INN
institute
nanoscience
nanotechnology

2021

ANNUAL REPORT

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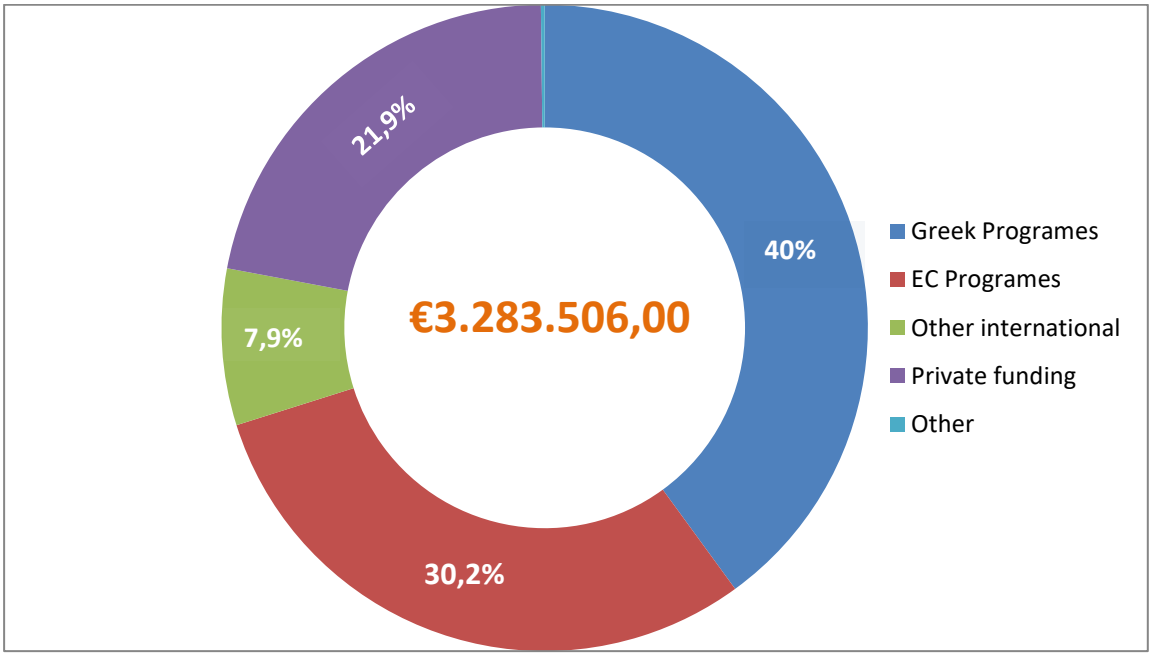
preface

This document contains mainly the scientific report of the research groups of INN for 2021, reflecting the high-quality scientific work performed at the Institute. It is preceded by financial and scientific data of the Institute, running projects, patents and spin-offs.

financials



717.852,63
Private Funding

1.312.306,12
National Research Grants

256.849,82
Other funding

990.381,17
EU Research Grants

year at a glance

358
PEOPLE

93
POSTDOCS

35
MASTER THESIS

97
PhD STUDENTS

12
DIPLOMA THESIS

214
PUBLICATIONS

11475
CITATIONS

17
NEW RESEARCH PROJECTS

excellent people & infrastructures

Marie Sklodowska-Curie Actions (MSCA)

Innovative Training Networks (ITN-ETN)

Training the next generation of archaeological scientists: Interdisciplinary studies of pre-modern Plasters and Ceramics from the eastern Mediterranean «PlaCe»
P.I.: V. Kilikoglou
NCSR Budget 486.035.28€

Individual Fellowships (IF)

THermIC

Local Thermal and thermoelectroic transport in 2D transition metal dichalcogenide based nanostructures and devices – Thermic

Fellow: Alexander El Sahat
P.I. A. Dimoulas
NCSR Budget 165.085,44€

ERC

MIX2FIX

Hybrid, organic-inorganic chalcogenide optoelectronics

P.I.: Th. Stergiopoulos
NCSR Budget 2.731.750,00€

Running infrastructure projects

Nanotechnology, Advanced Materials & Micro/Nanoelectronics

P.I.
V. Kilikoglou
NCSR Budget : 1.100.000,00

Plasma for Nano

Inorganic nanostructuring to the atomic limit via plasma nanotechnology

P.I.
E. Gogolides
NCSR Budget : 1.1439.424,00€

Att SENSE

AttSENSE

Attica Sensor Technology Center

P.I.
V. Kilikoglou
NCSR Budget : 44.330,00€

new projects in 2021

17 new research projects

NOOSE
NATO
P.I. E. Gogolides

5/4/2021 - 4/4/2024
NCSR Budget: 56.000,00€

PlaCe
E.E. / HORIZON 2020
P.I. V. Kilikoglou

1/3/2021 - 28/5/2025
NCSR Budget: 486.035,28€

GoHydro
Eranets
P.I. E Makarona

1/3/2021 - 28/2/2023
NCSR Budget: 101.700,00€

THERMIC
E.E. / HORIZON 2020
P.I. A. Dimoulas

1/11/2021 - 30/10/2023
NCSR Budget: 165.085,44€

3D-ΤΟΠΟΣ
National projects
P.I. P. Dimitrakis

29/7/2021 - 28/11/2023
NCSR Budget: 199.200,00€

ΜΕΤΑΛΛΩΝ ΤΟΠΟΙ
INTERREG V 204-2020
P.I. E, Filippaki

1/6/2021 - 31/5/2023
NCSR Budget: 221.200,00€

u-ArchaeoRoV
National Projects
P.I. E. Dotsika

30/9/2021 - 29/11/2023
NCSR Budget: 130.800,00€

CarbynSense
Eranets
P.I. T. Triantis

30/12/2021 - 29/06/2023
NCSR Budget: 200.000,00€

AttSENSE
National Projects
P.I. I. Karatasios

1/7/2021 - 31/12/2023
NCSR Budget: 44.300,00€

Plasma for Nano
National Projects
P.I. E. Gogolides

16/4/2021 - 15/4/2024
NCSR Budget: 1.439.424,00€

Παλίμψηστο
National Projects
P.I. E. Dotsika

29/7/2021-28/11/2023
NCSR Budget: 325.662,50€

Study of the photosynthetic water splitting by Electron Paramagnetic Resonance and X-ray spectroscopy
MAX PLANK Institute
P.I. M. Chrisina

1/12/2021-30/11/2026
NCSR Budget: 100.000,00€

Project kick off in 2022

LIMA-Chip
Logic-in-Memory Accelerator Chip
ESPA
P.I. P. Dimitrakis

14/1/2022-31/1/2025
NCSR Budget: 177.934€

REMAP
REusable MAsk Patterning
E.E. / HORIZON 2020
P. I. K. Trohidou

1/3/2022-28/2/2026
NCSR Budget:476.250€

AMASE
Advanced Materials science for Advanced STEMEducation
ERASMUS
P.I. K. Giannakopoulos

1/2/2022-31/1/2025
NCSR Budget: 42.226€

Vortex LC
Enhanced liquid chromatography for HbA1c monitoring based diabetes management in a globalized setting
E.E / HORIZON EUROPE
P.I. E. Goggolides

1/3/2022-28/2/2026
NCSR Budget: 555.000€

ΑΠΟΓΕΙΟΝ
Development of photoactive surfaces with antibacterial and antiviral activity for a clean and safe environment
ESPA
P.I. C. Trapalis

04/08/2022-31/12/2023
NCSR Budget: 140.000€

MOST-H2
Novel metal-organic framework adsorbents for efficient storage of hydrogen
E.E / HORIZON EUROPE CL4-XXX
P.I. T. Steriotis

1/6/2022-31/5/2026
NCSR Budget: 776.250€

SUSAAN
Sustainable Antimicrobial and Antiviral Nanocoating
E.E / HORIZON EUROPE CL4-XXX
P.I. F. Katsaros

1/6/2022-31/11/2025
NCSR Budget: 498.750€

Synthesis of the main long-term dihydroxylated metabolite of LGD-4033 as reference material for doping control analysis
OTHER EUROPEAN
P.I. E. Pitsinos

15/4/2022-14/4/2023
NCSR Budget: 133.784€

HeRISKtags
Systems for recording and monitoring the effects of climate change on the microenvironment and on the materials of the monuments
ESPA
P.I.I. Karatasios

01/06/2022-31/05/2025
NCSR Budget: 1.000.000,00€

Φωτοκαταλυτικοί αντιδραστήρες καθαρισμού υδάτων και υγρών αποβλήτων με ακινητοποιημένους φωτοκαταλύτες σε μικρο/νανομορφοποιημένες επιφάνειες
ESPA
P.I. T. Triantis

04/08/2022-31/12/2023
NCSR Budget: 200.000€

ΜΙΚΡΟΒΙΟΦΑΡΜ
Development of a BIOsensor MICROsystem for the Selective Detection of Phytopharmaceuticals
ESPA
P.I. S. Chatzandroulis

04/08/2022-31/12/2023
NCSR Budget: 60.000€

THERMOSKIN
A novel self-sterillizing surface for fighting community and hospital acquired infections
ESPA
P.I. N. Chronis

18/3/2022-17/6/2023
NCSR Budget: 98.172€

Adaptable Large Area META: Surfaces for customized applications
ESPA
P.I.F. Katsaros

01/07/2022-30/06/2025
NCSR Budget: 199.980€

spin-outs

The following is a list of youngest companies that are directly related to INN, and are using partly its facilities for production, or testing, or office space in the Technology Park.

AMEN Technologies	**The following is a list of youngest companies that are directly related to INN, and are using partly its facilities for production, or testing, or office space in the Technology Park.**
Established in 2013 AMEN Technologies develops advanced magnetic, thermoelectric and fuel cell materials "on demand" and tailored to the needs of the customers. The company also in-house fabricated bench-top RHS sintering systems, thermoelectric modules, optoelectronic components and sensors (In collaboration with CIDETE Ingenieros, Spain) as well as 3D-printing of nanocomposite materials.	

ThetaMetrisis S.A.	
ThetaMetrisis S.A. was established in 2008 and was the first spin-off company of the former Institute of Microleelctronics (now part of INN). It specializes in non-destructive characterization of coatings in the nano- and micro- scale and biosensors for PoN applications in Health & Food Safety. In 2014, ThetaMetrisis LLC in CA, USA was established, while the company has expanded into the point that of having sales representatives in several European countries and has also penetrated the Asian and Middle-Eastern market with sales representatives all the way to Japan and Korea. In April 2018 ,the growth of the company led it to its new, larger location.	

AISTHISIS Ltd	
Aisthisis Technologies Ltd provides intelligent hardware components and solutions on sensing applications bringing to market a novel silicon micromachining technology, SBE (Self-aligning, Binding & Etch-back) that is applied to capacitive, single crystal silicon pressure sensors and switches. Aisthisis also offers services in the field of MEMS development and in particular in MEMS design and process development. The company has been recently expanding in order to include in its products passive wireless RF sensor tags.	

Nanometrisis	

Nanometrisis is one of the two most recent spin-offs of INN established in 2016. The company creates software tools used for the measurement and quantification of geometric and morphological characteristics of micro and nanostructures during semiconductor manufacturing, or the manufacturing of other nanotechnology products. Nanometrisis software family incorporating state-of-the-art mathematical methodologies inspired by information science and complex theory can characterize the size, topography, roughness and morphology of nanostructures from the analysis of microscopy images.

Nanoplasmas	

Nanoplasmas is a company founded in 2016 as spin-off of INN and is the second of the two youngest companies emerging from the institute. The company uses an innovative, patented, plasma-based technology to produce healthcare and diagnostic consumables with enhanced performance. The Nanoplasmas team is highly experienced in surface modifications, plasma processing and device fabrication, and can offer customized solutions for a wide range of requests, such as wetting control, microfluidics fabrication, self-cleaning and antifouling surfaces, and optical properties control.

PLINIOS	

PLINIOS was founded in 2005 as a spin-off company of INN. Plinios, applying advanced microscopy methods, provides services in the field of evaluation of environmental risks in every kind of facility. The evaluation of these risks is necessary so that the health of the users of the facility will be safeguarded, hazardous substances will be properly managed, compliance with the environmental legislation will be ensured and future investments in that facility will be protected.

patents in 2021

Photonic chips with one sided optical ports self aligned to bifurcated fibers for the label free detection of biomolecular reactions through the use of integrated interferometers and resonators K Misiakos, I Raptis, A Salapatas - US Patent 11,119,040, 2021

Description: The present invention proposes a way for coupling light in and out of an integrated interferometer or resonator through the use of photonic chips with one-sided optical ports and the employment of bifurcated fibers. The bifurcated fiber at the common end matches the input and output waveguide pair at the one-sided optical port of the planar photonic chip

Encaplulated systems for the development of self-healing building materials, Karatasios, I., Papaioannou, S., Amenta, M., Gournis, D., Kilikoglou, V.
Application No./Patent No.: 21161152.0 – 1108
Application date: March 2021

Description: Concrete is the most used construction material as it is mechanically strong, rather inexpensive and presents a high degree of durability. However, crack formation is the primary reason for premature corrosion deterioration which leads to limitations in the durability of concrete structures.
The present invention relates to encapsulated systems and their application in the development of self- healing building materials, such as cement-based mortars, concrete and hydraulic mortars. Further, the invention relates to a method of manufacture of such self- healing systems

High-yield synthesis of nanozeolite-Y crystals of controllable particle size at low temperature, Marios S Katsiotis, Vasileios Tzitzios, Saeed Alhassan, High-yield synthesis of nanozeolite-Y crystals of controllable particle size at low temperature, US20210046463A1 (2021).

Description:

Hydrogel and xerogel active ingredient carriers made from dendritic polymers and silica for use as leather and textile additives, M. Arkas, E. Nikoli, M. Douloudi, G. Kythreoti, L. Arvanitopoulos, K. Arvanitopoulos, Application No / Patent No :GR20210122640
Application date: September 2021

Description: Hydrogels and dried counterparts xerogels consisting from silica, dendritic compounds and optionally metal nanoparticles are employed as coatings in order to immobilize active ingredients to leathers or textiles. The gel formation reaction takes place into the pores of the solid substrate.

Hydrogel and xerogel active ingredient carriers made from dendritic polymers and silica for solids substrate coating applications, M. Vardavoulias, E. Gkomoza, A. Tsetsekou, I. Kitsou, M. Arkas, M. Papageorgiou, S. Soto, L.Y. Cubillos, V. Cepas, M.E. Jensen Henrik, L.K. Jensen , S. Lopez-Ibanez, I. Cutierrez-Del,-Rio, C.J. Villar Granzia, F. Lombo Burgos, F. Lopez, M.J.I. Valdes-Solis, M.G. Soengas Raquel, PATENT GRANTED GR1010001B, 2021

Description: Hydrogels and xerogels containing silica, dendritic compounds, active ingredient and optionally, metal nanoparticles. These compounds are designed as coatings to solid metal and ceramic substrates, possessing rough porous surfaces. The dendritic compounds are selected so that they improve the encapsulation and conservation of the active ingredient and/or in order to achieve the desired release profile. Their methods of preparation and uses thereof are also described.

program 1

Chemical Sciences for Nanostructures and Biological Applications

LABORATORY OF STRUCTURAL AND SUPRAMOLECULAR CHEMISTRY (LSSC)

Project Leader: Dr. K. Yannakopoulou, Researcher A (also in charge of the High Resolution NMR facility for liquid samples)

Permanent Researcher Staff: Dr. E. Saridakis, Researcher B (also in charge of the Macromolecular Crystallographic Laboratory)

Research Collaborator: Dr. Irene M. Mavridis

PhD Candidates: Stylianos Panagiotakis, MSc (until 3/2021, project PCInano,), Eleni-Marina Kasimati, MSc (group funds)

Diploma thesis Student: Katerina Donta, senior undergraduate, Department of Chemistry, U. of Athens

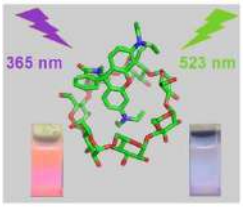
Objectives

The laboratory focuses on supramolecular systems comprising chemically modified cyclodextrin host macrocycles and organic guest molecules, as well as on biological macromolecules. The lab has strong expertise in cyclodextrin chemistry (synthesis, structure and function) and in X-ray crystallography of biological macromolecules and macromolecular crystallization methodology. The main objectives of the group involve:

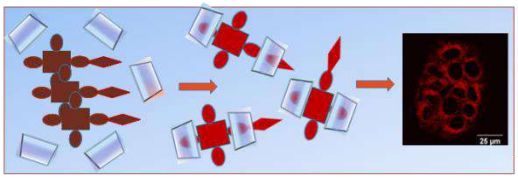
- Structure determination and intermolecular interactions in the crystalline state and in solution
- Development of cyclodextrin-based multimodal molecular/drug transport and release systems
- Macromolecular crystallization methods and crystal structure analysis of biological macromolecules

Main scientific results

A. <u>The supramolecular structure renders complete control over the photoswitching properties of Rhodamine B (Rho):</u> The conjugate (6-spirolactam rhodamine B-6-monodeoxy)-β-cyclodextrin (Rho-βCD) assembles as a self-included, rigid nanostructure where Rho is sequestered inside the βCD cavity and practically looses all degrees of freedom. The structure is identical in the crystalline state and in aqueous solution, as revealed by detailed X-ray and NMR analyses. The pathway to the synthesis of the Rho-βCD structure entails partial de-aggregation of the Rho molecules and perturbs the equilibrium zwitterion ←→spirolactone. The Rho-βCD conjugate is stable at pH 4.6 and displays controllable photoswitching between the colored, fluorescent, zwitterionic and the colorless, nonfluorescent closed structures, during several iterative cycles, a consequence of the self-locked Rho in the cavity. Rho-βCD is a water soluble photoresponsive nanosystem with improved photostability suggesting promising applications in super resolution bioimaging (*Chem. Asian J*. on-line: 25-11-2021).

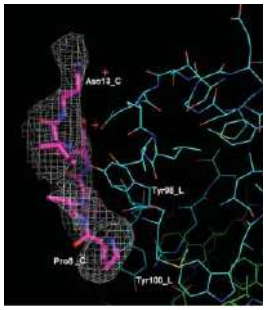


B. <u>Cyclodextrin-photosensitizer complexes for applications in phototherapy</u>: The well known tendency of photoactive porphyrinoid compounds to form water-insoluble aggregates hampers their biomedical applications. The contribution of cyclodextrins (CDs) is to restore/augment the photophysical response of the porphyrinoids, increase their solubility in aqueous solutions, modulate their uptake in cancer cells and finally exert a strong and controlled phototoxic outcome in tumors *via* various photodynamic therapy (PDT) approaches (Mavridis, I.M., Yannakopoulou, K. *J. Med. Chem.* **2020** *63, 7*, 3391-3424). Design and synthesis of suitable porphyrins as possible guest compounds for inclusion into selected CDs has been undertaken and their inclusion complexes with pMβCD have been studied. The resulting supramolecular complexes totally alleviate aggregation and reconstitute 100 % the photophysical characteristics



(absorption, emission intensity and lifetime) of the porphyrins in aqueous solution. The complexes produce singlet oxygen and are efficiently uptaken by cancer cells, where they are mainly distributed in the ER. Phototoxicity studies reveal that the complexes confer very high phototoxicity (and very low dark toxicity) to the tumor cells, suggesting applications in PDT protocols (*Carbohydrate Polymers* (on-line 21/9/2021).

C. HIV antibody bound to receptor epitope. C-C chemokine receptor 5 (CCR5) is a major co-receptor of HIV-1 in human cells. Blocking it by activating an antibody response would therefore prevent HIV infection. We have solved the crystallographic structures of anti-CCR5 antibody RoAb13 in complex with two synthetic peptides that encompass the epitope sequence for the antibody at the CCR5 N-terminus. The insights gained into the three-dimensional structure of the epitope sequence bound to the antibody may inform the design of better peptide analogues for use as immunogens. These synthetic analogues may ultimately provide the basis for active immunization vaccines to stimulate an antibody response to CCR5 that will block HIV infection, thus circumventing the current need for regular use of anti-viral drugs (*IUCrJ*, 2021).



Funding

1. **PCInano**: "Nanoparticle mediated photochemical internalisation (PCI) of small anticancer drugs". ERA-NET , EuroNanoMed-II, 2016-15/9/2021, Scientific Responsible: K. Yannakopoulou.

2. **INSPIRED**: The National Research Infrastructure on Integrated Structural Biology, Drug Screening Efforts and Drug target functional characterization, 2018-2021 (participating in the national GSRT-funded program). Contact point for Demokritos: E. Saridakis.

3. **NECTAR** COST ACTION: Network for Equilibria and Chemical Thermodynamics Advanced Research COST ACTION 18202. Management Committee members: K. Yannakopoulou (E. Saridakis)

OUTPUT

Publications in International Journals

1. Panagiotakis, S., Mavroidi, B., Athanasopoulos, A., Charalambidis, G., Coutsolelos, A. G., Paravatou-Petsotas, M., Pelecanou, M., Mavridis, I. M., Yannakopoulou, K. " Unsymmetrical, monocarboxyalkyl meso-arylporphyrins in the photokilling of breast cancer cells using permethyl-β-cyclodextrin as sequestrant and cell uptake modulator" *Carbohydrate Polymers* (on-line 21/9/2021) 275, 118666 (2022). **IF= 9.381, Q1.** doi.org/10.1016/j.carbpol.2021.118666

2. Govada, L., Saridakis E., Kassen, S.C., Bin-Ramzi, A., Morgan, R.M., Chain, B., Helliwell J.R., Chayen, N. E. "X-ray crystallographic studies of RoAb13 bound to PIYDIN, a part of the N-terminal domain of CC chemokine receptor 5" *IUCrJ* 8, 678-683(2021). **IF= 4.769, Q1.** doi.org/10.1107/S2052252521005340

3. Panagiotakis, S. Saridakis, E., Malanga, M., Mavridis, I. M., Yannakopoulou, K. "A self-locked β-cyclodextrin-rhodamine B spirolactam with photoswitching properties" *Chem. Asian J*. on-line: 25-11-2021; Early view 8-12-2021. **IF= 4.568, Q1.** https://doi.org/10.1002/asia.202101282

4. Agnes, M., Arabi, A., Caricato, M., Nitti, A., Dondi, D., Yannakopoulou, K., Patrini, M., Pasini, D. "Helical Nanofibers by Palladium-Mediated Assembly of Organic Homochiral Macrocycles Containing Binaphthyl and Pyridyl Units" *ChemPlusChem* 86 (2), 270-274 (2021). **IF= 2.863, Q1.** DOI: 10.1002/cplu.202100039

5. Saridakis, E. "The genetic informational network: how DNA conveys semantic information" *Hist. Philos. Life Sci.* **43,** 112 (2021). **IF= 0.559, Q2.** DOI: 10.1007/s40656-021-00470-y

International Conferences Presentations (invited, oral, poster)

1. Saridakis E., Kasimati E.-M., Yannakopoulou K., Mavridis I.M. "A novel, four subunit, 'dimer-within-a-dimer' γ-cyclodextrin self-assembly", *10th International Conference of the Hellenic Crystallographic Association*, October 15 - 17, 2021, Congress Center, NCSR Demokritos, Athens, Greece (oral).

2. Panagiotakis, S., Saridakis, E. Mavridis I.M., Yannakopoulou K. "The β-Cyclodextrin-rhodamine B spirolactam conjugate adopts a single, self-included structure in the crystalline state and in aqueous solution" *10th International Conference of the Hellenic Crystallographic Association*, October 15 - 17, 2021, Congress Center, NCSR Demokritos, Athens, Greece (poster).

3. Panagiotakis, S., Yannakopoulou, K. "Permethyl-β-cyclodextrin as a vehicle to transfer mono-carboxyalkyl meso-arylporphyrins in aqueous solution", *Supramolecular Chemistry days for young researchers*, October 13 - 15 2021, https://eventi.unibo.it/phdsuprachemdays20, virtual conference.

Teaching and Training Activities

Yannakopoulou, K. "High-resolution NMR spectroscopy in solution: basics - case studies of molecular structures" *INN Spectroscopy days,* May 6, 2021, on-line seminar.

Conference / Workshop Organisation

10th International Conference of the Hellenic Crystallographic Association, October 15 - 17, 2021, Congress Center, NCSR Demokritos, Athens, Greece.
E. Saridakis, K. Yannakopoulou, members of the Organizing Committee.

Scientific services

Scientific services to third parties (academic and private) are provided by the High Resolution Nuclear Magnetic Resonance Laboratory. The income is used exclusively for the maintenance of the facility that includes fixed operational costs, repairs of the instruments as well maintenance of the rooms.

Services to third parties (academic) were provided in the frame of the Macromolecular Crystallographic Laboratory. No income generated, but users participate in the maintenance costs.

ADVANCED EPR METHODS AND ELECTRON SPIN DYNAMICS IN MOLECULAR AND NANO-SCALE MATERIALS

Project Leader: Dr. George Mitrikas, Reseacher A

PhD Candidates: Maria Tsoukala, Nikolaos Kantartzis, Antonino Famulari

Research Collaborator: Assoc. Prof. Eleni K. Efthimiadou

Objectives

- Implementation of advanced EPR methods for quantum computation
- Development of pulsed EPR methods aimed at sensitivity enhancement
- Characterization of paramagnetic species including transition metal ions and free radicals

Main scientific results

A. The electronic structure of Tyrosyl D radical as probed by Pulsed EPR methods: The biological water oxidation takes place in Photosystem II (PSII), a multi-subunit protein located in thylakoid membranes of higher plant chloroplasts and cyanobacteria. The catalytic site of PSII is a Mn_4Ca cluster and is known as the oxygen evolving complex (OEC) of PSII. Two tyrosine residues D1-Tyr161 (Y_Z) and D2-Tyr160 (Y_D) are symmetrically placed in the two core subunits D1 and D2 and participate in proton coupled electron transfer reactions. Y_Z of PSII is near the OEC and mediates electron coupled proton transfer from Mn_4Ca to the photooxidizable chlorophyll species P^+_{680}. Y_D does not directly interact with OEC, but is crucial for modulating the various S oxidation states of the OEC. In PSII from higher plants the environment of Y_D· radical has been extensively characterized only in spinach (Spinacia oleracea) Mn-depleted non functional PSII membranes. Here, we present a 2D-HYSCORE investigation in functional PSII of spinach to determine the electronic structure of Y_D· radical. The hyperfine couplings of the protons that interact with the Y_D· radical are determined and the relevant assignment is provided. A discussion on the similarities and differences between the present results and the results from studies performed in non functional PSII membranes from higher plants and PSII preparations from other organisms is given.

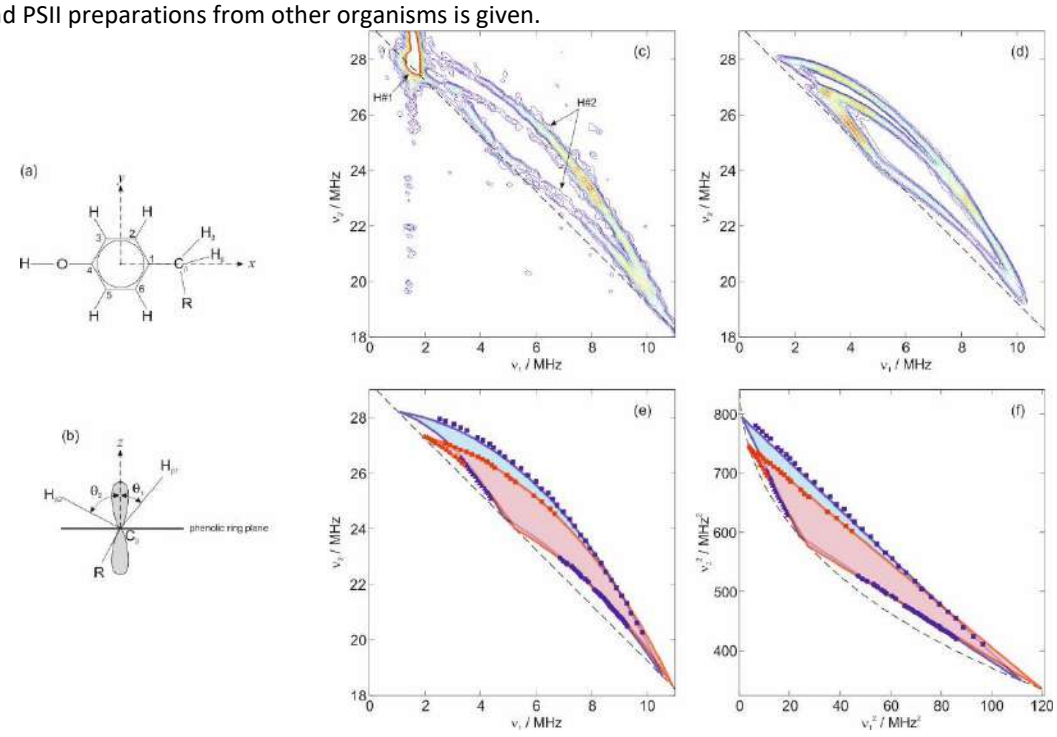


Figure 1: Schematic representation of a tyrosine (a) and the dihedral angles θ_1, θ_2 of the β-methylene protons (b). (c) Detail of the HYSCORE spectrum showing correlation ridges of β-type methylene (H#1) and 3,5-protons (H#2). (d) Full HYSCORE simulation of H#2. (e) Selected points from the experimental spectrum (filled symbols) and the corresponding fits (solid curves) using Dikanov analysis. Shaded areas in two different colors represent the two

different sets of ^{1}H principal hyperfine coupling constants obtained from this analysis. (f) Data as in (e) but in the (ν_1^2,ν_2^2) representation.

B. The role of isotope substitution on the electron spin relaxation of atomic hydrogen trapped in silsesquioxane cages: Encapsulated atomic hydrogen in silsesquioxane cages is a promising candidate for applications in emerging technologies like spin-based quantum computing, magnetic field sensing, and atomic clock devices. Previous studies on different polyhedral octasilsesquioxanes (POSS) of the type $Si_8O_{12}R_8$ have shown that key parameters for quantum computing like electron spin relaxation times T_1 and T_M depend strongly on the type of peripheral organic substituents. Herein we examine for the first time the effect of deuterium isotopic substitution on the spin relaxation properties of H@$h_{72}Q_8M_8$, the derivative with R = OSi(CH$_3$)$_3$, by applying pulsed electron paramagnetic resonance methods on its deuterated analogues H@$d_{72}Q_8M_8$ and D@$d_{72}Q_8M_8$ (Fig. 2(a)). For the latter species we measure a phase memory time of 60 μs at 190 K, the largest obtained so far for this family of molecular spins. We show that substitution of peripheral hydrogen atoms with deuterium reveals high-temperature relaxation mechanisms that were previously hidden by proton nuclear spin diffusion. Unusually short T_M values observed for all deuterated species even at liquid helium temperatures are discussed in terms of tunneling reorientation of methyl groups.

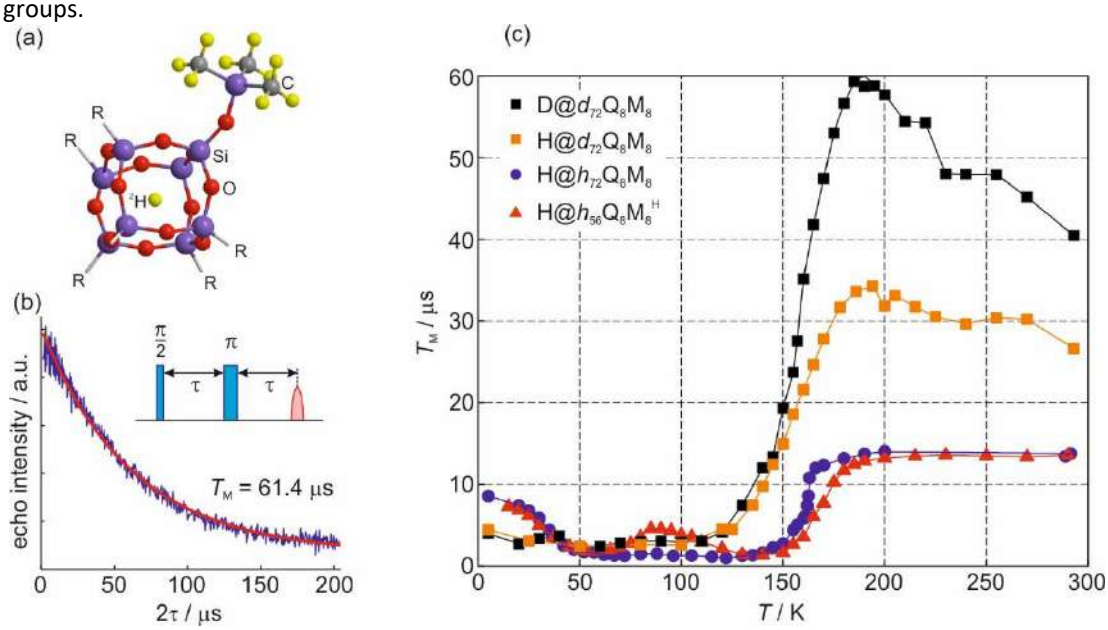


Figure 2: (a) Structure of the species D@$d_{72}Q_8M_8$, only one of the eight R groups is shown. (b) Two-pulse echo decay at T=190 K. (c) Temperature dependence of phase memory times T_M for three different isotopologues of the H@Q_8M_8 derivative. For comparison reasons, red triangles depicting previously published data for the H@$h_{56}Q_8M_8^H$ species (R = OSi(CH$_3$)$_2$H) are also shown. Straight lines connect data points.

Funding

1. "Photosynthetic Water Splitting: The Critical Stages before Oxygen Release" (MIS 5047814), co-financed by Greece and the European Union (European Social Fund-ESF) through the Operational Programme "Human Resources Development, Education and Lifelong Learning 2014–2020", budget 50 kEuros.
2. "PARACAT: Paramagnetic Species in Catalysis Research. A Unified Approach Towards Heterogeneous, Homogeneous and Enzyme Catalysis" H2020-EU.1.3.1. Project ID: 813209 (coordination of the project: Prof. Mario Chiesa, University of Torino, Italy), budget for INN, 18 kEuros.

OUTPUT

Publications in International Journals

1. Chrysina, M., Zahariou, G., Ioannidis, N., Sanakis, Y., Mitrikas, G. "Electronic Structure of Tyrosyl D Radical of Photosystem II, as Revealed by 2D-Hyperfine Sublevel Correlation Spectroscopy", *Magnetochemistry* **7**, 131 (2021). **IF: 3.336, Q2.** https://doi.org/10.3390/magnetochemistry7090131

2. Mitrikas, G., Carmieli, R. “Electron Spin Relaxation Mechanisms of Atomic Hydrogen Trapped in Silsesquioxane Cages: the Role of Isotope Substitution”, *J. Phys. Chem. C* **125**, 9899−9907 (2021). **IF: 4.177. Q1.** https://doi.org/10.1021/acs.jpcc.1c01582

International Conferences Presentations (invited, oral, poster)

1. Chrysina, M., Zahariou, G., Ioannidis, N., Sanakis, Y., Mitrikas, G. “2D-Hyperfine Sublevel Correlation Investigation of the Tyrosyl Radicals of Photosystem II”, *Athens Conference on Advances in Chemistry (ACAC 2020)*, March 10-14, 2021, Athens, Greece (oral)

Teaching and Training Activities

Mitrikas, G. “Pulsed Electron Paramagnetic Resonance Spectroscopy” *INN Spectroscopy days,* May 20, 2021, on-line seminar.

NATURAL PRODUCTS SYNTHESIS & BIOORGANIC CHEMISTRY

Project Leader: Dr. Emmanuel N. Pitsinos, Researcher A'

Permanent Research Staff: Dr. Veroniki P. Vidali, Researcher C'

Post Docs: Dr. Ioannis Mavridis, Research Associate

PhD Candidates: Aleksander Canko

Master Students: Evangelos Georgas , Georgia Athanassopoulou

Undergraduate students: Vassiliki Stamatiou

Objectives

Group's mission is to advance Synthetic Organic Chemistry (SOC) and to explore its applications in the fields of Life Sciences, Nanoscience and Nanotechnology.

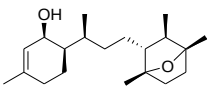
Natural Products (NPs) feature diverse, often complex and unprecedented, structures. Thus, their total synthesis historically defines the state of the art of SOC. Furthermore, they play a pivotal role in modern drug discovery. Interestingly however, in most cases the active ingredient of the end-product (i.e., drug) is not a NP but rather a semisynthetic modification or a totally synthetic compound with a NP-inspired pharmacophore. This highlights the importance of SOC in the exploitation of NPs. Nowadays, NPs continue to drive basic research in the field of SOC (for the discovery and validation of new methods and strategies) and are valuable tools for Chemical Biology (i.e., the study of biological systems using chemical techniques).

In this context and aiming to a) contribute in the advancement of modern SOC, b) facilitate further exploitation of bioactive NPs, and c) contribute in the training of young researchers in the "Art and Science" of NP total synthesis, the research focus of the group is the total synthesis of NPs and related medicinal chemistry studies. In parallel, the expertise of the team in the synthesis of complex organic molecules is exploited for the preparation of organic compounds of medicinal / agrochemical interest or with potential technological applications (e.g., photoresist etch enhancement additives).

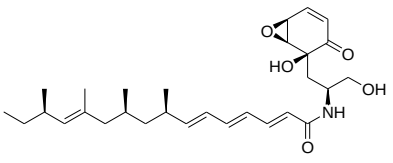
Highlights / main scientific results

-

Terpenes with selective anticancer activities: Stemming from the interest of our group in the synthesis and study of natural products with important biological activities and following past accomplishments in this area (e.g., total synthesis of Scyphostatin, a potent and selective N-SMase inhinitor; the first enantioselective total synthesis of Laurenditerpenol, a marine diterpene that targets hypoxic signalling in tumour cells), a research project focusing on the natural product Taepeenin D, a novel Hedgehog/GLI inhibitor, and related furanoditerpenoids that could target cancer stem cells (CSCs) has been initiated.

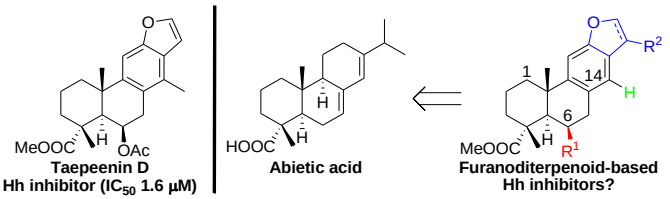


(-)-Laurenditerpenol



(+)-Scyphostatin

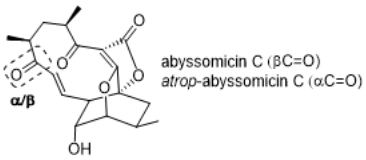
The Hedgehog (Hh) signalling pathway is one of the pathways that control embryonic patterning and cellular proliferation and differentiation. However, its abnormal activation has been linked with the occurrence of basal cell carcinoma and meduloblastoma while several other tumours (such as cancers of the skin, brain, lung, pancreas, digestive tract, prostate) are co-dependent on Hh signalling. Moreover, recent evidence suggests that Hh signalling is important for the self-renewal of cancer stem cells in pancreatic cancer, glioblastoma, multiple myeloma as well as in chronic myeloid leukemia. Thus, inhibition of Hh pathway has become an attractive strategy in anticancer therapy and several related clinical trials are underway.



Taepeenin D is a cassane-type diterpenoid originally isolated from *Caesalpinia crista* that has been identified as a constituent of *Acacia pennata* with significant Hh/Gli-mediated transcription inhibitory activity (IC_{50} 1.6 μM) and selective cytotoxicity against cancer cells with increased Hh signalling levels (IC_{50} 3.2-3.4 μM). Synthetic studies directed towards the total synthesis of this natural product were initiated. In parallel, a series of related analogues were prepared exploiting abietic acid (a readily available starting material; main constituent of rosin) and evaluation of their activity as Hh/Gli inhibitors has allowed the identification of important structural features (SAR studies). Efforts to complete the first total synthesis of Taepeenin D and related cassane-type diterpenoids are ongoing.

Drimanes as potential leads for new small-molecule RANKL inhibitors: Certain drimane natural products have recently been shown to inhibit RANKL-induced osteoclastogenesis without cytotoxicity. RANKL-blocking is a validated therapeutic strategy to treat osteoporosis and bone-metastasing cancer. Thus, small-molecule inhibitors are highly sought as attractive alternatives to a RANKL-targeted antibody that is already in clinical use. Building upon related preliminary studies of the group, a collaboration with the team of Dr. C. Mueller (CNRS UPR 3572, Strasbourg, France) has been initiated and the outcome of a joint research proposal, that has been submitted in response to the "2021 Medalis call" by the Strasbourg Drug Discovery and Development Institute (IMS), is pending.

Synthesis of spirotetronate polyketide antibiotics. Spirotetronate polyketides constitute a group of natural products with fascinating structures and important biological activities. Among them, abyssomicin C and its α-atropisomer were the first members that caught the eye of the scientific community. Their activity against methicillin-resistant *Staphylococcus aureus* mycobacteria and other Gram-positive bacteria, as well as their involvement in inhibiting *p*-aminobenzoic acid (*p*-ABA) biosynthesis, brought the abyssomicin pharmacophore to the attention of researchers for the development of novel antifolates.

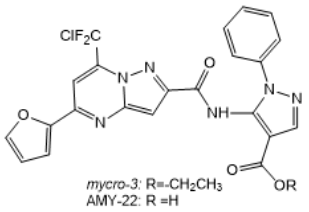


Based on previous work by members of our group (Dr V. Vidali, MSc A. Canko and E. Georgas) who worked on the improved formal synthesis of abyssomicin C via a scalable and high-yielding route, the developed methodology is being applied in the synthetic studies of other members of this family of products and analogues. This work is part of Mr Canko's PhD thesis (ongoing), which was funded by the State Scholarships Foundation and Mr Georgas' master thesis (completed in October 2021), under the supervision of Dr V. P. Vidali. This research is ongoing.

Synthesis of natural products and analogues with larvicidal activity and as pheromones. Natural products and analogues have been widely used in pest control. Among them, several terpenes have been active against the mosquito *Culex pipiens.* As part of this ongoing research, known and novel prenylated acylphloroglucinols were synthesized. Some of the synthesized compounds were evaluated for their larvicidal activity against *Cx. pipiens* and their structure-activity relationship was studied. This part of the work is ongoing and being implemented in our laboratory in collaboration with the Agricultural University of Athens and the Benaki Phytopathological Institute. Also, in partnership with the Benaki Phytopathology Institute, modified synthetic procedures are being developed for the scalable preparation of pheromones to control *Xylotrechus Chinensis* (Chevrolat), a harmful insect for mulberry trees. This research is ongoing and part of an undergraduate thesis implemented by the Agricultural University of Athens undergraduate student, Ms Vassiliki Stamatiou.

Synthesis of curcumine analogues and heterocyclic compounds for Alzheimer's disease. Curcumin and its derivatives have been shown as possible therapeutic tools against Alzheimer's disease. In collaboration with the Institute of Biosciences & Applications of NCSR "Demokritos", novel curcumin analogues were designed. Synthesis and biological evaluation of these compounds highlighted potent candidates, enriching our knowledge around the structure-activity relationship and setting the base for creating compounds with improved properties. Also, novel heterocyclic compounds were synthesized by developing optimized procedures showing high affinity for β-amyloid plaques, which will also be evaluated for other biological properties. Their synthesis was implemented in our laboratory by Georgia Athanassopoulou as part of her master thesis, under the supervision of Dr V. P. Vidali, in collaboration with Dr M. Sagnou (Institute of Biosciences & Applications of NCSR "Demokritos").

Synthesis of improved analogues of lead-compounds having the oncoprotein MYC as a therapeutic target. Oncoprotein MYC is one of the most promising and challenging therapeutic targets, involving several severe cancers, such as pancreatic, melanoma, breast cancer and others. Several small molecules, called anti-MYC compounds, have exhibited inhibitory activity against this oncoprotein via various modes of action. Recently, heterocyclic derivatives mycro-3 and later AMY-22 were shown to strongly inhibit MYC- dependent cell lines (TGR-1) over MYC-independent (HO15.19), selectively and with promising in vivo results in mice with pancreatic cancer.



Based on the above, Dr V. P. Vidali, in collaboration with the Biomedical Research Foundation Academy of Athens (BRFAA), participates in a research project (funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) for the development of novel anti-MYC small molecules. This research is ongoing.

Synthesis of dyes as tools for the study of pathophysiological pathways. A known nitroimidazole–indocyanine conjugate was synthesized in large amounts to study the factors affecting the HIF-1 aberrant expression and transcription activity in myelodysplastic syndrome. Although the synthetic route was known, several modifications were applied to produce the desired compound in the required amount and high purity. This work was in collaboration with Dr K. Kambas (Department of Immunology, Hellenic Pasteur Institute) and Prof M. Voulgarelis (School of Medicine, National and Kapodistrian University of Athens).

Polyaromatic compounds of nanotechnological interest: As part of a long-lasting collaboration with Dr P. Argitis and Dr M. Vassilopoulou and in the frame of the ongoing research grant OLED_Lumin_FoodPack (funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020), synthesis of polycarbocyclic anthracene derivatives was performed for their use in OLEDs. The compounds are currently used as tools for the construction of nanodevices used for the development of new sensors to check food quality. This research is ongoing.

- **Funding**

1. Title and reference Number of the grant: Participation in the institute's research grant "Development of Materials and Devices for Industrial, Health, Environmental and Cultural Applications", MIS 5002567
Funding Agency and funding Scheme: Ministry of Economy & Development; "Action for the Strategic Development on the Research and Technological Sector", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014–2020)
Amount of grant for the Team: € 48,860.00
Start date and end date of the grant: 27/10/2018–26/5/2021

2. Title and reference Number of the grant: PhD thesis scholarship for the research project "Synthesis of bioactive natural products". Contract No. 2018-050-0502-12856, MIS-5000432
Funding Agency and funding Scheme: Ministry of Development and Investments; Action: "Strengthening Human Resources Research Potential via Doctorate Research" implemented by the State Scholarships Foundation (IKY), funded by the Operational Programme "Human Resources Development, Education and Lifelong Learning" (NSRF 2014–2020).
Amount of grant for the Team: € 29,408.00
Start date and end date of the grant: 24/04/2018–31/12/2022.

3. Title and reference Number of the grant: Participation in the research grant "Innovative development of novel anticancer drugs for therapeutic targeting of the oncoprotein MYC", ΑΚΜΥ, Τ1ΕΔΚ 03532, MIS 5031813.
Funding Agency and funding Scheme: Ministry of Development and Investments; Action: "Research, Technological Development and Innovation: RESEARCH - CREATE - INNOVATE", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020)
Amount of grant for the Team: € 100,000.00
Start date and end date of the grant: 01/08/2020–31/07/2022.

4. Title and reference Number of the grant: Participation in the research grant "Using organic LED in intelligent food packaging for quality monitoring of meat products", OLED_Lumin_FoodPack, Τ2ΕΔΚ-04175, MIS 5075103.
Funding Agency and funding Scheme: Ministry of Development and Investments; Action: "Research, Technological Development and Innovation: RESEARCH - CREATE - INNOVATE B'", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020)
Amount of grant for the Team: € 25,000.00
Start date and end date of the grant: 26/11/2020–25/11/2023

OUTPUT

Publications in International Journals

1. Matiadis, D., Ng, S. T., Chen, E. H. L., Nigianni, G., Vidali, V. P., Canko, A., Chen*, R. P. Y., Sagnou, M. Synthesis and biological evaluation of hydroxylated monocarbonyl curcumin derivatives as potential inducers of neprilysin activity. *Biomedicines* **9**, pp. 955 - 972 (2021). DOI: 10.3390/biomedicines9080955
2. Moschona, F., Vagena, A., Vidali, V. P., Rassias, G. A novel dual organocatalyst for the asymmetric Pinder reaction and a mechanistic proposal consistent with the isoinversion effect thereof. *Molecules* **26**, pp. 6398 - 6421 (2021**)**. DOI: 10.3390/molecules26216398
3. Nicolaou, K. C., Rigol, S., Pitsinos, E. N., Das, D., Lu, Y., Rout, S., Schammel, A. W., Holte, D., Lin, B., Gu, C., Sarvaiya, H., Trinidad, J., Barbour, N., Valdiosera, A. M., Sandoval, J., Lee, C., Aujay, M., Fernando, H., Dhar, A., Karsunky, H., Taylor, N., Pysz, M., Gavrilyuk, J. Uncialamycin-based antibody-drug conjugates: Unique enediyne ADCs exhibiting bystander killing effect. *Proceedings of the National Academy of Sciences of the United States of America* **118**, e2107042118 (2021). DOI: 10.1073/pnas.2107042118
4. Stergiou, I. E., Kambas, K., Poulaki, A., Giannouli, S., Katsila, T., Dimitrakopoulou, A., Vidali, V., Mouchtouris, V., Kloukina, I., Xingi, E., Pagakis, S. N., Probert, L. Patrinos, G. P., Ritis, K., Tzioufas, A. G., Voulgarelis, M. Exploiting the role of hypoxia-inducible factor 1 and pseudohypoxia in the myelodysplastic syndrome pathophysiology. *International Journal of Molecular Sciences* **22** pp. 4099 - 4116 (2021). DOI: 10.3390/ijms22084099

International Conferences Presentations (invited, oral, poster)

1. Pitsinos E. N., "Natural Product-Driven Chemistry at the Interface with Biology" (invited plenary lecture) *18th Hellenic Symposium on Medicinal Chemistry* (Online symposium), 25–27 February 2021, Athens, Greece.
2. Vidali V.P., Canko A., Peroulias A.D., Athanassopoulou G.D., Georgas E.T., Bouzas E., Couladouros E.A., "Biomimetic Synthesis of abyssomicin C and atrop-abyssomicin C. Improvements and perspectives" (poster presentation) *18th Hellenic Symposium on Medicinal Chemistry* (Online symposium), 25–27 February 2021, Athens, Greece.
3. Vidali V.P., Nigianni G., Athanassopoulou G.D., Canko A., Mavroidi V., Matiadis D., Pelecanou M., Sagnou M., "Synthesis o novel pyrazolopyridines with affinity for β-amyloid plaques" (poster presentation) *18th Hellenic Symposium on Medicinal Chemistry* (Online symposium), 25–27 February 2021, Athens, Greece.

Master Dissertations completed in 2021

Name: Evangelos Georgas
Dissertation Title: Synthetic studies to the natural product abyssomicin C
Research Supervisor at NCSR: Dr Veroniki P. Vidali
University where the Thesis was presented: Department of Chemistry, National and Kapodistrian University of Athens

Awards

Best poster presentation award for the "Synthesis of novel pyrazolopyridines with affinity for β-amyloid plaques" presented in the *18th Hellenic Symposium on Medicinal Chemistry,* Hellenic Society of Medicinal Chemistry, February 25–27, 2021 by members of our group **Vidali Veroniki P.**, **Nigianni Georgia**, **Athanassopoulou Georgia D**, **Canko Aleksander**, Mavroidi Barbara, Matiadis Dimitris, Pelecanou Maria and Sagnou Marina.

MOLECULAR COMPUTATIONAL CHEMISTRY (MOLCOMPCHEM)

Project Leader: Dr. Yannis G. Lazarou

- **Objectives**

  Applications of theoretical chemistry methodologies in environmental quality issues
  Investigation of chemical reaction mechanisms

- **Highlights / main scientific results**

  Geochemical modeling of mercury-contaminated groundwaters

The seasonal appearance of toxic mercury (Hg) in the groundwater of Skiathos Island in concentrations occasionally exceeding the World Health Organization (WHO) limit of 1 μg/L was extensively studied by geochemical modeling in order to quantitatively reveal its origin and speciation. The program PHREEQC was employed, fed with all possible reaction equilibria for mercury species with well-known equilibrium constants. The geochemical system comprised the most abundant mineral of mercury, cinnabar (HgS) in equilibrium with saline water, dissolved organic matter as well as goethite (hydrous ferric oxide, FeOOH) as the adsorbent. By adjusting the relative abundance of cinnabar and goethite in the aquifer bedrock, an agreement was attained between modeled and measured total Hg concentrations as shown in Figure 1.

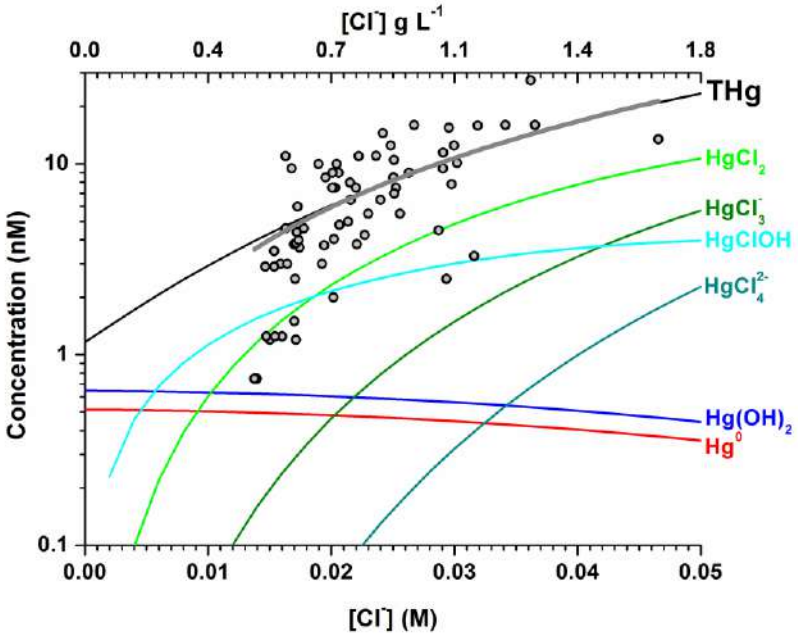


Figure 1. Concentrations of total mercury (THg) and its most prominent species in the groundwater of Skiathos, modeled at conditions of pH=8 and pε=6. The circles correspond to field measurements over a period of 9 years and the thick grey line represents their non-linear fit.

The results suggest that the mobilization of Hg in the presence of chloride anions is attributed to desorption of mercury hydroxide species from goethite surfaces via transformation to water soluble mercury chloride species. In aquifers prone to seawater intrusion, the majority of Hg in groundwater may be found in the form of chloride coordination complexes $[HgCl_n]^{2-n}$ (n=2-4) and HgClOH. Furthermore, the model was able to quantitatively reproduce the field concentrations of key species for previous groundwater contamination events in Italy. This study was performed in collaboration with Dr. Alexandra Spyropoulou and Prof. Chrysi Laspidou at the Department of Civil Engineering, University of Thessaly, Volos, Greece as well as with Dr. Andreas Sapalidis at INN, NCSRD ("Geochemical modeling of mercury in coastal groundwater", A.E. Spyropoulou, Y.G. Lazarou, A.A. Sapalidis, C.S. Laspidou, *Chemosphere* **2022**, 286, 131609).

STATISTICAL MECHANICS AND DYNAMICAL SYSTEMS

Project Leader: Astero Provata

Post Docs: Nefeli-Dimitra Tsigkri (until 31/08/2021)

PhD Candidates: Theodoros Kasimatis

Master Students: Anastasia Kosmou, Konstantinos Anesiadis

Undergraduate Students: Nikolaos Kartsonis (BSc thesis)

Research Collaborators: Georgios Sotiropoulos (01/09/2021-31/12/2021),
Marios Christopoulos (01/09/2021-31/12/2021)
Dr. Oleh Omelchenko (visiting from Potsdam University, Germany, September 2021)

- Objectives

The Laboratory of Statistical Mechanics and Dynamical Systems (STAT-DYN) was founded in 02/2004 as part of the former Institute of Physical Chemistry, while from 2014 belongs to the Institute of Nanoscience and Nanotechnology. Its research focuses on theoretical and numerical studies in the domains of :

1. Non-linear Dynamics & Statistical Mechanics
2. Computational Neuroscience
3. Networks of Interacting Neurons & Brain Dynamics
4. Complex Networks and their Applications
5. Reaction Diffusion Systems
6. Fractals, Multifractals and Hierarchical Systems
7. Long and Short Range Correlations in Conservative and Dissipative Systems

Our aim is the development of methods and models for understanding the emergence and evolution of mesoscopic and macroscopic spatial and temporal patterns and synchronization motifs in networks of interacting elements.A recent example comes from the domain of computational neuroscience: chimera states, which are synchronization motifs in neural networks composed by coexisting synchronous and asynchronous domains, come as a result of cooperation of a large number of interconnected neurons. A second example comes from the domain of reactive dynamics in hierarchical networks, where nonlinear interactions lead to agrregation phenomena and fractal morphologies. Other intricate spatiotemporal patterns induced by nonlinear interactions on complex systems/networks include aggregates, spirals and stripe formations, helices, fractals, long and short range correlations and can be experimentally observed in material science, physics, chemistry and biology.
Applications studied in the lab include, among others:
a) In the domain of Computational Neuroscience and Biocomplexity
Numerical simulations of brain dynamics, comparison of dynamics between healthy brains and brains with neurodegenerative disorders, recording and modelling of the complex fractal architecture of the neuron axons spanning the human brain, bioinformatics, DNA complexity and statistical analysis/modelling of cancerous biological tissues.
b) In the domain of Complex Networks and Applications
Reaction-diffusion processes on complex networks, studies of surface phenomena and aggregates with random and fractal morphology, pattern formation in nonlinear dynamics.
Regarding their complexity, natural systems may be categorized in two main classes: closed, conservative systems, and open, dissipative systems, in constant exchange with the environment. In our studies we focus:

- Away from the critical points in closed, isolated, conservative systems, where short range correlations and spatiotemporal patterns with well-defined length and time scales are studied (eg. spiral and stripe formations, helices etc.).

- At the critical points in closed conservative systems, where long range correlations (Levi distributions) are developed and information exchanges extend at long scales.
- In open, coupled dissipative systems the reduction of the phase space is studied, which leads to unexpected spatiotemporal phenomena such as the chimera states in coupled neuronal networks.

For the study of complex dynamical systems in the lab we develop a) statistical methods and algorithms describing the evolution of complex morphologies and b) modelling tools for the dynamics of pattern formation and synchronization phenomena. Statistical methods include thermodynamic approaches, entropic (extensive and non-extensive) approaches, theory of complex networks, theory of long and short range distributions, Levi distributions, theory of random walks. For the study of the mechanisms creating complex patterns, non-linear dynamical systems of hierarchical complexity are used, together with mean-field theories, exact enumeration methods, real-space renormalisation theory, theory of stochastic processes, numerical integration and kinetic Monte Carlo Methods.

- **Highlights / main scientific results**

1) We studied the influence of broken connectivity and frequency disorder in systems of coupled neuronal oscillators. Under nonlocal coupling, systems of nonlinear oscillators, such as Kuramoto, FitzHugh-Nagumo, or integrate-and-fire oscillators, demonstrate nontrivial synchronization patterns. One of these patterns is the “chimera state,” which consists of coexisting coherent and incoherent domains. In networks of biological neurons, the connectivity is not always perfect, but might be locally broken or interrupted due to pathologies, neuron degenerative disorders, or accidents. Our simulations show that destructed connectivity drastically affects synchronization, driving the coherent parts of the chimera state to cover symmetrically the region where the anomaly is located. The network synchronization decreases with the size of the destructed region as evidenced by the Kuramoto synchronization index. To the contrary, when keeping the connectivity of all nodes intact, altering the frequency in a block of oscillators drives the incoherent part of the chimera state toward the anomaly. This work is in line with recent dynamical approaches aiming to locate anomalies in the structure of brain networks, in particular when the anomalies have small, difficult-to-detect sizes.

2) We investigate the effects of reflecting connectivity in a network composed of FitzHugh–Nagumo (FHN) elements linked in a ring topology. Reflecting connectivity is inspired by the linking between theopposite hemispheres in the mammalian brain. To study synchronization phenomena and coexistence of synchronous and asynchronous domains (chimera states) under the influence of this connectivity, we use two versions of the FHN model: Version I where membrane and recovery potentials are interlinked via a rotational matrix (Omelchenko et al. PRL 110:224101, 2013), and version II where only the membrane potentials are linked and not the recovery ones (Shepelev et al., Phys. Lett. A 381:1398, 2017). In both realizations, the reflecting connectivity forces the activity to organise in two connected semirings. Our numerical results give evidence that, for FHN-I and positive (negative) coupling strength, coherent (incoherent) oscillatory regions develop and reside in the junctions between the two semirings. For the FHN-II model which supports multistability, our simulations indicate that for appropriate values of the parameters the two semirings are separated via oscillating elements. The center parts of the two semirings are composed either by elements which are frozen at the FHN fixed points (coexistence of fixed points and oscillatory states), or by coherent oscillatory elements (coexistence of coherent and incoherent nodes). Notable, here, is the case of oscillation death, which has also been reported for other oscillators coupled via one of their variables. These results can be useful for interpreting inhomogeneous and localised coordinated activity observed in the mammalian brain.

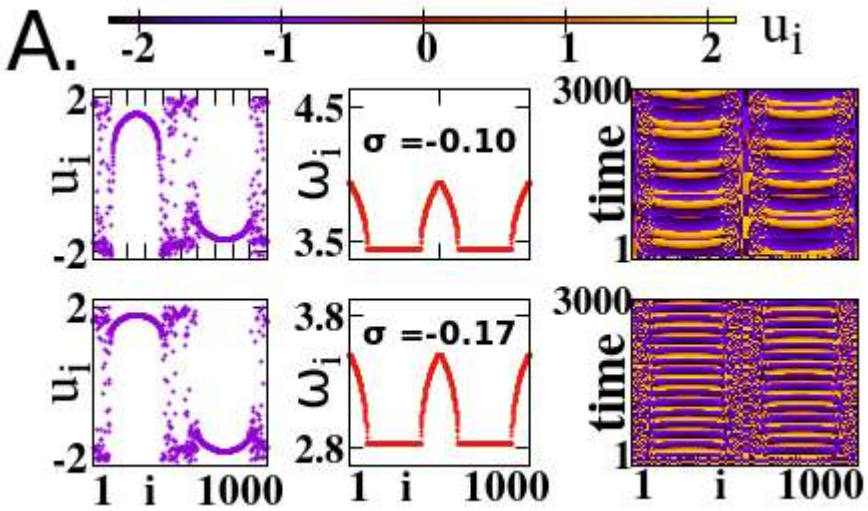


Figure 1: Chimera states of the FHN-I model, with inhibitory coupling. Typical potential profiles u_i (left panels), mean-phase velocities ω_i (middle panels) and spacetime plots (right panels) for (first row): $\sigma = -0.10$, $R = 120$ and (second row): $\sigma = -0.17$, $R = 180$. All simulations start from random initial conditions.

3) We study the synchronization properties in a network of leaky integrate-and-fire oscillators with nonlocal connectivity under probabilistic small-world rewiring. We demonstrate that the random links lead to the emergence of chimera-like states where the coherent regions are interrupted by scattered, short-lived solitaries; these are termed “shooting solitaries.” Moreover, we provide evidence that random links enhance the appearance of chimera-like states for values of the parameter space that otherwise support synchronization. This last effect is counter-intuitive because by adding random links to the synchronous state, the system locally organizes into coherent and incoherent domains.

4) The fractal dimension (FD) and the multifractal spectrum (MFS) are nonlinear quantitative measures which express the heterogeneity in the distribution of the tracer, F-18-fluorodeoxyglucose, (^{18}F-FDG), in the body of patients suffering from metastatic melanoma. Given the well-documented, high accumulation of the tracer in tumor/metastatic sites, the measures expressing the tracer distribution also express the extent of metastases in the body. As such, FD and MFS can be employed to detect the presence of melanoma and to monitor the therapeutic outcome using the PET-CT follow-up digitized scans of the patients. The FD and MFS measures of patients were evaluated before and during treatment with PD-1 inhibitors and are compared with the corresponding values of healthy controls. The MFS predictions agree with the PET Response Evaluation Criteria for Immunotherapy (PERCIMT) in 81% of the cases, while the FD agrees in 77% of all cases. Therefore, the quantitative MFS is proposed as an additional, alternative biomarker for monitoring the immunotherapy outcome in melanoma patients, after treatment with PD-1 inhibitors.

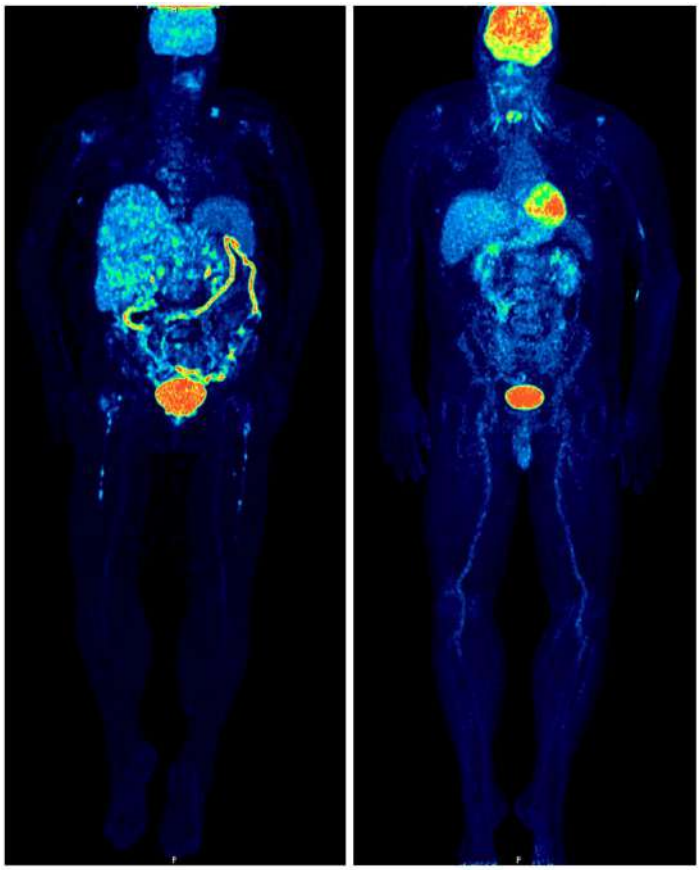


Figure 2: MIP PET-CT images for patients with metastatic melanoma: (**a**) Patient P16 at final stage with signs of colitis; (**b**) Patient P14 at interim stage without irAEs effects.

Funding
Participation to YPODOMES (2014-2020): MIS 5002772, implemented under the Action “Reinforcement of the Research and Innovation Infrastructure”, funded by Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020)

Participation to KRHPIS (2014-2020) : (MIS 5002567), implemented under the “Action for the Strategic Development on the Research and Technological Sector”, funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020)

GRNET-Greek Research and Technology Network: Computational Resources 500 000 CPU hours + 100 000 GPU hours on ARIS-HPC under project CoBrain5 (pr009012).

OUTPUT

Publications in International Journals

1. Rontogiannis, A., Provata, A., “Chimera states in FitzHugh–Nagumo networks with reflecting connectivity”. *Eur. Phys. J. B* **94,** 97 (2021).
DOI; https://doi.org/10.1140/epjb/s10051-021-00097-9

2. Tsigkri-DeSmedt, N. D., Sarlis, N. V., Provata, A., "Shooting solitaries due to small-world connectivity in leaky integrate-and-fire networks", Chaos **31**, 083129 (2021)
DOI: https://doi.org/10.1063/5.0055163

3. Kosmou, A., Sachpekidis, C., Pan, L., Matsopoulos, G.K., Hassel, J.C., Dimitrakopoulou-Strauss, A., Provata, A. “Fractal and Multifractal Analysis of PET-CT Images for Therapy Assessment of Metastatic Melanoma Patients under PD-1 Inhibitors: A Feasibility Study”. *Cancers **13***, 5170 (2021). DOI: https://doi.org/10.3390/cancers13205170

Papers in Refereed Conference Proceedings

1. Tsakalos, K. -A., Ntinas, V., Karamani, R.-E., Fyrigos, I.-A., Chatzinikolaou, T.-P., Vasileiadis, N., Dimitrakis, P., Provata, A., and Sirakoulis, G. Ch.. "Emergence of Chimera States with Re-Programmable Memristor Crossbar Arrays," *2021 IEEE International Symposium on Circuits and Systems (ISCAS),* pp. 1-5, (2021). DOI: 10.1109/ISCAS51556.2021.9401669.

Books/Chapters in Books

1. Provata, A., Antonopoulos, C.G., Vlamos, P., „Controlling the Chimera Form in the Leaky Integrate-and-Fire Model”. In: Vlamos, P. (eds) GeNeDis 2020. Advances in Experimental Medicine and Biology, vol 1338. Springer, Cham. DOI: https://doi.org/10.1007/978-3-030-78775-2_30

International Conferences Presentations (invited, oral, poster)

(please mark invited, oral, poster)

1. Provata, A., “Synchronization and information propagation in neuron networks”, 56th Summer School of NCSR “Demokritos” (online), July 12-16, Athens, Greece.
2. Provata, A., “Complex synchronization patterns in spatially correlated networks of coupled oscillators”, International Solvay Workshop in memory of Prof. Grégoire Nicolis on "Nonlinear Phenomena and Complex Systems" (invited, online), June 14 - 16, 2021, Brussels, Belgium.
3. Provata, A., “The role of fractal and reflecting connectivities in networks of FitzHugh-Nagumo oscillators”, International Conference “2021 Dynamics-Days – XL “ (invited, online), August 23 - 27, 2021, Nice, France.
4. Provata, A., “Pacemaker effects in Brain Dynamics”, International Conference “2021 Dynamics-Days – XL “ (invited, online), August 23 – 27, 2021, Nice, France.

5. Provata, A., "The role of reflecting connectivity in synchronization of neuronal oscillators", International workshop on "Nonlinear Dynamics of Oscillatory Systems (NWP-1)" (invited, online), September 19–22 2021, Nizhny Novgorod, Russia.
6. Provata, A., "The role of the network geometry in synchronization patterns", Physics Department, University of Potsdam (invited, in-person presentation), October 11 , 2021, Potsdam, German

Teaching and Training Activities

A. Provata
Methods of Computational Nonlinear Dynamics/ March 2021-June 2021/ 3 hours/week
MSc Program in "Applied Mechanics" at the National Technical University of Athens.

A. Provata
Special Topics in Complex Systems/ September 2020-February 2021/ 3 hours/week
MSc Program in "Mathematical Modelling in Modern Technology and Economics" at the National Technical University of Athens.

A. Provata
Special Topics in Complex Systems/ September 2021-February 2022/ 3 hours/week
MSc Program in "Mathematical Modelling in Modern Technology and Economics" at the National Technical University of Athens.

Master Dissertations completed in 2021

Name: Anastasia Kosmou
Dissertation Title: Fractal biomarkers describing the spread of metastases in patients with metastatic melanoma using PET/CT imaging
Research Supervisor at NCSR: Astero Provata
University where the Thesis was presented: School of Electrical and Computer Engineering,
National Technical University of Athens.

Undergraduate Theses and Internships completed in 2021

Name: Nikolaos Kartsonis (BSc thesis)
Dissertation Title: Entropic Analysis and Statistical Analysis of Nuclear Magnetic Resonance Images for the Detection of Alzheimer Disease
Research Supervisor at NCSR: Astero Provata
University where the Thesis was presented: Department of Physics, University of Athens

Name: Georgios Sotiropoulos (Internship)
Dissertation Title: Nontrivial dynamics in the control of oscillators
Research Supervisor at NCSR: Astero Provata
University where the Thesis was presented: Department of Physics, University of Athens

Name: Marios Christopoulos (Internship)
Dissertation Title: Analysis of nonlinear dynamical systems and neuronal oscillators
Research Supervisor at NCSR: Astero Provata
University where the Thesis was presented: School of Applied Mathematical and Physical Sciences, National Technical University of Athens.

Conference / Workshop Organisation

- Co-organization of the 27th PhD School-Conference on "Dynamical Systems and Complexity" (online), 19-24 July 2021, NCSR "Demokritos", Athens, Greece.

ELECTRONIC SPECTROSCOPY LABORATORY: MOLECULAR ENGINNERING OF PHOTOFUNCTIONAL SUPRAMOLECULAR NANOSYSTEMS

Project Leader: Dr George Pistolis, Researcher A

PhD Candidates: Adelajda Shahu, Vyron S. Petrakis

Masters Students: Theodora Menidiati

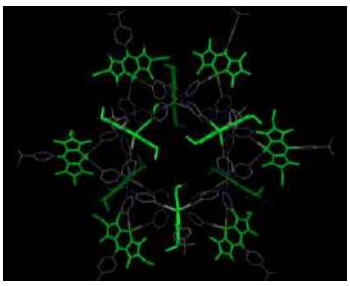
Objectives

The group focuses on the design and supramolecular synthesis – via various self-assembly protocols - of cleverly engineered self-assembled molecular networks capable of harvesting light for tuning and tailoring the properties of advanced photonic nanomaterials. More specifically, we are interested in constructing stiff and compact chromophoric arrays in a topologically well–defined way through programmable self-assembly in an effort to mimic photosynthetic light-harvesting antenna fragments and design the properties of artificial photosystems. Specific attention is being given to the formation of host-guest self-assembled multichromophoric scaffolds with remarkable rigidity and ordering. The realization of such supramolecular structures with fixed separation and orientation between peripheral and encaged chromophoric building blocks could make the structural basis for maximizing chromophore communication through donor - acceptor electronic energy / electron transfer phenomena. The main objectives of the group involve:

- Supramolecular synthesis - via coordination driven self-assembly – of artificial light-harvesting functional materials for performing specific light functions e.g., accumulation and tuning in fluorescence, Up-conversion of light, electronic energy transfer (EET), EET based sensing systems, solar energy conversion etc.
- Stability, dynamics and photoreactivity of certain guests in nanocavities.
- Photophysical and photochemical studies in organized supramolecular nanoarchitectures.
- Metallosupramolecular host nanoarchitectures for organic photovoltaics
- Color Tunability in Organic Light Emitting Diodes and Optical Lithography.
- Excited-state kinetics and thermodynamics of rotational phenomena in suitably tailored organic photosystems for molecular machinery.

Main scientific results

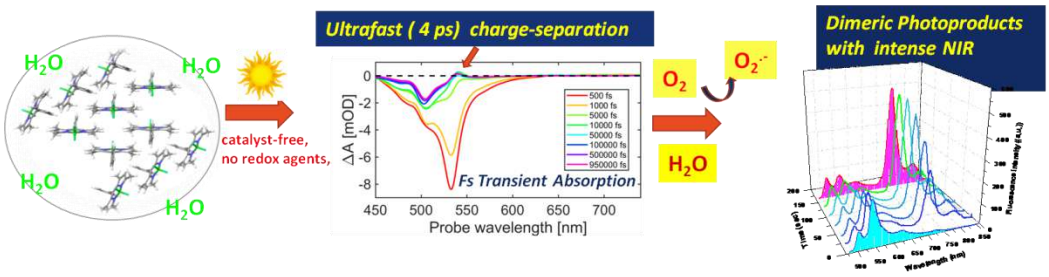
A. Macrocyclic self-assembled cages to rotaxanes consisting of functionalized BODIPY-dyes for light-harvesting and controlled energy transfer



This project is focused on the construction of 3D metallosupramolecular cages and macrocyclic cavitands and their threaded macromolecular architectures (Rotaxanes) onto a suitable polymeric chain via self-assembly with Pd(II) or Pt(II) organometallic acceptors of suitable chromophoric building blocks bearing the well known BODIPY dyes. In a first part of work we study the solvent dependent one step supramolecular synthesis - through coordination – driven self-assembly - of a 3D luminescent cage, in which the BODIPY dipoles are brought in close proximity leading to the appearance of exciton coupling. The above property is for the fist time used to record the evolution of the relaxation of such superstructures towards the most energetically favored conformation.

B **Novel green pathways on aggregation – induced photochemical synthesis**

Aggregation Induced Emission (AIE) by simple molecules and especially in the NIR region is of high novelty with a wide range of applications, spaning from OLEDs to photodynamic therapy and bio-imaging. In this new direction we inspect photophysical/photochemical aspects associated with the aggregated state of some BODIPY molecules in aqueous media towards NIR emission.



In the course of this activity we inspect photophysical/photochemical aspects associated with the aggregated state of some BODIPY molecules in aqueous solution. We observe interesting NIR emission bands due to the type of molecular packing in aggregates. We are currently working to correlate the intense NIR emission of Bodipys accompanied with a large-Stokes' shift with the type of aggregation.

Funding

1. **Project KRIPIS II**, MIS 5002567 "Development of Materials and Devices for Applications in Industry, Health, Environment and Culture", implemented under the "Action for the Strategic Development on the Research and Technological Sector", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF; start date 27/10/2017 End date 26/06/2021)

2. **Project Ereynw Kainotomw** - Industrial collaboration project for Food Packaging, 2020-2023: "Using organic LED in intelligent food packaging for quality monitoring of meat products" OLED_Lumin_FoodPack. T2ΕΔΚ-04175.

OUTPUT

Publications in International Journals

1. M. Vasilopoulou, A.R.M. Yusoff, M. Daboczi, J. Conforto, A. E. l. X. Gavim, W. J. d Silva, A. G. Macedo, A. Soultati, G. Pistolis, F. K. Schneider, Y. Dong, P. Jacoutot, G. Rotas, J. Jang, G. C. Vougioukalakis, C. L. Chochos, J-S. Kim, N. Gasparini, "*High efficiency blue organic light-emitting diodes with below-bandgap electroluminescence*" Nat. Commun. 2021, 12, 4868: https://doi.org/10.1038/s41467-021-25135-z
2. A. Verykios , G.Pistolis, L. Bizas, C. Tselios, D. Tsikritzis, S. Kennou, C. L. Chochos, D. E. Mouzakis, P. N. Skandamis A. R. M. Yusoff, L. C. Palilis, P. Argitis, M. Vasilopoulou, A. Soultati "*PEDOT:PSS:sulfonium salt composite hole injection layers for efficient organic light emitting diodes*" Organic Electronics, 2021, 93, 106155: https://doi.org/10.1016/j.orgel.2021.106155

International Conferences Presentations (invited, oral, poster)

1. Theodora Menidiati, Vyron Sotirios Petrakis, Adelajda Shahu, G. Pistolis Macrocyclic self-assembled cages to rotaxanes consisting of functionalized BODIPY-dyes for light-harvesting and controlled energy transfer. 13th Hellenic Polymer Society International Conference, University of Athens, December 10-16, 2021, Athens Greece (poster)

COMPUTATIONAL MODELING OF NANOSTRUCTURED MATERIALS

Project Leader: Dr K. Trohidou

Permanent Research Staff: Dr K. Trohidou

Post Docs: Dr M. Vasilakaki, Dr N. Ntallis

Research Collaborators (visiting): (1)Dr. G. Margaris, (2) Dr. D. Fiorani, Instituto Struttura della Materia- CNR, Rome, Italy, (3)Prof. D. Peddis University of Genova, Italy, (4) Dr. Roland Mathieu, Uppsala University (5) Dr. J. Nogués, Catalan Institute of Nanoscience and Nanotechnology, Barcelona (ICN2), Spain (6) Dr. A. Lappas, Forth, Crete, (7) Prof. Jose A. De Toro, University of Castilla-La Mancha Spain, (8) Dr. G. Papaefthymiou, Vilanova University, USA, (9) Dr. A. Juhin, CNRS, Sorbonne Université, France, (10) Prof. C. Binns, University of Castilla-La Mancha Spain, (11) Prof. J. Depeyrot, University of Brasilia, Brazil.

Objectives: Study of microscopic and macroscopic characteristics of the Magnetic NanoParticles (MNPs) and their assemblies thatl influence their thermomagnetic behavior.

Research Highlights

Magnetic Nanoparticle aggregates

Applications based on aggregates of magnetic nanoparticles (NPs) are gaining a lot of interest. However, in the nanoparticle-based materials some uses require a collective behavior, other need a more individual-like response, the conditions leading to either of these behaviors are still poorly understood. In our effort to investigate materials with enhanced magneto-thermal response:

(b) A mesoscopic scale approach and the Monte Carlo (MC) method has been employed to study the exchange bias behaviour of $MnFe_2O_4$ (soft) /maghemite (soft) and $CoFe_2O_4$ (hard) /maghemite (soft) nanoparticles (NPs) of size ~ 3nm in dense and diluted assemblies at low temperatures (Fig. 3). The analysis of our MC results clearly shows that in the powder samples the contribution to the exchange bias field (H_{ex}) and the coercivity (H_c) comes mainly from the intraparticle core/shell structure in the hard/soft sample and that the interplay between the internal characteristics and the interparticle interactions is more important in the soft/soft samples where the dipolar strength is enhanced. In the diluted frozen ferrofluid samples where interparticle exchange interactions are absent and the role of the dipolar interactions is not significant the exchange bias effects are reducing, and they come from the intra particle structure. The variation of H_{ex} and H_c with the applied cooling field well reproduces the experimental findings and sheds light on the key mechanisms of the observed magnetic behaviour. Our results demonstrate the possibility to control the magnetic behaviour of nanostructures by using properly chosen core/shell bimagnetic nanoparticles. The experimental results produced in the University of Brasilia, Brazil and the Sorbone Universite, Paris, France.

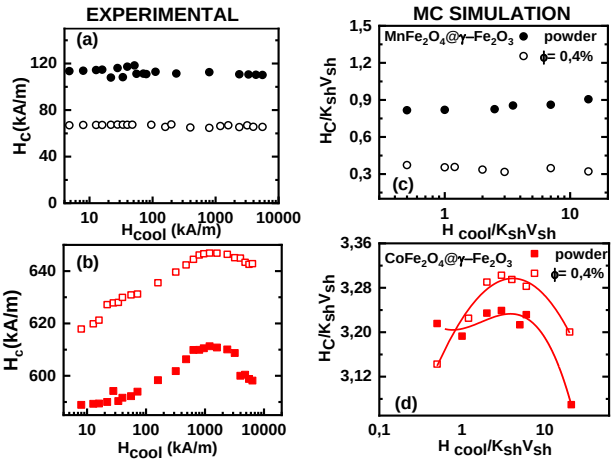


Fig. 1 Cooling field dependence of the coercivity H_c Experimental data (a,b) are compared with Monte Carlo simulations results (c,d) for frozen ferrofluid (open symbols) and powder (full symbols) of the $MnFe_2O_4$@γ-Fe_2O_3 (a, c) and $CoFe_2O_4$@γ-Fe_2O_3 (b,d) core/shell nanoparticles respectively. The solid lines are guides to the eye.

(a) We studied a series of particle assemblies with similarly strong dipolar interactions but widely varying anisotropy. The effective anisotropy (K_{ef}) is tuned through different amount of cobalt-doping in maghemite nanoparticles,

resulting in a variation of nearly an order of magnitude. All the particle compacts display collective glassy behavior (as evident from the shape of the FC/ZFC irreversibility and a significant ZFC memory effect), except the one made with the highest anisotropy particles (f_{Co} =0.23), which exhibits "marginal" behavior (Fig. 2). Thus, a threshold of volume anisotropy energy to dipole-dipole interaction energy $K_{ef}V/E_{dd} \approx 130$ to suppress collective behavior is derived, in good agreement with Monte Carlo simulations. This translates into a crossover value of ≈1.7 for the easily accessible parameter T_{MAX}(interacting)/T_{MAX}(non-interacting) (ratio of the peak temperatures of the zero-field-cooled magnetization curves of interacting and dilute particle systems), which is successfully tested against the literature to predict the individual-like/collective behavior of any given interacting particle assembly comprising relatively uniform particles. The memory curves have been also simulated.

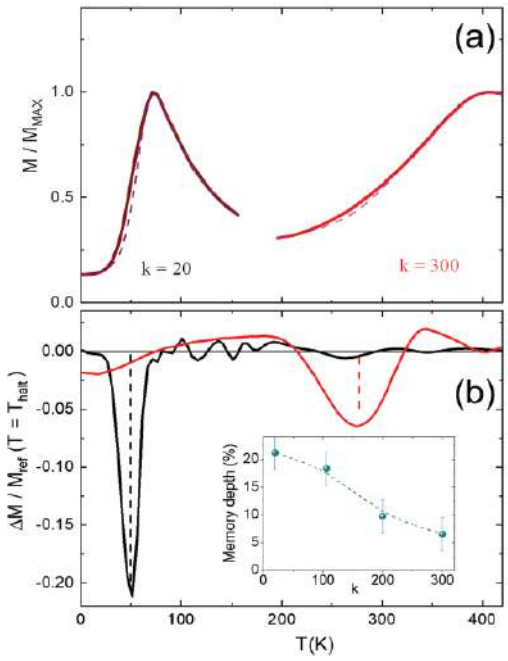


Fig. 2 o-doped samples show weaker memory than the bare maghemite ones, barely noticeable in the 23% doped sample. This trend can be ascribed to the net increase of the K_{ef} with Co-doping, in turn slowing down the individual nanoparticle relaxation and, thus, the overall collective effect. These was a collaborative work with the experimental groups of the University Castilla La Mancha and the Catalan Institute of Nanoscience and Nanotechnology in Spain, The Genova University in Italy and University of Upsalla in Sweden.

Magnetic Nanoparticles for biomedical applications

The effect of cobalt incorporation/substitution in spherical heterostructured iron oxide nanocrystals (NCs) of sub-critical size, produced by colloidal chemistry methods from the group of Dr. A Lappas (IESL-FORTH, Crete), have been numerically studied in our group.

Our simulations show that:

(1) Designed NCs, with desirable enhanced magnetic properties, have enhanced magnetic anisotropy at low content of Co and (2) the protected from oxidation rock salt core, play a key role in magnetically-mediated heating efficacies, for hyperthermia applications (Fig. 3). SAR value is raised almost 3 times for spherical defected FeO/Fe_3O_4 with 12% Co-substitution nanoparticles than that without Co-incorporation.

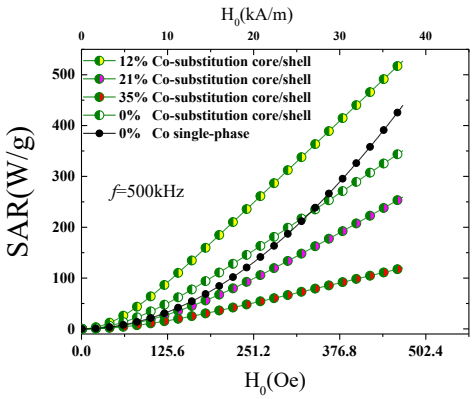


Fig. 3 Specific absorption rate (SAR) for Co-substituted heterostructured NCs (15nm), compared with 8nm (black) and 15 nm (dark green) Fe-containing only Fe-oxide NCs.

- **Funding**

MAGnetic nanoparticle based liquid **EN**ergy materials for **T**hermoelectric device **A**pplications (MAGENTA, Contract No 731976 1/1/2017-30/6/2021), European Union Horizon 2020- Research and Innovation Program (FETProactive – Boosting emerging technologies). https://www.magenta-h2020.eu

OUTPUT

Publications in International Journals

1. Antonaropoulos G., Vasilakaki M., Trohidou K. N., Iannoti V., Ausanio G., Abeykoon M., Bosin E. S., Lappas A.,Tailoring defects and nanocrystal transformation for optimal heating power in bimagnetic $Co_yFe_{1-y}O@Co_xFe_{3-x}O_4$ particles, *Nanoscale*, **Nov 2021 (Early Access)** | **14,** 382 – 401 (2022). DOI:10.1039/D1NR05172E
2. Omelyanchik A., Villa S., Vasilakaki M., Singh G., Ferretti A. M., Ponti A., Canepa F., Margaris G., Trohidou K. N., Peddis D.. Interplay between inter- and intraparticle interactions in bi-magnetic core/shell nanoparticles, *Nanoscale Adv.***3,** 6912-6924 (2021). DOI: 10.1039/d1na00312g
3. Abdolrahimi M., Vasilakaki M., Slimani S., Ntallis N., Varvaro G., Laureti S., Meneghini C., Trohidou K. N., Fiorani D. and Peddis D., Magnetism of Nanoparticles: Effect of the Organic Coating, *Nanomaterials* **11,** 1787 (2021). DOI:10.3390/nano11071787
4. Peddis D., Trohidou K. N., Vasilakaki M., Margaris G., Bellusci M., Varsano F., Hudl M., Yaacoub N., Fiorani D., Nordblad P., Mathieu R. Memory and superposition in a superspin glass, *Scientific Reports* **11,** 7743 (2021). DOI: 10.1038/s41598-021-87345-1
5. Vasilakaki M., Gementzi F., Devlin E., Yi D. K., Riduan S. N., Lee S. S., Ying J. Y., Papaefthymiou G. C., Trohidou K. N., Size effects on the magnetic behavior of γ-Fe_2O_3 core/SiO_2 shell nanoparticle assemblies. *JMMM* **522,** 167570 (2021). DOI: 10.1016/j.jmmm.2020.167570

Books/Chapters in Books

Vasilakaki M., Margaris G., Trohidou K., *Interparticle Interactions: Theory and Mesoscopic Modeling* in New Trends in Nanoparticle Magnetism , Edited by D. Peddis, S. Laureti, D. Fiorani, , Springer Series in Materials Science Springer Nature Switzerland AG, Vol. 308, Ch. 2, pp 39-63 (2021).

International Conferences Presentations (invited, oral, poster)

1. Trohidou K., Ntallis N., Vasilakaki M., Peddis D. and Fiorani D.,
Organic coating effects on the magnetic behavior of nanoparticles systems,
International Baltic Conference on Magnetism, 29/8-2/9 2021, Svetlogorsk, Russia (invited)

2. Vasilakaki M., Chikina J., Shikin V. B., Ntallis N., Peddis D., Trohidou K.,
Magnetic Nanoparticle Systems as high-performance thermoelectric materials: A Numerical study,
4th Workshop Jornada Franco-Brasileira Francisco Tourinho, 8-12 March 2021, University of Brasilia, Brazil (invited)

program 2

Magnetism and Superconductivity: Advanced Materilas and Applications

MAGNETIC THIN FILMS, METAMATERIALS AND THERMOELECTRICS

Project Leader: Dr. E. Devlin.
Permanent Research Staff: Dr V. Tzitzios, Dr. Dr. M. Gjoka, Dr. Th. Speliotis.
Other Staff: R. Tarkhanyan.
Post Docs: Dr V. Alexandrakis,Dr .A. Kaidatzis.
PhD Candidates: George Sempros, Alexandra Pilidi, Nikolaos Koutsokostas, Athanasios Tzanis.
Master Students: Zoi Plevri.
Research Collaborators (emeritus or visiting) :Dr. D. Niarchos, G. Hadjipanayis

Objectives

1. Rare-earth lean permanent magnets (zero or reduced critical material content)
2. Magnetocaloric Materials
3. Chemical Synthesis of Multi-Functional Nanomaterials
4. Magnetic – Dielectric Nanocomposites
5. Mössbauer Spectroscopy of Magnetic Compounds

Activities and Main Results

1. Non-Rare-Earth (RE) Permanent Magnets (PMs) with zero or reduced critical material

a) A series of $(Nd_{1-x}Sm_x)Fe_{11}Ti$ alloys with the $ThMn_{12}$ crystal structure have been fabricated and characterized in order to promote a strong uniaxial anisotropy in $NdFe_{11}Ti$ without the need of nitrogenation. The compounds show small changes in the lattice parameters and cell volume, as well as Curie temperature and spontaneous magnetization. The anisotropy field, however, rapidly increases with the incorporation of Sm and overcomes the effect of nitrogenation, reaching values>4 T for a 30% Sm content. These alloys are good candidates for permanent magnets, provided the correct microstructure is developed to increase coercivity.

b) In this work we extend the last research on stability of modified MnBi alloys by small partial addition of (Co, Fe, Cu) instead of substitution, and small substitution of Bi for Sn. $Mn_{1.05}Co_xBi_{1-y}Sn_y$ alloys were produced in bulk form by arc-melting high purity constituents in high purity Ar atmosphere followed by annealing at 563 K under high vacuum for 24 hours. The main phase of $Mn_{1.05}Co_xBi_{1-y}Sn_y$ alloys is the desired LTP phase (hexagonal close-packed structure S.G. No 194, $P6_3/mmc$), which was obtained in all cases. No traces of metallic Co or Mn were detected, proving their successful incorporation within the structure. Unit cell parameters were determined by Rietveld analysis to be a = 0.426 and c = 0.611 nm for $Mn_{1.05}Co_{0.02}Bi_{0.96}Sn_{0.04}$ alloy annealed at 290° C.

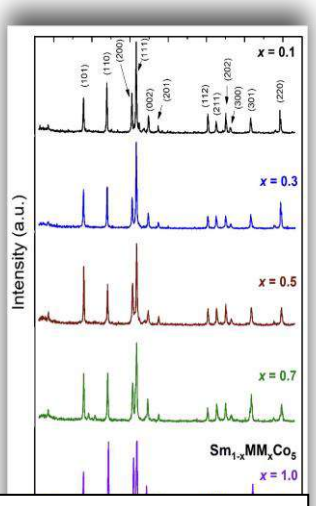


Fig.1 1 XRD patterns of MbBi alloys

The saturation magnetization and coercivity of this sample are 50.2 emu/gr and 4.9 kOe respectively.

Increasing the Co addition to 0.04 (keeping Sn =0.04), the saturation magnetization decreases to the value 42.4 emu/gr and coercivity increases to 5.44 kOe. However, the coercivity of all samples decreases after planetary ball-milling. Microstructure after ball milling was consisted of small particles of few microns and with Scanning Electron Microscopy. Agglomerates of different sizes were observed, while EDX analysis confirmed the chemical composition.

c) $SmCo_5$ magnets exhibit high anisotropy. Nevertheless, both Sm and Co need to be reduced or replaced by other elements due to cost, availability and environmental issues. Sm can be substituted by the mischmetal alloy (MM) which typically consists of cerium (Ce) and lanthanum (La). Ab initio atomistic simulations were

used to determine the energetically favorable lattice sites in the P6/mmm hexagonal structure for the replacement of Sm atoms with the ones of the MM compound in the $Sm_{1-x}MM_xCo_5$ alloy for various stoichiometry. A series of samples with nominal stoichiometry $Sm_{1-x}MM_xCo_5$ (x = 0.1 – 1.0) was prepared with Ar arc-melting and subsequent heat treatment. Annealed samples were studied with X-Ray diffraction and patterns show good crystallinity and small changes in unit cell parameters as expected. Curie temperature is reduced with increasing MM content almost linearly from 920 K (x = 0.1) to 800 K (x = 0.7) while in the case of the full-MM sample an enhanced Curie temperature is observed. Mass magnetization is not affected significantly across the series. It is deduced that the introduction of MM in $SmCo_5$ system may reduce the demand of Sm in some applications.

d) Intermetallic compounds such as $SmCo_5$ are already used as high-performance PMs. Reducing the high content of the expensive cobalt in $SmCo_5$ from low-priced transition metals can lead in a cost reduction. Our study examines by computational methods the effect of substituting cobalt atoms in the crystal structure of $SmCo_5$ by nickel atoms. The aim is to specify the structure that will be stable and at the same time will maintain high values of magnetization. A series of atomistic simulations are implemented based on Density Functional Theory calculations. Various simulations are performed by considering all possible crystallographic positions of Co and Ni atoms in a $SmCo_{5-X}Ni_X$ compound. Based on energy minimization and maximizing the magnetization we pinpointed the interesting cases. An experimental implementation based on the sample with x = 1 is presented to translate the findings from atomistic simulations to realizable bulk materials. Interestingly, it is concluded that in many cases an energetically favorable atomistic configuration does not exhibit maximum magnetization. It should be noted that for the experimentally investigated case of $SmCo_4Ni$, both the energetically favorable as well as the magnetically maximum configuration have been identified.

2. Magnetocaloric Materials

Metamagnetic off-stoichiometric Heusler alloys are actively being investigated for their great potential as magnetocaloric materials. These properties are intimately related to the nanoscale homogeneity of their magnetic properties. In our work, a spontaneous exchange bias phenomenon on a Ni-Co-Mn-Sn metamagnetic Heusler sputtered film was studied in detail. In particular, a series of DC magnetization curves measured as a function of the temperature demonstrated that the system exhibits canonical spin-glass-like features.

After careful measurements of the field-cooling and zero field-cooling curves on this system the existence of magnetic inhomogeneities is inferred, as a consequence of the competition between ferromagnetic and antiferromagnetic exchange interactions between Mn atoms. Further AC susceptibility measurements on this system demonstrated that the underlying exchange bias phenomenon can be interpreted using a magnetic clusters model based on the superferromagnetic-like interactions present in the film. Actually, we probed, for first time, the evolution of a superferromagnetic-like state using AC susceptibility measurements at different dc bias fields.

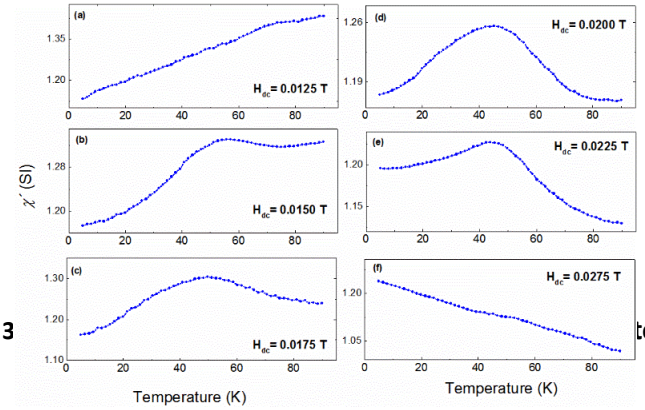
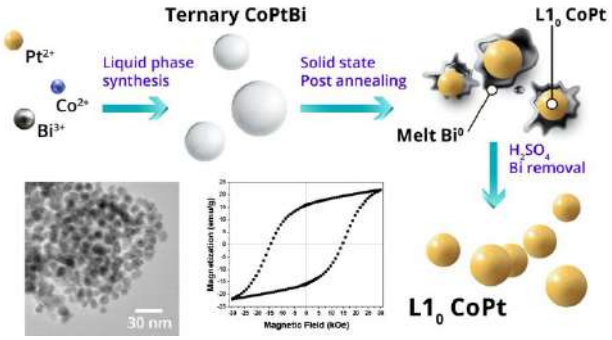


Figure 1. Evolution of the AC susceptibility peak close to 42K, after Zero Field Cooling, as a function of the DC-bias field at 178 Hz.

3 terials

Colloidal magnetic nanoparticles, with well-defined morphology and dimensionality, are of primary importance for both fundamental studies and prospective applications in many technological areas including magnetic storage devices, ferrofluids, magnetic resonance imaging, drug delivery, bio-separation, hyperthermia, sensing and catalysis. Fe and Co based colloids including core/shell morphologies and bimetallic ordered nanoalloys were synthesized by novel chemical protocols and their properties were estimated by various techniques. TEM images of Fe based colloids in the form of core/shell, yolk/shell Fe/Fe-oxide, and hollow Fe oxides, as well as the corresponded room temperature magnetic hysteresis loops are presented in the **Figure 1**.



Among the significant finding we are mentioning the $L1_0$ ordecring in the CoPt nanoalloys by the presence of bismuth and the $L1_2$ ordering in the FePt alloys by the presence of iodine. The CoPt nanoparticles even in the as-made state reveal a relatively high room-temperature coercivity, up to 1.7 kOe, while after thermal annealing at 700 °C for 1 h, the coercivity reaches ~14.6 kOe; these values are among the highest observed for CoPt nanoparticles. Furthermore, the excess bismuth phases could be removed by a simple acid treatment, leaving the structure and magnetic properties nearly unchanged for the annealed nanoparticles. The schematic representation of the overall synthetic pathway is shown in the adjacent figure. Concerning the FePt alloys the results shows that the iodine presence enhance the formation of the ordered $L1_2$ $FePt_3$ phase. These $L1_0$ and $L1_2$-structured bimetallic MPt nanoalloys have potential applications in the fields of permanent magnets as well as low Pt-based catalysts.

Nanostructured transition metal phosphides, in the last few years, have attracted increased scientific interest, due to their unique physicochemical properties. Nickel phosphide nanoparticles, with controllable crystal structures, from metal-rich tetragonal $Ni_{12}P_5$ to phosphorous-rich hexagonal Ni_2P, and hexagonal close-packed (*hcp*) Ni_2P-decorated reduced graphene oxide (r-GO) nanohybrid materials have been synthesized via a novel one-step liquid-phase approach in

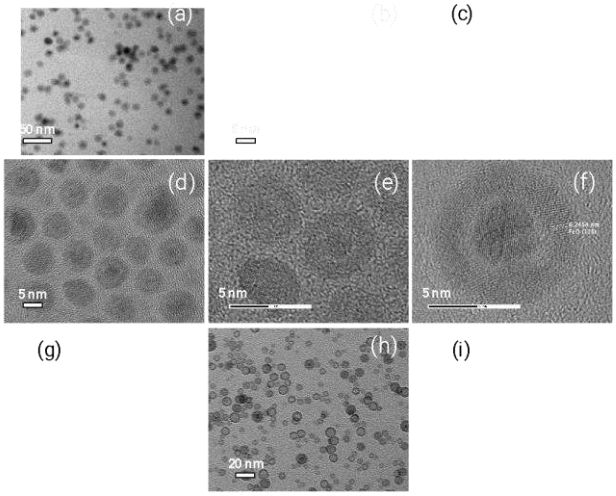


Figure 1. TEM images and room temperature magnetic hysteresis loops of Fe/Fe-

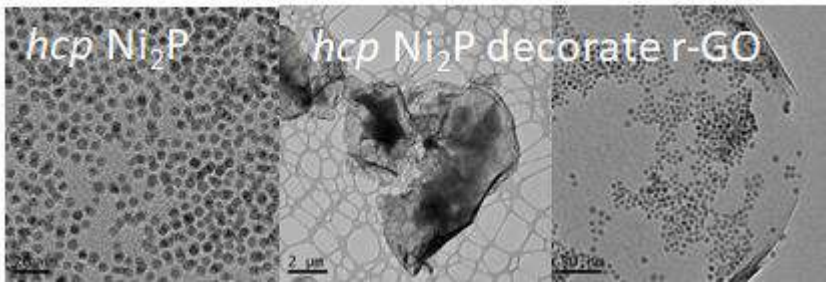


Figure 2. TEM images of Ni_2P and Ni_2P decorated r-GO.

primary−tertiary aliphatic amine mixtures. The nanoparticles are monodispersed, have a spherical shape and a controllable size in the sub-10 nm regime, and uniformly decorate the surface of r-GO, leading to the formation of Ni_2P/r-GO hybrid materials (see **Figure 2**). The materials were characterized using powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and Raman spectroscopy and catalytically evaluated for the dibenzothiophene hydro-desulfurization (HDS) reaction. The results clearly demonstrated that the role of the tertiary amine is crucial for the phosphidation process. In addition, r-GO has been proven to be ideal alternative support to the traditional inorganic ones for the immobilization of the catalytically active component, preventing significant sintering effects.

5. Mössbauer Spectroscopy of Magnetic Compounds

Mössbauer Spectroscopy (MS) has been applied to a range of materials in collaboration with many research groups from within the NCSR Demokritos and abroad. It continues to be a technique which provides a depth of information, both on the macroscale and hyperfine parameters. In the figure below we see the application of MS in the characterization of core-shell Fe_2O_3/SiO_2 magnetic nanoparticles. Blocking temperatures, and the origin of the magnetic anisotropy are investigated by magnetic measurements and Mossbauer spectroscopy. These data are compared with theoretical simulations to assess the role of weaker dipolar effects and stronger magnetic surface effects as the core size is reduced.

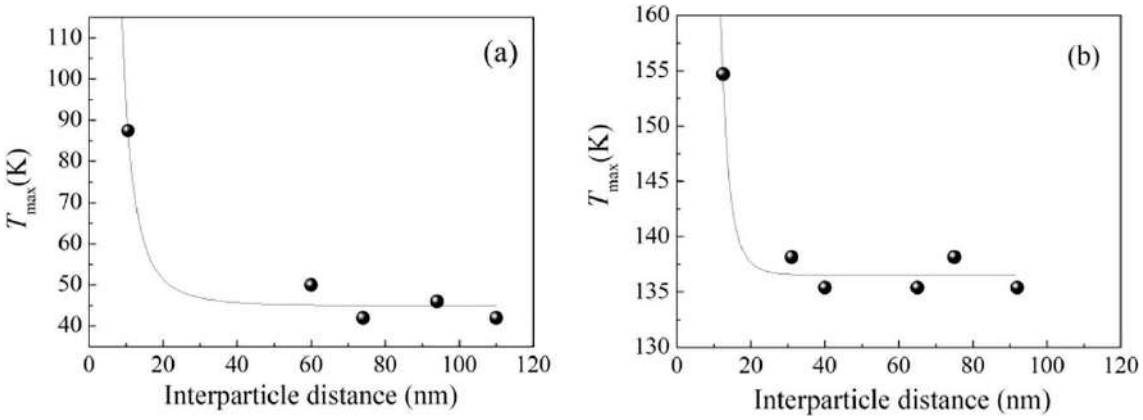


Fig. 3 : T_{max} as a function of the interparticle distance *d* for an assembly of spherical nanoparticles with γ-Fe_2O_3 core/SiO_2 shell morphology and a core diameter of *D* = 10 nm: (a) experimental data, and (b) Monte-Carlo simulation results. The solid lines are guides to the eye.

Funding

"Magnetostructural transitions and magnetocaloric effect in metamagnetic Heusler alloys"
Funding institution: Hellenic Foundation for Research and Innovation (HFRI)
Coordinator: Vasilis Alexandrakis: 200,000€

NATO Science for Peace and Security programme Multi-Year Project "Spintronic Devices for Microwave Detection and Energy Harvesting Applications" (G5792).
Duration: 1/12/2020 to 30/11/2023.
Coordinator A. Kaidatzis
Budget: 300 k€ (NCSR "Demokritos": 68k€.

Mössbauer Spectroscopy Services 2021 20,000 €

OUTPUT

Publications in International Journals

1. Cordoyiannis G., Lavrič M., Tzitzios V., Trček M., Lelidis I., Nounesis G., Kralj S., Thoen J., Kutnjak Z., Experimental advances in nanoparticle-driven stabilization of liquid-crystalline blue phases and twist-grain boundary phases. *Nanomaterials,* 11(11), 2968, (2021). DOI: https://doi.org/10.3390/nano11112968

2. Abel F.M., Basina G., Tzitzios V., Alhassan S.M., Sellmyer D.J., HadjipanayiS G.C., Ferromagnetic $L1_0$-Structured CoPt Nanoparticles for Permanent Magnets and Low Pt-Based Catalysts, *ACS Applied Nano Materials*, 4(9), 9231-9240, (2021). DOI: https://doi.org/10.1021/acsanm.1c01754
3. Deepchand V., Tzitzios V., Hadjipanayis G.C., Structural and magnetic properties of iodide-mediated chemically synthesized $L1_2$ $FePt_3$ nanoparticles, *AIP Advances*, 11(1), 015312, (2021). DOI: https://doi.org/10.1063/9.0000102
4. Basina G., Khurshid H., Tzitzios N., Hadjipanayis G., Tzitzios V., Facile Organometallic Synthesis of Fe-Based Nanomaterials by Hot Injection Reaction, *Nanomaterials,* 11(5), 1141, (2021). DOI: https://doi.org/10.3390/nano11051141
5. Tzitzios V., Pillai V., Gioti C., Katsiotis M., Karagiannis T., Gournis D., Karakassides M.A., Alhassan S., Ultrafine Ni_2P Nanoparticle-Decorated r-GO: A Novel Liquid-Phase Approach and Dibenzothiophene Hydro-desulfurization, *Industrial & Engineering Chemistry Research*, 60(11), 4300, (2021). DOI: https://doi.org/10.1021/acs.iecr.0c05544
6. Papawassiliou W., Carvalho J.P., Panopoulos N., Wahedi Y., Wadi V.K.S., Lu X., Polychronopoulou K., Lee J.B., Lee S., Kim C.Y., Kim H.J., Katsiotis M., Tzitzios V., Karagianni M., Fardis M., Papavassiliou G., Pell A.J., Crystal and electronic facet analysis of ultrafine Ni2P particles by solid-state NMR nanocrystallography, *Nature Communications*, 12(1), 4334 (2021). DOI: https://doi.org/10.1038/s41467-021-24589-5
7. Vasilakaki, M., Gemenetzi, F., Devlin, E., Yi, D.K., Riduan, S.N.,Lee, S.S., Ying, J., Papaefthymiou, G.C., Trohidou, K. N., Size effects on the magnetic behavior of γ-F**e**$_2O_3$ core/SiO_2 shell nanoparticle assemblies", (2021) *Journal of Magnetism and Magnetic Materials*, 522, art. no. 167570, DOI: 10.1016/j.jmmm.2020.167570
8. Intrinsic magnetic properties of $(Nd_{1-x}Sm_x)Fe_{11}Ti$, Niarchos D., Gjoka M., Schönhöbel A. M. Schönhöbel, Aubert A., Madugundo R., Garitaonanda J. J. S. a, Barandiaran J. M, Hadjipanayis G. *Journal of Alloys and Compounds* 864 (2021) 158097
9. Structural and magnetic properties of $SmCo_{5-X}Ni_X$ intermetallic compounds, E. Antoniou, G. Sempros, M. Gjoka, C. Sarafidis, H.M. Polatoglou, J. Kioseoglou, *Journal of Alloys and Compounds* 882 (2021) 160699.
10. e2O3 core/SiO2 shell nanoparticle assemblies, J*ournal of Magnetism and Magnetic Materials,* 52215 March 2021 Article number 167570,
11. A. E. Hafarov, S. M. Voloshko, A. Kaidatzis, and I. A. Vladymyrskyi. "Nanoscale Materials for State-of-the-Art Magnetic Memory Technologies". *Prog. Phys. Met*. 22, 175–203 (2021)
12. E. Hourdakis, A. Kaidatzis, D. Niarchos."Shadow effect photodetector with linear output voltage vs light intensity*". J.Appl. Phys*. 129, 203102 (2021)
13. Sanida, A., Stavropoulos, S.G., Speliotis, T., Psarras, G.C., "Evaluating the multifunctional performance of polymer matrix nanodielectrics incorporating magnetic nanoparticles: A comparative study", (2021) *Polymer*, 236, art. no. 124311, DOI: 10.1016/j.polymer.2021.124311
14. Choi, B.C., Jordan, K., Rudge, J., Speliotis, T., "Coherent Magnetization Dynamics in Ni80Fe20Thin Films Incorporated in Fe/Au Spintronic Terahertz Emitters", (2021) *IEEE Transactions on Magnetics*, 57 (2), art. no. 9139443, DOI: 10.1109/TMAG.2020.3009037
15. Tzanis, A., Zeibekis, M., Pilidi, A., Koutsokostas, N., Kollia, C., Speliotis, T., "Villari magnetomechanical coupling at hcp-Cobalt thin films on flexible substrates", (2021*) Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, 264, art. no. 114945, DOI: 10.1016/j.mseb.2020.114945
16. Pilidi, A., Speliotis, T., Litsardakis, G., "Magnetotransport Phenomena in Topological Insulator / Superconductor Bi2Te3/Nb Bilayer and Trilayer Thin Films", (2021) *Digests of the Intermag Conference*, 2021-April, DOI: 10.1109/INTERMAG42984.2021.9579518

Papers in Refereed Conference Proceedings

1. Antoniou E. , Sempros G. ,**Gjoka M.** , Sarafidis C. , Polatoglou H.M. , Kioseoglou J. Experimental synthesis and ab-initio theoretical calculations of $Sm_{1-x}MM_xCo_5$ (x= 0 –1, MM = mischmetal) (**paper**) Proceedings of 26th International Workshop on Rare Earth and Future Permanent Magnets and Their Applications (REPM2021) June 7-10, 2021.
2. Gjoka M., Sarafidis Ch. , Khalifa W. , Niarchos D. , Structural stability and magnetic properties of $Mn_{1.05}Co_xBi_{1-y}Sn_y$ (Co, Sn: x, y=0.02-0.04) compounds, Proceedings of 26th International Workshop on Rare Earth and Future Permanent Magnets and Their Applications (REPM2021)

Other type of publications (non-refereed Conference Proceedings, magazine, etc)

1. Gjoka M. Mischmetal-Co-Ni based Permanent Magnets (oral), 'PHYSICS AND TECHNOLOGICAL APPLICATIONS', School of Applied Mathematical and Physics Science, Polytechnic University, Athens, STUDENT INFORMATION DAY, June 14th, 2021.
2. Gjoka M. "The challenge of producing reduced rare earth permanent magnets (or free rare earths)", 56 SUMMER SCHOOL, Demokritos July 12-16-2021, (oral).

International Conferences Presentations (invited, oral, poster)

1. Antoniou E. , Sempros G. , **Gjoka M.** , Sarafidis C. , Polatoglou H.M. , Kioseoglou J.Experimental synthesis and ab-initio theoretical calculations of Sm1- xMMxCo5(x= 0 –1, MM = mischmetal)
26th International Workshop on Rare Earth and Future Permanent Magnets and Their Applications (REPM2021) Maryland (oral), June 7-10, 2021.,
2. Gjoka M., Sarafidis Ch. , Khalifa W. , Niarchos D. , Structural stability and magnetic properties of $Mn_{1.05}Co_xBi_{1-y}Sn_y$ (Co, Sn: x, y=0.02-0.04) compounds , 26th International Workshop on Rare Earth and Future Permanent Magnets and Their Applications (REPM2021), Maryland, (poster), June 7-10, 2021.

Undergraduate Theses and Internships completed in 2021

1. Name Kovani Eleni, graduate student of the Chemistry Department of the National and Kapodistrian University of Athens
   Activity Title Internship, 01/09/2021-31/10/202 ./2 months/training Research topic: Advanced materials for permanent magnets: Production of intermetallic compounds of type Sm1-xMmx (CoFeNi)5 (Mm = mischmetal) and their characterization.
   place: Laboratory of Magnetic Materials/EKEFE Demokritos
2. Name Konstandinos Stamatis, graduate student of the Chemistry Department of the Aristotle University
   Activity Title: Internship, Interval time 01/09/2021-31/10/2021/2 months/training and research: Research topic: Advanced materials for permanent magnets: Production of rare earth intermetallic compounds and their characterization.
   place: Laboratory of Magnetic Materials/EKEFE Demokritos

3. Name: George Semvrios, PhD student, Research topic: demonstration and teaching how to produce and characterize (XR, SEM-EADAX, TGM) intermetallic compounds of type Sm1-xMmx (CoFeNi)5 (Mm = mischmetal).
4. Name: Stergiou Evaggelos, Dissertation Title: Synthesis and characterization of superparamagnetic, ferromagnetic and antiferromagnetic colloids.
   Research Supervisor at NCSR: Vasileios Tzitzios
   University where the Thesis was presented: University of Ioannina

Patents - Technology transfer
Marios S Katsiotis, Vasileios Tzitzios, Saeed Alhassan, High-yield synthesis of nanozeolite-Y crystals of controllable particle size at low temperature, US20210046463A1 (2021).

SOLID STATE NUCLEAR MAGNETIC RESONANCE (ssNMR) LABORATORY

Project Leader: Dr. G. Papavassiliou

Permanent Research Staff: Dr. M. Fardis

Other Staff (scientific, appointed research fellows, administrative, technical, auxiliary, etc.):

Post Docs: Dr. M. Karagianni, Dr. N. Panopoulos

PhD Candidates: A. Anastasiou, S. Orfanidis

Master Students: S. Katopodis

Research Collaborators (emeritus or visiting): Dr. F. Milia, Dr. L. Gkoura, Dr. G. Tsorbatzoglou

- Objectives

- Development and implementation of novel broadband solid-state NMR methods.
- NMR studies of Topological Quantum Materials and the fundamental physics underlying topological quantum computation combining ssNMR crystallography with advanced DFT calculations.
- Solid-state NMR nanocrystallography studies of Transition Metal based Nanocatalysts combined with HRTEM and advanced DFT calculations.
- NMR studies of nanofluidic processes extending from water transport in biomimetic nanochannels to Ionic Liquids confined in silica and carbon nanoporous systems for energy storage applications.
- Studies of gelation and diffusion-controlled physicochemical processes in e.g. hydrogels, hydrating cement slurries and rock-pore structure analysis, using advanced two-dimensional (2D) ^{1}H ssNMR relaxation and diffusion methods

- Highlights / main scientific results

- **NMR guided facet engineering of Transition Metal based Nanocatalysts**

Unraveling the surface crystal and electronic structure of nanosized catalysts is crucial for optimizing the morphology of the nanoparticle terminating surfaces (facet engineering) to improve catalytic performance in important catalytic processes, such as Oxygen and Hydrogen Evolution Reactions. At the nanoscale, however, even state-of-the-art experimental methods such as ARPES, HRTEM, or XRD lack satisfactory resolution and become impractical.

Implementation of NMR nanocrystallography methods (combining NMR with DFT calculations) to obtain at atomic scale resolution the structural and electronic properties of nanosized Transition Metal -based Nanocatalysts is one of the major research topics of the group in recent years.

^{31}P NMR nanocrystallography combined with HRTEM and XRD crystal structure analysis was successfully employed **for the first time** to identify the individual crystal facets and the electron energy band structure of terminating surfaces of Ni_2P nanoparticles. Figure 1 shows HRTEM of a Ni_2P nanoparticle together with DFT calculated TEM, as well as experimental (black line) and theoretical (red line) NMR spectra. Work was published in *Nature Communications* **12**, 4334 (2021) and has been featured in Editors' Highlights webpage in section "Materials science and chemistry" http://www.nature.com/collections/eecgdgijhh). The method which is applicable in a great variety of Transition Metal based nanocatalysts is amiming towards NMR guided facet engineering of nanocatalysts.

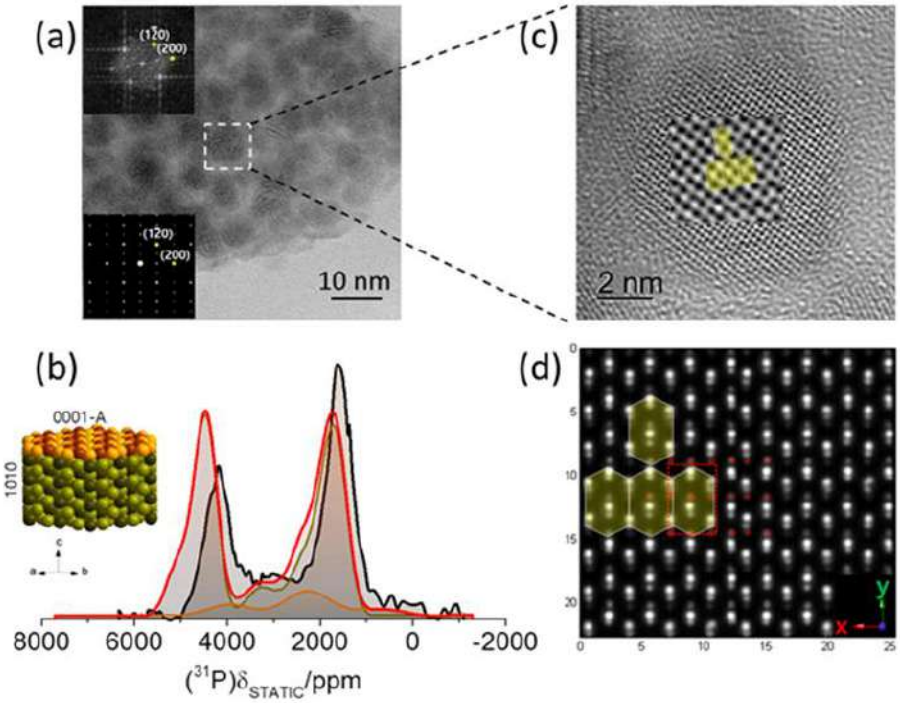


Figure 1. Papawassiliou, W., et al. (2021), *Nature Communications* **12**, 4334; Featured in Nature Communications Editors' Highlights webpage

- **NMR studies of nanosized topological Insulators (ultrathin Bi_2Se_3 and Bi_2Te_3 nanoplateletes).**

Topological Quantum Materials (TQMs) such as Topological Insulators (TI) and Dirac and Weyl semi-metals are a major research activity of our group over the last years. TQMs attract great scientific and technological interest owing to the exotic properties deriving from the distinctive topology of their electronic energy bands and to a plethora of applications in cutting-edge technologies. The efforts of our group are focused on experimentally elucidating the intriguing topological electronic properties by combining advanced Nuclear Magnetic Resonance (NMR) methods with Density Functional Theory (DFT) calculations and ultra-high resolution Transmission Electron Microscopy (HRTEM), to monitor topological electrons and their low energy excitations, i.e. Dirac and Weyl fermions.

In our previous work (**Nature Communications** | (2020) 11:1285 | https://doi.org/10.1038/s41467-020-14838-4) we have succeeded for the first time to detect topological electrons on the surface of a nanostructured topological insulator (Bi_2Te_3). In the last year, implementation of broadband High Resolution Static and Magic Angle Spinning (MAS) ^{125}Te NMR methods on the WTe_2 Weyl semimetal allowed to disciminate Weyl fermions, which are impossible to be detected with ARPES, as the relevant energy bands disperse in an extemely narrow region of the k-space. Figure 2 shows experimental and DFT calculated 1-D ^{125}Te MAS (black lines) and static (red line) NMR spectra of WTe_2 in the T_d phase (293K) together with HRTEM images where the change of the (002)/(202)/(200) intersection angle from 90° to 87.3° marks the $T_d \rightarrow 1T'$ phase transition.

This work is conducted in collaboration with the Stockholm University (Sweden), the University of Lyon (France), the Korea Basic Science Institute (S. Korea), and the Khalifa university of Science and Technology at Abu Dhabi (UAE) and was published in *arXiv:2110.01300* [cond-mat.mtrl-sci] (2021) (*see publ. no 5 under: Publications in International Journals*)

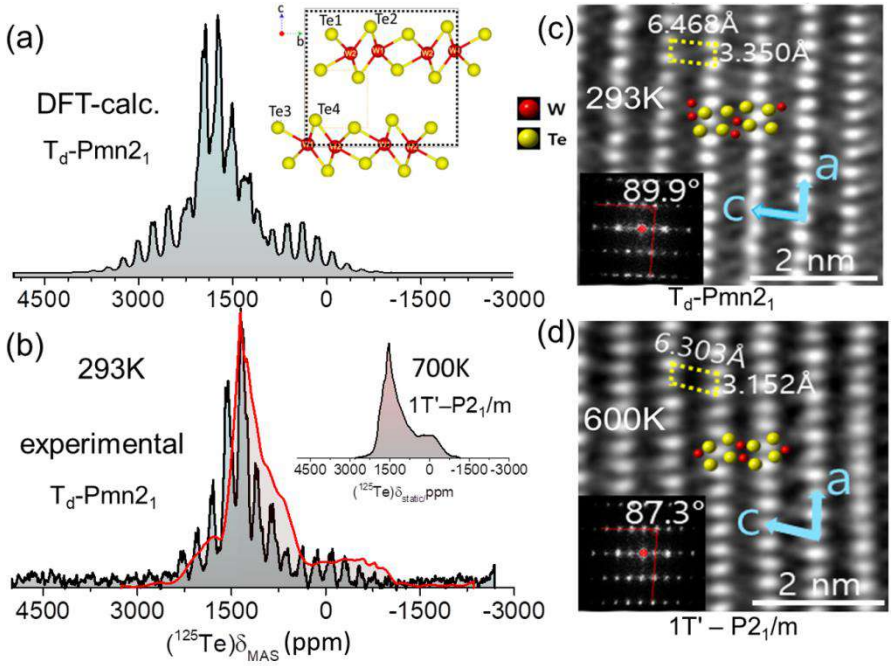
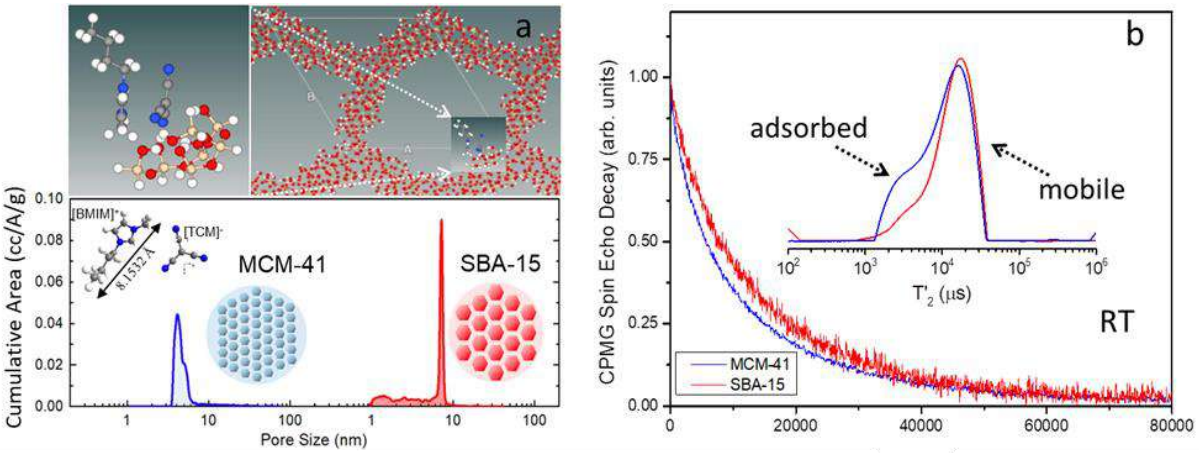


Figure 2. Papawassiliou, W., et al., *arXiv:2110.01300* [cond-mat.mtrl-sci] (2021)

- **NMR studies of single and multiphase fluids in restricted geometries.**

Understanding the basic mechanisms of fluid transport and the complex dynamics of guest liquid molecules confined in nanoporous systems is of great interdisciplinary interest for a wide range of important technological applications and biological processes (such as the development of high-readout single-molecule detectors, water purification and the regulation of cellular traffic of important biological solutes). In a previous work (Biomicrofluidics **14**, 034114 (2020); https://doi.org/10.1063/5.0005398), by implementing a fast and scalable method combining diffusion - relaxation ssNMR experiments with advanced inversion algorithms developed for NMR relaxation data analysis, we were able to disentangle experimentally distinct water groups with characteristic diffusion and relaxation profiles and confirmed the predictions of molecular dynamics simulations visualizing a stratified arrangement of water inside the nanotube.

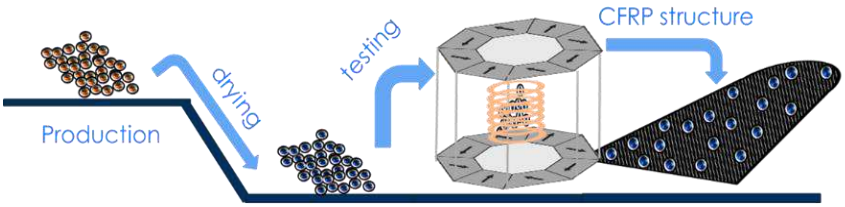


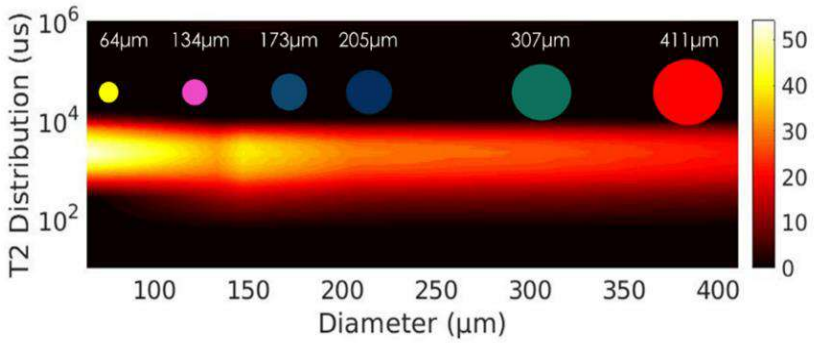
In the last year, ^{1}H NMR diffusion experiments were conducted to monitor the motion of ionic liquids in nanocarbon and nanosilica channels. To this aim we developed an elaborate time-resolved diffusion NMR method, in which diffusion is recorded in different relaxation windows thus allowing resolving at a molecular level multiple modes of diffusion in complex multiphasic nanofluidic processes (*preprint:* https://www.researchsquare.com/article/rs-1052911/v1).

- **NMR studies of self-healing polymeric composites materials (for the aerospace technology)**

Self-healing materials are a cutting-edge technology that attracts considerable scientific and industrial interest owing to their ability to automatically repair large-scale matrix damages in polymer composites. Over the last years, systematic ^{1}H ssNMR relaxation and diffusion studies have been conducted to monitor the polymerization process in microcapsule-based self-healing materials.

A miniaturized portable NMR spectrometer has been developed for the study of gelation and diffusion-controlled physicochemical processes in a broad range of systems ranging from hydrogels, to hydrating cement slurries and rock-pore structure analysis.





- **Funding**

1. *CIRA-2020-051: "Carbon nanotubes for water transport".*
Partner (NCSRD) Principal Investigator: Georgios Papavassiliou.
The project is a Competitive Internal Research Award (CIRA) funded by the Khalifa University (United Arab Emirates).
INN budget: 276,000 AED.

2. *CIRA-2018-007: "Morphology Engineered Nanocatalysts for Sulfur Hydrogenation"*.
Partner (NCSRD) Principal Investigator: Georgios Papavassiliou.
The project is a Competitive Internal Research Award (CIRA) funded by the Khalifa University (United Arab Emirates).
INN budget: 250,360 AED.

3. *MIS 5047810: "Study of the Peculiar Water Flow in Hydrophobic Carbon Nanotubes using 2D - NMR Spectroscopy"* funded by the Operational Programme «Human Resources Development, Education and Lifelong Learning 2014-2020» and co-financed by Greece and the European Union (European Social Fund- ESF). Budget: 41,542 €.

OUTPUT

Publications in International Journals

1. Papawassiliou, W., Carvalho, J.P., Panopoulos, N., Alwahedi, Y., Wadi V. K. S., Lu X., Polychronopoulou, K., Lee, J-B., Lee, S-G., Kim C-Y., Hae Jin Kim, H-J., Katsiotis, M., Tzitzios, V., Karagianni, M., Fardis, M., Papavassiliou, G., and Pell, A.J. (2021) Crystal and electronic facet analysis of ultrafine Ni_2P particles by solid-state NMR nanocrystallography, *Nature Communications* 12, 4334; https://doi.org/10.1038/s41467-021-24589-5. - Featured in Nature Communications Editors' Highlights webpage.
2. Giousis, T., Potsi, G., Kouloumpis, A., Spyrou, K., Georgantas, Y., Chalmpes, N., Dimos, K., Antoniou, M-K., Papavassiliou, G., Bourlinos, A.B., Kim, H-J., Wadi, V.K.S., Alhassan, S., Ahmadi, M., Kooi, B.J., Blake, G., Balazs,

D.M., Loi, M.A., Gournis, D., Rudolf, P. (2021) Synthesis of 2D Germanane (GeH): a New, Fast, and Facile Approach, *Angew. Chem. Int. Ed.* **60**, 360–365, https://doi.org/10.1002/anie.202010404
3. Lu, X., Baker, M.A., Anjum, D.H., Papawassiliou, W., Pell, A.J., Fardis, M., Papavassiliou, G., Hinder, S.J., Gaber, S.A.A., Gaber, D.A.A., Al Wahedi, Y., Polychronopoulou, K. (2021) Nickel Phosphide Nanoparticles for Selective Hydrogenation of SO_2 to H_2S, *ACS Appl. Nano Mater.* **4**, 6568–6582, https://doi.org/10.1021/acsanm.1c00044
4. Lu, X., Baker, M.A., Anjum, D.H., Basina, G., Hinder, S.J., Papawassiliou, W., Pell, A.J., Karagianni, M., Papavassiliou, G., Shetty, D., Gaber, D., Gaber, S., Al Wahedi, Y., Polychronopoulou, K. (2021) Ni_2P Nanoparticles Embedded in Mesoporous SiO_2 for Catalytic Hydrogenation of SO_2 to Elemental S", *ACS Appl. Nano Mater.* **4,** 5665–5676, https://doi.org/10.1021/acsanm.0c02853
5. W. Papawassiliou, J. P. Carvalho, H. J. Kim, C-Y. Kim, S. J. Yoo, J. B. Lee, S. Alhassan, S. Orfanides, V. Psycharis, M. Karagianni, M. Fardis, G. Papavassiliou, A. J. Pell. (2021). Detection of Weyl Fermions and the Metal to Weyl-Semimetal phase transition in WTe_2 via broadband High Resolution NMR. arXiv:2110.01300 [cond-mat.mtrl-sci], https://arxiv.org/abs/2110.01300

Papers in Refereed Conference Proceedings

1. Georgios Papavassiliou, Nikolaos Panopoulos, Michael Fardis, Jamal Hassan, Saeed Alhassan, Hae Jin Kim, "Tracing the "invisible" Polarons in Ferromagnetic Manganites. A combined NMR and HRTEM study in the temperature range 3.2–1000 K". *in Proceedings of* 18th International School-Conference *MAGNETIC RESONANCE AND ITS APPLICATIONS SPINUS,* p.p.59-60 29 March – 2 April 2021, Saint-Petersburg, Russia.
2. L. Gkoura, M. Karagianni, M. Fardis, J. Hassan and G. Papavassiliou, "2D NMR diffusion-relaxation (DT2) studies of water in hydrophobic carbon nanotubes". *in Proceedings of* 18th International School-Conference *MAGNETIC RESONANCE AND ITS APPLICATIONS SPINUS,* p.p.100-101 29 March – 2 April 2021, Saint-Petersburg, Russia.
3. W. Papawassiliou, J. P. Carvalho, M. Fardis, H. J. Kim, G. Papavassiliou, A. J. Pell, "Broadband high resolution NMR studies of Topological Matter". *in Proceedings of* 18th International School-Conference *MAGNETIC RESONANCE AND ITS APPLICATIONS SPINUS,* p.p.156-157 29 March – 2 April 2021, Saint-Petersburg, Russia.

International Conferences Presentations (invited, oral, poster)

1. M. Karagianni, L. Gkoura, M.Fardis and G. Papavassiliou, "The Peculiar Size and Temperature Dependence of Water Diffusion in Carbon Nanotubes studied with 2D NMR Diffusion–Relaxation D–T_{2eff} Spectroscopy", *The 62nd ENC Experimental Nuclear Magnetic Resonance Conference,* March 29 – 31, 2021 Virtual (**poster**)
2. S. Orfanidis, M. Raimondo, L. Guadagno , A.S. Paipetis , M. Fardis , G. Papavasilliou, "Thermal profiling of self-healing process simulating flight conditions. A solid-state NMR study", *11th International Conference of Innovation in Aviation & Space*, 01-03/09/2021 (**poster**).
3. S. Orfanidis, M. Raimondo, L. Guadagno , A.S. Paipetis , M. Fardis , G. Papavasilliou, "Solid-state NMR as an Innovative Non-Destructive Evaluation methodology in composite self-healing systems for aerospace engineering applications", *17th EUROMAR*, July 5 – 8, 2021, Portoroz, Slovenia (**poster**).

Teaching and Training Activities

G. Papavassiliou

Solid State NMR Spectroscopy (theory & experimental exercises). / Interdepartmental Postgraduate Course in Materials Chemistry and Technology / Spring 2021 / University of Ioannina

M. Fardis

Nuclear Magnetic Resonance / Laboratory Course of the undergraduate course "Methods of Materials Characterization", co-organized by the School of Applied Mathematical and Physical Sciences of National Technical University of Athens and NCSR Demokritos / Spring 2021 / NMR lab INN, NCSR Demokritos.

Undergraduate Theses and Internships completed in 2021

Name: Charitini Kontopidi
INTERNSHIP 2 months fall 2021
Dissertation Title
Research Supervisor at NCSR
University where the Thesis was presented

SUPERCONDUCTIVITY AND MAGNETIC OXIDES

Project Leader: Michael Pissas

PhD Candidates: Varouti, V. Panagopoulos

Master Students: T. Poulis

Diploma thesis students: Dimitriadis Anastasis

Research Collaborators: I. Sanakis, V. Psycharis, C. Raptopoulou, C. Christides, D. Stamopoulos D. Niarchos and E. Devlin.

Objectives

Our aim is to conduct high quality research in selected topics of superconductivity, magnetism, molecular magnetic materials, magnetoelectric materials, strongly correlated electronic systems, transition metal oxides, hybrid systems, application of magnetism in non-destructive evaluation, magnetic materials for medical applications and lithium oxides for batteries and microwave applications.

Activities and Main Results

(1) Magnetostructural characterization of α-$LiFeO_2$

The objective of this activity is the study of the magnetostructural physical properties of α-LiFeO2 compound which can be potentially used as cathodes in Li ion batteries. Fig. 1 shows representative TEM results measured in STEM microscopy of INN. The diffraction data are consistent with the F m-3m space group (NaCl crystal structure) a=4.16 A. Panel a of this figure displays a characteristic diffuse intensity with a nearly sinusoidal variation along the horizontal direction. The other two panels depict real space TEM images. Atomic planes (middle panel) and atomic columns (right panel of Fig. 1) can be seen. The disordered arrangement of the bright spots in the right panel is since Li atoms scatter the electrons lower than iron.

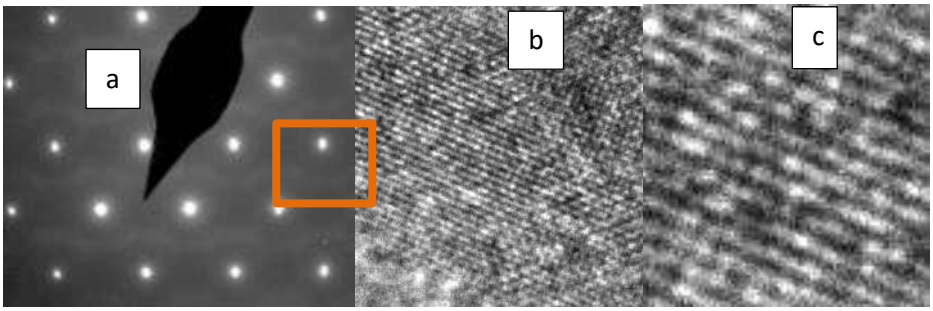


Figure 1 (a) Electron diffraction pattern taken from α-$LiFeO_2$. (b) and (c) TEM images.

Figure 2 depicts Mossbauer spectra (MS) of α-$LiFeO_2$ compound measured at T=290 K, 60K, 40 K, 20K and 5 K. The upper panel of Fig. 2 shows the MS (experimentally and theoretically calculated), fitted with the Le Caer-Dubois method. The lower panel of Fig. 2 shows the distribution $p(\Delta E_Q)$ of the quadrupole splitting parameter (ΔE_Q), extracted from the fitting procedure with the Le Caer-Dubois method. The middle part of Fig. 2 depicts the MS fitted with a two doublet model. The paramagnetic spectra of α-$LiFeO_2$ consist of two, relatively broad, absorption lines, in comparison to the ideal state of our spectrometer (Γ=0.24 mm/s). An initial attempt to fit the spectra with only one doublet was unsuccessful. By adopting a second doublet the fitting significantly improved. The estimated hyperfine parameters for the two site model are: $\Gamma_1/2$=0.181 mm/s, δ_1=0.377(1) mm/s, ε=0.238(1) mm/s, $\Gamma_2/2$=0.168(2) mm/s, δ_2=0.377(1) mm/s, ε_2=0.436 mm/s, and relative spectra area A_1:A_2=63:37. The non-zero value of ΔE_Q and more significantly the existence of at least two doublets is an unexpected result, because α-$LiFeO_2$ compound crystalizes in the cubic crystallographic system with iron occupying only one site. The observed behavior can be explained taking into account the high disorder of the iron site due to the presence of Li ions (both Li and Fe ions occupy (50:50) the same site). Below T=80 K the spectra broaden and for T<25 K they display a well resolved six-line spectrum. Similarly with the paramagnetic spectra the MS at T=5 K can be fitted with two sextets. A possible interpretation of the MS

can be the existence of short-range ordering. A reasonable model could be the existence of crystallographic planes of (111) family of planes, where some of them are rich in iron whereas the remaining ones are rich in Li. Despite this kind of clustering the average stoichiometry of Li and Fe is 1:1.

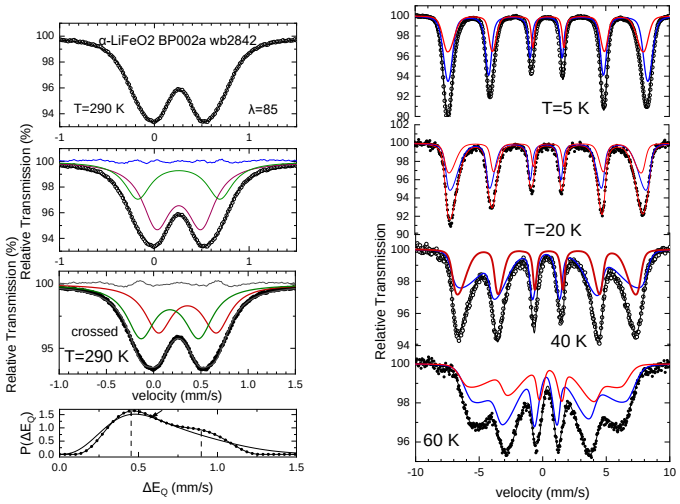


Figure 2. (a) Mossbauer spectra of α-$LiFeO_2$ at T=290 K. The upper panel shows the experimental and the theoretically calculated spectra using the methodology of Le Caer. The obtained distribution of the quadrupole splitting is shown in the lower panel. The other two panels depict the analysis of the MS using a model with two components (two doublets). The model with the two nested doublets better reproduces the experimental data. The hyperfine parameters, for both sites, indicate Fe(III). (b) (Right panels). Magnetically split MS of α-$LiFeO_2$ compound measured at T=5K, 20, 40 and 60 K.

(2) Vortex matter properties of $Ba_{1-x}K_xFe_2As_2$

As a continuation of our research on the properties of vortex matter in type II superconductors, we have studied the magnetic properties in a single crystal of the $Ba_{1-x}K_xFe_2As_2$ compound, in the region where the peak effect at the critical current disappears. This crystal was of better quality (Tc=37.2 K ΔTc=0.2 K) than the quality of crystals we have studied in the past for this compound. Fig. 3 (left panel) depicts a representative set of magnetic ac-susceptibility measurements as a function of temperature, for several dc magnetic fields Hdc=0, 0.5, 1.5, 2.5, 4, 5, 7.5, 10, 30, 40, 50 60, 70, 80 and 90 kOe. Presented are measurements for Hac=1 Oe and 10 Oe. The ac and the dc-fields are applied parallel to the crystal c-axis. The right panel of Fig. 4 depicts the vortex matter phase diagram of $Ba_{1-x}K_xFe_2As_2$ superconductor in linear and semi-logarithmic scales. Shown are data for angles, between crystal c-axis and external magnetic field: Θ=0, 60°,80°, and 90°.

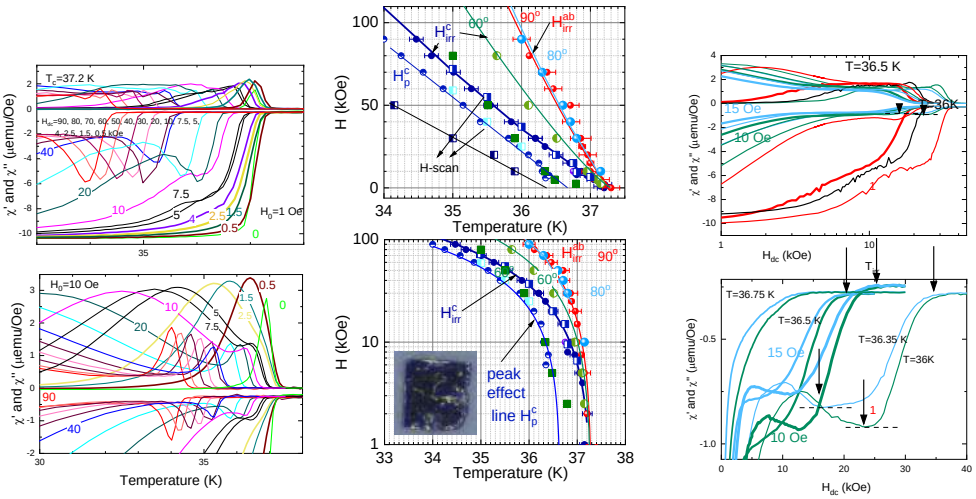


Figure 3 (Left panel) A representative set of ac-susceptibility measurements as a function of temperature for several dc magnetic fields. The ac and the dc fields are applied parallel to the crystal c-axis. (Middle panel) Vortex matter phase diagram of $Ba_{1-x}K_xFe_2As_2$ superconductor. Shown are data for angles between crystal c-axis and external magnetic field Θ =0, 60°, 80°, and 90°. (Right panel) Real and imaginary parts of the magnetic ac-susceptibility as a function of dc-magnetic field.

The data were collected at constant temperatures T=36 K, 36.5 K 36.5 and 36.75 K. The local minimum curves (arises from a peak of critical current as function of the dc-magnetic field) near the diamagnetic onset of the χ'(Hdc) disappears for T>35.5 K. The peak-effect was observed in all the studied angles Θ. Also, for this crystal, the peak effect is not observed for Hdc<5 kOe. The irreversibility line and the peak effect line can be described by power low relations. If we suppose that the irreversibility lines coincide with the second critical field the anisotropy of this crystal is about 2. Fig. 3 (right panel) displays measurements, at constant temperature, of the magnetic ac-susceptibility as function of the dc-magnetic field. It is obvious that the local minimum in the real part of ac-susceptibility bellow the diamagnetic onset is absent in the measurements for T=36.75 K. The estimated vortex matter phase diagram illustrated in Fig 3 (middle panel). The similarity of the vortex matter phase diagrams and the disappearance of the peak effect below (T,H)-point, observed in crystals with different quality is an interesting finding. A possible explanation of the disappearance of the peak effect above a certain temperature, below and near the zero-field critical-temperature, can be given supposing that inside the crystal exist nanoregions with slightly lower critical temperature (slightly different Ba/K stoichiometry) in comparison with the remaining part of the crystal. The existence of those nanoregions is not detected in zero dc-magnetic field measurement because the largest part of the crystal produces superconducting currents which magnetically screen all the crystal. Only when the vortex-lattice spacing becomes comparable with the average distance of the nanoregions they are acting collectively as pinning centers.

OUTPUT

Publications in International Journals

1. **Synthesis and characterization of modified magnetic nanoparticles as theranostic agents: *in vitro* safety assessment in healthy cells** Danai Prokopiou, Michael Pissas, Gabriella Fibbic, Francesca Margheri, Beata Kalska-Szostko, Giorgos Papanastasiou, Maurits Jansen, Jansen Wang, Anna Laurenzana, Eleni Efthimiadou, *Toxicology in Vitro*, **72,** 105094, (2021) https://doi.org/10.1016/j.tiv.2021.105094
2. **A single-chain magnet based on bis(end-on azido/alkoxo)-bridged linear [Mn(III)2Mn(II)] repeating units,** Georgopoulou A., Pissas M., Psycharis V., Sanakis Y., Raptopoulou C., *Polyhedron*, **206,** 115334, (2021) https://doi.org/10.1016/j.poly.2021.115334
3. **Synthesis, crystal structures, magnetic and magnetocaloric studies of heterometallic enneanuclear {Cu7Gd2} complexes**, Dermitzaki D., Pissas M., Psycharis V., Sanakis Y., Raptopoulou C., *Polyhedron*, 195, 114960, (2021), https://doi.org/10.1016/j.poly.2020.114960
4. **Di-2-pyridyl ketone-based ligands as evergreen "trees" in the "forest" of manganese chemistry: Mononuclear Mn(III) complexes from the use of MnF3,** Stoumpos C., Danelli P., Zahariou G., Pissas M., Psycharis V. , Raptopoulou C., Sanakis Y. Perlepes S., **207,** *Polyhedron,* 115350 (2021) https://doi.org/10.1016/j.poly.2021.115350

Conference presentations

1. **Mössbauer and crystallographic studies of disordered $LiFe_{5-x}Mn_xO_8$ ferrite**, XXXV Panhellenic Conference on Solid State Physics and Materials Science, Congress Center, NCSR "Demokritos", 26-29 September 2021, Athens, Greece, V. Panagopoulos, V. Psycharis, E. Devlin, Y. Sanakis, and M. Pissas
2. **Nanosized phase separation in $LiFe_{5-x}Mn_xO_8$**, Proceedings of the 10th International Conference of the Hellenic Crystallographic Association (HeCrA), NCSR "Demokritos", Athens, Greece, 15-17 October 2021, Vassilis Panagopoulos, Vassilis Psycharis, Yiannis Sanakis, and Michael Pissas.

Teaching and Training Activities

M. Pissas: One semester course in graduate "Electromagnetism", 1/10/2020-21-01/2021, of the graduate program "Physics and technological applications", co-organized by the School of Applied Mathematical and Physical Sciences of National Technical University of Athens and NCSR Demokritos.

M. Pissas: Participation in the graduate course “Experimental methods” of the graduate program “Physics and technological applications”, co-organized by the School of Applied Mathematical and Physical Sciences of National Technical University of Athens and NCSR Demokritos. Michael Pissas is responsible for the experimental lesson Magnetic measurements.

M. Pissas: Participation in the undergraduate course “Methods of material characterization” (School of Applied Mathematical and Physical Sciences of National Technical University of Athens and IMS Demokritos). Michael Pissas is responsible for the experimental lesson Magnetic measurements.

Administrative positions

M. Pissas, Member of the executive committee of graduate program “Physics and technological applications”, co-organized by the School of Applied Mathematical and Physical Sciences of National Technical University of Athens and NCSR Demokritos. For the academic 2020-21.

Masters diploma thesis

Poulis Thomas
“Theoretical simulation of the electromagnetic field penetration in type II superconductors” Presented at The School of Applied Mathematical and Physics Science, NTUA, Research Supervisor at NCSR: Michael Pissas, completed 2021.

Degree Diploma projects

Dimitriadis Anastasis
“Electromagnetic characterization of small scale wind turbine with double side topology”, Department of Physics, University of Athens, Supervisor M. Pissas,. completed in (2021)

Practical Courses

1) **Magafas Ioannis-Polichronakos**
   Simulation of the flux lines penetration in type II superconductor (Cambpell model)”, School of Applied Mathematical and Physical Sciences of National Technical University of Athens, Supervisor M. Pissas (completed 2021)
2) **Stergiou Vasiliki,**
   Simulation end experimental study of the levitation of a type II superconductor above a permanent magnet, School of Applied Mathematical and Physical Sciences of National Technical University of Athens, Supervisor M. Pissas (completed 2021)

MOLECULAR MAGNETIC AND BIOINORGANIC SPECTROSCOPY

Project Leader: Dr Yiannis Sanakis

Permanent Research Staff: Dr Nikolaos Ioannidis

Other Staff: Michael Tzifas

Post Docs: Dr Georgia Zahariou, Dr Maria Chrysina

Research Collaborators: E. Devlin, M. Pissas, C. Raptopoulou, V. Psycharis, G. Mitrikas

- **Objectives**
- The understanding and synthetic simulation of the function of active centres in biological systems, which catalyze important chemical processes. The study of the Mn_4O_5Ca complex of Photosystem II, whose function constitutes a fundamental biochemical process empowering life on Earth, and sets the paradigm for engineering solar fuel–production systems, is exemplified.
- Spin trapping and identification of Reactive Oxygen Species formed during UV/vis irradiation of various photocatalysts.
- The study of the electronic and magnetic properties of synthetic multinuclear complexes of transition metals.
- Characterization of metal-based pharmaceuticals by application of low temperature spectroscopic techniques.

Our main methodology is based on the application of spectroscopic techniques such as Electron Paramagnetic Resonance (EPR) and Mössbauer Spectroscopy as well as on the application of magnetic measurements (static and dynamic).

- **Highlights / main scientific results**

Metalloradical intermediates in Ca^{2+} - depleated Photosystem II. Photosystem II (PSII) catalyzes the biologically fundamental reaction of light-driven oxygen evolution from water. The active site of water oxidation, the Oxygen oxidation steps denoted as $S_0 \rightarrow S_1$, $S_1 \rightarrow S_2$, $S_2 \rightarrow S_3$, and $S_3 \rightarrow [S_4] \rightarrow S_0$, accompanied by progressive removal of four protons from two bound water molecules. O_2 evolution occurs during the last transition, $S_3 \rightarrow [S_4] \rightarrow S_0$, where the S_4 is a metastable state. The intermediates of the S-state transitions are known as metalloradical intermediate states ($S_iY_z^{\bullet}$) and involve the free radical of Tyrosine$_Z$ (Y_z), which magnetically interacts with the Mn-cluster and plays a critical role in the proton and electron transfer reactions during the water oxidation process. In most metalloradical states it was established that $Y_z^{\bullet}$ interacts magnetically with the Mn_4CaO_5 cluster. However, at the $S_2Y_z^{\bullet}$ intermediate state of the Ca^{2+} - depleted PSII membranes, which gives rise to the well-known '$Y_z^{\bullet}$ doublet' EPR signal, the idea of metal-radical spin–spin interaction is disputed. Particularly, while the prevailing view supports the idea of the Mn_4-$Y_z^{\bullet}$ magnetic interaction, alternative investigations suggest that after the formation of the $S_2Y_z^{\bullet}$ metalloradical state, the Mn_4 is reduced to the S_1 state, together with the formation of the His190$^{\bullet}$ radical, which interacts magnetically with the $Y_z^{\bullet}$. Hence, according to this model, the splitting of the '$Y_z^{\bullet}$ doublet' EPR signal is assigned to the spin-spin interaction between the two free radicals, Tyr$_Z^{\bullet}$ and His190$^{\bullet}$, while the inorganic cluster is in the resting S_1 oxidation state. We aimed at investigating whether the manganese cluster interacts magnetically with the tyrosyl Z radical in calcium-depleted PSII preparations, as holds in the functional PSII. The EPR spectra of S_2 and $S_2Y_z^{\bullet}$ (figure 1), accompanied by their theoretical simulation (figure 2), show that the reversible modification of the spin configuration of the Mn_4 being at the S_2 state, by NIR illumination, results in the reversible change of the splitting of the '$Y_z^{\bullet}$ doublet' EPR signal. These observations strongly support the idea of magnetic interaction between the Mn_4 and Tyr$_Z$, upon the formation of the $S_2Y_z^{\bullet}$ metalloradical state in Ca_{2+}- depleted PSII preparations. For the simulation of the 185 G width signal (trace a) we assumed two interacting species $S_1 = S_2 = 1/2$ with $g_1 = g_2 = 2$, and an effective distance of $R_{12} = 5.8$ Å (red trace), which is quite similar to that of the respective species for the $S_2Y_z^{\bullet}$ state in functional PSII preparations. The more asymmetric signal with a splitting of 165 G (trace b) is well described by assuming a dipolar interaction between $S_1 = 5/2$ and $S_2 = 1/2$, with $g_1 = g_2 = 2$, the zero-field splitting parameters for the $S_1 = 5/2$ of $D_1 = 0.455$ cm^{-1}, $E_1/D_1 = 0.25$, and an effective distance of $R_{12} = 7.7$ Å (blue trace). The different effective distances that describe the two aforementioned $S_2Y_z^{\bullet}$ split signals is assigned to the modification of the Mn_4 spin configuration that changes the nature of the magnetic interaction between the Mn_4 and $Y_z^{\bullet}$.

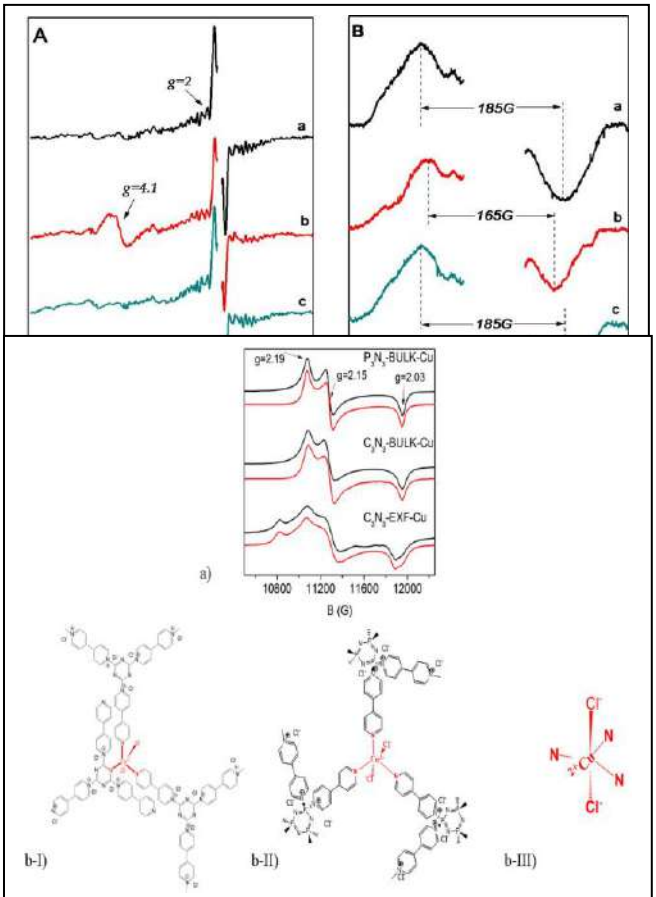


Fig. 3. (a) Q-band EPR spectra from compounds (i) P_3N_3-BULK-Cu, (ii) C_3N_3-BULK-Cu, and (iii) C_3N_3-EXF-Cu. Black lines: experimental. Red lines: simulations obtained as described in the text. EPR experimental conditions: microwave frequency, 34.01 GHz; microwave power, 1.3 mW; modulation frequency, 100 kHz; modulation amplitude 10 G; temperature, 298 K. (b) Proposed structural motif of the (I) C_3N_3-BULK-Cu and (II) P_3N_3-BULK-Cu covalent organic networks and (III) the binding sites of Cu(II) in a trigonal bipyramidal configuration.

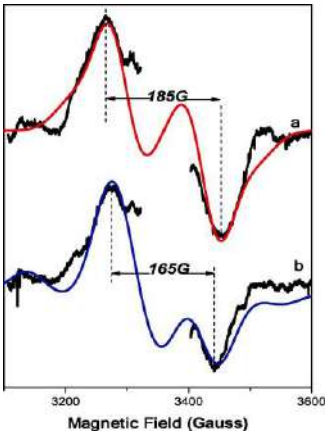


Fig. 2. Theoretical simulations of the $S_2Y_z^{\bullet}$ EPR signals with splitting of 185 G (trace a) and 165 G (trace b), by using point-dipole approximation for two interacting species (see text).

Redox-active triazine frameworks. Covalent organic frameworks (COFs) represent an emerging class of semiconducting materials with high chemical stability, tunable optical properties and porosity that have demonstrated great performances in various applications. Triazine central cores have been established lately as versatile building blocks for the design and synthesis of such frameworks (CTFs) with molecular precision. Dr P. Dallas (recipient of an ELIDEK grant) and his Ph.D student P. Bika, from the group of C. Trapalis at INN, synthesized organic frameworks through substitution of a triazine core with an aromatic nitrogen heterocycle under heating. The resultant polymeric systems had a π-stacked 2D sheets configuration, expanding perpendicularly to 3D structures. In particular, they have demonstrated that the 4,4′-bipyridine based covalent organic frameworks are efficient absorbers of copper, with a significantly high capacity that depends on the 3D or 2D character of the networks. A direct comparison among three different morphologies revealed the structural rearrangement of the frameworks after the absorption of copper, which induces significant changes in terms of morphology, crystallinity, and thermal stability. On the basis of our EPR measurements, we traced that the divalent copper ions are coordinated in a trigonal bipyramidal configuration with the N of core units, 4,4′-bipyridine, and the chlorine ions (figure 3), which can be hindered and converted to a square-planar geometry after the addition of glycerol.

Dependence of spectroscopic parameters upon the coordination environment (symmetry, coordination number) of transition metal ions.

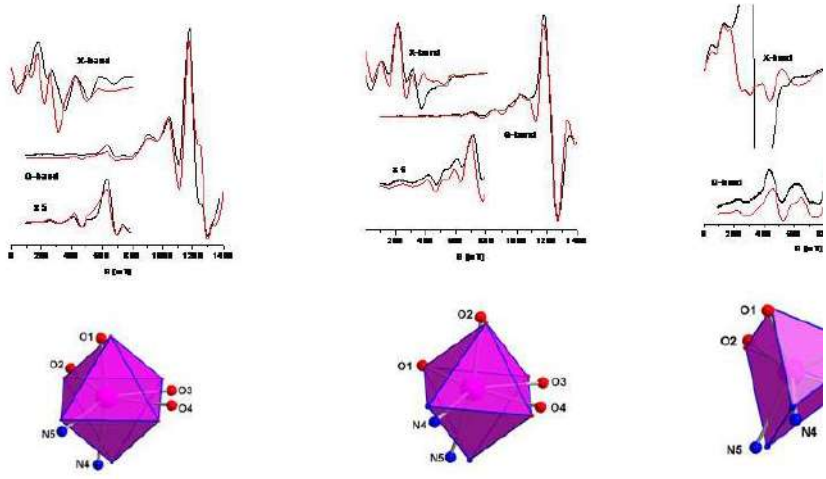


Fig.4. Upper panel. X- and Q-band EPR spectra from powder samples of compounds (1), (2) and (3) at room temperature. Lower panel: Idealized polyhedral based on Continuous Shape Measure calculations for 1, 2, and 3

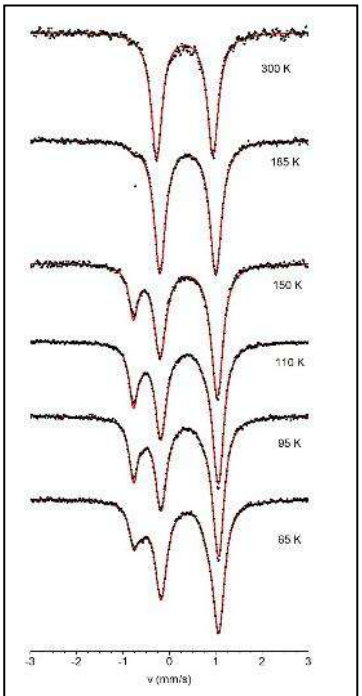
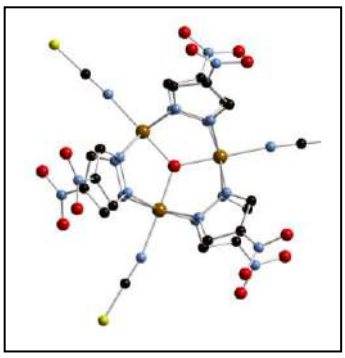


Fig. 6 . Mossbauer spectra from powdered samples of **4** at the indicated temperatures.

The spectroscopic parameters of paramagnetic transition metal ions are related to a number of properties of the relevant compounds such as structural features, magnetic behavior and reactivity. As part of our ongoing interest in this field, X- and Q-band EPR spectroscopy was applied to study the electronic properties of the $[Mn(O,O)(N,N)(NO_3)]$ complexes, (O,O) = $[PhC(O)NP(O)PPh_2]^-$, (N,N) = phenanthroline (1), neocuproine (2) and 2,2′-bipyridine (3) in collaboration with the group of Prof. P. Kyritsis, University of Athens. In **1** and **2**, the Mn(II) ion is closer to an octahedral environment, whereas in **3** the symmetry is closer to trigonal prismatic. Analysis of the EPR spectra determined the zero-field splitting parameters of these S = 5/2 systems and revealed a small but significant difference in the magnitude of $|D|$ for complex **3** compared to those of **1** and **2**. These differences are attributed to the structural and electronic properties of complexes **1**-**3**. The latter were probed by DFT calculations, which showed different D_{SOC} contributions among the three complexes.



Spin Crossover (SCO) in a triferric compound. Spin Crossover is a phenomenon observed in some transition metal compounds in which the spin state of the metal ion changes due to an external stimulus such as temperature, pressure or light. Compounds with SCO properties have potential uses such as sensors, switches, data storage devices and optical displays. The potential SCO behavior of an iron ion containing compound can be monitored by using Mössbauer spectroscopy. In

collaboration with the group of Prof. R. G. Raptis, Florida International University, U.S.A., we studied the electronic properties of the iron sites in a compound containing the unit $[Fe_3(\mu_3\text{-}O)(\mu\text{-}4\text{-}NO_2\text{-}pz)_6(NCS)_3]^{2-}$ (**4**) (Fig. 5). In figure 6 we present representative Mössbauer spectra from powder samples of **4** recorded at the indicated temperatures. The spectrum at 300 K (Fig. 5) gives rise to a quadrupole doublet with parameters consistent with three equivalent high spin ferric ions (Fe(III), S = 5/2) in an octahedral environment comprising N/O ligands. The temperature dependence of the spectra indicate that this electronic configuration persists down to ~200K. In the spectrum recorded at 195 K a shoulder appears at ~ -0.8 mm/s, indicated by an arrow in figure 6. This peak is the left part of doublet with the right part lying in the more intense absorption peak at ~ +1.03 mm/s. As the temperature decreases the intensity of the novel doublet peak increases reaching at an equilibrium at ~ 110 K. The parameters of the novel doublet are consistent with a low spin ferric ion (Fe(III), S = 1/2). The Mössbauer properties of **4** are consistent with a compound exhibiting thermally assisted SCO behavior.

Funding

MIS 5047814, "Photosynthetic Water Splitting: The Critical Stages before Oxygen Release", "Human Resources Development, Education and Lifelong Learning 2014-2020", PI: George Mitrikas, Deputy PI: Yiannis Sanakis. Duration 2020-2021 (15 months).

MIS 5002567, KRIPIS II. "Action for the Strategic Development on the Research and Technology sector" funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

MIS 5002772, INNOVATION -EL. "National Infrastructure in Nanotechnology, Advanced Materials and Micro-/ Nanoelectronics, "Reinforcement of the Research and Innovation Infrastructure". Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund)

"Multifunctional Metal Organic Frameworks and the Fine Tuning of their Magnetic, Photoluminescence and Sorption Properties through Single - Crystal Ligand Exchange Reactions, Program EXCELLENCE/1216/0076, Research Promotion Foundation of Cyprus, University of Cyprus (Prof. A. Tasiopoulos), Role: Foreign Research Organization (Y. Sanakis) Duration: 2019 – 2021 (36 months).

"Helium Liquefaction and Low Temperature Spectroscopy", ELKE #11143, PI: Y. Sanakis, 2013-.

OUTPUT

Publications in International Journals

1. Chrysina, M., Zahariou, G., Ioannidis, N., Sanakis, Y., Mitrikas, G. Electronic Structure of Tyrosyl D Radical of Photosystem II, as Revealed by 2D-Hyperfine Sublevel Correlation Spectroscopy. *Magnetochemistry*, **7**, 131 (2021).
2. Nano, K., Zahariou, G., Ioannou, P.-C., Alam, Md M., Pantazis, D. A., Raptopoulou, C. P., Psycharis, V., Sanakis, Y., Kyritsis, P. Electronic properties of the S = 5/2 Mn(II) complexes [Mn{ PhC(O)NP(O)PPh_2}(N,N)(NO_3)], (N,N) = phenanthroline, neocuproine, 2,2 –bipyridine. *Polyhedron*, **207**, 115374 (2021).
3. Stoumpos, C. C., Danellia, P., Zahariou, G., Pissas, M., Psycharis, V., Raptopoulou, C. P., Sanakis, Y., Perlepes, S. P. Di-2-pyridyl ketone-based ligands as evergreen "trees" in the "forest" of manganese chemistry: Mononuclear Mn(III) complexes from the use of MnF_3. *Polyhedron*, **207**, 115350, (2021).
4. Zahariou, G., Sanakis, Y., Ioannidis, N. Evidence for the Mn_4-Yz• Magnetic Interaction in Ca^{2+}-depleted Photosystem II. *Polyhedron*, **206**, 115335 (2021).
5. Georgopoulou, A., Pissas, M., Psycharis, V., Sanakis, Y., Raptopoulou, C. P. A single-chain magnet based on bis(end-on azido/alkoxo)-bridged linear [$Mn^{III}_2Mn^{II}$] repeating units. *Polyhedron*, 206, 115334 (2021).
6. Mathivathanan, L., Sanakis, Y., Raptis, R. G., Turek, P., Boudalis, A. K. Observation and deconvolution of a unique EPR signal from two cocrystallized spin triangles. *Phys. Chem. Chem. Phys.*, **23**, 14415–14421. (2021).
7. Kalra, A., Bagchi, V., Paraskevopoulou, P., Das, P., Ai, L., Sanakis, Y., Raptopoulos, G., Mohapatra, S., Choudhury, A., Sun, Z., Cundari, T. R., Stavropoulos, P. Is the Electrophilicity of the Metal Nitrene the Sole Predictor of Metal-

Mediated Nitrene Transfer to Olefins? Secondary Contributing Factors as Revealed by a Library of High-Spin Co(II) Reagents. *Orgnanometallics*, **40**, 1974-1996 (2021).
8. Dimiza, F., Hatzidimitriou, A. G., Sanakis, Y., Papadopoulos, A. N., Psomas, G.Trinuclear and tetranuclear iron(III) complexes with fenamates: Structure and biological profile. *J. Inorg. Biochem.*, **228**, 111410 (2021).
9. Dermitzaki, D., Pissas, M., Psycharis, V., Sanakis, Y., Raptopoulou, C. P. Synthesis, crystal structures, magnetic and magnetocaloric studies of Enneanuclear $\{Cu_7Gd_2\}$ molecular magnetic refrigerants. *Polyhedron*, **195**, 114960 (2021).
10. Zahariou, G., Ioannidis, N., Sanakis, Y., Pantazis, D. A. Arrested substrate binding resolves catalytic intermediates in higher-plant water oxidation. *Angew. Chem. Int. Ed.*, **60**, 3156-3162 (2021).
11. Zahariou, G., Drosou, M., Pantazis, D. A. Orientational Jahn-Teller Isomerism in the Dark-Stable State of Nature's Water Oxidase. *Angew. Chem. Int. Ed.*, **60**, 13493-13499 (2021).

International Conferences Presentations

1. Georgia Zahariou, Maria Chrysina, 2D-Hyperfine Sublevel Correlated Investigation of the Tyrosyl Radicals of Photosystem II, *Athens Conference on Advances in Chemistry,* 10-14 March 2021, Athens, Greece. (oral)
2. Maria Chrysina, HYSCORE spectroscopy as an alternative tool in the study of systems that are not feasible to crystallize: the example of the stable Tyrosyl D radical of Photosystem II, *10th International Conference of the Hellenic Crystallographic Association*, Athens, 15-17 October 2021, Athens, Greece. (oral)
3. Yiannis Sanakis, Homo- and Hetero- Iron based Polynuclear Transition Metal Clusters, *1st Panhellenic Workshop on Inorganic Chemistry*, 19-21 November 2021, Patras, Greece.

Teaching and Training Activities

Ioannis Sanakis
Graduate course "Molecular Magnetism", Spring 2021, 3 hrs
University of Ioannina.

Administrative positions

Ioannis Sanakis
Member of the Scientific Council of INN

CRYSTALLOGRAPHY AND COORDINATION CHEMISTRY MATERIALS

Project Leader: VASSILIS PSYCHARIS

Permanent Research Staff: CATHERINE RAPTOPOULOU

Post Docs: DESPINA DERMITZAKI

PhD Candidates: SOFIA TZANI

Master Students: GIORGOS BAKLAVAS

- Objectives

The research objectives of the Laboratory of Crystallography and Coordination Chemistry of Materials cover two main fields:

1. X-ray crystallographic studies from powder samples or thin films and single crystal techniques ranging from routine crystal structure determination to twinned and/or disordered crystals.
2. Synthesis, structural and spectroscopic characterization, and magnetic studies of molecular magnetic materials in collaboration with other national and international research groups.

- Highlights / main scientific results

We have continued our synthetic activities in the field of heterometallic 3d/4f complexes and isolated two $\{Cu_7Gd_2\}$ compounds with the polydentate Schiff base ligands *o*-OH-$C_{10}H_6$-CH=NC(R)$(CH_2OH)_2$ (R = CH_3, H_3L1; R = C_2H_5, H_3L2), namely $[Cu_7Gd_2(L1)_4(HL1)_2(piv)_4(H_2O)(MeOH)_3]$ (**1**) and $[Cu_7Gd_2(L2)_4(HL2)_2(piv)_4(MeOH)_5]$ (**2**) [*Polyhedron* **195** (2021) 114960, 7 pages]. Both complexes are isostructural and consist of a central core $\{Cu_7Gd_2(\mu_3\text{-}O_{alkoxo})_6(\mu_2\text{-}O_{alkoxo})_4(\mu_2\text{-}O_{pivalato})_2\}^{8+}$ which is observed for the first time in the literature (Figure 1). Peripheral ligation and bridging are provided by four triply and two doubly deprotonated Schiff base ligads, two μ_3-pivalates, two chelate pivalates, and terminal aqua and/or MeOH molecules. The seven Cu^{II} ions show five different coordination environments and three different coordination geometries, i.e. square planar, square pyramidal and octahedral. The two Gd^{III} ions show O_9 coordination which is described as spherical capped square antiprism CAAPR-9. The magnetic susceptibility measurements for both **1** and **2** revealed the presence of dominant ferromagnetic intramolecular interactions between the metal ions, whilst magnetization measurements suggested that some of the Cu^{II} ions are antiferromagnetically coupled. The magnetocaloric effect of both **1** and **2** was estimated by isothermal magnetization measurements and found ~13 $Jkg^{-1}K^{-1}$ at 2 K for ΔH = 5 T.

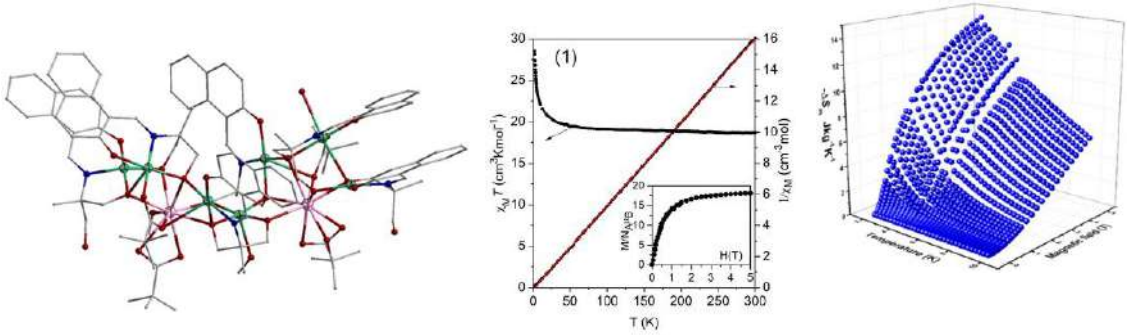


Figure 1. The molecular structure (left), magnetic (middle) and magnetocaloric (right) measurements of the $\{Cu_7Gd_2\}$ complex **1**.

We have continued our synthetic efforts on Molecular Magnetic Materials and reported a Single-Chain Magnet (SCM) [*Polyhedron* **206** (2021) 115334 (7 pages)], i.e. the 1D coordination polymer $[Mn^{III}_2Mn^{II}(L)_2(N_3)_2(MeOH)_2]_n$ [H_3L is the Schiff base ligand *o*-OH-C_6H_4-CH=NC$(CH_3)(CH_2OH)_2$]. The coordination polymer consists of Mn^{III}-Mn^{II}-Mn^{III} strictly linear trinuclear repeating units with bis(end-on azido/alkoxo) bridges between the central Mn^{II} ion and each one of the terminal Mn^{III} ions, defining two rhombic units $[Mn^{III}Mn^{II}(\mu_{1,1}\text{-}N_3)(\mu\text{-}OR)]$. Each repeating unit is further linked to its neighboring ones through two μ-OR groups, defining rhombic units $[Mn^{III}_2(\mu\text{-}OR)_2]$, thus promoting the

chain structure of the compound (Figure 2). The magnetic studies revealed that the 1D coordination polymer displays Single-Chain Magnet behavior (SCM) with energy barrier $\Delta = 53 \pm 1$ K. This compound is the first example of SCM based on a mixed-valence linear trinuclear unit $[Mn^{III}_2Mn^{II}(\mu_{1,1}\text{-}N_3)_2(OR)_2]$.

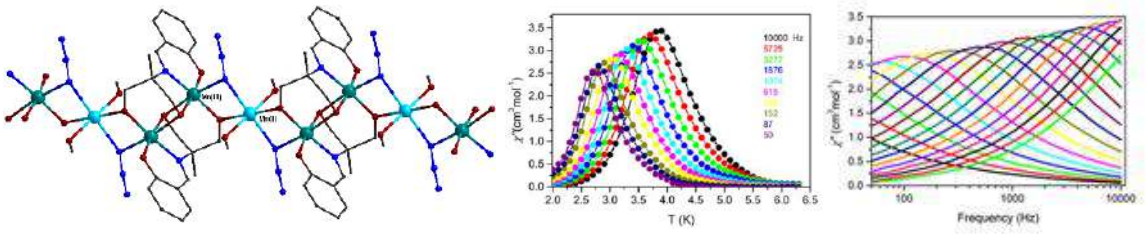


Figure 2. A part of the 1D Single-Chain Magnet (left) and temperature (middle) and frequency (right) dependence of the imaginary part of the susceptibility at zero external magnetic field.

A review monograph on "Metal-Organic Frameworks: Synthetic Methods and Potential Applications" was published in *Materials* **14** (2021) 310 (32 pages). The review summarizes the synthetic methods reported in the literature for the preparation of MOFs and their derived materials, and their potential applications in gas adsorption/separation/storage for energy and environmental purposes, in catalysis, and as sensor, piezo/ferroelectric, thermoelectric, dielectric, proton-conducting, magnetic, biomedical and analytical materials.
The first Pentanuclear Thorium (IV) coordination cluster presenting a Kuratowski type topology was studied in collaboration with the University of Patras [*Inorganic Chemistry* **60** (2021) 60, 11888 (5 pages)]. The graph theoretical analysis has proven that the bonding topologies in analogous pentanuclear units contain the nonplanar $K_{3,3}$ graph. This is also valid for the cluster under study, as it is clearly seen in the structural (Figure 3, middle) and schematic paths for the derivation of the $K_{3,3}$ graph (Figure 3, right top, bottom respectively) which is a subgraph of the bonding topology of the $Th^{IV}5$ cluster. This feature of the cluster places it among the members of the family of Kuratowski-type coordination compounds, which is the first with tetravalent metals and a rare example in which the central metal has a coordination number higher than 6. This topology creates holes in a structure and it is useful in the synthesis of MOFs.

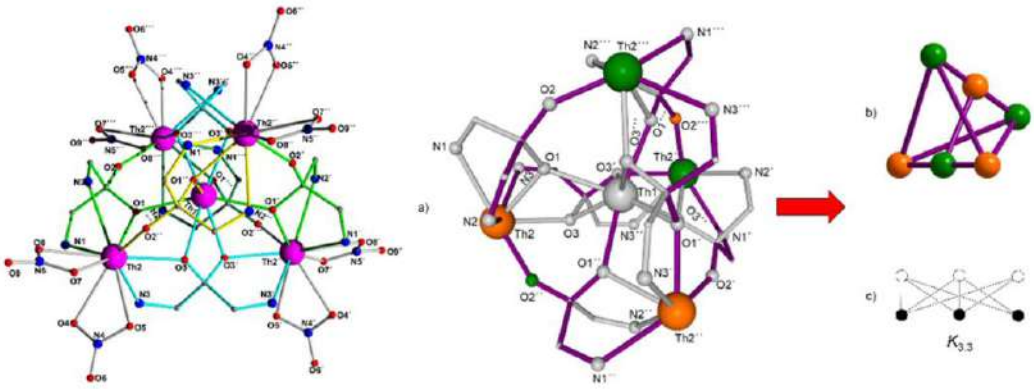


Figure 3. A part of the molecular structure of the Pentanuclear Thorium (IV) cluster (left). The structural centers and the schematic paths (right) for the derivation of $K_{3,3}$ graph of Kuratowski-type coordination compounds; The green and orange spheres indicate the nodes and the thick violet lines the edges of the graph.
In collaboration with the group of Prof. Hadjikakou (Laboratory of Biological Inorganic Chemistry, Department of Chemistry, University of Ioannina, we have studied the structure of Silver-Nitrate Urea compound (Figure-4, left), which together with a series of silver(I) covalent polymers were tested for their antibacterial efficiency against microbes which colonize in contact lenses [Dalton Trans **50** (2021) 13712 (16 pages)]. The specific compound presents moderate activity but the others present superior one. The graphical abstract of this work was selected as the back cover of the Issue 39, 2021 of Dalton Transactions journal.

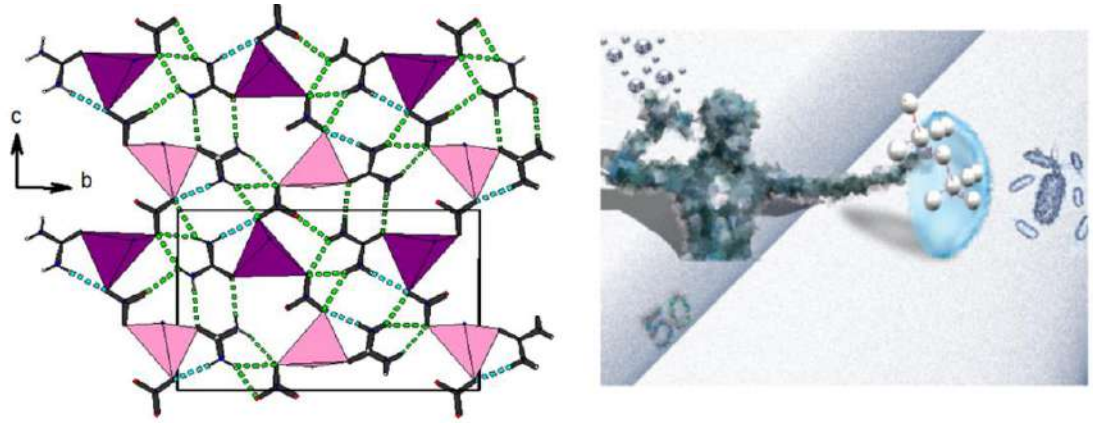


Figure 4 Layers formed parallel to the (100) plane of the structure of compound Silver-Nitrate Urea (left). The graphical abstract which was selected as the back cover of the Issue 39, 2021 of Dalton Transactions journal (right).

The study of Industrial samples concerns the research on alternative cement clinkers which have been proposed as building materials with improved carbon footprint compared to conventional Portland Cement (PC) whose production is a highly energy-intensive industrial process. In a study [CEMENT AND COCONRETE RESEARCH, **147** (2021)106529)] performed in collaboration with the Group Ceramics and Composite materials of INN, the effect of

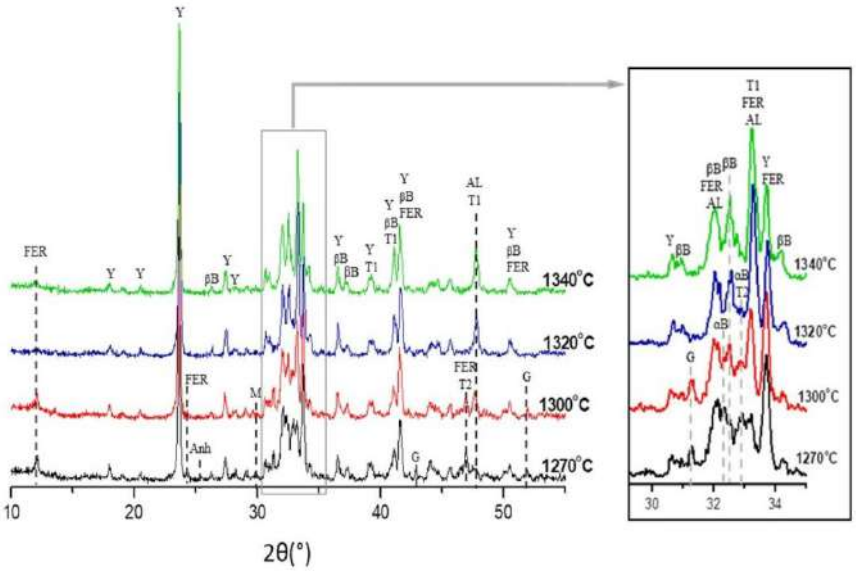


Figure 5 Diffraction patterns of the clinker produced at different temperatures for 30 min, indicating the effect of temperature on the mineralogy of the clinker and belite polymorphs in the detail. (Y – C4A3$, βB – β-C2S, αH'B – αH'-C2S, FER – ferrite, T1 – CaTiO3, T2 – Ca3Fe2TiO8, G – C2AS, AL – C3A, Anh – C$, M – C12A7).

clinkering temperature and duration on the production of low energy Belite Calcium-Sulpho-Aluminate (BCSA) clinkers, targeting a composition belite and ye'elimite at 40 wt. % each was examined. The mineralogy and microstructure of BCSA clinker were studied by XRD/QXRD (Figure-5) and SEM/EDS analysis. The target concentration of belite was achieved at temperatures between 1270 and 1300 ^{o}C, while that of ye'elimite was only marginally reached at 1300 and even at 1320 ^{o}C. In all clinkering conditions belite was detected in both α_H'- and β-polymorphs. The extensive use of bauxite to produce BCSA clinker lead to a Ti - rich raw mix and the formation of perovskite in all clinkers. At low clinkering conditions the presence of Ti and S-ions in belite crystals contributed to the stabilization of belite α_H'- polymorph, while at elevated temperatures their partial release from belite crystal favors the stabilization of β - polymorph.

- **Funding**

1. Dr. Vassilis Psycharis, Supervisor of Dr Despina Dermitzaki who has attracted funding of an IKY Scholarships Programme which is co-financed by the European Union (European Social Fund - ESF) and Greek national funds through the action entitled "Reinforcement of Postdoctoral Researchers", in the framework of the Operational Programme "Human Resources Development Programme, Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) 2014 – 2020». Total funding for Demokritos for 2021 (12 months): 13.200,00 €.
2. Characterization of polycrystalline materials with X-ray Powder Diffraction Method, mainly from QC and RND departments of Pharmaceutical Industries. Income: 71.011,40 € for 2021.

OUTPUT

Publications in International Journals

1. Dermitzaki, D., Pissas, M., Psycharis, V., Sanakis, Y., Raptopoulou, C.P. Synthesis, crystal structures, magnetic and magnetocaloric studies of heterometallic enneanuclear $\{Cu_7Gd_2\}$ complexes. *Polyhedron* **195**, 114960 (7 pages) (2021). DOI: 10.1016/j.poly.2020.114960
2. Dermitzaki, C., Raptopoulou, C.P., Psycharis, V., Escuer, A., Perlepes, S.P., Mayans, J., Stamatatos, T.C. Further synthetic investigation of the general lanthanoid(III) [Ln(III)]/copper(II)/pyridine-2,6-dimethanol/carboxylate reaction system: $\{Cu_{II}_5Ln_{III}_4\}$ coordination clusters (Ln = Dy, Tb, Ho) and their yttrium(III) analogue. *Dalton Trans.* **50**, pp. 240-251, (2021). DOI: 10.1039/D0DT03582C
3. Raptopoulou, C.P. Metal-organic frameworks: Synthetic methods and potential applications. *Materials* **14**, 320 (32 pages) (2021). DOI: 10.3390/ma14020310
4. Polyzou, C.D., Nikolaou, H., Raptopoulou, C.P., Konidaris, K.F., Bekiari, V., Psycharis, V., Perlepes, S.P. Dinuclear lanthanide(III) complexes from the use of methyl 2-pyridyl ketoxime: Synthetic, and physical studies. *Molecules* **26**, 1622 (18 pages) (2021). DOI: 10.3390/molecules26061622
5. Ioannou, P.-C., Grigoropoulos, A., Stergiou, K., Raptopoulou, C.P., Psycharis, V., Svoboda, J., Kyritsis, P., Vohlídal, J. Structural and catalytic properties of the $[Ni(BIPHEP)X_2]$ complexes, BIPHEP = 2,2'-diphenylphosphino-1,1-biphenyl; X = Cl, Br. *Inorg. Chim. Acta* **522**, 120300 (7 pages) (2021). DOI: 10.1016/j.ica.2021.120300
6. Gabriel, C., Tsave, O., Yavropoulou, M.P., Architektonidis, T., Raptopoulou, C.P., Psycharis, V., Salifoglou, A. Evaluation of insulin-like activity of novel zinc metal-organics toward adipogenesis signaling. *Int. J. Molec. Sci.* **22**, 6757 (34 pages) (2021). DOI: 10.3390/ijms22136757
7. Banti, C.N., Raptopoulou, C.P., Psycharis, V., Hadjikakou, S.K. Novel silver glycinate conjugate with 3D polymeric intermolecular self-assembly architecture; an antiproliferative agent which induces apoptosis on human breast cancer cells. *J. Inorg. Biochem.* **216**, 111351 (13 pages) (2021). DOI: 10.1016/j.jinorgbio.2020.111351

8. Stoumpos, C.C., Danelli, P., Zahariou, G., Pissas, M., Psycharis, V., Raptopoulou, C.P., Sanakis, Y., Perlepes, S.P. Di-2-pyridyl ketone-based ligands as evergreen 'trees' in the 'forest' of manganese chemistry: Mononuclear Mn(III) complexes from the use of MnF_3. *Polyhedron* **207**, 115350 (9 pages) (2021). DOI: 10.1016/j.poly.2021.115350

9. Georgopoulou, A., Pissas, M., Psycharis, V., Sanakis, Y., Raptopoulou, C.P. A single-chain magnet based on bis(end-on azido/alkoxo)-bridged linear [$Mn_{III}{}_2$ Mn_{II}] repeating units" *Polyhedron* **206**, 115334 (7 pages) (2021). DOI: 10.1016/j.poly.2021.115334

10. Tsantis, S.T., Danelli, P., Tzimopoulos, D.I., Raptopoulou, C.P., Psycharis, V., Perlepes, S.P. Pentanuclear thorium(IV) coordination cluster from the use of di(2-pyridyl) ketone. *Inorg. Chem.* **60**, pp. 11888-11892 (2021). DOI: 10.1021/acs.inorgchem.1c01800

11. Shegani, A., Ischyropoulou, M., Roupa, I., Kiritsis, C., Makrypidi, K., Papasavva, A., Raptopoulou, C., Psycharis, V., Hennkens, H.M., Pelecanou, M., Papadopoulos, M.S., Pirmettis, I. Synthesis and evaluation of new mixed "2+1" Re, $_{99m}$Tc and $_{186}$Re tricarbonyl dithiocarbamate complexes with different monodentate ligands. *Bioorg. & Med. Chem.* **47**, 116373 (11 pages) (2021). DOI: 10.1016/j.bmc.2021.116373

12. Banti, C.N., Kapetana, M., Papachristodoulou, C., Raptopoulou, C.P., Psycharis, V., Zoumpoulakis, P., Mavromoustakos, T., Hadjikakou, S.K. Hydrogels containing water soluble conjugates of silver(I) ions with amino acids, metabolites or natural products for non infectious contact lenses. *Dalton Trans.* **50**, pp. 13712-13727 (2021). DOI: 10.1039/D1DT02158C

13. Lazopoulos, A., Triantis, C., Shegani, A., Papasavva, A., Raptopoulou, C.P., Psycharis, V., Chiotellis, A., Pelecanou, M., Pirmettis, I., Papadopoulos, M.S. Effective labelling of amine pharmacophores through the employment of 2,3-pyrazinedicarboxylic anhydride and the generation of *fac*-[M(CO)$_3$(PyA)P] and *cis-trans*-[M(CO)$_2$(PyA)P$_2$] complexes (PyA = pyrazine-2-carboxylate, P = phoshine, M = Re, $_{99m}$Tc. *Inorg. Chem.* **60**, pp. 17509-17516 (2021). DOI: 10.1021/acs.inorgchem.1c01968

14. Psycharis, V., Dermitzaki, D., Raptopoulou, C.P. The use of Hirshfeld surface analysis tools to study the intermolecular interactions in single molecule magnets. *Crystals* **11**, 1246 (9 pages) (2021). DOI: 10.3390/cryst11101246

15. Nano, K., Zahariou, G., Ioannou, P.-C., Alam, M.M., Pantazis, D.A., Raptopoulou, C.P., Psycharis, V., Sanakis, Y., Kyritsis, P. Electronic properties of the S = 5/2 Mn(II) complexes [Mn{PhC(O)NP(O)PPh$_2$}(N,N)(NO$_3$)], (N,N = phenanthroline, neocuproine, 2,2'-bipyridine" *Polyhedron* **207**, 115374 (9 pages) (2021). DOI: 10.1016/j.poly.2021.115374

16. Beka, G., Papageorgiou, G., Chatzichristidi, M., Karydas, A.G., Psycharis, V., Makarona, E. CuO/PMMA polymer nanocomposites as novel resist materials for E-beam lithography. *Nanomaterials* **11**, 762 (22 pages) (2021). DOI: 10.3390/nano11030762

17. Koumpouri, D., Karatasios, I., Psycharis, V., Giannakopoulos, I.G., Katsiotis, M.S., Kylikoglou, V. Effect of clinkering conditions on phase evolution and microstructure of Belite Calcium-Sulpho-Aluminate cement clinker. *Cement and Concrete Res.* **147**, 106529 (14 pages) (2021). DOI: 10.1016/j.cemconres.2021.106529

Other type of publications (non-refereed Conference Proceedings, magazine, etc)

1. Banti C.N., Raptopoulou C.P., Psycharis V., Hadjikakou S.K. Natural products ingredients with metal ions for new efficient targeted chemotherapeutics. *in 10th International Conference of the Hellenic Crystallographic Association (HeCrA)*, NCSR Demokritos, Athens, Greece, 15-17 October (2021).
2. Dermitzaki D., Panagiotopoulou A., Raptopoulou C.P., Psycharis V. 3d/4f chiral complexes: The case of $\{Cu_8 Ln_4\}$ (Ln_{III} = Dy, Ho) clusters. *in 10th International Conference of the Hellenic Crystallographic Association (HeCrA),* NCSR Demokritos, Athens, Greece, 15-17 October (2021).
3. Tzani S., Pissas M., Psycharis V., Sanakis Y., Raptopoulou C.P. Iron molecular magnetic materials based on polydentate ligands. *in 10th International Conference of the Hellenic Crystallographic Association (HeCrA),* NCSR Demokritos, Athens, Greece, 15-17 October (2021).
4. Stamou C., Danelli P., Michalopoulou P., Psycharis V., Raptopoulou C.P., Dechambenoit P., Perlepes S.P. The "periodic table" of di-2-pyridyl ketone: Zirconium(IV) and hafnium(IV) complexes. *in 10th International Conference of the Hellenic Crystallographic Association (HeCrA),* NCSR Demokritos, Athens, Greece, 15-17 October (2021).
5. Koulouri C., Raptopoulos G., Paraskevopoulou P., Sanakis Y., Psycharis V., Raptopoulou C.P., Perlepes S.P. Reactions of cobalt(II) with 2-aminophenylmethanol: Synthetic, reactivity and structural studies. *in 10th International Conference of the Hellenic Crystallographic Association (HeCrA),* NCSR Demokritos, Athens, Greece, 15-17 October (2021).
6. Chaikali C., Tsantis S.T., Raptopoulou C.P., PSycharis V., Papaioannou D., Tzimopoulos D.I., Perlepes S.P. Coordination chemistry and metal-mediated transformation of 2-pyridyl oximes: The case of pyridine-2-chloroxime. *in 10th International Conference of the Hellenic Crystallographic Association (HeCrA)*, NCSR Demokritos, Athens, Greece, 15-17 October (2021).
7. Iliopoulou M., Tsantis S., Papaioannou D., Raptopoulou C.P., Psycharis V., Dechambenoit P., Tzimopoulos D.I., Perlepes S.P. Efforts to structurally model the $\{UO_2\}_{2+}/V_{IV},V_V$ competition in seawater extraction of uranium using extractants containing the amidoxime functional group. *in 10th International Conference of the Hellenic Crystallographic Association (HeCrA),* NCSR Demokritos, Athens, Greece, 15-17 October (2021).
8. Perlepes S.P., Iliopoulou M., Chaikali C., Tzimopoulos D.I., Raptopoulou C.P., Psycharis V., Tsantis S.T. Aspects of the chemistry of thorium(IV) and uranium(VI): Our recent efforts. *in 1st Panhellenic*

Workshop on Inorganic Chemistry, GRIC-2021, University of Patras, Patras, Greece, 19-21 November (2021).

9. Dermitzaki D., Pissas M., Raptopoulou C.P., Sanakis Y., Psycharis V. Chiral $\{Cu_8 Ln_4\}$ complexes from chiral ligands. *in 1st Panhellenic Workshop on Inorganic Chemistry, GRIC-2021,* University of Patras, Patras, Greece, 19-21 November (2021).
10. Dermitzaki D., Pissas M., Psycharis V., Sanakis Y., Raptopoulou C.P. Chiral-at-metal and achiral complexes from achiral ligands: The case of linear trinuclear Ni_{II}-Ln_{III}-Ni_{II} complexes. *in 1st Panhellenic Workshop on Inorganic Chemistry, GRIC-2021,* University of Patras, Patras, Greece, 19-21 November (2021).

International Conferences Presentations

1. Dermitzaki D., Panagiotopoulou A., Raptopoulou C.P., Psycharis V. 3d/4f chiral complexes: The case of $\{Cu_8 Ln_4\}$ (Ln_{III} = Dy, Ho) clusters. *in 10th International Conference of the Hellenic Crystallographic Association (HeCrA),* NCSR Demokritos, Athens, Greece, 15-17 October (2021), poster.
2. Tzani S., Pissas M., Psycharis V., Sanakis Y., Raptopoulou C.P. Iron molecular magnetic materials based on polydentate ligands. *in 10th International Conference of the Hellenic Crystallographic Association (HeCrA),* NCSR Demokritos, Athens, Greece, 15-17 October (2021), invited oral.
3. Dermitzaki D., Pissas M., Raptopoulou C.P., Sanakis Y., Psycharis V. Chiral $\{Cu_8 Ln_4\}$ complexes from chiral ligands. *in 1st Panhellenic Workshop on Inorganic Chemistry, GRIC-2021,* University of Patras, Patras, Greece, 19-21 November (2021), invited oral.
4. Dermitzaki D., Pissas M., Psycharis V., Sanakis Y., Raptopoulou C.P. Chiral-at-metal and achiral complexes from achiral ligands: The case of linear trinuclear Ni_{II}-Ln_{III}-Ni_{II} complexes. *in 1st Panhellenic Workshop on Inorganic Chemistry, GRIC-2021,* University of Patras, Patras, Greece, 19-21 November (2021), invited oral.

Teaching and Training Activities

V. Psycharis
Powder X-ray Diffraction, 1 day (22-10-2021)
Academic Institute: post-graduate programs "Physics and Technological Applications" at the Faculty of Applied Mathematics and Physics of the National Technical University of Athens, Practical Laboratory exercise.
V. Psycharis, C. Raptopoulou
A series of 9 lectures on X-ray Crystallography and study of intermolecular interactions of biological interest in the crystalline state were given in the framework of the Lesson Biophysics of pharmaceutical action. International Graduate Program in Biological Inorganic Chemistry. Laboratory of Biological Inorganic Chemistry, Department of Chemistry Ioannina.

Doctoral Dissertations completed in 2021

Name: SOFIA TZANI
Dissertation Title: "Synthesis, Structural Characterization and Study of Magnetic and Spectroscopic Properties of Homometallic Fe(II/III) and Heterometallic Fe(III)/M [M = Co(III), Ni(II)] Clusters with Multidentate Ligands"
Research Supervisor at NCSR: CATHERINE RAPTOPOULOU
University where the Thesis was presented: UNIVERSITY OF PATRAS, DEPT. OF CHEMISTRY

Conference / Workshop Organisation

V.PSYCHARIS

1. 10_{th} International Conference of the Hellenic Crystallographic Association (HeCrA), NCSR Demokritos, Athens, Greece, 15-17 October (2021)
2. 1_{st} Panhellenic Workshop on Inorganic Chemistry, GRIC-2021, University of Patras, Patras, Greece, 19-21 November (2021)

Patents - Technology transfer

Patent No 1008941, Issued by Greek Industrial Property Organization, with title Cifroxacin-Silver with antibacterial properties for S. K. Hadjikakou, C. N. Banti, I. Milionis, I. Sainis, N. Kourkoumelis, C. P. Raptopoulou, N. Kourkoumelis, V. Psycharis and C. P. Raptopoulou. Int. Cl.: C07D 401/04, C07D 471/04, C07F 1/10

Guest-Editing of Special Issue

Catherine Raptopoulou served as invited Guest Editor for the Special Issue "Advanced Coordination Polymers" of *Materials* (ISSN 1996-1944). This special issue belongs to the section 'Smart Materials'. The journal Materials has I.F. 3.748. The special issue consists of five peer-reviewed articles, including a review monograph by the Guest Editor.

SYNCHROTRON AND NEUTRON SCATTERING STUDIES OF QUANTUM MATERIALS AND NANOPARTICLES

Permanent Research Staff: Evangelia Moschopoulou

Research Collaborators (emeritus or visiting): Olivier Isnard

- Objectives

- Synthesis of $CoFe_2O_4$ nps, doped derivatives and related nanocomposites ($CoFe_2O_4$@0.5Ba($Zr_{0.2}Ti_{0.8}$)O_3−0.5($Ba_{0.7}Ca_{0.3}$)TiO_3.
- Synthesis of selected Ce-based quantum materials in single crystalline form.
- Structural and morphological characterization of the above materials at various length and time scales by advanced synchrotron and neutron-based scattering, spectroscopy and imaging probes.
- Determination of their physical properties down to very low temperatures, medium pressures and up to high magnetic fields
- Establishment of the synthesis-structure-properties-function relationship of the above systems.
- Understanding the role of dimensionality, interface states and strong electron correlations of the above complex materials.
- Understanding the role of structure (local and at short, nano- and meso- length scales) and composition on the cooperative phenomena of magnetism, superconductivity and multi-ferroelectricity in quantum materials (single crystals, powders and nanoparticles).
- Understanding the role of dimensionality, geometrical frustration, strain and disorder on the cooperative phenomena of magnetism, superconductivity and multi-ferroelectricity in quantum materials and as a result on the materials' functionalities.

- Highlights and Main Scientific Results

1. Quantum Materials

Quantum materials are systems where quantum effects remain manifest over a wide range of energy and length scales. When strong electron-electron correlations are present in those quantum materials there is strong coupling and competition between the basic degrees of freedom of the material: lattice, charge, spin, orbital degrees of freedom. Studying and understanding these couplings down to low temperatures, medium pressures and high magnetic fields is the key prerequisite to understand why the material adopts a superconducting or other ground state.

Our overarching aim was to study the couplings of fundamental degrees of freedom (lattice, charge, spin and orbital) in quantum systems, by using a combination of complementary Synchrotron X-ray and/or Neutron scattering methods with subsystem selective sensitivity. We were thus mostly interested in the structural characterization of Ce-based quantum materials which are of key importance in understanding broader classes of quantum systems. Our structural investigations (at various length and time scales) are the base to place the observed properties of the materials into the appropriate physics context. In addition, our studies elucidate the role of dimensionality, geometrical frustration, strain and disorder to the functionalities of these materials, namely unconventional superconductivity, novel magnetism and topology.

Most of our effort was focused on the heavy-fermion superconductor $CeIrIn_5$. $CeIrIn_5$: exhibits intriguing low-temperature properties. It is a HF superconductor with Sommerfeld coefficient ≈ 750 mJ/(moleK^2), resistivity = 0 below T_0= 1.2 K and bulk superconducting transition at T_c = 0.4 K. The temperature dependence, down to 300 mK) of the crystal structure of $CeIrIn_5$ has been determined by powder neutron diffraction at the HRPD (RAL). The structure refinements (carried out by GSAS) are presented below. They reveal the role of strain and disorder on the structure response to superconductivity of this system.

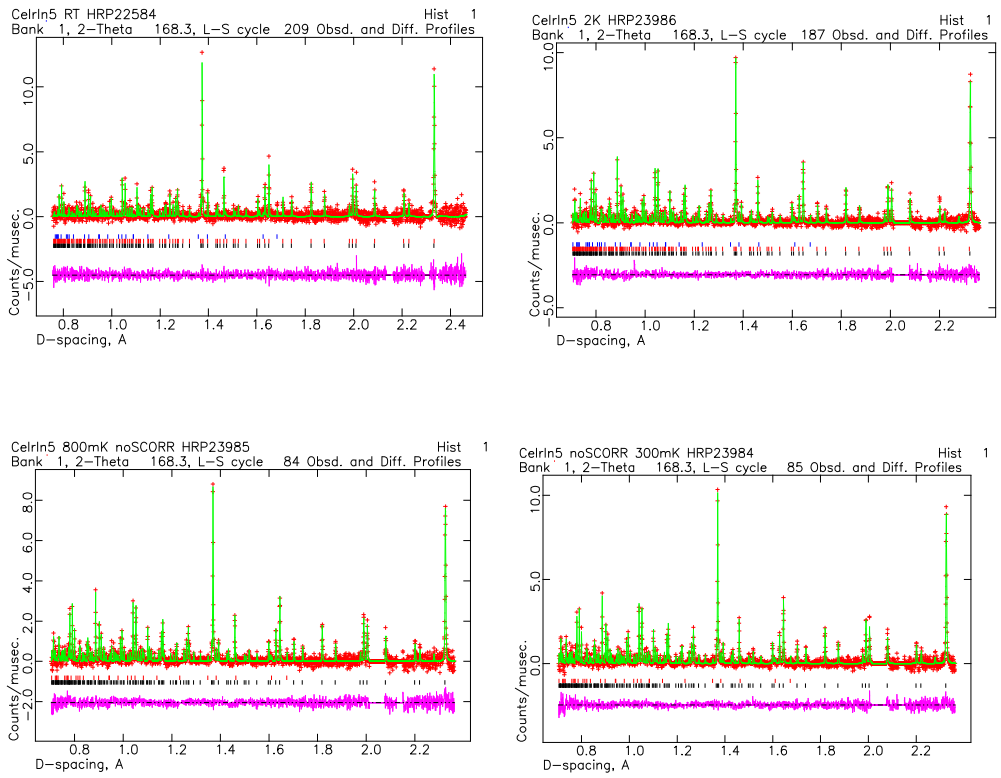


Fig. 1. Temperature dependence of the crystal structure of the heavy fermion material $CeIrIn_5$ down to 300 mK.

2. Nanoparticles

Magnetoelectric (ME) core–shell nanoparticles (nps) are composed of two separate but intimately connected compounds: a **magneto**strictive core and a piezo**electric** shell which possess cross-coupled **magnetic** and **electric** polarization respectively (fig. 2). Their properties and thus functionalities result from a delicate balance of the synthesis method, structure, composition, size and interfacial strain and state.

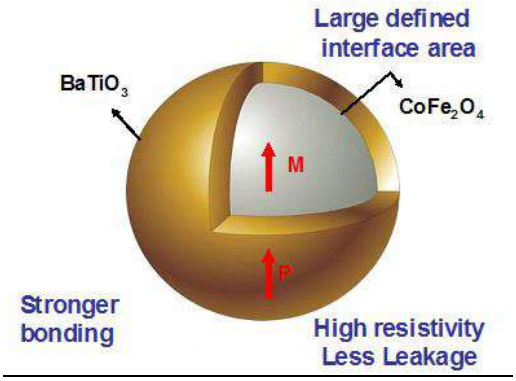


Fig. 2. $CoFe_2O_4$-$BTiO_3$ ME core-shell np.

Most of our effort has been focused on the synthesis of monodisperse $CoFe_2O_4$ nanoparticles that form the magnetic core of the complex magnetoelectric nanoparticles pictured at fig. 2.

$CoFe_2O_4$ nps have been synthesized by several methods including co-precipitation, sol-gel auto-combustion and forced hydrolysis in attempting to address the most important difficulty: agglomeration of nps. We used the co-precipitation method which has low production cost and it provides monodisperse small (≈20-30 nm) nps with almost no agglomeration. A key finding of our synthetic efforts is that increase of the amount of NaOH decreases the

np sizes, but the degree of agglomeration increases. The optimal concentration is 1 mol/L NaOH to produce non-agglomerated nps of d≈20 nm. Higher sizes were achieved by calcinations up to 1000 °C.

- **Funding**

COST Action "Materials, Physics and Nanosciences" with the project "Nanoscale Coherent Hybrid Devices for Superconducting Quantum Technologies" (NANOCOHYBRI); 18 October 2017 through 17 April 2022.
Principal investigator, Member of the Management Committee and National Representative.

OUTPUT

International Conferences Presentations (invited, oral, poster)

Oral
1. Moshopoulou E.G. "Structure response to superconductivity in the heavy fermion superconductor $CeIrIn_5$" COST online-Meeting 22 February, 2021.

Oral (invited)
2. Moshopoulou E.G. "Role of strain in the establishment of coherence in quantum systems" COST online-Meeting 24 June, 2021

Oral
2.Moshopoulou E.G, "Synthesis of monodisperse $CoFe_2O_4$ nanoparticles" COST online-Meeting 21 September, 2021.

Teaching and Training Activities

Participation in the organization of the graduate course: "Science at Large Scale Synchrotron and Neutron Facilities" at the Aristotle University of Thessaloniki.

Administrative positions

Member of the core committee for the participation of Greece to the ESRF.

NANOFUNCTIONAL AND NANOCOMPOSITE MATERIALS LABORATORY

Project Leader: Christos Trapalis

Permanent Research Staff: Christos Trapalis

Other Staff (scientific): Panagiotis Dallas, Tatiana Giannakopoulou, Nadia Todorova, Androniki Vrettou

Post Docs: Ilias - Ioannis Papailias, Niki Bardi

PhD Candidates: Sofia Karapati, Niki Plakantonaki, Michalis Vagenas, Panagiota Bika

Objectives

- Development of novel photocatalytic coatings for air pollutants oxidation.
- Novel Electrochemical Processes and nanocarbon electrodes for water desalination.
- Synthesis of Conductive Polymer/Carbon nanocomposites for CDI electrodes.
- CO_2 waste gases conversion to valuable solid-state nanocarbons.
- COFs as sensors, photocatalysts and platforms for metal removal.
- 2D MXene nanocrystals for antistatic, photocatalytic and EMI Shielding applications.
- CNTs and graphene-based composites for supercapacitors.
- Accreditation of the laboratory with ISO 17025:2017, ISO 22197-1:2016,ISO 22197-2:2016, 27447:2019, standards.

Activities and Main Results

1. Pilot application of novel g-C_3N_4/TiO_2 coatings

The evaluation of the photocatalytic activity of the novel coatings in real conditions was carried out by recording the change in the concentration of gaseous pollutants in indoor environment under visible light irradiation. Specifically, plasterboard surfaces were coated with the photocatalytic coatings containing g-C_3N_4/TiO_2, as well as the commercial coating containing only TiO_2. They were then placed in a reactor of appropriate dimensions manufactured at NCSR Demokritos and irradiated with a low-intensity visible light lamp (Fig. 1). Similarly, the evaluation of the efficiency of the new coatings on an urban scale was carried out by studying the change in the concentration of gaseous pollutants NOx in outdoor environment, utilizing concrete slab surfaces (Fig. 2).

Fig. 1. Setup for indoor pilot measurements.

Fig. 2. Concrete surfaces for outdoor pilot.

The activity of the coatings during the oxidation of gaseous pollutants is presented in Fig. 3. The addition of only a small amount of g-C_3N_4 significantly enhances the photocatalytic activity of the coatings. Thus, even with the low irradiation intensity that was applied, the TiCN0.1 and TiCN0.5 coatings showed at least twice the activity compared to the commercial coating, both for the removal of NOx and the oxidation of acetaldehyde.

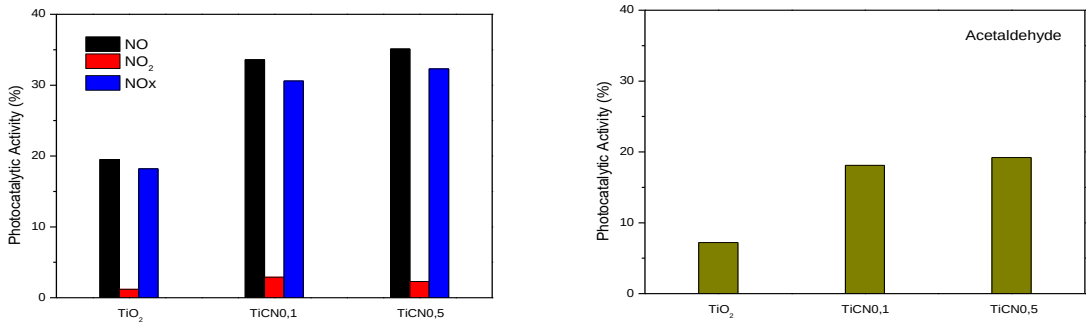


Fig. 3. Photocatalytic activity for the removal of gaseous pollutants NOx (left) and acetaldehyde(right).

2. Evaluation of desalination performance of nanocarbon electrode materials

Composites containing carbon and conductive polymers were tested as electrode materials for water treatment application. In brief, nanocomposite electrodes were manufactured by mixing the active material with a small quantity of binder and stirring until a homogeneous slurry is formed. The slurry was then deposited on graphite substrates as a coating. Furthermore, hybrid electrodes with carbon nanotubes (HTC-A@CNTs) and polypyrrole nanotubes (HTC-A@PNTs) as additives were also tested to delineate the impact of specific surface area and conductivity of different active materials (Fig. 4) on electrode performance.

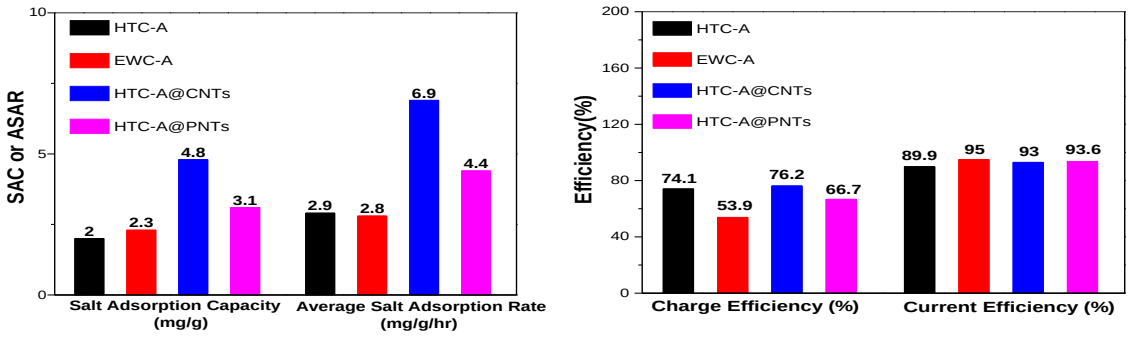


Fig. 4. Comparative analysis of desalination performance of HTC-A, EWC-A, HTC-A@CNTs and HTC-A@PNTs nanocomposite electrodes.

3. Capacitive deionization (CDI) process optimization and scale-up

In this work, egg-white derived activated carbon electrode (EWC-A) acted as the anode while the HTC-A@PNTs electrode acted as the cathode. The nanocomposite electrodes were also tested in the opposite direction (with EWC-A as the cathode and HTC-A@PNTs as the anode) but no significant change in the electrochemical performance of the electrodes was observed. This CDI cell configuration led to an increase in the salt adsorption capacity of the system and especially in terms of charge efficiency of the system as evidenced by the comparative diagram (Fig.5). Data obtained from the experimental study of the CDI on a lab scale were then used for the simulation of the process and the design of scale-up for pilot plan application. Batch-mode electrosorption experiments were conducted in a CDI configuration composed of two electrochemical cells of dimensions 10cm x 10cm. Regarding the electrical connection, the same potential was applied to the electrode pairs (parallel connection). In this direction, nanocomposite electrodes containing sucrose-derived activated carbon with 1% CNTs (HTC-A@CNTs) additive were tested as they were the ones that proved to have the best electrochemical performance. This configuration led to an increase in the salt adsorption capacity of the system thus, it is recommended for the treatment of aqueous solutions with higher concentrations of total dissolved solids (TDS >1000ppm).

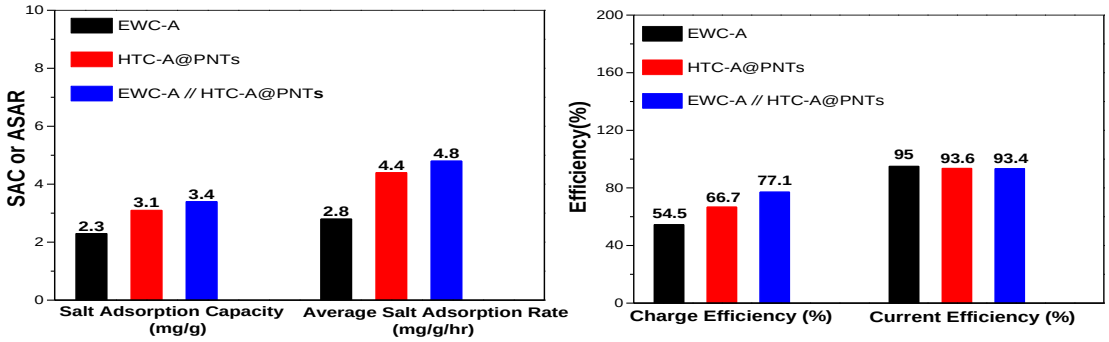
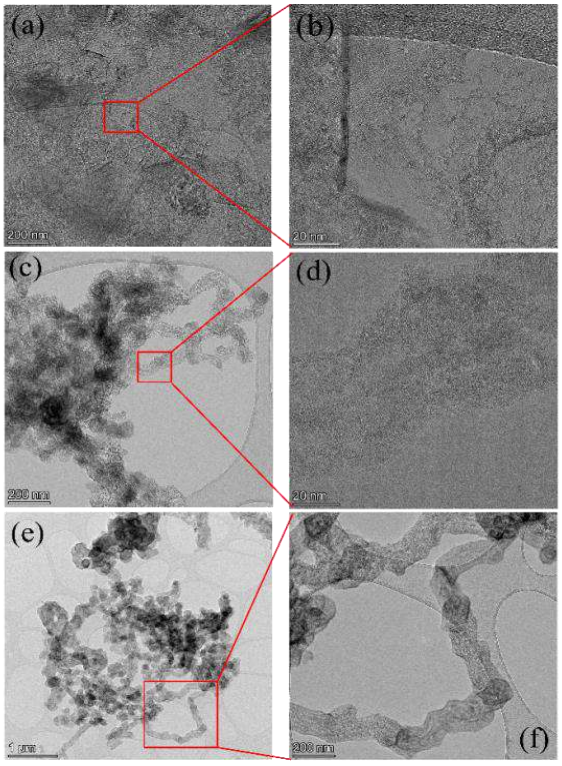
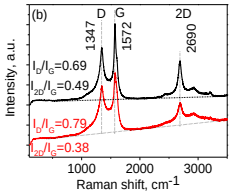


Fig. 5. Comparative analysis of desalination performance of EWC-A, HTC-A@PNTs and asymmetric EWC-A//HTC-A@PNTs nanocomposite electrodes

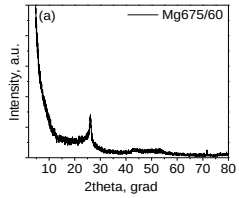
5. Metallothermic technique for CO_2 conversion

The reduction of CO_2 using Mg reducing agent was performed by variation the experimental conditions (temperature, flow rates, mixture of reductants/catalysts, etc.). Some of the results are given in Fig. 6 for the reduction over single Mg reductant at 675 ^{o}C which demonstrate the formation of nanocarbons with plethora of morphologies such as graphene, nanotubes and nanospheres.





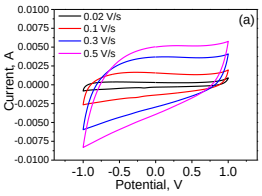
(g)



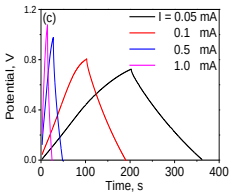
(h)

(i)

C from CV		C from CH-DCH		C from EIS
Scan rate (V/s)	C (F/g)	Current (mA)	C (F/g)	(F/g)
0.02	407.3	0.05	290.9	
0.05	368.7	0.1	302.8	266.8
0.1	**325.0**	0.5	334.5	
0.2	267.4	1.0	336.9	
0.3	228.7			
0.5	179.9			



(j)



(k)

Fig. 6. TEM micrographs of the prepared material: crumpled graphene sheets with mesopores (a, b), entangled fibers (c) and a fragment of fiber (d), single and jointed spherical segments (e, f) at different magnifications: 46 kx, scale bar 200 nm (a, c, f), 500 kx, scale bar 20 nm (b, d) and 11 kx, scale bar 1 μm

(e). XRD pattern of the prepared material (g) and its Raman spectra taken at two different points for limiting (as for I_D/I_G and I_{2D}/I_G ratios) cases (h). Table with calculated capacitance (C) of electrode material measured via different electrochemical techniques (i). CV loops for different scan rates (j) and CH/DCH diagram (k) of the prepared electrode material measured in 0.5 M Na_2SO_4 electrolyte.

The prepared materials possess high crystallinity and are good candidates for supercapacitor applications since they exhibit ~ 407 F/g and 325 F/g at scan rates of 0.02 V/s and 0.1 V/s, correspondingly.

6. Covalent organic frameworks as sensors, photocatalysts and platforms for metal removal

Triazine based covalent organic frameworks were synthesized in bulk quantities and tested as sensors, (Fig.7) photocatalysts and towards heavy metal removal from aquatic environments. The materials are tested as photocatalysts for carbon dioxide reduction and decomposition of selected organic pollutants under visible and UV-A light irradiation. EPR experiments revealed the formation of reactive oxygen species and optical measurements demonstrated the tuning of the band gap upon exfoliation and formation of heterojunction materials.

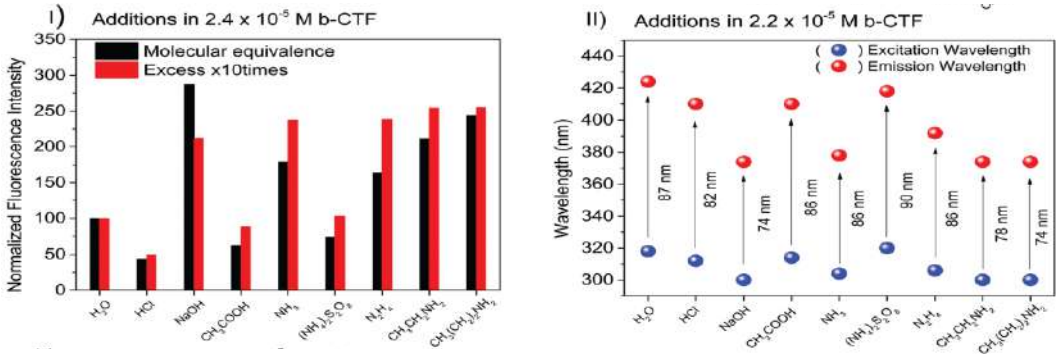


Fig. 7. (I) Emission response chart of fluorescent covalent organic frameworks for various analytes and (II) the corresponding excitation and emission position maxima. By P.Bika et al. [7]

7. 2D MXene nanocrystals for EMI Shielding applications

Composite MXene-based materials with CNTs, TiO_2 and graphene were prepared and incorporated in water and solvent-based formulations. MXene-containing coatings were deposited on glass and flexible polymeric substrates and the functional properties of the obtained coatings, namely conductivity, electromagnetic interference (EMI) shielding effectiveness (SE) and photocatalytic activity in NOx oxidation were investigated. Photocatalytic activity superior to common commercial photocatalyst (Fig. 8) and SE 30-40 dB by epoxy coating with 20 % loading and thickness 125 μm (Fig. 9) were achieved.

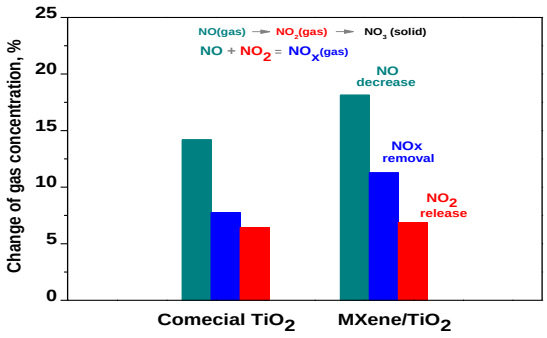


Fig. 8. *Photocatalytic efficiency in NOx oxidation of TiO_2/MXene and commercial TiO_2*

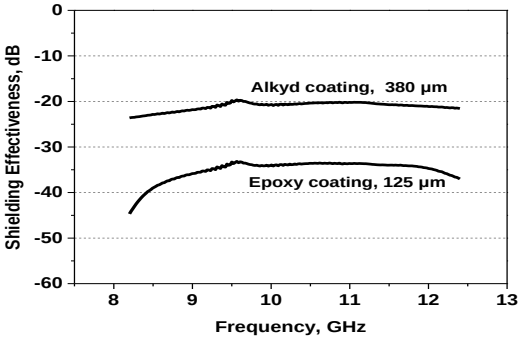


Fig. 9. *EMI SE of coatings with 20 % active component and different thicknesses*

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8. Flexible supercapacitors via inkjet printing

Solid-state supercapacitors were made using a common inkjet printer and aqueous inks from carbon nanomaterials, such as Graphene, CNTs and gold nanoparticles (AuNPs). Lithium dodecyl sulfate (LDS) was used as a dispersing

agent in nanocarbon inks. Tip dispersion was applied to obtain individual graphene sheets and CNTs. This nanocarbon formulation was further enhanced by incorporating conductivity additives, such as 0D Au nanoparticles. Using the above aqueous dispersions of nanomaterials, flat electrodes of the supercapacitors were printed using a commercial inkjet printer on PET film and on PET modified with two polymers, polyethylenemine (PEI) and polystyrene sulfonate (PSS) applying from 1 to 15 layers of ink. Then a gel electrolyte was placed between the two printed electrodes, and wires were connected to the printed electrodes in the PET sheets using silver paint. The electrochemical performance of the printed supercapacitors was measured in a two-electrode system using an Autolab potentiostat/galvanostat and a capacity higher than 400 mF/cm^2 was recorded.

Funding

(1) "2D Photocatalytic Heterostructures for Air Pollutants Oxidation", 2018-2021, T1EDK-05545, GSRT, 350.000€, 120.000€.
(2) "Nanocarbons from greenhouse gases of cement industry", 2019-2023, T1EDK-01719, GSRT, 390.000€, 150.000€.
(3) "Development of Novel Electrochemical Processes for Water Treatment Applications Using Composite Electrodes based on Nanocarbon Materials and Conductive Polymers", 2018-2021, T1EDK-02663, GSRT, 200.000€, 80.000€.
(4) "2D Lightweight Materials and Coatings for EMI Shielding Applications", 2019-2020, ESA, 180.000€.
(5) "Graphene Based Nanocomposite Electrodes for High Energy Density Supercapacitors", 2017-2020, ISN, 90.000 €, 20.000 €.
(6) "Novel 2D Nanocrystals for Smart Coatings Applications", 2017-2021, ISN, 120.000 €, 25.000€.
(7) "2-D semiconductors coupled with plasmonics as advanced photocatalysts and light emitters", Hellenic Foundation for Research & Innovation. 2018-2022. 190.000 €.

Publications in International Journals

1. Edelmannová M., Reli M., Kocí K., Papailias I., Todorova N., Giannakopoulou T., Dallas P., Devlin E., Ioannidis N., Trapalis C., "Photocatalytic Reduction of CO_2 over Iron-Modified g-C_3N_4 Photocatalysts", *Photochem 1* (2021) 462-476. https://doi.org/10.3390/photochem1030030
2. Mavrikos, A., Papoulis, D., Todorova, N., Papailias, I., Trapalis, C., Panagiotaras, D., Chalkias, D.A., Stathatos, E., Gianni, E., Somalakidi, K., Sygkridou, D., Komarneni, S., "Synthesis of Zn/Cu metal ion modified natural palygorskite clay-TiO_2 nanocomposites for the photocatalytic outdoor and indoor air purification". *J. Photochem. Photobiol. A.* **423,** 113568 (2022) https://www.sciencedirect.com/science/article/pii/S1010603021004378
3. Papailias, I., Todorova, N., Giannakopoulou, T., Dvoranova, D., Brezova, V., Dimotikalic, D., Trapalis, C. "Selective removal of organic and inorganic air pollutants by adjusting the g-C_3N_4/TiO_2 ratio". *Catal. Today* **361,** pp. 37-42 (2021). https://doi.org/10.1016/j.cattod.2019.12.021
4. Bika, P., Giannakopoulou, T., Osokin, V., Li, M., Todorova, N., Kaidatzis, A., Taylor, R.A., Trapalis, C., Dallas, P. "An insight study into the parameters altering the emission of a covalent triazine framework". *J. Mater. Chem. C* (2021) https://pubs.rsc.org/en/content/articlehtml/2021/tc/d1tc02985a
5. Giannakopoulou, T., Pilatos, G., Todorova, N., Boukos, N., Vaimakis, T., Karatasios, I., Trapalis, C. "Effect of processing temperature on growing bamboo-like carbon nanotubes by chemical vapor deposition". *Mater. Today Chem.* **19**, 100388 (2021). https://doi.org/10.1016/j.mtchem.2020.100388
6. Athanasoulia, I.-G., Giachalis, K., Todorova, N., Giannakopoulou, T., Tarantili, P., Trapalis, C. Preparation of hybrid composites of PLLA using GO/PEG masterbatch and their characterization. *J. Therm. Anal. Calorim.* **143,** pp. 3385–3399 (2021). https://doi.org/10.1007/s10973-019-09227-z
7. Tomšík, E., Dallas, P., Šeděnková, I., Svoboda, J., Hrubý, M. "Electrochemical deposition of highly hydrophobic perfluorinated polyaniline film for biosensor applications". *RSC Advances* **11**, pp 18852-18859 (2021) https://pubs.rsc.org/en/content/articlehtml/2021/ra/d1ra02325j
8. Gatou, M-A., Bika, P., Stergiopoulos, T., Dallas, P., Pavlatou, L. "Recent Advances in Covalent Organic Frameworks for Heavy Metal Removal Applications". *Energies* **14**, pp. 3197-3223 (2021) https://www.mdpi.com/1996-1073/14/11/3197

International Conferences Presentations (invited, oral, poster)

1. Todorova, N., Giannakopoulou, T., Papailias, I., Trapalis, C., "MXene-based composites for EMI shielding and photocatalysis", *4th International Symposium on Energy and Environmental Photocatalytic Materials (EEPM4)*, July 25-29 2021, Xi'an, China, Presentation (Oral, virtual presentation).
2. N. Plakantonaki, M. Vagenas, N. Todorova, T. Giannakopoulou, O. Kotrotsiou, C. Kiparissides, M. Karakassides , C. Trapalis, "Biomass-derived hierarchical porous carbon as highly-efficient electrode material", 5th International

Conference On Capacitive Deionization & Electrosorption (CDI&E), May 9th-13th 2021, Atlanta, USA (Poster presentation).

3. N. Plakantonaki, M. Vagenas, N. Todorova, T. Giannakopoulou, M. Karakassides, C. Trapalis, "Tailoring Capacitive Deionization process by nanocomposite electrodes", 5th International Conference On Capacitive Deionization & Electrosorption (CDI&E), May 9th-13th 2021, Atlanta, USA (Poster presentation).
4. Gıannakopoulou T., Plakantonaki N., Vagenas M., Papailias I., Boukos N., Todorova N. and Trapalıs C., "CO_2 Utilization for Preparation of Carbon Nanostructures", 17th International Conference on Environmental Science and Technology (CEST 2021), September 1st-4th 2021, Athens, Greece, (poster presentation).
5. P. Bika, T.Giannakopoulou, V.Osotkin, M.Li, R.A.Taylor, C.Trapalis, P.Dallas. "A covalent triazine framework of tunable emission for sensor applications". EMRS (European Materials Research Society), Strasbourg, France. May 31-June 3, 2021 (oral presentation).
6. P.Bika, N.Ioannidis, T.Giannakopoulou, P.Dallas. "A redox active triazine framework for photocatalytic applications." Acac2020 (Athens Conference on Advances in Chemistry), Athens, Greece. From March 10-14, 2021 (Oral presentation).

Teaching and Training Activities

Name: Christos Trapalis
Activity Title, Dates/Duration of lectures/training: Pollution Abatement Processes / 5/10/2021 - 31/12/2021.
Location/Academic Institute: Athens/Hellenic Open University.

Doctoral Dissertations completed in 2021

Name: Sofia Karapati
Dissertation Title: Development of modified TiO_2 nanoparticles for photocatalytic oxidation of air pollutants.
Research Supervisor at NCSR: Christos Trapalis
University where the Thesis was presented: National Technical University of Athens (NTUA).

Services

Determination of Supercapcitors properties. Industrial partner, 50.000€.


program 3
Cultural Heritage

CERAMICS AND COMPOSITE MATERIALS

Project Leader: Vassilis Kilikoglou

Permanent Research Staff: Anno Hein, Ioannis Karatasios

Research fellows: Peter M. Day

Post Docs: M. Amenta, D. Koumpouri, A. Michalopoulou.

PhD Candidates: S. Papaioannou, A. Panagopoulou, K. Christodoulou, K. M. Pollatou, H. Bartlet-Balicki

Objectives

- Development of analytical methods and approaches for statistical data processing applied in the study of the compositional variation of raw materials and the provenance of finished products in view of the investigation of trade routes and exchange networks.
- Development of experimental and computational methods for the investigation of function and performance of archaeological materials and objects and the study of ancient technologies
- Study of deterioration mechanisms and patterns of inorganic materials, in relation to environmental and burial conditions
- Development and design of new materials, with physicochemical compatibility to the original ones, self-healing and self-sensing properties for the conservation and restoration of monuments and buildings.

Main scientific results and highlights

Self-healing and self-sensing nano-composite conservation mortars

Cement-based spherical capsules, prepared in the lab, were incorporated in cement mixtures in different concentrations in order to study their effect on cement properties and healing efficiency. The representative results presented belowindicated the beneficial effect of capsules addition on the self-healing efficiency of cement-basedmortars.

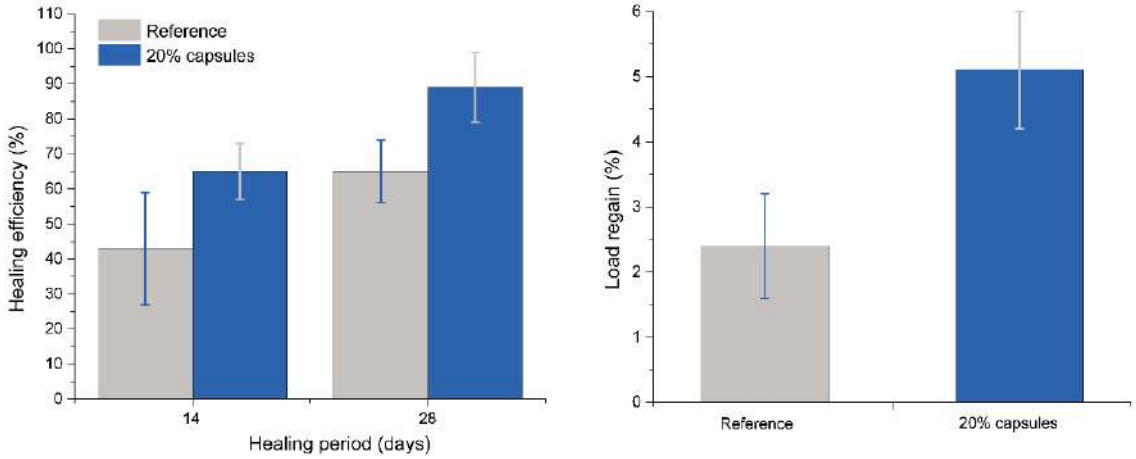


Figure 1. Effect of capsules addition on the healing efficiency of cement specimens, in terms of water permeability test (left) and strength recovery after 28 d of healing (right).

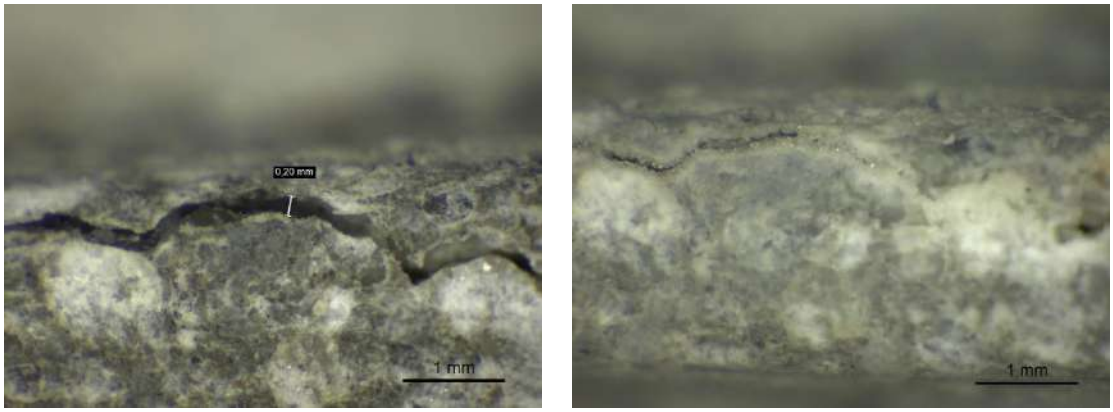
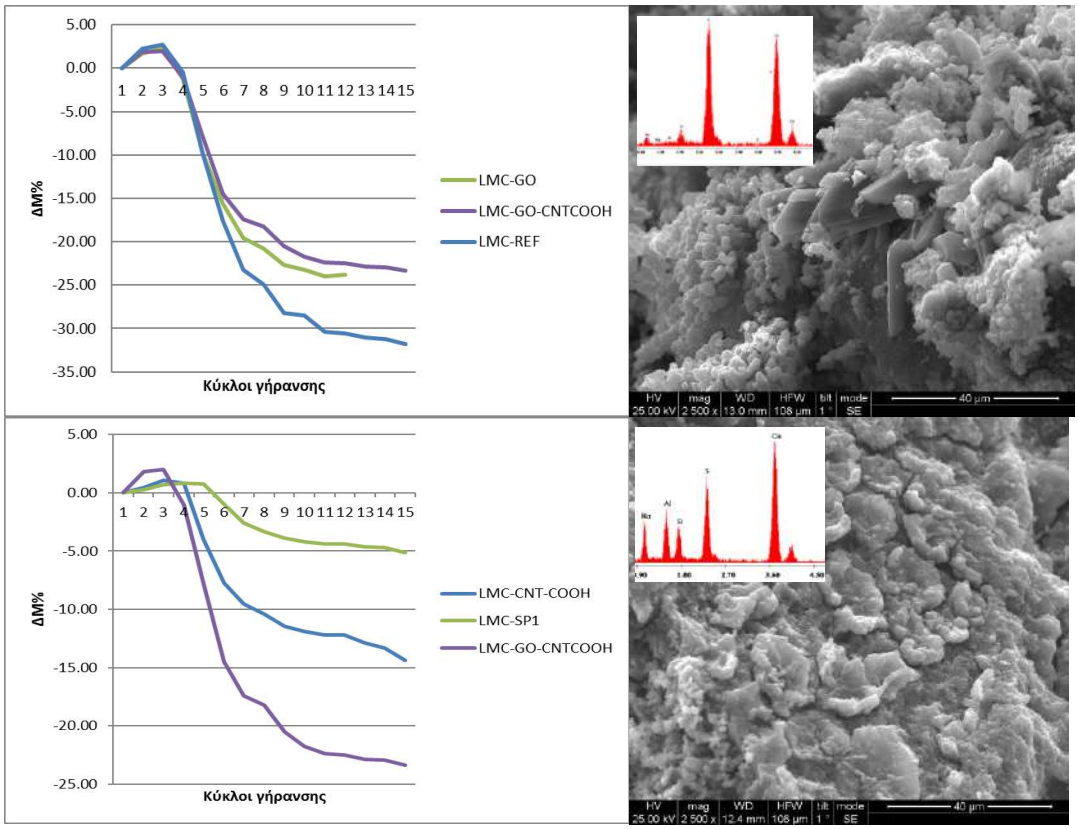


Figure 2. Stereomicroscope images of capsule containing specimens after cracking (left) and after 28 d of healing under water (right).

Durability of nanocomposite restoration mortars through accelerated aging test

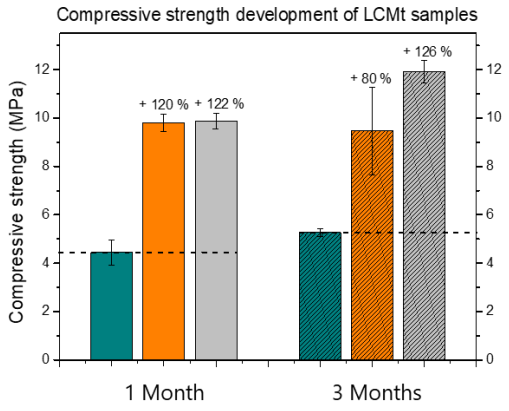
The durability of nanocomposite mortars was studied through accelerated aging cycles with soluble salts (Na_2SO_4) according to EN12370. It was shown that the durability of restoration mortars is enhanced by the addition of Graphene Oxide and is further enhanced by the cumulative effect of Graphene Oxide and Carboxylated CNTs addition. Furthermore, when superplasticizer is added to the mixture the resistance to salt crystallization is greatly improved, masking the effects of the nanomaterials. Moreover, SEM studies revealed that the chemical composition of the crystallized salts differed between the Graphene Oxide and the Carboxylated CNTs mortars where Gypsum or Thenardite were observed respectfully.



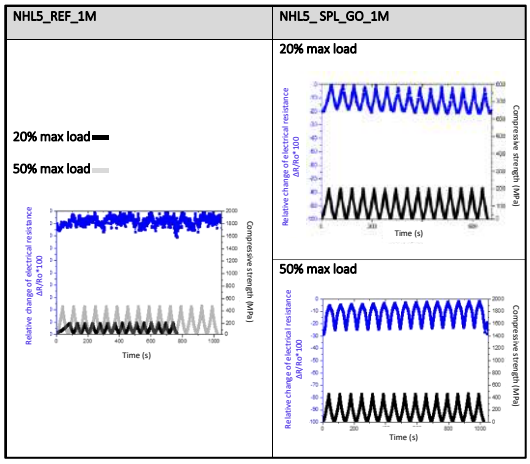
Development of carbon nano-reinforced groutswith piezoelectric properties

The current project investigated the development of novel grouts with the incorporation of carbon nano-structures (CNT), for attributing piezoelectric properties on the grouts. Three types of grouts were studied (Natural Hydraulic Lime_NHL5, Natural Hydraulic Lime and Metakaolin_NHL5Mt and hydraulic Lime, Cement and Metakaolin_LCMt), in combination with two types of superplasticizers (sulphonated and polycarboxylate) and graphene oxide (GO). The

studywas focused on the rheological and stability properties of the fresh grouts, along with porosity, 3 pond bending and compressive strength properties. The electrical and piezoelectrical properties of the grouts were evaluated at 1 and 3 months of hydration.



Results of compressive strength *development of hydraulic Lime – Cement – Metakaolin (LCMt) grouts. On the graph are the reference grouts as well as with superplasticizer (SPL) and superplasticizer – graphene oxide (SPL_GO) addition for 1 and 3 months of hydration.*



Experimental curves of the piezoelectric measurements *of Natural Hydraulic Lime (NHL5) reference (REF) samples and samples with the addition of superplasticizer – graphene oxide (SPL_GO) for 1 and 3 months of hydration and for loads of 20% and 50% of the max load.*

Non-invasive Compositional Characterization of archaeological materials

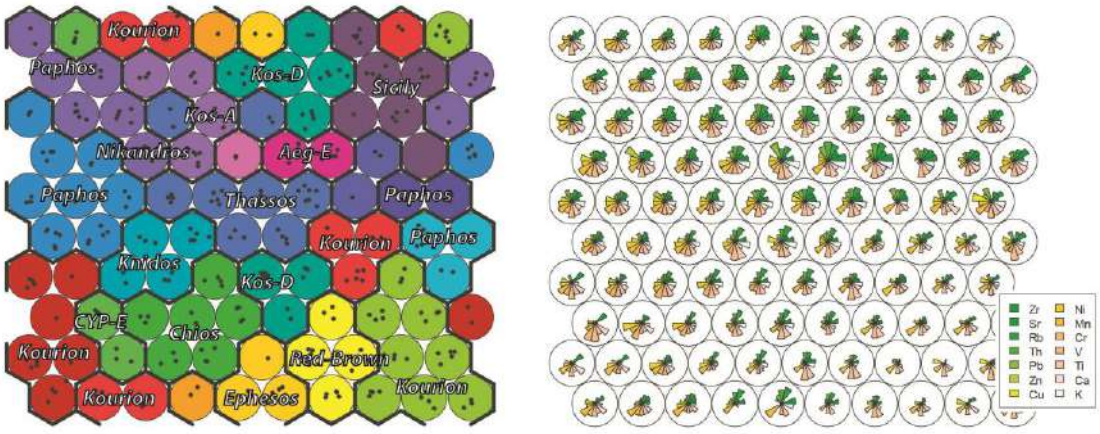
The compositional characterization of archaeological objects and structures as well as of the raw materials used for their manufacture remains an essential focus of research. The elemental analysis of ceramics and clayey raw materials is investigated with neutron activation analysis (NAA) in collaboration with the Missouri University Research Reactor (MURR). Apart from NAA handheld portable X-Ray fluorescence spectroscopy (pXRF) is applied as non-invasive analytical method for the categorization of different categories of archaeological, such as ceramics, metals, pigments, marble or obsidian. In 2021 a case study was published, in which the feasibility of pXRF as survey method in view of optimizing the sampling strategy of large ceramic assemblages has been tested. Furthermore, a large assemblage of more than 500 stamped clay nodules of the Minoan Period was analysed non-invasively by pXRF, for which sampling would have been impossible. The pXRF allowed for defining different groups of nodules, which provided information about Palatial administration in Minoan Crete.

Set up of the pXRF system in the Archaeological Museum of Heraklion

Artifical Neural Networks in the evaluation of comporisitional data

During the recent years portable energy dispersive XRF (pXRF) has been introduced in the study of archaeological materials allowing for fast and non-invasive measurements of their elemental compositions. In the case of pottery analyses, though, several issues arise. The method is extremely surface sensitive, which has to be considered for

measurements of slipped, painted or weathered surfaces. The determined element concentrations are commonly less precise and accurate than compositional data collected with laboratory measurements. The suite of elements potentially measured is smaller and concentrations might be below the lower limit of determination. The sample geometry introduces additional uncertainty as the systems are calibrated for measurements of plane surfaces in direct contact. Hence, the statistical evaluation of pXRF data following traditional approaches of multivariate statistics applied to data collected by laboratory analyses becomes inappropriate. For the evaluation of the considerably fuzzier pXRF data a rather flexible approach is expected to be more feasible taking into account the actual data structure rather than assumptions regarding geochemistry. For this, the application of artificial neural networks (ANN) is tested and the multivariate data are evaluated using self organizing maps (SOM).



Self Organizing Map (SOM) based on a pXRF dataset of c. 300 amphora fragments from the Hellenistic Agora in Palaio Paphos (Cyprus)

Funding

AKEISTHAI – Self-healing and self-sensing nano-composite conservation mortars (MIS 5031866), Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE, GSRT.

PlaCe - MSC-ITN Training the next generation of archaeological scientists: Interdisciplinary studies ofpre-modern Plasters and Ceramics from the eastern Mediterranean , (PlaCe – GA no. 956410)

HELIOKERAMOS– Developmentof building integrated organic solar cells (OSC), on a new type ofmultifunctional roof-tiles for energyproduction. 2019-2023 (MIS 5066858)

OUTPUT

Publications in International Journals

1. Amenta, M., Metaxa, Z. S., Papaioannou, S., Katsiotis, M.S., Kilikoglou, V., Kourkoulis, S. K., Karatasios, I., "Quantitative evaluation of self-healing capacity in cementitious materials," Mater. Des. Process. Commun., vol. 3, no. 3, p. e152, Jun. 2021
2. Chrysoula Litina, C., Bumanis, G., Anglani, A., Dudek, M., Maddalena, R., Amenta, M., Papaioannou, S., Pérez, G., García Calvo, G. L., Asensio, E., Cobos, R. B., Pinto, F. T., Augonis, A., Davies, R., Guerrero, A., Moreno, M. S., Stryszewska, T., Karatasios, I., TullianI, J. M., Antonaci, P., Bajare, D., Al-Tabbaa, A. Evaluation of Methodologies for Assessing Self-Healing Performance of Concrete with Mineral Expansive Agents: An Interlaboratory Study, Materials Vol. 14 (2021). DOI: 10.3390/ma14082024
3. Hein, A., Jung, R., Kardamaki E., Kilikoglou, V. Pottery Production in Mycenaean Laconia: NAA Results from the Palace of Ayios Vasileios, Praehistorische Zeitschrift (2021). DOI: 10.1515/pz-2021-0002
4. Hein, A. Dobosz, A., Day, P.M., Kilikoglou, V., Portable ED-XRF as tool for optimizing sampling strategy – Case study of a Hellenistic amphora assemblage from Paphos (Cyprus), Journal of Archaeological Science 133 105436 (2021). DOI: 10.1016/j.jas.2021.105436

5. Koumpouri, D., Karatasios, I., Psycharis, V., Giannakopoulos, I.G., Katsiotis, M.S., Kilikoglou, V. Effect of clinkering conditions on phase evolution and microstructure of Belite Calcium-Sulpho-Aluminate cement clinker. Journal of Cement and Concrete Research **vol** 147, (2021). DOI: 106529
6. Panagopoulou, A.P., Vroom, J., Hein, A., Kilikoglou, V., Production Technology of Glazed Pottery in Chalcis, Euboea during the Middle Byzantine Period, Heritage 4 4473–4494 (2021). DOI: 10.3390/heritage4040247
7. Papaioannou, S., Amenta, M., Kilikoglou, V., Gournis, D., Karatasios, I. Critical Aspects in the Development and Integration of Encapsulated Healing Agents in Cement and Concrete, Journal of Advanced Concrete Technology, Vol. 19, 301-320 (2021). DOI: 10.3151/jact.19.301
8. Cutillas-Victoria, B., Buxeda i Garrigos, J. and Day, P.M. Technological change and cultural resistance among southeast Iberian potters: analytical characterisation of Early Iron Age pottery from Castellar de Librilla. Archaeological and Anthropological Sciences, Volume 13, Article number: 174
9. Gilstrap, W.D., Meanwell, J.L., Paris, E.H., López Bravo, R. and Day, P.M. Post-depositional alteration of calcium carbonate phases in archaeological ceramics: depletion and accretion effects. Minerals, 11, 749. https://doi.org/10.3390/ min11070749

Papers in Refereed Conference Proceedings

- Hein, A., Revisiting the groups – Exploring the feasibility of portable EDXRF in provenance studies of transport amphorae in the Eastern Aegean, in M. Hegewisch, M. Dazkiewicz and G. Schneider (eds.) Application of portable energy-dispersive X-ray fluorescence to the analysis of archaeological ceramics and glass, Topoi - Berlin Studies of the Ancient World - Vol. 75 43-61. (2021) DOI: 10.17171/3-75
- Panagopoulou, A. Vroom, J. Kilikoglou, V. Hein, A. ProductIon Technology of ByzantIne ceramics at Chalkis: some PrelImInary results, in P. Petridis, G. Yangaki, N. Liaros, E.-E. Bia (eds.) 12th Congress AIECM3 On Medieval and Modern Period Mediterranean Ceramics – Proceedings, Athens 339-343 (2021).

Books/Chapters in Books

- Hein, A., Kilikoglou, V., Examination of terracotta figurines from the excavation at Ancient Halasarna, in G. Kokkorou-Alevra, S. Kalopisi-Verti, M. Panagiotidi-Kesioglou (eds.) ΑΛΑΣΑΡΝΑ VII, Athens, pp. 87-96 (2021).
- Pautasso, A., Rizza, S., Pappalardo, E., Hein, A., Biondi, G., Gigli, R., Perna, K., Guarnera, V., Priniàs. Scavi e ricerche nel 2021, in Annuario della Scuola Archeologica Italiana di Atene 99.II, 2021, Scuola Archeologica Italiana di Atene, Athens pp. 9-53 (2021).
- Gilstrap, W.D., Day, P.M. and Kilikoglou, V. Compositional Analysis of LH IIIB-IIIC early Ceramics from the Cave of Euripides, Salamis, Greece. (Appendix 2) In C. Marabea, Salamis II, The Cave of Euripides at Peristeria Salamina: The Mycenaean Use, 215-243

Other type of publications (non-refereed Conference Proceedings, magazine, etc)

- Hein, A., Ονόματα γυναικών σε ενσφράγιστες λαβές αμπορικών αμφορέων - Women and amphora production - Appendix, in K. Kopanias and G. Doulfis (eds.) Τέχνης ἐμπειρία - Νέα Αρχαιολογικά Ευρήματα και Πορίσματα, 268-269 (2021).

International Conferences Presentations (invited, oral, poster)

- Bartlet Balicki, H., Considering social network analysis: A Black Sea case study investigating trade dynamics in the ancient Greek world. Computer Applications and Quantitative Methods in Archaeology - Greece (CAA-GR), 21-22 Oct 2021, Athens. (oral)
- Christodoulou, K. Pollatou, K. Grigoropoulos, D. Hein, A., Preliminary results from a mineralogical and chemical study of clayey raw materials from the area of East Phokis and East Lokris, Waiting for EMAC2023@Pisa, 6-8 Jul 2021, Pisa. (poster)

- Hein, A. Ceramic cooking pots and cooking structures: Thermo-mechanical and performance, Archeology of Cooking in Ancient Greece, International Round Table, 27 May 2021 Athens. (invited)
- Hein A. and Kilikoglou, V. Modeling the material performance of ceramic vessels in view of their function and utilization, Computer Applications and Quantitative Methods in Archaeology, 14-18 Jun 2021, Limassol (virtual). (oral)
- Hein, A., Compositional variation of clays and archaeological ceramics in the Eastern Mediterranean, Neutron activation analysis (NAA) and its relevance to the Archaeology of the ancient Mediterranean, 17-18 Jun 2021, Tuebingen (virtual). (invited)
- Hein, A. Categorization of archaeological ceramics - based on their elemental composition using self organizing maps (SOM), Computer Applications and Quantitative Methods in Archaeology - Greece (CAA-GR), 21-22 Oct 2021, Athens. (oral)
- Mentesana, R. Buxeda i Garrigòs, J. Kilikoglu, V. Hein, A. Madrid i Fernàndez, M. Making, Producing and Consuming Sugar on the East Coast of the Iberian Peninsula: The Contribution of the Ceramic Study to the Understanding of the "Sugar Cycle", Waiting for EMAC2023@Pisa, 6-8 Jul 2021, Pisa. (oral)
- Mentesana, R. Buxeda i Garrigòs, J. Kilikoglou, V. Hein, A. Madrid i Fernàndez, M. Adaption and Transformation of the Ceramic Manufacture for Sugar Production in Medieval Europe, EAA Annual Meeting, , 6-11 Sep 2021, Kiel. (oral)
- Palacios O. and Hein, A. Investigating Technological Properties of Bone-tempered ceramics in Prehistoric Europe, EAA Annual Meeting, 6-11 Sep 2021, Kiel. (oral)
- Panagopoulou, A.P. Vroom, J. Hein A. and Kilikoglou, V. Kütahya wares versus porcelain in Mytilene - Original Manufacturing Technology or a 'Peasant Porcelain'? 13th International Congress on Medieval & Modern Period Mediterranean Ceramics, 8-13 Nov 2021, Granada. (poster)
- Mentesana, R. Buxeda i Garrigòs, J. Kilikoglu, V. Hein, A. Madrid i Fernàndez, M.The production and circulation of sugar pots in the Iberian peninsula in the 15th-16th century: old and new data examined with the contribution of archaeological science, 13th International Congress on Medieval & Modern Period Mediterranean Ceramics, 8-13 Nov 2021, Granada. (oral)

Teaching and Training Activities

Anno Hein
Summer Course: Conservation and Physicochemical Study of Nisyros Shipwreck Pottery, Apr 2021/1h lecture
Athens, Netherlands Institute in Athens (virtual)

Anno Hein
'Archaeological Ceramics' (MSc CultTech), Nov 2021, 2 x 3h lectures
Kalamata, University of Peloponnese, Department of History, Archaeology and Cultural Resources Management

Anno Hein
CCC52 'Materials Science' (MSc 'Protection of Cultural Heritage and Monuments of Nature from the Effects of Climate Change (CCC)'), Oct 2021 – Jul 2022, c. 10 h per month
Patras, Hellenic Open University, School of Applied Arts and Sustainable Design, (web seminars)

Ioannis Karatasios
MSc CultTech, Archaeometry I, Two lectures in December
Kalamata, Department of History, Archaeology and Cultural Resources Management, University of Peloponnese

Ioannis Karatasios
MSc Cultural Heritage Conservation, Four lectures in March
Athens, Department of Conservation of Antiquities and Works of Art, University of West Attica

Vassilis Kilikoglou
MSc CultTech, Archaeometry I, Two lectures in May and two lectures in November
Kalamata, Department of History, Archaeology and Cultural Resources Management, University of Peloponnese

Anastasia Michalopoulou
MSc Cultural Heritage Conservation, Two lectures in March

Athens, Department of Conservation of Antiquities and Works of Art, University of West Attica

Conference / Workshop Organisation

Computer Applications and Quantitative Methods in Archaeology - Greece (CAA-GR), 21-22 Oct 2021, Athens. (virtual)

AKEISTHAI Conference & Workshop, 10 & 13 December 2021, National Centre for Scientific Research “Demokritos”

Patents

ENCAPSULATED SYSTEMS FOR THE DEVELOPMENT OF SELF-HEALING BUILDING MATERIALS
Application No./Patent No.: 21161152.0 – 1108
Application date: March 2021

MATERIAL AND ENVIRONMENTAL ISOTOPE GEOCHEMISTRY (STABLES ISOTOPES AND RADIOCARBON

Project Leader: Dr. Elissavet Dotsika

Permanent Research Staff: Dr. Elissavet Dotsika

Associate Researchers: G. Diamantopoulos, M. Tassi

PhD Candidates: P. Karalis, E. Iliadis., E. Palaigeorgiou, O. Kourakis

Research Collaborators (emeritus or visiting):

- Memorandum between Hellenic National Defense General Staff, Hellenic Team of Experts of the Joint Committee of Experts, 251 General Hospital of Hellenic Air Force and National Centre for Scientific Research "Demokritos" (Stable Isotope Unit)
- Internship agreement between University of Sidney, Australia and National Centre for Scientific Research "Demokritos" (Stable Isotope Unit) (Dr. A, Tindell)
- Internship agreement between University of Pisa, Italy and National Centre for Scientific Research "Demokritos" (Stable Isotope Unit), (Dr. B. Raco, CNR, Pisa).
- Internship agreement between University of Calabria, Italy and National Centre for Scientific Research "Demokritos" (Stable Isotope Unit), (Prof. C. Apollaro).
- Internship agreement between University of Warsovia and National Centre for Scientific Research "Demokritos" (Stable Isotope Unit), Prof. Roksana Chowaniec, University of Warsaw, Institute of Archaeology, krakowskie przedmiescie 26/28, pl 00-927, Warsaw, Poland.
- Internship agreement between University Helsinki, with Dr. Kati Salo (finno-ugrian gene project), dr. Mika Lavento (Archaeology dep.) and dr. Kati Salo (National board of Antiquities, Finland)
- Collaboration with the Ministry of Culture and all the Ephorates of Antiquities of Museums of Greece.
- Collaboration with Centre for Research and Technology Hellas (Dr. D. Tzovaras)
- Collaboration with the National Technical University of Athens
- Collaboration with the University of Volos (Prof. A. Mazarakis)
- Collaboration with the National and Kapodistrian University of Athens
- Collaboration with the University of Patras

Research Objectives

A) Material and Environmental Isotope Geochemistry

- Development of novel and combined methodologies for the determination of stable isotope composition of different materials: geological, biological, composite and natural.
- expanding the existing spectrum of isotope diagnosis (Geochemistry-Isotope fingerprinting) with novel isotope tracers
- Characterization and investigation of the technology of ancient –historic structural materials (marbles, glass and mortars)
- Damage diagnosis and scientific determination of weathering and decay mechanisms of ancient-historic materials and development of conservation materials.
- Provenance determination and weathering of ancient and modern materials
- Palaeoenvironmental and paleoclimatic reconstruction
- Palaeodiet
- Origin of geofluids-pollution, palaeohydrology
- Origin of raw materials
- Authenticity and fingerprinting of food and natural products

B) Analytical Work

- Stable isotopes of inorganic carbonate materials ($\delta^{13}C$, $\delta^{18}O$), organic materials ($\delta^{13}C$, $\delta^{15}N$), water ($\delta^{18}O$, $\delta^{2}H$), sulfates ($\delta^{34}S$) as well as elemental analysis of C, N and S in geological, biological, composite and natural materials.
- Application of boron, strontium and neodymium isotopes in archaeological and geological materials
- Development and the appropriate measuring new protocols for isotopic measurements in different materials (bone, teeth enamel, glass and mortars).
- Construction of database of local food products, raw materials, natural products, water (precipitation, lakes, spring) and further development of existing ones. These databases are the baselines and reference points for archaeological, hydrology, forensic, agricultural studies etc.

Activities and Main Results

1. **Glass artefact - Investigation of Early vitreous Technology Construction Materials and Glass.**

In this project we investigate

- the geographical origin of raw material using in the production of ancient glass,
- the geographic identification of glass artifacts i.e. local or foreign provenance
- the evolution of production technologies ex. (coloring and opacifying agents used, recycling of broken glasses)
- the distinction of primary and secondary workshops

2. **Palaeo-Environment reconstruction**

In this project we investigate:

- Water systems sediment deposition and erosion in caves, tombs and other environments that can provide information for dating, origin as well as evolution and recovery of palaeoenvironment and palaioecology. The concentration of ^{13}C and ^{18}O in materials such as bones, spileothems, shells, carbonate sediments, etc., which varies depending on climatic changes, can also supply information for palaeoenvironment reconstruction.
- Human and animal tissue (bones, teeth). During the last four decades, the analysis of stable isotopes in terrestrial teeth and bones has provided valuable information about the palaeoclimatic and palaeoenvironmental conditions on the Quaternary period as well as palaeodiet habits for a variety of species. Oxygen, nitrogen, carbon, boron, strontium, and neodymium comprise principal structural materials of skeleton and teeth. These elements mainly originate from the water and food that the animal consumes and reflect the respective isotopic fingerprints of their original sources. From 2015 up to today research was conducted on palaeoclimatic, diet and mobility information from isotopic signatures of bone and teeth apatite.

3. **Mortar**

In this project we investigate mortar samples from historic masonries dated from classical to Ottoman period with stable isotope analysis. The study focuses on the analysis of stable isotopes of oxygen and carbon (^{13}C and ^{18}O) in order to determine the origin of calcite and to diagnose the state of preservation of historic mortars. Investigation of the provenance of the raw materials of the ancient mortars is conducted in order to determine the most appropriate compositions for contemporary restoration mortars.

4. **Isotopes fingerprint and Natural genetic indeX.**

Common methods for identifying remains include examination of the biological profile, dental records, forensic facial reconstruction (2D and 3D, with age regression), inspection of personal effects and artifacts from medical or surgical procedures (birthmarks, surgical scars, implants, etc.), fingerprints and DNA analysis, photographic documentation and documentation of the burial site. Even so, positive identification may not be possible, in all cases, due to luck of databases (in order to match the DNA profile of a single individual remains there must be a record of relatives of that individual in forensic DNA databases for comparative analysis - in consequence, individuals whose DNA profiles are unknown cannot be identified). In cases where only partial remains, including some

scattered bones, few personal effects, and mass of hair, are found and no comparative materials are available for DNA analysis, none of these investigative techniques or tools can provide the needed evidence to give the decedent its name.
In this project we implement a methodology for identifying the geographic origin of unidentified persons (recent and ancient), their residence and moving patterns while providing information on lifestyle, diet and socio-economic status by combining stable isotopic data, with the biological information (from the skeleton). This is accomplished by comparing the oxygen isotopic composition of the spring water that an individual was drinking, during his living period, with the oxygen isotopic composition of tooth enamel and bone apatite.

- We perform stable isotope analysis in human bones and teeth for the identification of Greeks killed in military operations during the Greek-Italian War 1940-41, by categorizing human remains (e.g. bones, teeth) according to the predicted geographical area that the individual lived before death and their eating habits, which could facilitate the overall task of genetic identification. Specifically, we correlate the ^{13}C, ^{15}N, ^{18}O isotopes of human bones and teeth with the geographically controled ^{18}O isotope of water in order to estimate the place in which they lived before death and to reconstruct their dietary habits.

5. Natural products.

In this project, we intergraded and transferred knowledge to industries in the food branch. Specifically, the research activities on meteoric waters and on fractionation of the isotopic values in different biological systems contributed to the development of methodologies for authenticating the provenance of food products and ensuring the purity with fraud detection, thus providing added value to food products and self-guarding the consumer's rights. In the last five years the results were implemented to wine, oil, honey cereals producers and contributed to the authentication of their products.

6. Geothermy

The use of stable isotopes (^{13}C, ^{18}O, ^{34}S, ^{18}O (SO_4), ^{18}O (CO_2), ^{2}H, 18O, ^{11}B, $^{87}Sr/^{86}Sr$) and radiocarbon (^{14}C) allows the study of aquatic environment (the source of dissolved carbonate, source of water, source of data, mixing), the deep geothermal fluids (water source, source of elements, water-rock interaction, geothermometria) of geological materials (origin of carbonate rocks, travertine, etc.), of the atmosphere (the source of infection through the study of CO_2 and CO and control of human intervention in the surrounding cities or industrial zones)

Funding Projects

1. Develoment of novel technologies and methods for highlighting and protecting monuments of cultural heritage (Palimpsisto)
   Funding source: The Management and Implementation Authority for Research, Technological Development and Innovation Action (MIA-RTDI) / Operational Program Competitiveness, Entrepreneurship and Innovation (Call: Research-Create-Innovate), 2021-today
2. Novel RoV with Haptic Arms for Underwater Archaeological Research (u-ArchaeoRoV)
   Funding source: The Management and Implementation Authority for Research, Technological Development and Innovation Action (MIA-RTDI) / Operational Program Competitiveness, Entrepreneurship and Innovation (Call: Research-Create-Innovate), 2021-today
3. Restoration of ancient theatre in Thasos
   Funding source: Ephorate of Antiquities of Kavala – Thasos, Ministry of Culture, 2021-today
4. Development of a holistic methodology for the verification of authenticity, for the improvement of the quality of traditional products, for the protection of consumers from fraud or adulteration (BACCHUS)
   Funding source: The Management and Implementation Authority for Research, Technological Development and Innovation Action (MIA-RTDI) / Operational Program Competitiveness, Entrepreneurship and Innovation (Call: Research-Create-Innovate), 2020-today

5. Application of modern analytical and chemometric techniques for the quality control-fraud of olive products (Holea)

Funding source: The Management and Implementation Authority for Research, Technological Development and Innovation Action (MIA-RTDI) / Operational Program Competitiveness, Entrepreneurship and Innovation (Call: Research-Create-Innovate), 2018-today

7. Food Authenticity and Food Traceabilitiy
   Funding source: Private commercial funding, 2019-today

OUTPUT

Publications in International Journals

1. Dotsika, E., Dalampakis, P., Spyridonos, E., Diamantopoulos G., Karalis P., Tassi M., Raco B., Arvanitis A., Kolios N. And Michelot J.L..Chemical and isotopic characterization of the thermal fluids emerging along the North–Northeastern Greece. Scientific Reports (Nature), (2021) 11, 16291, DOI: 10.1038/s41598-021-95656-6
2. Theodorakopouloy K., Kyriakopoulos K., Athanassa C.D., Galanopoulos E., Economou G., Maniatis Y., Godelitsas A., Dotsika E., Mavridis F., Darlas A., 2021. First Speleothem Evidence of the Hiera Eruption (197 BC), Santorini, Greece, Environmental Archaeology, 26(3), pp. 336-348, DOI: 10.1080/14614103.2020.1755196

Publications in Conferences

1. Vespasiano, G., Marini, L., Muto, F., Auqué, L.F., Cipriani, M., De Rosa, R., Critelli, S., Gimeno, M.J., Blasco, M., Dotsika, E., Apollaro, C., Chemical, isotopic and geotectonic relations of the warm and cold waters of the Cotronei (Ponte Coniglio), Bruciarello and Repole thermal areas, (Calabria - Southern Italy) (2021) Geothermics, 96, 102228

Publications in Books

1. Dotsika E., Diamantopoulos G., Longinelli A., Ignatiadou D., Analyses of Methone glasses, In Methone, D. Ignatiadou, Early glass in Methone (J. Papadopoulos et. al (eds), (Book, in press. 2021).
   Chrysostomou, A. Agras - Edessa In The Iron Age; Edessa: 2021.
2. Prohitech 2021, 4th International Conference On Protection Of Historical Constructions 25-27 October 2021, Athens, Greece “Stable Isotopic Composition Of Carbonate Materials For Determination Of The Origin Of Marble Artifacts” Karalis P., Tassi M., Heliades E., Diamantopoulos G., Christaras V., Spathis P., Godelitsas A. and Dotsika E.
3. Prohitech 2021, 4th International Conference On Protection Of Historical Constructions 25-27 October 2021, Athens, Greece “Stable Isotope For Tracing The Salt Involved In The Degradation Of Stone Monuments” Karalis P., Tassi M., Gougoura S., Diamantopoulos G., Kyropoulou D., Heliades E., Palaigeorgiou E., Godelitsas A. And Dotsika E.
4. Prohitech 2021, 4th International Conference On Protection Of Historical Constructions 25-27 October 2021, Athens, Greece “Δ13c And Δ18o Stable Isotope Analysis Applied To Indicate Sources Of Water-Induced Degradation In Historic Monuments” Kyropoulou D., Heliades E., Karalis P., Diamantopoulos G., Gougoura S. and Dotsika E.
5. Prohitech 2021, 4th International Conference On Protection Of Historical Constructions 25-27 October 2021, Athens, Greece “Technological Evolution Of Historic Mortars: From Lime-Based Mortars To Roman Opus Caementicium” Kyropoulou D., Heliades E., Karalis P., Diamantopoulos G., Gougoura S. and Dotsika E.
6. 22aihv International Conference, 13-17 September 2021, Lisbon, Portugal “Glass Opera Sectilia From The South Stoa Roman Bath In Ancient Corinth’s Agora” Antonaras A., Karalis P., Tassi M. and Dotsika E.
7. 17th International Conference On Environmental Science And Technology (Cest2021), 1-4 September 2021, Athens, Greece “Chemical And Isotopic Characterization Of The Thermal Fluids Emerging From Nestos River Delta Basin In North Greece” Tassi M., Karalis P., Dalampakis P., Spyridonos E., Diamantopoulos G., Dotsika E. and Pagonis G.
8. 17th International Conference On Environmental Science And Technology (Cest2021), 1-4 September 2021, Athens, Greece “Chemical And Isotopic Characterization Of The Thermal Fluids In The South-Western Margin Of The Louros-Feres-Soufli Tertiary Basin In Northern Greece. Case Study: Geothermal Area Of Aristino” Dalampakis P., Spyridonos E., Tassi M., Karalis P., Dotsika E. and Pagonis G.

Teaching and Training Activities

Doctoral Dissertations

2018-Today	
Title	Isotopical Traceability of raw materials of Ancient Glass
Ph.D. Candidate	P. Karalis
Academic Institute	National Centre for Scientific Research "Demokritos" (Stable Isotope Unit) in Collaboration with University of Athens, Geology Department
Research Supervisor at NCSR	E. Dotsika
2015- Today	
Title	The Degree of Corrosion of Structural Materials and Excavations Finds of Archaelogical monuments in Eastern Macedonia and Thrace, using methods of Isotopical Geochemistry and Ultrasound Velocity.
Ph.D. Candidate	E. Iliadis
Academic Institute	National Centre for Scientific Research "Demokritos" (Stable Isotope Unit) in Collaboration with University of Thessaloniki, Geology Department
Research Supervisor at NCSR	E. Dotsika
2019- Today	
Title	Stable Isotope Contribution in the analysis of bio-hydrogeological systems.
Ph.D. Candidate	E. Palaigeorgiou
Academic Institute	National Centre for Scientific Research "Demokritos" (Stable Isotope Unit) in Collaboration with National Technical University of Athens
Research Supervisor at NCSR	E. Dotsika
2019-Today	
Title	The mineralogy, isotopical geochemistry and photographical capture contribution in the identification colorants on glass objects
Ph.D. Candidate	O. Kourakis
Academic Institute	National Centre for Scientific Research "Demokritos" (Stable Isotope Unit) in Collaboration with University of Athens, Geology Department
Research Supervisor at NCSR	E. Dotsika

Master Dissertations

2021-Today	
Title	Isotope analysis of pygmy hippo's fossil bone and tooth apat from Aghia Napa, Cyprus for palaeoclimate studies
M.Sc. Student	M. Nakasi
Academic Institute	National Centre for Scientific Research "Demokritos" (Stable Isotope Unit) in
Research	Collaboration with University of Athens, Geology Department
Supervisor at NCSR	E. Dotsika

RADIOCARBON DATING, PROVENANCE OF MARBLE AND COLOUR TECHNOLOGIES

Project Leader: Dr. V. Kilikoglou

Permanent Research Staff: Dr. G.S. Polymeris

Other Staff (technical): M.E. Kyriazi

Post Docs: -

PhD Candidates: E. Tsoutsoumanos

Master Students: Dr. A. Pentedeka

Research Collaborators (emeritus or visiting): Dr. Y. Maniatis

Objectives

Extending the applications of radiocarbon dating for monitoring and comparing human cultural phases of the past in an absolute time framework.
Developing methodologies and databases for precise determination of the origin of marble from artifacts, sculptures and monuments.
Basic research in age assessment using luminescence techniques – Age limit extension in luminescence dating – improving the accuracy of ages beyond 500 ka.
Application of computational technologies in age assessment

Highlights / main scientific results

- Tracing with Carbon-14 dating the beginning and spread of *Neolithization* in the Aegean. A long-standing project aiming at the identification of the geographic locations of the earliest settlements of the first farmers and stockbreeder in Greece. A time when the humans from hunter/gatherers acquired the knowledge/technology of agriculture and animal husbandry and founded the first permanent settlements. The so far results have shown that this started first in Central and West Macedonia and then spread to other locations. The project is now expanded in collaboration with the Democritus University of Thrace (Prof. D. Urem-Kotsou) and other Institutions to investigate the beginning and spread of Neolithization in Thrace a geographic area between Anatolia and Greece which may reveal the pattern of spreading.
- Dating of monumental olive trees located in the Ionian islands (Corfu, Paxoi, Cephalonia, Ithaca, Lefkada and Zakynthos). This project in collaboration with the Ionian University (Prof. A. Martinis) aims at identifying the oldest olive trees in the above areas and hence the history of olive tree cultivation in Greece. The dating of these old trees is quite challenging as they have lost their initial part. We use the following three approaches: (a) calculation of the radial growth rate from the preserved wood pieces and extrapolating to the total number of rings (thus the age) that would correspond to the radius of each tree according to the measured respective perimeter; (b) radiocarbon dating of sequential tree rings from the preserved older parts and applying the wiggle matching technique for a precise dating of the remaining part and calculation of the annual growth and (c) OSL and IRSL dating of the palaeo-sediments either surrounding or beneath the roots of the olive trees.
- Radiocarbon dating of samples from numerous archaeological sites and monuments in the region of Mediterranean.
- A number of projects on the marble provenance of ancient sculptures and monuments in Greece. Among these, the provenance of a series of 40 marble statuettes of the Roman period from the Athenian Agora stands as the most important. This project is now extended to roman portraits in the Acropolis and National Archaeological Museums in Athens.
- Developing tools for analysis of experiment data, modeling and machine learning approaches to archaeometry using common computing environments such as MATLAB, R, Python and Excel.

Funding

Collaborators to the European Project entitled MapFarm; Mapping the early farmers in Thrace (Democritus University of Thrace)
Collaborators to the European Project entitled Biomemories (Ionian University)

OUTPUT

Publications in International Journals

1. J.M. Kalita, Ş. Kaya-Keleş, G.Ö. Çakal, N. Meriç, G.S. Polymeris. Thermoluminescence and optically stimulated luminescence properties of ulexite mineral. *Journal of Luminescence* **230**, 117759 (2021). https://doi.org/10.1016/j.jlumin.2020.117759
2. E. Aşlar, E. Şahiner, G.S. Polymeris, N. Meriç. Thermally and optically stimulated luminescence properties of BeO dosimeter with different main dosimetric peak. *Applied Radiation and Isotopes* **170**, 109635 (2021). https://doi.org/10.1016/j.apradiso.2021.109635
3. E. Aidona, S.Spassov, D. Kondopoulou, G.S. Polymeris, K. Raptis, A.Tsanana. Archaeo-magnetism and Luminescence on Medieval kilns in Thessaloniki and Chalkidiki (N. Greece): implications for geomagnetic field variations during the last two millennia. *Physics of the Earth and Planetary Interiors* **316***,* 106709 *(2021)*. https://doi.org/10.1016/j.pepi.2021.106709
4. N. Meriç, E. Şahiner, G. Kitis, G.S. Polymeris. Component-Resolved Analysis Towards Correlation between Thermoluminescence and Optically Stimulated Luminescence in Commercial Magnesium Oxide. *Geochronometria* **48**, 222–231 (2021). https://doi.org/10.2478/geochr-2020-0011
5. E. Şahiner, G. S. Polymeris, M.Z. Öztürk, Y.K. Kadioğlu, N. Meriç. Component resolved equivalent dose estimation using TL glow curves of travertine samples from Anatolia, Turkey. *Geochronometria* **48**, 171–178 (2021). https://doi.org/10.1515/geochr-2015-0116
6. G.S. Polymeris, S. Çoskun, E. Tsoutsoumanos, P. Konstantinidis, E. Aşlar, E. Şahiner, N. Meriç, G. Kitis. Dose response features of quenched and reconstructed, TL and deconvolved OSL signals in BeO. *Results in Physics* **25,** 104222 (2021). https://doi.org/10.1016/j.rinp.2021.104222
7. S. Geranmayeh, E. Aşlar, E. Şahiner, G.S. Polymeris, N. Meriç. Comparison of TL and OSL properties of various porcelain-based items from Turkey towards their effective use in accidental retrospective dosimetry. *Nuclear Instruments and Methods in Physics Research B* **499**, 89 – 99 (2021). https://doi.org/10.1016/j.nimb.2021.05.007
8. L. Malletzidou, G.S. Polymeris, I.K. Sfampa, S. Stoulos, K.M. Paraskevopoulos, G. Kitis. Methodological aspects and practical limitations for luminescence dating applications in calcium sulfate samples implied by dose response and dose recovery measurements. *Microchemical Journal* **168,** 106382 (2021). https://doi.org/10.1016/j.microc.2021.106382
9. V. Pagonis, N. Brown, J. Peng, G. Kitis, G.S. Polymeris. On the deconvolution of unfaded luminescence signals in feldspars. *Journal of Luminescence* **239,** 118334. https://doi.org/10.1016/j.jlumin.2021.118334
10. P. Konstantinidis, S. Kioumourtzoglou, G.S. Polymeris, G. Kitis. Stimulated luminescence; Analysis of complex signals and fitting of dose response curves using analytical expressions based on the Lambert W function implemented in a commercial spreadsheet. *Applied Radiation and Isotopes* **176,** 109870 (2021). https://doi.org/10.1016/j.apradiso.2021.109870
11. A.E. Erginal, G.S. Polymeris, O. Erenoğlu, V. Giannoulatou, E. Meriç, A. Karataş, E. Şahiner, H. H. Selim. New record of calcarenite in Hatay, Turkey: an evidence of the Late Pleistocene Eastern Mediterranean–Red Sea connection. *Arabian Journal of Geosciences* **14**, 2104 (2021). https://doi.org/10.1007/s12517-021-08521-1
12. Y. Maniatis and F. Adaktylou-Pappas. Revenia-Korinos: one of The Earliest Neolithic Settlements in North Greece as Evidenced by Radiocarbon Dating. *Radiocarbon* **63(3)**, 1025-1051 (2021). https://doi.org/10.1017/RDC.2021.26
13. Y. Maniatis, D. Tambakopoulos, L. Lazzarini, M.C. Sturgeon. Provenance Investigation of Three Marble Relief Sculptures from Ancient Corinth: New Evidence for the Circulation of the White Marble from Mani. *Archaeometry* **63(4)**, 684-704 (2021). https://doi.org/10.1111/arcm.12647
14. F. Mavridis, P. Zafeiriadis, A. Papadea, E. Stravopodi, K. Trantalidou, K. Theodorakopoulou, K. Athanassas and Y. Maniatis. Kouvaras Cave: a new Early Holocene site in East Attica, Greece. *Past* **98**, 14-16 (2021).
15. I. Bald Romano, D. Tambakopoulos, Y. Maniatis. A Roman Portrait of Alexander the Great from Beth Shean. The most important Hellenistic sculpture found in the Holy Land. *Israel Museum Studies in Archaeology* **10**, 2-28 (2020–2021).
16. A.Reingruber, G. Toufexis, and Y. Maniatis. Elateia 1 in northeastern Thessaly 8000 years ago: relative and absolute chronology of a flat extended settlement. *Documenta Praehistorica* **XLVIII**, 2-19 (2021). https://doi.org/10.4312/dp.48.22

Books/Chapters in Books

1. Georgios S. Polymeris, Evrypidis Hatzikraniotis, Theodora Kyratsi. *Highly efficient Mg_2Si-Based Thermoelectric Materials: A Review on the Micro- and Nanostructure Properties and the Role of Alloying,* In: Highly Performed Silicide Thermoelectric Materials, Thermoelectric Energy Conversion: Theories and Mechanisms, Materials, Devices, and Applications, Editor: Ryoji Funahashi, Elsevier Publishing (2021).

Other type of publications (non-refereed Conference Proceedings, magazine, etc)

1. E. Tsoutsoumanos, G.S. Polymeris, P. Konstantinidis, Th. Karakasidis, G. Kitis, General Order Kinetics (GOK) vs One Trap One Recombination model (OTOR); Kinetic order – Retrapping ratio correlation in simulated LM-OSL curves using Deconvolution, Peak Shape Methods and Machine Learning, *XXXV Panhellenic Conference on Solid State Physics and Materials Science*, 26 - 29 September 2021, Athens, Greece.
2. G. Kioselaki, K. Prevezanou, P. Konstantinidis, E. Tsoutsoumanos, G.S. Polymeris, V. Pagonis, G. Kitis, Fitting modelling on Stimulated Luminescence dose response curves using Python, *XXXV Panhellenic Conference on Solid State Physics and Materials Science*, 26 - 29 September 2021, Athens, Greece.
3. K. Prevezanou, G. Kioselaki, E. Tsoutsoumanos, G.S. Polymeris, P. Konstantinidis, V. Pagonis, G. Kitis, Implementation of expressions based on Lambert-W function for deconvolution of stimulated luminescence curves using Python, *XXXV Panhellenic Conference on Solid State Physics and Materials Science*, 26 - 29 September 2021, Athens, Greece.

International Conferences Presentations (invited, oral, poster)

1. E. Tsoutsoumanos, G.S. Polymeris, G. Kioselaki, K. Prevezanou, P. Konstantinidis, T. Karakasidis, G. Kitis, Python: An innovative, cutting-edge tool in Luminescence for Cultural Heritage purposes, *eRA 2021: 14th International Scientific Conference, "Industry 4.0", Session: Digitization and non-destructive techniques in Cultural Heritage*, June 2021, Athens, Greece (Oral Presentation).
2. G.S. Polymeris, V. Pagonis, K.M. Paraskevopoulos, G. Kitis, Athermal fading studies in ther-moluminescence signal of 10 different K-feldspar samples; fading rate versus TL glow curve temperature analysis and correlation to structural state characteristics, *16th International Conference on Luminescence and Electron Spin Resonance Dating (LED)*, 13 – 17 September 2021, Burgos, Spain (Poster Presentation).
3. C. Schmidt, D.C.W. Sanderson, A. Cresswell, A. Chruścińska, M. Fasoli, G.S. Polymeris, S. Kreutzer, M. Biernacka, G. Adamiec, M. Martini, A systematic multi-technique comparison of two reference quartz samples, *16th International Conference on Luminescence and Electron Spin Resonance Dating (LED)*, 13 – 17 September 2021, Burgos, Spain (Oral Presentation).
4. E. Tsoutsoumanos, P. Konstantinidis, G.S. Polymeris, V. Pagonis, T. Karakasidis, G. Kitis, Dependence of the LM-OSL peak shape on trap filling and trap emptying - Comparison with TL, *16th International Conference on Luminescence and Electron Spin Resonance Dating (LED)*, 13 – 17 September 2021, Burgos, Spain (Poster Presentation).
5. P. Konstantinidis, E. Tsoutsoumanos, G.S. Polymeris, G. Kitis, Recombination pathways in a BeO yielding two main dosimetric TL peaks, *16th International Conference on Luminescence and Electron Spin Resonance Dating (LED)*, 13 – 17 September 2021, Burgos, Spain (Poster Presentation).
6. K. Prevezanou, G. Kioselaki, E. Tsoutsoumanos, G.S. Polymeris, P. Konstantinidis, V. Pagonis, G. Kitis, Implementation of Lambert-W function in deconvolution and dose response phenomena using Python, *16th International Conference on Luminescence and Electron Spin Resonance Dating (LED)*, 13 – 17 September 2021, Burgos, Spain (Poster Presentation).
7. A. Vafiadou, L. Malletzidou, I.K. Sfampa, G. Kitis, I. Liritzis, G.S. Polymeris, On the OSL, IRSL And TA-OSL signals in limestones; contribution and possible implications to dating of ancient stone structures, *2nd Sinno – Hellenic Conference on Global Issues on Environment and Culture*, 18 – 19 September 2021, Delphi, Greece (Oral Presentation).
8. G.S. Polymeris, TA – OSL as an effective tool for extending the luminescence age limits beyond 1 Million years; preliminary results from a number of sites, *3rd Symposium on Dating using physical methods; applications in archaeology and geosciences*, 11 – 13 October 2021, Sao Paulo, Brazil (***Invited*** Oral Presentation).
9. G. Kioselaki, K. Prevezanou, P. Konstantinidis, E. Tsoutsoumanos, V. Pagonis, G.S. Polymeris, G. Kitis, Fitting of stimulated luminescence dose response curves using the Lambert-W function; implementation with Python, *4th Conference in Computer Applications and Quantitative Methods in Archaeology*, October 21 – 22 2021, Athens, Greece (Oral Presentation).

Teaching and Training Activities

Name: Dr. Georgios S. Polymeris

1. Absolute Dating Techniques, M.Sc. Course on Physical and Chemical Methods for the Diagnosis of Corruption in Materials of Cultural Heritage, one semester, Aristotle University of Thessaloniki.
2. Radiometric Dating Techniques, M.Sc. Course on European Master Course in Archaeological Materials Science – ARCHMAT, 4 hours, April 2021, Aristotle University of Thessaloniki.

Name: Dr. Yannis Maniatis

1. Radiocarbon dating, M.Sc. Course on Cultural technologies, University of Peloponnese, Kalamata, January 2021, 6 hours.

Doctoral Dissertations completed in 2021

Name: ***Vasiliki Angeli***
Dissertation Title: *TL and OSL characterization of new materials towards ionizing radiation dosimetry applications.*
Research Supervisor at NCSR: Dr. Georgios S. Polymeris
University where the Thesis was presented: Aristotle University of Thessaloniki, Greece.

Name: ***Lamprini Malletzidou***
Dissertation Title: *Contribution to the restoration of paintings: Study of the interaction between binders and pigments and/via characterization of fresh, artificially aged and authentic samples from old paintings.*
Research Supervisor at NCSR: Dr. Georgios S. Polymeris
University where the Thesis was presented: Aristotle University of Thessaloniki, Greece.

Master Dissertations completed in 2021

Name: ***Ebru Yildiz***
Dissertation Title: *Optimization of annealing parameters for using BeO dosimeters.*
Research Supervisor at NCSR: Dr. Georgios S. Polymeris
University where the Thesis was presented: Ankara University, Ankara, Turkey.

Undergraduate Theses and Internships completed in 2021

Name: ***Konstantina Prevezanou***
Dissertation Title: *Deconvolution of stimulated luminescence curves using the Lambert W function; implementation with python programming*
Research Supervisor at NCSR: Dr. Georgios S. Polymeris
University where the Thesis was presented: Aristotle University of Thessaloniki, Greece.

PALAEOENVIRONMENT AND ANCIENT METALS STUDIES

Project Leader: Eleni Filippaki

Permanent Research Staff: Eleni Filippaki

Other Staff : Associate Prof. C. Kopanias, National and Kapodistrian UoA, Faculty of Philosophy, Department of History and Archaeology, Associate Prof. I. Papadatos, UoA, Faculty of Philosophy, Department of History and Archaeology, Prof. P. Vassiliou, National Technical University of Athens, NTUA, School of Chemical Engineering, Department of Materials Science and Engineering, Prof. Th. Rondoyanni, NTUA, School of Mining and Metallurgical Engineering, Department of Geological Sciences, Prof. G. Sanidas, Université de Lille (Lille 3), Histoire, Archéologie et Littérature des Mondes Anciens, f. Prof. C. Xaplanteris, Greek Military Academy, Dr. N. Nerantzis, Université de Lille (Lille 3), Histoire, Archéologie et Littérature des Mondes Anciens, Dr. M. Georgakopoulou, UCL Qatar, Prof. A. Hauptmann, Deutsches Bergbau-Museum, Dr. M. Bode, Deutsches Bergbau-Museum, Dr. M. Kiderlen, Winkelmann-Institut, Humboldt University at Berlin, Prof. Aiming Lin, University of Kyoto, Department of Geophysics, Japan.

Post Docs: Evangelos Tsakalos, Maria Kazantzaki, Georgios Mastrotheodoros

PhD Candidates: Athina Nikolopoulou, Michel Ronggenbucke, Despoina Fountoulaki, Erato Vemou, Katerina Sidiropoulou, Isidoros Kambolis, Ioannis Margaritis, Dimitra Oikonomou, Margarita Arvanitaki

Researchers Emeritus: Dr. Yannis Bassiakos

Objectives

- Ancient/historic metals: characterization, technology, provenance
- Ancient metallurgical residues studies
- Prehistoric copper-smelting simulations
- Metal corrosion studies
- Conservation and restoration of metallic archaeological objects by plasma chemistry methods
- Study of the materials and techniques of portable and monumental paintings
- Characterisation of archaeological and historical assets
- Ancient landscapes reconstruction
- Palaeoenviromental studies, sea-land diachronic interaction
- Palaeoseismological studies
- Chronometric studies (absolute dating)

Activities and Main Results

1) Dating the traces of the last hunters and gatherers on the island of Cyprus

Archaeological investigations at the Late Epipaleolithic/Pre-Neolithic campsite of Roudias, Cyprus, have revealed that this location was repeatedly visited by hunter-gatherer groups during the beginning of the Holocene. Despite the placement of the deeper lithic assemblages of the site within the Late Epipaleolithic tradition, the main obstacle of the site has been its lack of absolute ages. Previous attempts to date bone samples recovered from the site using radiocarbon were unsuccessful since the samples did not contain enough collagen to return reliable dates. The absolute chronology of the site within early Cypriot developments—Late Pleistocene or Early Holocene—has been eagerly awaited by researchers who try to document the arrival of the first human groups to the island. This study places the campsite of Roudias in its temporal setting using optically stimulated luminescence dating. Absolute ages (ranging from 7.251.3 to 12.851.6 ka) provide evidence for the duration of the occupation of the Roudias site from the Late Epipaleolithic (or even earlier) to the Late Aceramic Neolithic, but more importantly, they push back the time of the first colonization of Cyprus and the onset of seagoing practices in the southeastern Mediterranean.

2) Post-byzantine Epirus panel paintings materials and techniques

Red and yellow pigments on more than 50 panel paintings were investigated. The studied artefacts dated from the mid-15th to the mid-19th centuries and came from regions in modern-day Greece. Cinnabar and yellow ochres predominated. In the case of the region of north-west Greece there was a persistent use of orpiment and the employment of a peculiar ochre-type pigment, while the rare lead-antimony-tin yellow was identified in an early 18th-century Greek icon. Trends in pigments use during the post-Byzantine period are revealed and compared with contemporary Western European ones. Recipes and terms of the Hermeneia manual are revisited in light of the analytical data, and pertinent misconceptions are restored.

3) Archaeometallurgical studies of ancient metal objects Mesi Glygada sea, Northern Greece

An archaeological treasure of metal objects, dated back to Early Helladic (EBA) period, was discovered in the sea area between the contemporary settlements of Mesi and Glyfada of North Aegean, Rhodope Prefecture in 2008. The assemblage is consisted of 136 finds and came to light by the Ephorate of Underwater Antiquities. More specifically, 115 objects belong to the category of tools, while equally interesting are the 19 ingots, which are considered as the raw material of the tools.

Of the total 134 metal finds, analyses were carried out on 64 of them by the non-destructive XRF method in the frame of a PhD project. The results of the XRF analysis showed that all the objects are made of arsenical copper. Moreover, the presence of arsenic within the ingots is also interesting. We sampled 32 objects in order to draw more conclusions about the proportion of their components as well as their manufacturing technology. Our research aims at reconstructing the early metallurgical techniques practiced in the above region and Northern Greece in general.

4) A combined archaeological, archaeometric and experimental approach for Mycenaean 'gold-embroidery'

A combined archaeological, archaeometric and experimental approach was followed to a demanding gold-working technique attested in some of the wealthiest tombs of Early Mycenaean Greece. The technique, known as 'gold-embroidery' required exceptional skills and was used only for decorating prestigious weapons (Figure 4). Emphasis was laid on the experimental reconstruction of the technique. The reconstruction was based on microscopic observations and archaeometric data and sought to identify the various stages of manufacture. Particularly important was the creation of special tools, which helped us to deal with the minute size of the gold particles and the delicate movements involved in this technique.

Figure 4. Mycenaean gold-embroidery: Style B decoration. Possibly Dendra chamber tomb 12, sword 14417 (National Museum of Denmark, Copenhagen)

Funding

"Prediction and modelling of coastal zone changes using luminescence dating techniques (MIS 5047809)", Operational Programme «Human Resources Development, Education and Lifelong Learning 2014- 2020», 01/06/2020 – 30/09/2021, budget: 50,050 €.

"METAL PLACES: Culture crossroads in eastern Mediterranean", MIS: 5050657, Interreg VA Greece – Cyprus Program "2014-202001/06/2020-31/05/2023", budget: 221.200,00€,

Services

Geo-chronological research concerning the absolute dating and other required laboratory work, producing OSL and ESR individual dating results on a number of samples from Greece and Cyprus, 25,000 €.

OUTPUT

Publications in International Journals

1. Mastrotheodoros G., Beltsios K.G., Bassiakos Y. On the red and yellow pigments of post-Byzantine Greek Icons, Archaeometry 63/4, pp753-758 (2021) https://doi.org/10.1111/arcm.12642
2. Mastrotheodoros, G.P.,Beltsios, K.G. Original Varnish Recipes in Post-Byzantine Painting Manuals. Heritage 2021, 4, 3572–3582. https://doi.org/10.3390/heritage404019
3. Evangelos Tsakalos, Nikos Efstratiou, Yannis Bassiakos, Maria Kazantzaki, and Eleni Filippaki, Early Cypriot Prehistory: On the Traces of the Last Hunters and Gatherers on the Island—Preliminary Results of Luminescence Dating, Current Anthropology 2021 62:4, 412-425 https://doi.org/10.1086/716100

Books/Chapters in Books

1. Μ. Ρογκενμπούκε, Ε. Φιλιππάκη, 2021. Συντήρηση μεταλλικών αρχαιολογικών ευρημάτων με τη μέθοδο της πλασματικής επεξεργασίας και με συμβατικές μεθόδους: Πολλαπλή αναλυτική αξιολόγηση, Αλάσαρνα VII, ΚΟΡΟΠΛΑΣΤΙΚΗ – ΝΟΜΙΣΜΑΤΑ - ΜΕΤΑΛΛΙΚΑ ΕΥΡΗΜΑΤΑ ΤΩΝ ΕΛΛΗΝΟΡΩΜΑΪΚΩΝ ΧΡΟΝΩΝ από το Ιερό του Απόλλωνα Πυθαίου/Πυθαέως και τον Πρώιμο Βυζαντινό Οικισμό, Γ. Κοκκορού-Αλευρά (εκδότης), Πανεπιστήμιο Αθηνών, Φιλοσοφική Σχολή, Τομέας Ιστορίας και Αρχαιολογίας, 271-301
2. Y.Bassiakos, C.Apostolaki, V.Perdikatsis, E.Filippaki, S.Sotiropoulou, 2021. Technological Observations Based on the Analyses of Metal and Steatite Finds from the Early Minoan IB Cemetery Gournes, Pediada A Minoan Cemetery in Crete, Instap, Academic Press Philadelphia, Pennsylvania, 161-170

International Conferences Presentations (invited, oral, poster)

1. E. Filippaki, K. Karaindrou and Y. Bassiakos, A closer look at the metallurgical activities of the two Early Helladic settlements of Raphina and Askitario, East Attica, Greece. FORGING VALUES, Metals Technologies and Social Interactions in Greece and the Mediterranean from the 4th to the 1st millennium BC, International Online Symposium, 15-16 April 2021 **(invited)**
2. Y. Bassiakos, E. Filippaki, Crucible: a multipurpose metallurgical utensil and its diachronic trajectory in the Aegean world. FORGING VALUES, Metals Technologies and Social Interactions in Greece and the Mediterranean from the 4th to the 1st millennium BC, International Online Symposium, 15-16 April 2021 **(invited)**
3. Nikolopoulou A., Filippaki E**.,** 2021, Archaeometallurgical analyses of ancient metal objects from Mesi Glyfada sea, North Aegean, Greece: preliminary data, 3rd European Mineralogical Conference (EMC), Materials Sciences and Archaeometry for Cultural Heritage, 29/08-02/09 2021, Poland **(oral)**
4. Kazantzaki M., Tsakalos E., Filippaki E., Bassiakos Y., 2021. Sea Level Rise and Implications for Low-lying areas: Coastal Evolution and Impact of Future Sea Level Rise Scenarios in Mirabello Gulf - NE Crete. ICGMGTA 2021: XV International Conference on Geomorphological Mapping, Geospatial Technologies and Applications, October 25-26, Istanbul, Turkey **(oral)**
5. Tsakalos E., Kazantzaki M., Filippaki E., Bassiakos Y., 2021. Forecasting Impacts on Vulnerable Shorelines: Vulnerability Assessment along the Coastal Zone of Messologi Area - Western Greece. ICGMGTA 2021: XV International Conference on Geomorphological Mapping, Geospatial Technologies and Applications, October 25-26, Istanbul, Turkey **(oral)**

Teaching and Training Activities

1. E. Filippaki, Archaeometallurgy in Greece during the prehistoric period, University of Ioannina, 26th of March 2021, Ioannina, Postgraduate program “Ancient world: History and Archaeology”, Interdisciplinary Seminar of Prehistoric Archaeology, School of Philosophy, Department of History and Archaeology

Undergraduate Theses and Internships completed in 2021

1. Giorgos Mendrinos

X-ray fluorescence: Study of overlapping trace elements
Research Supervisor at NCSR: Eleni Filippaki
University of Athens

program 4

Nanoelectronics, Photonics and Microsystems

CIRCUITS & DEVICES FOR SENSOR NETWORKS & SYSTEMS

Group Leader: S.Chatzandroulis

Researchers: A.Tserepi, P. Petrou

Research Associates: V.Tsouti (Adjunct Researcher), M-K. Filippidou, S. Douskas, A. Kanaris

External Collaborators: I.Zergioti, M.Chatzichristidi, G.Tsekenis

Ms Students: Nikitas Melios

Objectives

- Lab-on-Chip and PoC Systems
- Sensors and Micro- Electro- Mechanical Systems
- Intelligent Microsystems
- RF harvesting/telemetry

Activities and Main Results

I. Point-of-care and Lab-on-Chip Systems

Ia. RPA-on-PCB chip for bacteria detection

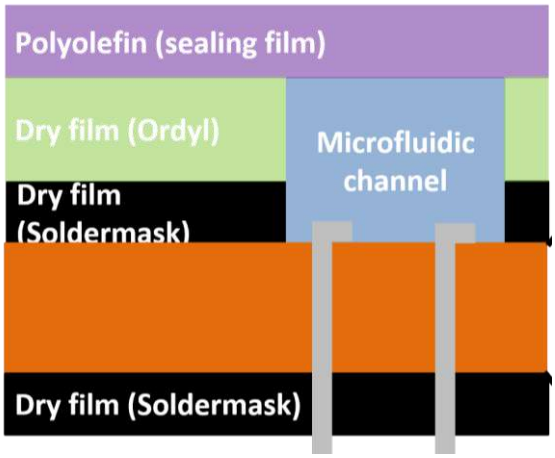


Figure 1. Schematic cross-sectional view of the RPA-on-PCB chip.

A RPA-on-PCB chip was implemented for bacteria identification in urine. PCB technology allows for low-cost and standardized mass production, while the PCB substrate enables all the electrical connections required for the operation of the device. The chip has a size of 65 mm x 42 mm x 1.55 mm and includes a meandering microfluidic channel on one side of the PCB substrate and a copper (Cu) microheater on the other side. The microchannel is patterned on a laminated photosensitive dry film and has a volume of 30 µl. It was partly commercially fabricated on the solder mask layer while for increased microfluidic channel height, the solder mask layer was combined in house with an ORDYL SY 300 film. A cross-sectional view of the device is shown in Fig. 1. The micro-heater was implemented in the inner 18 µm-thick Cu layer of the PCB substrate in the area below the microfluidic channel, to allow for proper heating of the DNA amplification cocktail during the amplification. The chip was validated for RPA-based amplification of two E. coli target genes compared to a conventional thermocycler. The RPA performance of the PCB microchip was found to be comparable to that of a thermocycler while requiring only 0.6 W. This chip is intended for seamless integration with biosensors in the same PCB substrate for the development of a point-of-care (POC) molecular diagnostics platform.

II. Microsystems for obstructive sleep apnea treatment

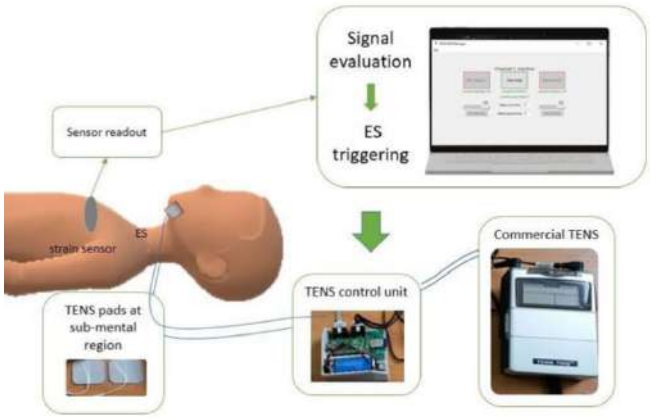


Figure 2. Schematic representation of the overall system design including images of the developed parts such as the control circuit of the TENS device and the user interface of the control program.

A prototype system (Figure 2) has been developed during the MiSleep project that includes a resistive strain sensor which is placed over the patient's chest to monitor breath during sleep, a program that analyzes the signal of the sensor using signal processing and machine learning (ML) algorithms, a commercial transcutaneous electrical nerve stimulation (TENS) device that generates electric pulses, a control circuit based on Arduino–nano intervened between the TENS device and the electrode pads for controlling the electrical stimulation (ES) at the patient's submental region and a Python program running on a PC that controls the whole system.

The system was tested on the human body by attaching the flexible strain sensor on the five regions shown in Figure 3. It is observed that the regions that are typically used for breath effort monitoring (1 and 4) give the best signals for our sensor too. The region of the neck, in which typically a microphone is used, also results in a measurable signal, however it has an opposite sign compared to the other 4 regions, namely, when breathing in the resistance decreases and when breathing out the resistance increases. Regions 1 and 4 are proposed as the best for placement of our strain sensor.

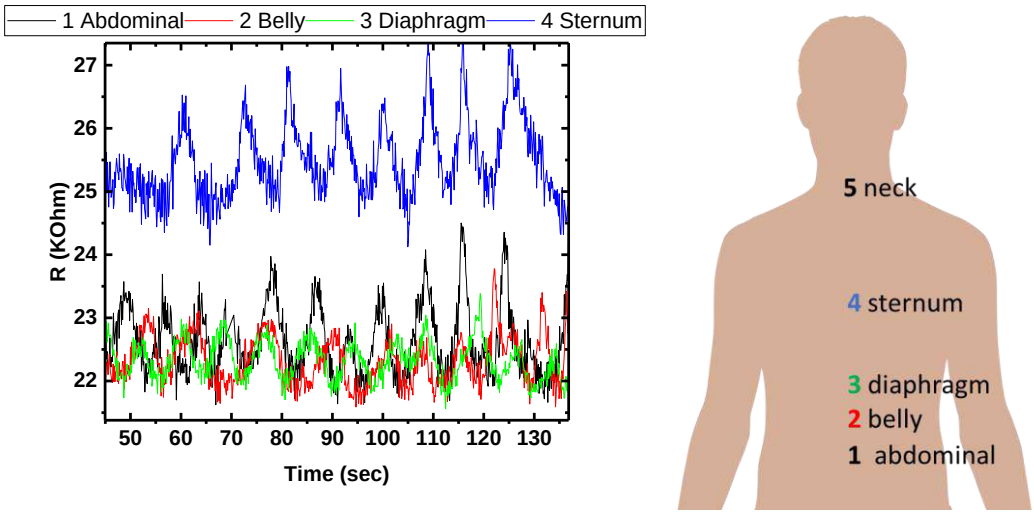


Figure 3. Real breath effort signals using the Misleep system when placing the sensor on various regions of the human body

III. Epidermal patch for glucose monitoring sensor in sweat

This work focuses on the development of an epidermal patch comprising a sweat collector microfluidic and a solution based electrochemical sensor for the detection of analytes in this biofluid. The sensor is realized on a flexible polyimide film using a carbon based ink which is subsequently bonded with the PDMS microfluidic to form the final patch. Glucose is selected as the analyte of interest. Detection of glucose in sweat removes the painful invasive blood sampling step, while paving the road for the continuous monitoring of glucose levels.

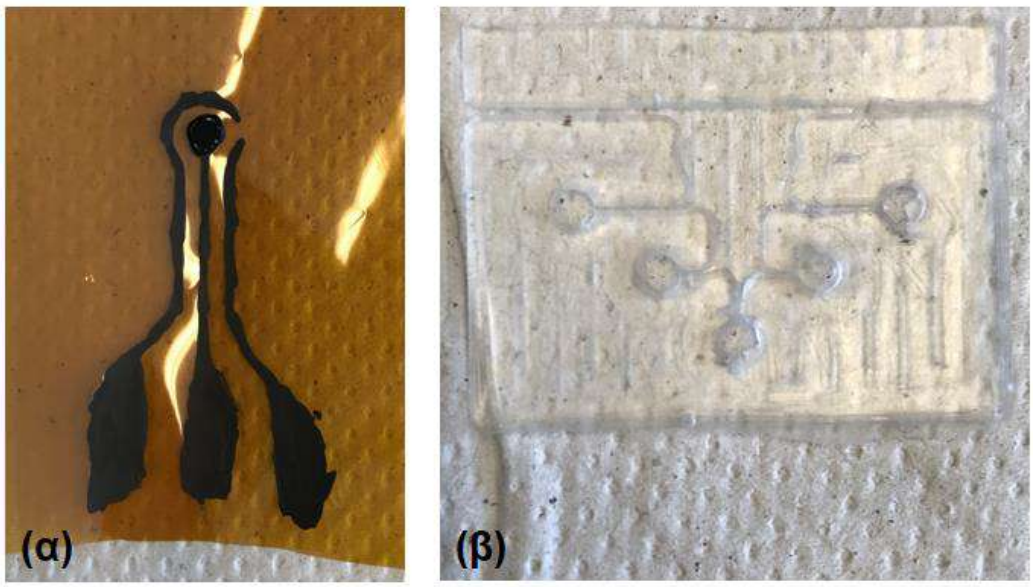


Figure 4. Epidermal glucose patch components: Solution based electrochemical sensor and PDMS microfluidic

Funding
Title: DIAMOND, "Rapid, timely diagnosis and monitoring of microbial infections by means of an automated, point-of-care, diagnostic system", GSRT ΔΡΑΣΗ ΕΘΝΙΚΗΣ ΕΜΒΕΛΕΙΑΣ: «ΕΡΕΥΝΩ-ΔΗΜΙΟΥΡΓΩ-ΚΑΙΝΟΤΟΜΩ», ΚΩΔΙΚΟΣ ΕΡΓΟΥ Τ1ΕΔΚ-03565
Duration: 18/7/2018 – 17/7/2021
Budget: 393.292,60 €
Budget for 2020: 45.000

Title: Microsystems for obstructive sleep apnea treatment (MiSleep), Stavros Niarchos Foundation
Duration: 7/2017 – 6/2021
Budget: 120.000
Budget for 2021: 30.000

Title: MICSYS, "A microfluidic chip-based system for the detection of contaminants in water", GSRT, ΔΡΑΣΗ ΕΘΝΙΚΗΣ ΕΜΒΕΛΕΙΑΣ: «ΕΡΕΥΝΩ-ΔΗΜΙΟΥΡΓΩ-ΚΑΙΝΟΤΟΜΩ», ΚΩΔΙΚΟΣ ΕΡΓΟΥ Τ2ΕΔΚ-02144
Duration: 29/10/2020 –28/4/2023
Budget: 202.500 €
Budget for 2020: 50.000

OUTPUT

Publications in International Journals

1. G.Spyridonos, M.Filippidou, G.D.Kaprou, D.C.Mastellos, S.Chatzandroulis, A.Tserepi, "Isothermal recombinase polymerase amplification (RPA) of E. coli gDNA in commercially fabricated PCB-based microfluidic platforms", (2021) Micromachines, 12 (11), art. no. 1387, https://doi.org/10.3390/mi12111387 IF 2.942

Teaching and Training Activities

1. Nikitas Melios Ms Thesis (2021) "Development of an epidermal, patch-type, electrochemical sensor for the detection of analytes in sweat", NTUA/SAMPS, MSc on "Microsystems and Nanodevices".

ENERGY HARVESTING AND AUTONOMOUS SENSORS

Project Leader: C. Tsamis

Post Doc: M. Hourdakis

PhD Candidates: A. Bardakas, D. Barmpakos, A. Segkos, M. Stramarkou

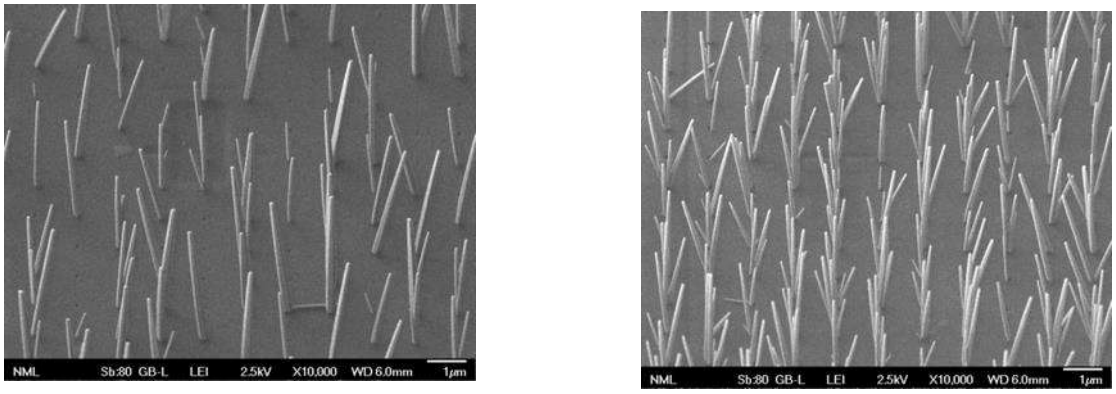
Objectives

- Exploitation of low cost, biocompatible and environmentally friendly material synthesis technologies for sensing and energy harvesting materials (based mainly on ZnO nanostructures and Carbon Quantum Dots).
- Development of environmentally friendly, biocompatible energy storage systems based on Porous Silicon technology.
- Design and development of multi-energy harvesting systems (triboelectric, piezoelectric, solar, hybrid systems).
- Design and development of low power sensors on silicon and flexible substrates.
- Integration of energy harvesters and sensors for self-powered systems for IoT applications, especially in the field of personalized healthcare, safety and security and smart cities.

Highlights / main scientific results

Templated growth of ZnO nanorods using EBL for sensor applications.
A. Bardakas, G. Papageorgiou, C. Tsamis

During this year we expanded our activities regarding the templated growth of ZnO nanorods (NR) using electron beam lithography. ZnO nanorod arrays were grown on seeded Si substrates patterned using EBL. A ZnO seeding layer was deposited on the Si substrates via magnetron RF sputtering and spinning coating, using a sol-gel solution. For the EBL process, ARP and PMMA photoresists were spin coated on top of the seeded substrates with a thickness of 300 and 90nm respectively. An array pattern was created consisting of 50 and 100nm holes at a pitch size 1, 2 and 5μm. ZnO nanorods were grown through the template via an aqueous equimolar solution of zinc nitrate hexahydrate and hexamethylenetetramine, at a concentration of 2 and 50mM at 87oC. The seeding layers where characterized by atomic force microscopy (AFM), grazing incident X-ray diffraction (GIXRD) and scanning electron microscopy (SEM). The influence of the seeding layer crystallinity, surface roughness and grain size on the density of ZnO NRs per hole was studied. The morphology and dimensions of the grown ZnO NRs were characterized via SEM, shown in Figure 1.



(a) (b)

Figure 1 ZnO NR arrays grown at 50 and 2mM at an aperture size of 50 (a) and 100nm (b).

Modification of surface roughness with plasma etching and its influence on the performance of triboelectric generators

S. Arvaniti, A. Segkos, A. Bardakas and C. Tsamis

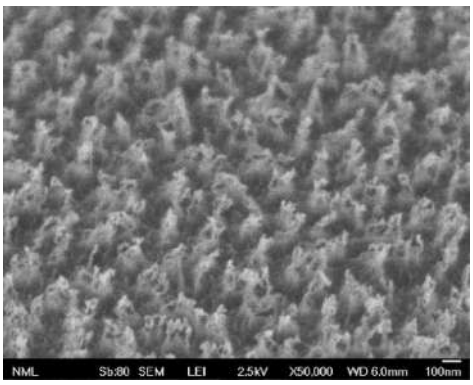
In collaboration with A. Zeniou and E. Gogolides

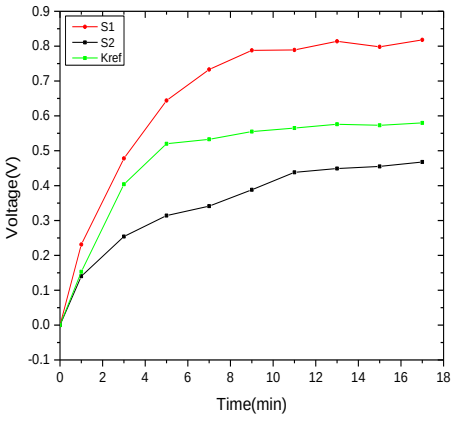
We investigated the modification of Kapton surfaces using plasma processing on the electrical performance of TENGs. As a starting material, Kapton sheets were used. Controlled surface roughness was induced on Kapton surfaces with plasma treatment. Etching and roughening of Kapton was conducted in oxygen plasma, at 6,6 mTorr pressure, 100sccm Oxygen gas flow, 1800W source power, 250W bias power, with two different etching time (Fig 2a).

Electrical characterization of the surfaces was performed in contact-separation mode (Fig 2b). As a second surface for the tribogenerator two different electrodes were used, corresponding to a “hard” and a “soft” substrate: a) Electrode 1: a silicon wafer with a 100nm oxide on the top and with aluminum contact, deposited at the back side and b) Electrode 2: commercially available PET/ITO sheet. The output voltage was monitored as a function of time using an oscilloscope. In addition, charging experiments were performed. In this case the triboelectric generator is connected to a capacitor through a rectifier and the capacitor voltage is monitored as a function of time. Charging phenomena of the triboelectric surfaces were considered.

We noticed that the charging behavior of the capacitor does not depend on whether plasma surface treatment has been performed on the surface of the Kapton. Such a result could be explained if we consider a load-dependent contact area between the two surfaces. Experimental as well as simulation results show that the electrical output can be expected to be tiny at low contact loads but should converge to an upper-bound at higher loads as the contact area approaches complete contact. In our case this would mean that for the combination of the specific load in combination with “hard” would create the necessary condition to reach a complete contact, independent of the surface roughness.

It was also observed that when two soft substrates were used, after a certain degree of roughness the “true contact surface” between the two surfaces of the triboelectric generator decreases resulting in reduced triboelectric signal. This could also mean that the maximum value for the load dependent contact area is not yet reached.





(a) (b)

Figure 2 a) SEM images of Kapton surface after oxygen plasma processing for 6min and b) Capacitor voltage as a function of time for the three different samples using PET/ITO as electrode

Simple method for determining Si p-n junction depth using anodization

E. Hourdakis, C. Tsamis

During this year, we developed a simple method for the determination of a Si p+/n junction. The method was designed to delineate the specific junction due to its importance in the field of Si solar cells where cost effective and fast characterization techniques are necessary. It consists of the electrochemical transformation of the p+ Si to porous Si. The determination of the porous Si depth with the use of cross-sectional Scanning Electron Microscope (SEM) images provides a direct, fast and easy to implement measurement of the junction depth. In addition, through

a simple 4-point probe electrical measurement of the sheet resistance, the average dopant concentration is determined, which allows the creation of an abrupt junction approximation of the p+/n junction. The method is shown to produce accurate results in two types of doping techniques, namely implantation and spin-on-doping and a range of junction depths between 200nm and 1500nm, as compared to the well-established secondary ion mass spectrometry (SIMS) technique. An image of the results achieved by the method, in comparison to SIMS for a characteristic sample is presented in figure 3.

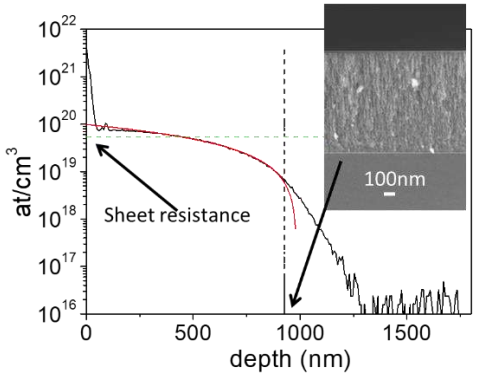


Figure 3 SIMS measurement (black line) of the doping concentration of boron atoms in a Si p+/n junction. The black dotted line represents the junction depth (SEM image of the inset) while the green dotted line is the average concentration from the sheet resistance measurements. The red solid line represents a linear fit of the data.

Study of the photoluminescence of N-doped, Carbon Dot-based nanocomposite materials from citric acid and urea
A. Segkos, E. Alexandratou1, I. Sakellis, N. Boukos, S. Gardelis2, K. Kordatos3 and C. Tsamis
In collaboration with 1Dept. of Electrical Engineering NTUA, 2Dept. of Physics NKUA and 3Dept. of Chemical Engineering NTUA

We studied different synthetic processes and their effect on structural and optical properties of Carbon Dots (CDs). It was observed that the synthetic conditions have profound effects on the structure of resulting CDs; namely, increased pressure appears to inhibit the formation of HPPT, a molecular fluorophore often observed in the synthesis of CDs and which is responsible for the green emission component observed in the photoluminescence spectra. On the other hand, both synthetic routes produced citrazinic acid derivatives, a type of fluorophore molecule responsible for the blue photoluminescent emission. The fluorophores were found to partake in energy transfer mechanisms both in solution (graphitic cores) and in the solid state (inter-molecular) (Fig. 4).

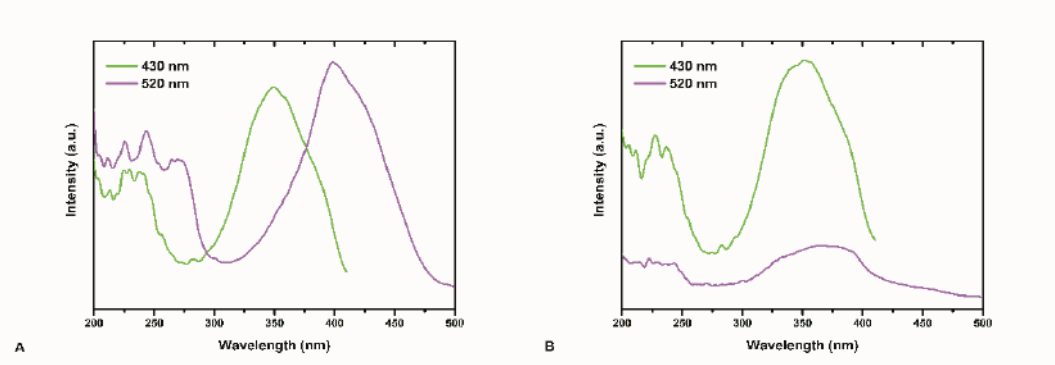


Figure 4 Excitation spectra of CDs with (A) and without HPPT molecular fluorophores (B).

“Shadow effect” photodetector with linear output voltage vs light intensity
E. Hourdakis, C. Tsamis

A novel concept for a simple, cost effective, readily integrable with Si electronics and self-powered photodetector was developed within 2021. The device consisted of a semitransparent Au film deposited on an n-type Si substrate with contacts on the Au layer. The operation of the device relied on the recently demonstrated “shadow effect”. The

device was shown to consist of back-to-back Schottky diodes with a built-in parallel resistance caused by the Au layer. Shadowing half of the device area under illumination caused anisotropy in the diodes' behavior creating a measurable open circuit voltage and a short circuit current. The presence of the built-in parallel resistance, along with a large series resistance, caused the open circuit voltage to have a linear term with respect to illumination power, in addition to the logarithmic term normally present in Schottky solar cells. We demonstrated that under certain combinations of series and parallel resistances the open circuit voltage of the device is linear with respect to illumination power for a range between 50mW/cm2 (0.5suns) and 0.5mW/cm2 (0.005suns) as is presented in figure 5. This allows the device to be used as a photodetector operated as a self-powered voltage source, instead of a current source which is the case with most photodetectors operated in the photovoltaic mode.

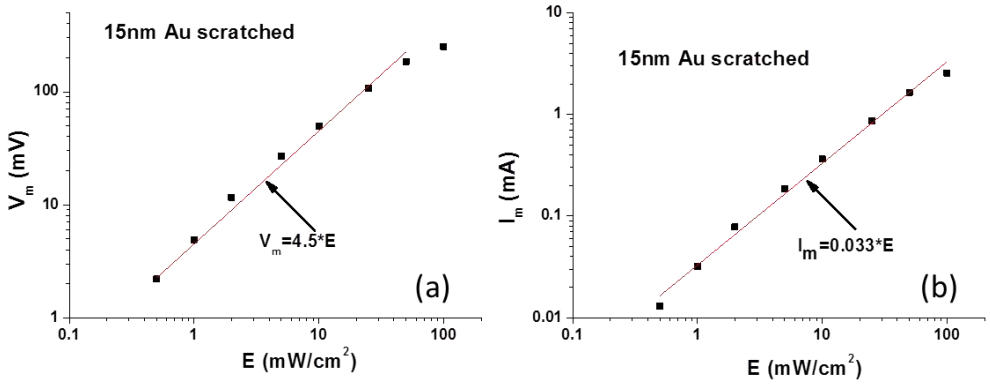


Figure 5 (a) Open circuit voltage Vm and (b) short circuit current Im as a function of illumination power E for the developed devices. The red lines represent linear fits of the data. In the presented relations the constants are presented without units for clarity.

Funding

1. "Perpetual Power Supply for IoT – PERPS", RESEARCH – CREATE – INNOVATE, T1EDK-00360, 10/2018, 30 months, 140KEuros
2. "Development of Autonomous Atmospheric Recorder of Electrical Field for Ships- EFOS", RESEARCH – CREATE – INNOVATE, T2ΕΔΚ-00350, 11/2020, 30 months, 199KEuros
3. "A multi parametric measurement and control system implemented on flexible substrates with printed technologies", D. Barmpakos, Industrial PhD Fellow, Stavros Niarchos Foundation, 8/2017, 48 months, 46.4KEuros
4. "Smart Packaging using electronic sensors on flexible substrates for the activation of food bioactive compounds encapsulated with innovative methods", M. Stramarkou, Industrial PhD Fellow, Stavros Niarchos Foundation, 8/2017, 48 months, 46.4KEuros
5. "Experimental and theoretical study of magnetic strain-gated transistors based on semiconducting nanowires", A. Bardakas (State Scholarships Foundation – IKY), 4/2018, 36 months, 29KEuros

OUTPUT

International Conferences Presentations (invited, oral, poster)

1. M. Kanidi, A. Bardakas, A. Kerasidou, A. Anastasopoulos, C. Tsamis, M. Kandyla, Hierarchical surfaces with reversible photoinduced and heat-induced wettability: ZnO nanorods on laser-microstructured silicon, Micro and Nano Engineering Conference, 20-23 September 2021, Turin, Italy.
2. Segkos A., Alexandratou E., Sakellis I., Boukos N., Gardelis S., Kordatos K., Tsamis C., Photoluminescence mechanisms of citric acid-derived, Photoluminescence mechanisms of citric acid-derived N-doped Carbon Quantum Dots for sensing applications, Micro and Nano Engineering Conference, 20-23 September 2021, Turin, Italy.

3. Arvaniti S., Segkos A., Bardakas A., Zeniou A., Tsamis C., Influence of plasma induced surface roughness on the performance of triboelectric generator, Micro and Nano Engineering Conference, 20-23 September 2021, Turin, Italy.
4. Arvaniti S., Segkos A., Bardakas A., Zeniou A., Gogolides E., Tsamis C., Modification of surface roughness with plasma etching and its influence on the performance of triboelectric generators, XXXV Panhellenic Conference on Solid State Physics and Materials Science, 26-29 September 2021, (Virtual Conference)
5. Stramarkou M., Bardakas A., Segkos A., Krokida M., Tsamis C., Fabrication of Na-doped ZnO nanostructured films for CO2 sensing at room temperature, XXXV Panhellenic Conference on Solid State Physics and Materials Science, 26-29 September 2021, (Virtual Conference)

Teaching and Training Activities

Christos Tsamis
MSc course, “Advanced Studies in Physics- Physics and Technology of Materials-Photonics”
Lectures for the lesson “Physics and technology of materials and Solid-State Devices”, 12h
Physics Dept., University of Patras

Doctoral Dissertations completed in 2021
Dimitris Barmpakos
Dissertation Title: A multi parametric measurement and control system, implemented on flexible substrates with printing technologies
Research Supervisor at NCSR: Dr. Christos Tsamis
University where the Thesis was presented: Department of Physics, University of Patras

Conference / Workshop Organisation
XXXV Panhellenic Conference on Solid State Physics and Materials Science, 26-29 September 2021, (Virtual Conference)

ELECTRON MICROSCOPY AND NANOMATERIALS LAB

Project Leader: A. Travlos

Permanent Research Staff: N. Boukos, K. Giannakopoulos

Other Staff : M. Lasithiotakis

Post Docs: E. Sakellis, A. Kaidatzis

PhD Candidates: E. Chatzigeorgiou

Master Students: A. Douzenis, N. Mouti, G. Gravvani

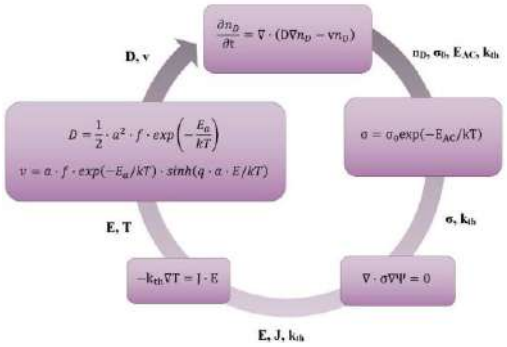
Objectives

- Growth and study of oxide nanostructures with applications in optoelectronics and energy
- Research and Development of electron microscopy methods
- Study of nanomaterials utilizing electron microscopy methods in order to optimize their properties
- Study of the fabrication of nanoparticles from aerosol and their deposition
- Fabrication of coatings for self-cleaning surfaces

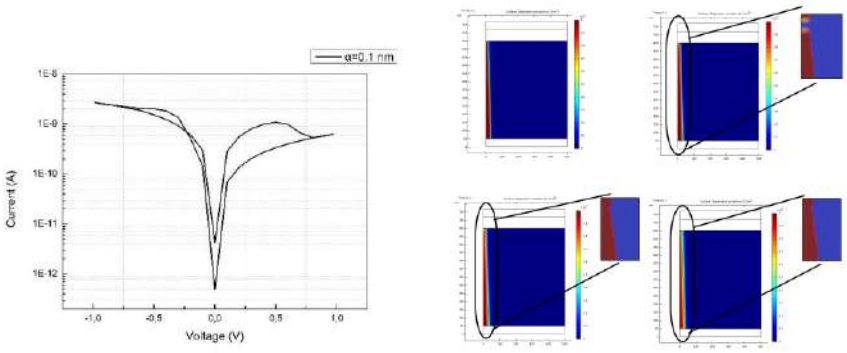
Activities and Main Results

ZnO MSM memristors

Heterojunction diodes MSM (Metal-Semiconductor-Metal) based on Zinc Oxide nanoparticles, as the active electrode material, were fabricated and characterized electrically and structurally. Simulations, using



Schematic illustration of the mathematical model used to perform simulations of the memory devices.

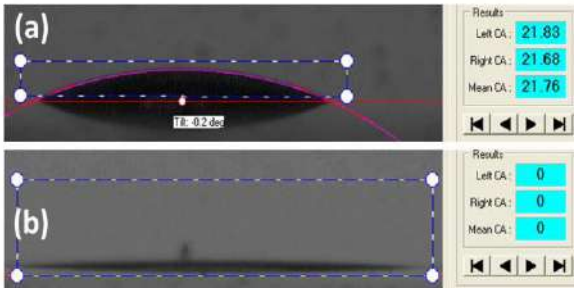


Schematic illustration of a simulated I-V curve of the Au/Zn/ZnO/Au/Si/SiO2 structured device, as well as snapshots of the

the finite element method, were performed in order to simulate zinc oxide based variable resistance memory devices.

Fabrication of Titania films for self-cleaning CSP mirrors

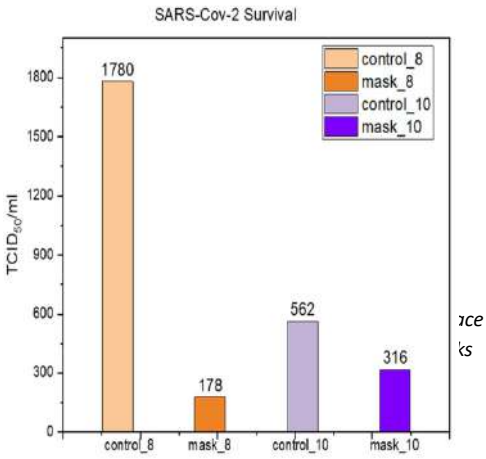
Within the framework of the Solar Eranet project Nano4CSP a range of TiO_2 coatings were deposited on glass, i.e. in low iron glass and in already existing Concentrated Solar Power mirrors; a range of processes and analyses were performed to evaluate the stability of the films, their hydrophilicity, their phase etc. Durable, transparent, superhydrophyilc coatings were achieved for cost reduction in manufacturing and in cleaning costs.



Contact angle measurement on mirrors: a) untreated b) coated at

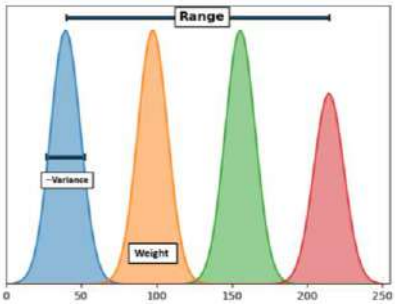
Fabrication of nanoparticles by the use of Spark Discharge method

A wide range of depositions of Au, Pt, Pd, CuO/Cu nanoparticles
on fibrous substrates (carbon cloths, borosilicate glass etc)
using the Spark discharge aerosol technique were performed in collaboration with the lab for Environmental radiation of NCSR Demokritos. An in situ characterization technique (SMPS) was employed to tune the system for the maximum particle production and monitor cluster size. We compared the findings with SEM and TEM results, monitoring the depth of particle intrusion in the fibrous substrates and the primary particle size. Also the CuO/Cu particles were deposited on standard face masks and we introduced antibacterial and antiviral (against SARS-CoV-2) properties.

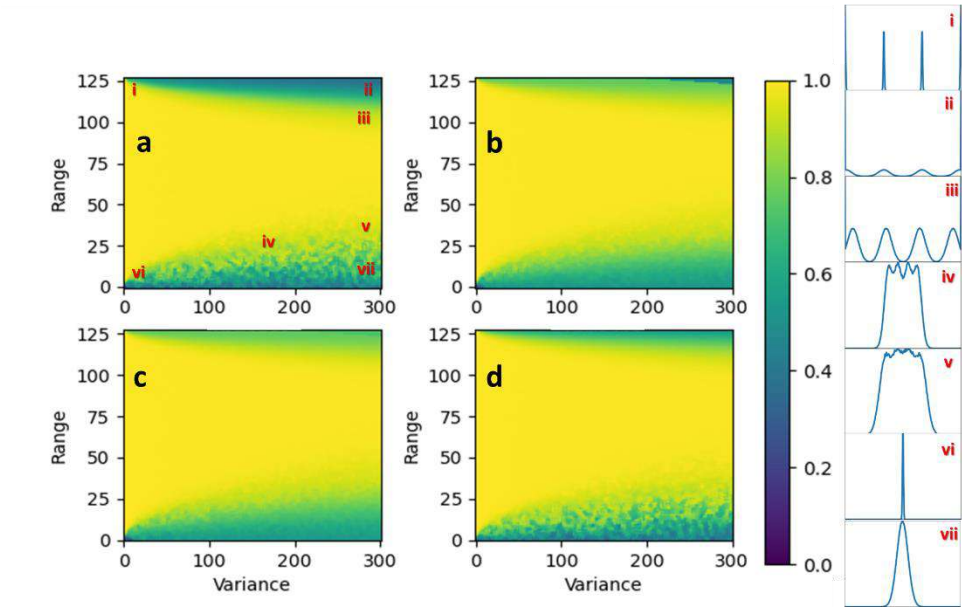


Electron microscopy methods development

One of the main challenges of the SEM-based analysis is the calculation of the fractions of material components constituting a multiphase material by means of the segmentation of their back scattered electron SEM images. In order to segment multiphase images, Gaussian mixture models (GMMs) are commonly used, based on the deconvolution of the image pixel histogram. Despite its extensive use, the accuracy of GMM predictions has not been validated yet. A systematic study of the evaluation of the accuracy and the limitations of the GMM method, when applied to the segmentation of a four-phase material, was performed. A modelling framework was built and a novel index, named distribution similarity index (DS), was introduced to quantify the accuracy of GMM predictions for all phases. In order to simplify mathematical representation three collective parameters were defined, i.e. Range, Variance, and Weight. This framework was applied in synthetic as well as hybrid-synthetic SEM back-scattered electron images of model samples having small differences in their back-scattered coefficients.

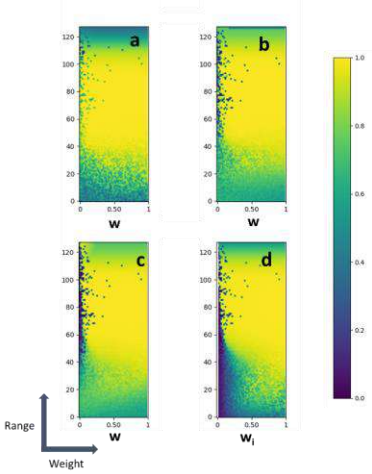


Schematic representation of the Gaussian distributions of four phases indicated with different colors showing the meaning of the parameters Range, Weight and Variance.



DS versus Range and Variance for all 4 distributions as calculated for a constant and equal weight of all distributions. In the top left figure (a) DS of the first distribution is depicted. For a better understanding of this figure, a set of histograms are shown along with their positions in the Range and Variance parametric space.

DS versus the collective parameter Range and the normalized

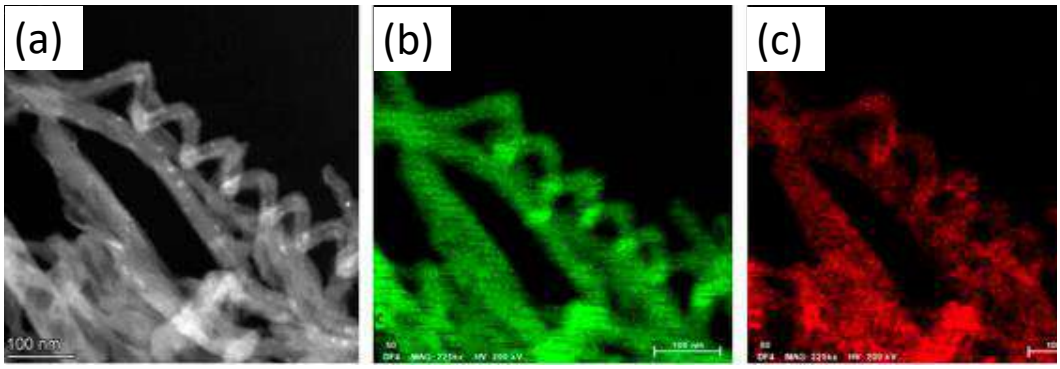


Weight (w_i) of one external distribution (d)

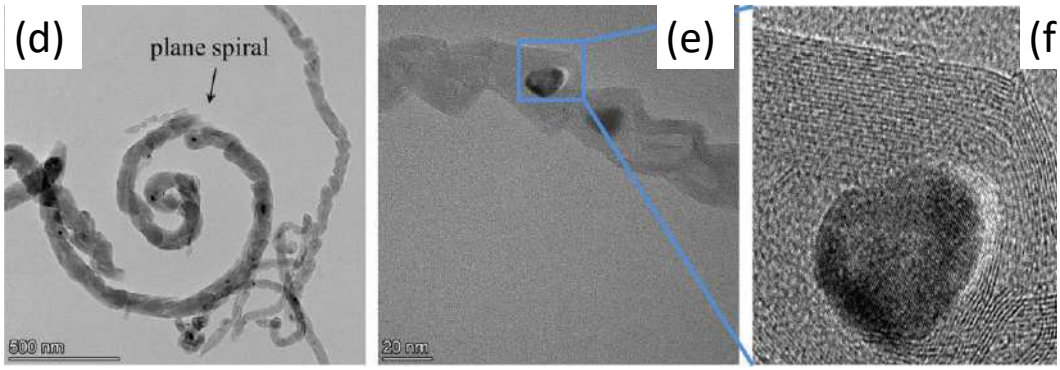
The effect of the collective parameters of the image histogram on the accuracy of GMM was studied. Some rules of thumb are concluded to guide SEM users about the suitability of using GMM for the segmentation of SEM images based only on the inspection of the image histogram. A suitable histogram for GMM is a histogram with number of peaks equal to the number of Gaussian components, and if that is not the case, kurtosis and skewness should be smaller than 2.35 and 0.1 respectively.

Study of nanomaterials utilizing electron microscopy methods in order to optimize their properties

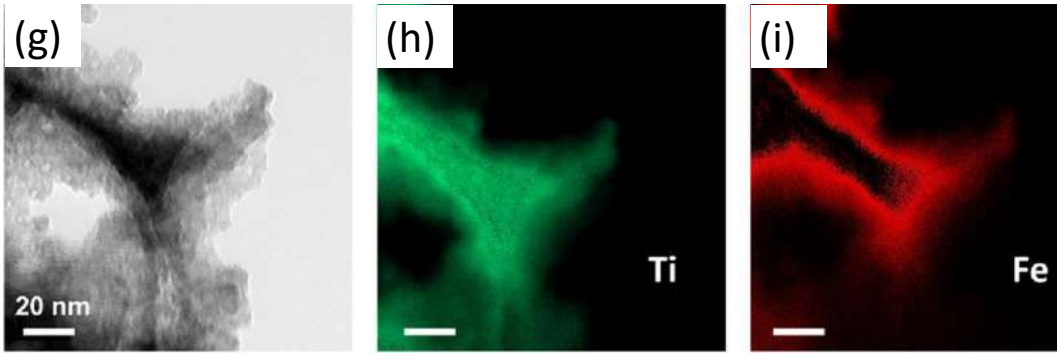
Characterization of nanoparticles and thin films with TEM, S/TEM and SEM for opto- micro- electronics, nanosafety evaluation, polymeric processes, catalysis, health, energy and environmental applications



High angle annular dark field STEM image (a) and carbon (b), nitrogen (c) EDS/STEM map of guanidinylated hyperbranched polyethyleneimine functionalized oxidized CNTs



Bright field TEM images of bamboo-like CNTs grown over pozzolans and corresponding HR-TEM image of tube walls



Bright field TEM image of nanocrystalline TiO_2/FeO_x inverse opal heterostructures (g) and corresponding titanium (h) and iron (i) EFTEM images.

Funding

Nano4CSP: Nanomaterials for reduced maintenance costs in Concentrated Solar Power plants, Solar-ERANET, 770.000 € (K. Giannakopoulos, Coordinator)

Development of a DNA biosensor with the use of low dimensional materials, in collaboration with NTUA, European Structural and Investment Funds, Partnership Agreement for the Development Framework 2014-2020, 50.000 € (K. Giannakopoulos, Co-Supervisor)

Spintronic Devices For Microwave Detection And Energy Harvesting Applications, North Atlantic Treaty Organization (NATO) - Emerging Security Challenges Division, 300.000 Euro, 50.000 for NCSR Demokritos (A. Kaidatzis, Scientific Director)

Electronic Switching Resistance Devices for Neuromorphic Applications in collaboration with NTUA, European Structural and Investment Funds, Partnership Agreement for the Development Framework 2014-2020, 50.000 € (Co-Supervisor)

Development of a novel characterization method for new types of clinker combining Scanning Electron Microscopy and X-ray Powder Diffraction techniques, Industrial Research Fellowship Scheme co-funded by Stavros Niarchos Foundation and Industry, 47.600 €

OUTPUT

Publications in International Journals

1. Kochylas I., Gardelis S., Likodimos V., Giannakopoulos K.P., Falaras P., Nassiopoulou A.G. Improved Surface-Enhanced-Raman Scattering Sensitivity Using Si Nanowires/Silver Nanostructures by a Single Step Metal-Assisted **Chemical Etching. *Nanomaterials* 11 (7), p.1760 (2021). DOI: https://doi.org/10.3390/nano11071760**
2. Tsigkourakos M.C., Kainourgiaki M., Skotadis E., Giannakopoulos K., Tsoukalas D., Raptis Y. Capping technique for chemical vapor deposition of large and uniform MoS2 flakes. *Thin Solid Films* **733**, 138808 (2021). DOI: https://doi.org/10.1016/j.tsf.2021.138808
3. N., Liao C-W, Wang C-Y, Kondo J. N., Tampaxis C., Steriotis T, Giannakopoulos K., Kontos A.G., Hinder S., Baker M., Bousser E, Matthews A., Rebholz C., Mitterer C., Effect of Pt nanoparticle decoration on the H2 storage performance of plasma-derived nanoporous graphene, *Carbon* **171**, pp.294-305 (2021). DOI: https://doi.org/10.1016/j.carbon.2020.08.061
4. Pylarinou, M., Toumazatou, A., Sakellis, E., Xenogiannopoulou, E., Gardelis, S., Boukos, N., Dimoulas, A., Likodimos, V., *Visible light trapping against charge recombination in feox–tio2 photonic crystal photocatalysts*, Materials **14** (23), art. no. 7117, (2021) DOI: 10.3390/ma14237117
5. Kaminari, A., Nikoli, E., Athanasopoulos, A., Sakellis, E., Sideratou, Z., Tsiourvas, D., *Engineering mitochondriotropic carbon dots for targeting cancer cells*, Pharmaceuticals **14** (9), art. no. 932 (2021) DOI: 10.3390/ph14090932
6. Sakellis, E., Markopoulos, A., Tzouvelekis, C., Chatzigeorgiou, M., Travlos, A., Boukos, N., *Low-cost electrodeposition of size-tunable single-crystal zno nanorods,* Fibers **9** (6), art. no. 38, (2021) DOI: 10.3390/fib9060038
7. Kolonelou, E., Loupou, E., Klonos, P.A., Sakellis, E., Valadorou, D., Kyritsis, A., Papathanassiou, A.N., *Thermal and electrical characterization of poly(vinyl)alcohol)/poly(vinylidene fluoride) blends reinforced with nano-graphene platelets* Polymer **224**, art. no. 123731, (2021) DOI: 10.1016/j.polymer.2021.123731

8. Lyra, K.-M., Kaminari, A., Panagiotaki, K.N., Spyrou, K., Papageorgiou, S., Sakellis, E., Katsaros, F.K., Sideratou, Z., *Multi-walled carbon nanotubes decorated with guanidinylated dendritic molecular transporters: An efficient platform for the selective anticancer activity of doxorubicin*, Pharmaceutics **13** (6), art. no. 858, (2021) DOI: 10.3390/pharmaceutics13060858
9. Papavasiliou, A., Deze, E.G., Papageorgiou, S.K., Sideratou, Z., Boukos, N., Poulakis, E., Philippopoulos, C.J., Glisenti, A., Van Everbroeck, T., Cool, P., Katsaros, F.K*., A hyperbranched polymer synthetic strategy for the efficient fixation of metal species within nanoporous structures: Application in automotive catalysis* Chemical Engineering Journal, **421**, art. no. 129496 (2021) DOI: 10.1016/j.cej.2021.129496
10. Bousoulas, P., Panagopoulou, M., Boukos, N., Tsoukalas, D. *Emulating artificial neuron and synaptic properties with SiO2-based memristive devices by tuning threshold and bipolar switching effects* Journal of Physics D: Applied Physics, **54** (22), art. no. 225303 (2021) DOI: 10.1088/1361-6463/abea3b
11. Malakopoulos, A., Chatzigeorgiou, M., Boukos, N., Salifoglou, A. *Durability performance of Portland limestone cement mortar containing butyl and zinc stearate admixtures* Materials and Structures/Materiaux et Constructions, **54** (2), art. no. 60 (2021) DOI: 10.1617/s11527-021-01638-5
12. Giannakopoulou, T., Pilatos, G., Todorova, N., Boukos, N., Vaimakis, T., Karatasios, I., Trapalis, C. *Effect of processing temperature on growing bamboo-like carbon nanotubes by chemical vapor deposition* Materials Today Chemistry, **19**, art. no. 100388 (2021) DOI: 10.1016/j.mtchem.2020.100388

International Conference Presentations (invited, oral, poster)

Giannakopoulos K., Kaidatzis A., Mouti N., Magnetron sputtered titania films on CSP mirrors EUROMAT 2021, 13-17 September 2021, Virtual, (Oral)

Giannakopoulos K., Douzenis A., Lasithiotakis M., Eleftheriadis K., Vratolis S, Gini M.I., Mouti N., Optimization of Production Parameters for Copper and Gold Nanoparticles by Spark Discharge Generator EUROMAT 2021, 13-17 September 2021, Virtual, (Poster)

Papadopoulos N.D., Koutsaftiki P., Vourna P., Xafakis S., Giannakopoulos K., Designing a facile preparation mode for the development of transparent and durable antisoiling coatings with enhanced anti-static properties EUROMAT 2021, 13-17 September 2021, Virtual, (Oral)

Teaching and Training Activities

1. K. Giannakopoulos
   Contribution in the ECOWEEK Book#2: "When nanotechnology inspires design" N. Mouti, K. Giannakopoulos, 2021 https://issuu.com/ecoweek/docs/ecoweek_book2_sample_lr
2. K. Giannakopoulos
   Presentation at the Online SciFY Academy | Prometheus: The Future of Science is here. Title: "Nanocoatings, the answer to the overuse of biocidal materials" 15/12/2021, online http://www.scify.gr/site/el/news/13-news/631-online-scify-academy-prometheus-the-future-of-science-is-here
3. K. Giannakopoulos
   Presentation of the new electron microscope, Researcher's Night 2021, Online, https://www.ntua.gr/ntuaren/research-centers.php#Research_Centers12
4. K. Giannakopoulos
   Presentation at the ECOWEEK EU Green Week 2021, 5 June 2021, Online, https://www.archisearch.gr/press/ecoweek-2021-aegina-greece-history-tourism-sustainability/
5. N. Boukos / E. Sakellis
   Nanomaterials lab, MSc course "Microsystems and Nanodevices"/Fall Semester 2021/NTUA/Athens, Greece
6. N. Boukos / E. Sakellis
   Experimental Methods lab, MSc course "Technological Applications of Physics"/Fall Semester 2021/NTUA/Athens, Greece
7. N. Boukos / E. Sakellis
   Weekly educational school visits to EM laboratory and demonstration of the electron microscopes.

Master Dissertations completed in 2021
Name: Apostolos Douzenis
Dissertation Title: Gold Nanoparticle Fabrication in Aerosols, study of their deposition and of their properties
Research Supervisor at NCSRD: K. Giannakopoulos
University where the Thesis was presented: National Technical University of Athens

Name: Georgia Gravvani
Dissertation Title: Synthesis and characterization of ZnO nanoparticles and study of M/ZnO NPs/Au (M:Au,Ag,Zn) heterostructures with ReRAM characteristics.
Research Supervisor at NCSRD: N. Boukos / E. Sakellis
University where the Thesis was presented: National Technical University of Athens

Undergraduate Theses and Internships completed in 2021
Name: Maria Modestou
Dissertation Title: Spark Discharge Aerosol Particle Generator
Research Supervisor at NCSRD: K. Giannakopoulos
University where the Thesis was presented: National Technical University of Athens

Name: Chrysa Diamantopoulou
Dissertation Title: Metallic coatings for antibacterial activity
Research Supervisor at NCSRD: K. Giannakopoulos
University where the Thesis was presented: National Technical University of Athens

Name: Chryssanthi Anagnostopoulou
Dissertation Title: Experimental setup for the study of magnetoresistance phenomena on thin magnetic films
Research Supervisor at NCSRD: K. Giannakopoulos
University where the Thesis was presented: National Technical University of Athens

Conference / Workshop Organisation

1. Member of the International Scientific Board of the Fourteenth ECerS Conference for Young Scientists in Ceramics, CYSC-2021, October 20-23, 2021 in Novi Sad, Serbia
2. Symposium organiser at EUROPEAN CONGRESS AND EXHIBITION ON ADVANCED MATERIALS AND PROCESSES - EUROMAT 2021, Sept. 13th – 17th, 2021, virtual
3. Member of the International Technical Program Committee of the MNE2021 - 47th international conference on Micro and Nano Engineering, September 2021, Turin, Italy

Services

Electron Microscopy characterization of materials and products to industrial entities in Greece.
Total income of 20.000 Euros

GRAPHENE AND TWO-DIMENSIONAL MATERIALS FOR NANOELECTRONICS

Project Leader: Dr Athanasios Dimoulas

Post Docs: P. Tsipas, S. Chaitoglou, E. Xenogiannopoulou, N. Kelaidis, P. Pappas, A. El Sachat

PhD Candidates: C. Zacharaki, S. Fragkos, N. Siannas, E. Symeonidou, E. Georgopoulou-Kotsaki, A. Lintzeris

- Objectives

- 2D metal dichalcogenide materials and van der Waals heterostructures
- HfO_2-based ferroelectrics focusing on the compatibility with Si semiconductor processing.
- Skyrmion-Topological insulators and Weyl semimetal heterostructures

- Highlights / main scientific results

1. Magnetic skyrmion manipulation in $CrTe_2/WTe_2$ 2D van der Waals heterostructure

Magnetic skyrmions in two-dimensional van der Waals materials provide an ideal platform to push skyrmion technology to the ultimate atomically thin limit. In this work, we theoretically demonstrate the Dzyaloshinskii–Moriya interaction and the formation of a Néel-type skyrmion lattice at the $CrTe_2/WTe_2$ bilayer van der Waals heterostructure. Our calculations suggest a field-contolled Néel-type skyrmion lattice — ferromagnet transition cycle. In addition, a spin-torque induced by spin-polarized current injection was simulated in order to study the motion of a skyrmion on a racetrack, where an increase in the skyrmion Hall angle is observed at high temperatures. Consequently, this study suggests that generation and annihilation of skyrmions can be achieved with temperature or field control and also manipulate the velocity and the direction of the Néel-type skyrmions through ultra-low current densities and temperature, thus shedding light on the general picture of magnetic skyrmion control and design of two-dimensional van der Waals heterostructures.

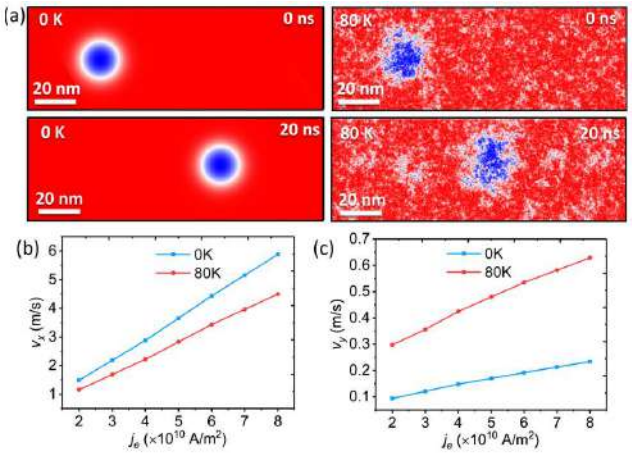


FIG. 1. (a) Screenshots of Neel-type skyrmion motion at 0 and 80 K under the same spin-polarized current density j_e = 4×10^{10} A/m^2. (b) and (c) v_x and v_y as a function of j_e, respectively.

2. Ultrafast Spin-Charge Conversion at $SnBi_2Te_4$/Co Topological Insulator Interfaces Probed by Terahertz Emission Spectroscopy

Spin-to-charge conversion (SCC) involving topological surface states (TSS) is one of the most promising routes for highly efficient spintronic devices for terahertz (THz) emission. Here, the THz generation generally occurs mainly via SCC consisting in efficient dynamical spin injection into spin-locked TSS. In this work, sizable THz emission from a nanometric thick topological insulator (TI)/ferromagnetic junction—$SnBi_2Te_4$/Co—specifically designed to avoid bulk band crossing with the TSS at the Fermi level, unlike its parent material Bi_2Te_3 is demonstrated. THz emission time

domain spectroscopy (TDS) is used to indicate the TSS contribution to the SCC by investigating the TI thickness and angular dependence of the THz emission. This work illustrates THz emission TDS as a powerful tool alongside angular resolved photoemission spectroscopy (ARPES) methods to investigate the interfacial spintronic properties of TI/ferromagnet bilayers.

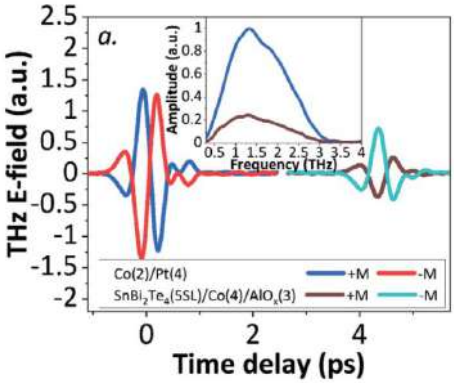


FIG. 2. THz emission spectroscopy acquired from $SnBi_2Te_4$/Co TSS mediated conversion. THz E-field of $SnBi_2Te_4$(5SL)/Co(4)/AlO_x(3) compared to the Co(2)/Pt(4) reference acquired under different ±M polarities. The phase difference between interface states and Pt indicates identical conversion sign for $SnBi_2Te_4$ and Pt. The inset represents the signal in the frequency domain (Fourier transform for +M).

3. The role of interface defect states in n and p-type Ge Metal-Ferroelectric-Semiconductor structures with $Hf_{0.5}Zr_{0.5}O_2$ ferroelectric

The discovery of ferroelectricity in doped HfO_2 represents an excellent opportunity to overcome the obstacles in manufacturing reliable ferroelectric field effect transistors (FeFET) for nonvolatile memory applications, considering that HfO_2 is compatible with Si and Ge and it is already used in semiconductor industry. The presence of interface defects may have detrimental effects on the operation of FeFETs, so their role is systematically investigated in this study in correlation with the substrate doping. Metal–ferroelectric–semiconductor (MFS) structures are fabricated by depositing $Hf_{0.5}Zr_{0.5}O_2$ (HZO) layers on n-type Ge substrate. Their electric properties are compared with those of MFS structures obtained by depositing HZO on p-type Ge, to study the influence of the doping. It is found that, although the ferroelectric properties of HZO are similar, the capacitance and impedance of the MFS structures behave differently. For n-Ge, the occupation probability of a large number of low-lying interface defect acceptor states, charges the interface negatively which adversely affects the *C*–*V* response of the MFS, albeit without harming the ferroelectric (*P*–*V*) hysteresis. Although the interface defects do not harm ferroelectricity, they could inhibit inversion in p-type Ge or accumulation in n-type Ge so they should be taken into account when designing Ge FeFET devices.

- **Funding**

- SKYTOP (Skyrmion-Topological insulator and Weyl semimetal technology), EU-funded Horizon 2020 project in FETPROACT-01-2018.
- 3eFERRO- (Energy Efficient Embedded Non-volatile Memory Logic based on Ferroelectric Hf(Zr)O2) EU-funded Horizon 2020 project
- BeFerrosynaptic-871737 (BEOL technology platform based on ferroelectric synaptic devices for advanced neuromorphic processors) EU-funded Horizon 2020 project
- Smart-X (Study of carrier transport in Materials by time-Resolved spectroscopy with ultrashort soft X-ray light) EU-Funded Marie Curie Innovative Training Network
- 2D-TOP (2D crystalline thin films with non-trivial topology)-ELIDEK, funded by the Hellenic Foundation for Research and Innovation (HFRI) and the General Secretariat for Research and Technology (GSRT).
- MELoDICA (Revealing the potential of transition metal dichalcogenides for thermoelectric applications through nanostructuring and confinement), FLAG-ERA JTC 2017.

- Marie Curie Individual Fellowship-"THERMIC"-101029727 "Local thermal and thermoelectric transport in 2D transition metal dichalcogenide based nanostructures and devices".

OUTPUT

Projects

Project MCSA-THERMIC-IEF started on November 2021. Researcher: Dr. Alex ElSachat

Publications in International Journals

1. Fragkos, S., Tsipas, P., Xenogiannopoulou, E., Panayiotatos, Y., Dimoulas, A., Type-III Dirac fermions in HfxZr1−xTe2 topological semimetal candidate, J. Appl. Phys. 129, 075104 (2021). DOI: https://doi.org/10.1063/5.0038799
2. Fragkos, S., Baringthon, L., Tsipas, P., Xenogiannopoulou, E., Le Fèvre, P., Kumar, P., Okuno, H., Reyren, N., Lemaitre, A., Patriarche, G., George, J.-M., Dimoulas, A., Topological surface states in epitaxial (SnBi2Te4)n(Bi2Te3)m natural van der Waals superlattices, Phys. Rev. Materials 5, 014203 (2021). DOI: https://doi.org/10.1103/PhysRevMaterials.5.014203
3. Tsipas, P., Pappas, P., Symeonidou, E., Fragkos, S., Zacharaki, C., Xenogiannopoulou, E., Siannas, N., Dimoulas, A., Epitaxial HfTe2 Dirac semimetal in the 2D limit, APL Materials 9 (10), 101103 (2021). DOI: https://doi.org/10.1063/5.0065839
4. Xenogiannopoulou, E., Tsoutsou, D., Tsipas, P., Fragkos, S., Chaitoglou, S., Kelaidis, N., Dimoulas, A., Ultrathin epitaxial Bi film growth on 2D HfTe2 template, Nanotechnology 33 (1), 015701 (2021). DOI: https://doi.org/10.1088/1361-6528/ac2d08
5. Chaitoglou, S., Spachis, L., Zisis, G., Raptis, I., Papanikolaou, N., Vavouliotis, A., Penedo, R., Fernandes, N., Dimoulas, A., Layer-by-layer assembled graphene coatings on polyurethane films as He permeation barrier, Progress in Organic Coatings 150, 105984 (2021). DOI: https://doi.org/10.1016/j.porgcoat.2020.105984
6. Xiao, P., Chavez-Angel, E., Chaitoglou, S., Sledzinska, M., Dimoulas, A., Sotomayor Torres, C. M., El Sachat, A., Anisotropic Thermal Conductivity of Crystalline Layered SnSe2, Nano Letters 21 (21), 9172-9179 (2021). DOI: https://doi.org/10.1021/acs.nanolett.1c03018
7. Rongione, E., Fragkos, S., Baringthon, L., Hawecker, J.; Xenogiannopoulou, E., Tsipas, P., Song, C., Mičica, M., Mangeney, J., Tignon, J., Boulier, T., Reyren, N., Lebrun, R., George, J.-M., Le Fèvre, P., Dhillon, S., Dimoulas, A., Jaffrès, H., Ultrafast Spin-Charge Conversion at SnBi2Te4/Co Topological Insulator Interfaces Probed by Terahertz Emission Spectroscopy, Adv. Opti. Mater. 10, 2102061 (2021). DOI: https://doi.org/10.1002/adom.202102061

International Conferences Presentations (invited, oral, poster)

1. Fragkos, S., et al, Type-I, II and III topological Dirac semimetals in 1T transition metal ditelluride family, 35th Panhellenic Conference on Solid State Physics and Materials Science, Virtual, 26-29 September 2021. Oral presentation
2. Dimoulas, A., et al, 2D ferromagnet/Bi2Te3 TI heterostructures grown by Molecular Beam Epitaxy, EUROMAT 2021, Virtual, 13-17 September 2021. Oral presentation
3. Fragkos, S., et al, Ultrathin epitaxial Bi film growth on $HfTe_2$/InAs(111) template, EUROMAT 2021, Virtual, 13-17 September 2021. Oral presentation
4. Fragkos, S., et al, Type-I, II and III topological Dirac semimetals in group IV 2D transition metal ditelluride family, EUROMAT 2021, Virtual, 13-17 September 2021. Oral presentation
5. Fragkos, S., et al, Epitaxial HfTe2, ZrTe2 and type-III Dirac fermions in HfxZrx-1Te2 topological semimetal candidate, APS March Meeting, Virtual, 15-19 March 2021. Oral presentation

MATERIALS FOR NANOLITHOGRAPHY AND ORGANIC ELECTRONICS

Project Leader: Dr. Panagiotis Argitis

Permanent Research Staff: Dr. Maria Vasilopoulou, Dr. Antonios Douvas, Dr. Nikos Kehagias

Post Docs: Dr. Anastasia Soultati, Dr. Ermioni Polydorou, Dr. Marinos Tountas

PhD Candidates: Apostolis Verykios, Charis Katsogridakis, Konstantina Tourlouki, Varvara Marazioti, Petros P. Filippatos

Undergraduate Students: Konstantina K. Armadorou

Objectives

- Research on materials for organic and perovskite optoelectronic devices of advanced performance.
- Research on photosensitive polymeric materials, nanostructured metal oxides and polyoxometalates for micro-nanopatterning processes, and drug delivery.
- Development of nanostructured materials, with emphasis on hybrid materials and metal oxides/polyoxometalates, for applications in electronic devices, photocatalysis, and art conservation.
- Development of functional resist materials suitable for micro/nano patterning.

- **Highlights / main scientific results**

High efficiency blue organic light-emitting diodes with below-bandgap electroluminescence *(Nature Communications 12, Article number: 4868 (2021))*

Blue thermally activated delay fluorescent organic light-emitting diodes with a below-bandgap turn-on voltage of 2.5 V and an external quantum efficiency (EQE) of 41.2% were successfully fabricated. These devices also showed suppressed efficiency roll-off maintaining an EQE of 34.8% at 1000 cd m^{-2}. The high OLED performance was made possible through the application of a low ET (2.14 eV) hole transport material (HTM), rationally designed with a high hole mobility of 7.5 × 10^{-3} cm^2 $(V\ s)^{-1}$ .This HTM served as a hole "reservoir" influencing both hole and electron carrier injection, and transport and subsequent exciton formation at the EML/electron transport material (ETM) interface. Effective exciton confinement due to the formation of an interface exciplex between the ambipolar host and the ETM prevents exciton diffusion towards the low ET HTM, resulting in minimal energy loss, below-bandgap electroluminescence (EL), high efficiency, improved lifetime, and reduced efficiency roll-off.

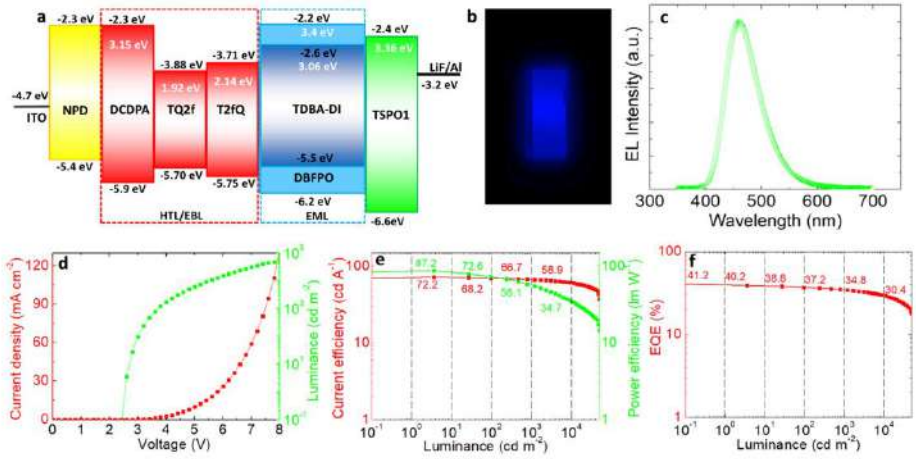


Fig. 1 *Performance of optimized blue TADF OLEDs and efficiency roll-off.* ***a*** *The energy-level diagram of the layers sequence in the blue TADF OLED device architecture considering vacuum level alignment before contact. Besides HOMO and LUMO energies of organic layers, the triplet energy of the emitter, host, and interlayer materials are also presented.* ***b*** *Photograph of a working OLED pixel with an active area of 25mm² and* ***c*** *electroluminescence spectrum of the same device. d Current density–luminance–voltage characteristics, e current and power efficiency vs. luminance, and f EQE vs. luminance characteristics for the OLED.*

- **PEDOT:PSS:sulfonium salt composite hole injection layers for efficient organic light emitting diodes** ***(Organic Electronics 93, pp. 106155 [1–9] (2021))***

  Two triphenylsulfonium (TPS) salts that consist of the same TPS cation and two different counter anions, in particular, hexafluoroantimonate (SbF_6) and trifluoromethane sulfonate (Triflate) were added in the PEDOT:PSS solution in various concentrations and the composite films were fully characterized for surface and optoelectronic properties and subsequently we employed as hole injection layers (HILs) in OLEDs. It is demonstrated that both, the counter anion and the concentration of TPS-salts in the PEDOT:PSS matrix play significant role in the optoelectronic properties of the composite and thus in the device performance. Although all TPS-salt modified PEDOT:PSS films exhibited higher work function (WF) values relative to the undoped one thus resulting in more efficient hole injection than pristine PEDOT:PSS, the PEDOT:PSS:TPS-Triflate with the lower concentration (10:1 v/v) showed the highest luminous (LE) and power efficiency (PE) values of 27.04 cd A^{-1} and 6.26 lm W^{-1}, respectively. This extraordinary performance was ascribed to a significant increase in the conductivity of the composite film combined with the formation of an interface exciplex between the TPS-Triflate (acceptor) and the emissive copolymer (donor). This interfacial electroplex strongly confines the generated excitons and prevents their diffusion towards aluminum cathode which acts as exciton quencher.

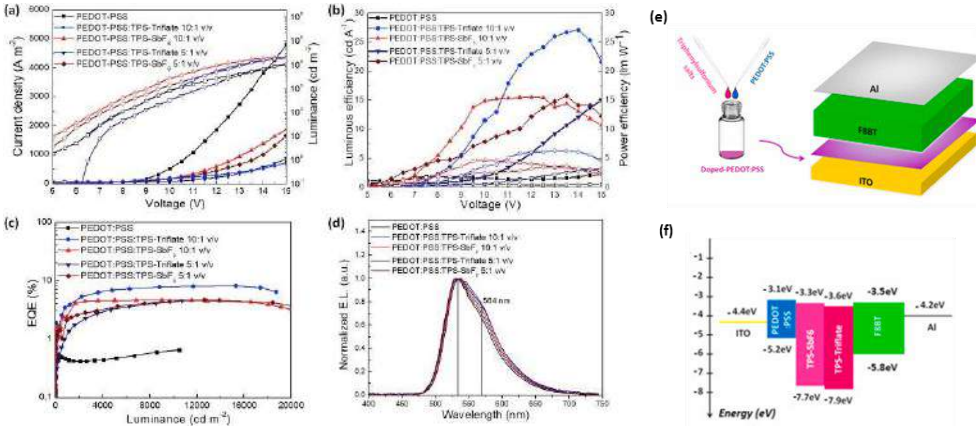


Fig. 2 ***(a)*** *Current density-luminance-voltage (J-V-L) characteristics (J-V at linear scale and L-V at semilog-scale),* ***(b)*** *luminous efficiency-power efficiency-voltage (LE-PE-V) characteristic curves (in linear scale),* ***(c)*** *EQE-luminance characteristics (in semilog-scale) and* ***(d)*** *Electroluminescent (EL) spectra of OLEDs based on F8BT emissive layer with pristine and TPS-salt-doped PEDOT:PSS HILs. (e)Schematic representation of the OLEDs with TPS-salt-doped PEDOT:PSS HIL. (f) Illustration of energy levels of the materials used in the OLED, considering the vacuum level alignment of the OLED layers before physical contact.*

- **Nanoimprint lithography (NIL)**

  During 2021 emphasis was placed on setting up a nanoimprint lithography (NIL) laboratory with new equipment both for the replication and imprinting of micro/nano structures, devices and surfaces as well as for their optical characterization. At the same time, novel lithography systems were developed to scale up the fabrication of nano-enabled devices and surfaces. In the same context, 3D printers have been installed to provide additional support to the laboratory's research activities. The aim of the NIL lab is to create a useful laboratory which will strengthen the collaborations and synergies of the INN researchers.

  The relevant research activity focused on the development of nanostructured polymeric surfaces for the control of thermal dissipation (surface cooling) effects as well as for the fabrication of optical surfaces (metasurfaces) with personalized optical characteristics. Additionally, functional surfaces were designed and developed which were studied for both their superhydrophobic and antimicrobial properties.

- **Development of nanostructured materials**

  During 2021 the relevant research activity focused on

  Physicochemical investigation of polyoxometalates for photocatalytic and energy applications

  Physicochemical characterization of spray-paints used in street artworks (graffiti), for the investigation of the pathology of these materials (mainly due to aging) and their removal from licensed public murals.

- **Funding**

1. Adhesive polymeric materials and non-destructive characterization methods for abrasive coatings (collaboration with Smirdex S.A. Coated Abrasives Industry), Stavros Niarchos Foundation (Industrial Adjunct Researchers)-12149, Dimitra Niakoula, 112,000 Euros, 7/3/2017- 7/6/2021.
2. Novel organic and perovskite solar cells of high efficiency using porphyrins as transport layers and/or molecular linkers, IKY Scholarship Post-Docs 2019, 2019-050-0503-18494, Anastasia Soultati, 25,000 Euros, 2/15/2020- 2/15/2022.
3. Colloidal quantum dot-in-perovskite light emitting diodes with high efficiency in the second near-infrared window, IKY Scholarship Post-Docs 2019, Marinos Tountas, 25,000 Euros, 1/15/2020- 1/15/2022.
4. High efficiency and stability organic solar cells employing metal oxide and nanoparticle interlayers, MONACELL, K. KARATHEODORI 2020, Maria Verouti, 2/1/2021, 700 Euros/month.
5. Experimental and theoretical studies of physical properties of low dimensional quantum nano- electronic systems, EINSTEIN, T4ΔΡΩ-00031, Greek-Russian Bilateral Collaboration, GSRI, 13,500 Euros, 2/13/2018- 8/13/2021.
6. HELIOKERAMOS, Industrial Materials Project for OPV incorporation in Buildings (OPV Tiles), ΗΚ, Τ6ΥΒΠ-00367, GSRI - EIDIKES DRASEIS (BIOMHXANIKA YLIKA), 100,000 Euros, 5/26/2020- 5/25/2023.
7. Advanced inline nano-metrology techniques for roll to roll nanoimprint lithography manufacturing processes, NanoMet, GSRI - EIDIKES DRASEIS (BIOMHXANIKA YLIKA), 50,000 Euros, 2/28/2020- 2/27/2023.
8. Intelligent food packaging implementing Organic Photonics for Food Quality Monitoring, iPHOTO-PACK, HFRI-FM17-3268, ELIDEK Faculty Members and Researchers, Collaboration with Agricultural University of Athens, 80,000 Euros, 9/2/2020- 9/8/2023.
9. Using organic LED in intelligent food packaging for quality monitoring of meat products, OLED_Lumin_FoodPack, Τ2ΕΔΚ-04175, GSRI - EREYNW KAINOTOMW, 200, 000 Euros, 11/26/2020 - 5/25/2023.

OUTPUT

Publications in International Journals

1. Filippatos, P.-P., Soultati, A., Kelaidis, N., Petaroudis, C., Alivisatou, A.-A., Drivas, C., Kennou, S., Agapaki, E., Charalampidis, G., Yusoff, A. R. b. M., Lathiotakis, N. N., Coutsolelos, A. G., Davazoglou, D., Vasilopoulou, M., Chroneos, A., Preparation of hydrogen, fluorine and chlorine doped and co-doped titanium dioxide photocatalysts: A theoretical and experimental approach, *Scientific Reports* **11**, Article number: 5700 (2021).DOI: https://doi.org/10.1038/s41598-021-81979-x
2. Filippatos, P.-P., Kelaidis, N., Vasilopoulou, M., Davazoglou, D., Chroneos, A., Impact of boron and indium doping on the structural, electronic and optical properties of SnO_2, *Scientific Reports* **11**, Article number:13031 (2021). DOI: https://doi.org/10.1038/s41598-021-92450-2
3. Fakharuddin, A., Vasilopoulou, M., Soultati, A., Haider, M. I., Briscoe, J., Fotopoulos, V., Di Girolamo,D., Davazoglou, D., Chroneos, A., Yusoff, A. R. b. M., Abate, A., Schmidt-Mende, L., Nazeeruddin, M. K., Robust inorganic hole transport materials for organic and perovskite solar cells: insights into materials electronic properties and device performance, *Solar RRL* **5**, pp. 2000555 [1–44] (2021). DOI: https://doi.org/10.1002/solr.202000555
4. Filippatos, P.-P., Kelaidis, N., Vasilopoulou, M., Davazoglou, D., Chroneos, A., Defect processes in halogen doped SnO_2, *Applied Sciences* **11**, pp. 551 [1–14] (2021). DOI: https://doi.org/10.3390/app11020551
5. Filippatos, P.-P., Kelaidis, N., Vasilopoulou, M., Davazoglou, D., Chroneos, A., Structural, Electronic, and Optical Properties of Group 6 Doped Anatase TiO_2: A Theoretical Approach, *Applied Sciences* **11**, 1657 (2021). DOI: https://doi.org/10.3390/app11041657
6. Yusoff, A. R. b. M., Vasilopoulou, M., Georgiadou, D. G., Palilis, L. C., Abate, A., Nazeeruddin, M. K., Passivation and process engineering approaches of halide perovskite films for high efficiency and stability perovskite solar cells, *Energy & Environmental Science* **14**, pp. 2906–2953 (2021). DOI: https://doi.org/10.1039/D1EE00062D
7. Fakharuddin, A., Li, H., Di Giacomo, F., Zhang, T., Gasparini, N., Y Elezzabi, A., Mohanty, A., Ramadoss, A., Ling, J., Soultati, A., Tountas, M., Schmidt-Mende, L., Argitis, P., Jose, R., Nazeeruddin, M. K., Yusoff, A. R. b. M., Vasilopoulou, M., Fiber-shaped electronic devices, *Advanced Energy Materials* **11**, pp. 2101443 [1–58] (2021). DOI: https://doi.org/10.1002/aenm.202101443
8. Tsevas, K., Smith, J. A., Kumar, V., Rodenburg, C., Fakis, M., Yusoff, A. R. b. M., Vasilopoulou, M., Lidzey, D. G., Nazeeruddin, M. K., Dunbar, A. D. F., Controlling PbI_2 Stoichiometry during Synthesis to Improve the

Performance of Perovskite Photovoltaics, *Chemistry of Materials* **33**, pp. 554–566 (2021). DOI: https://doi.org/10.1021/acs.chemmater.0c03517

9. Nikolaou, V., Charalambidis, G., Ladomenou, K., Nikoloudakis, E., Drivas, C., Vamvasakis, I., Panagiotakis, S., Landrou, G., Agapaki, E., Stangel, C., Henkel, C., Joseph, J., Armatas, G., Vasilopoulou, M., Kennou, S., Guldi, D. M., Coutsolelos, A. G., Controlling Solar Hydrogen Production by Organizing Porphyrins, *ChemSusChem* **14**, pp. 961–970 (2021). DOI: https://doi.org/10.1002/cssc.202002761
10. Di Giacomo, F., Schmidt-Mende, L., Vasilopoulou, M., Soultati, A., Gasparini, N., Ramadoss, A., Mohanty, A., Yusoff, A. R. b. M., Zhang, T., Fakharuddin, A., Free-standing nanopaper electrode for all-printed super-flexible perovskite solar cells, *Advanced Energy Materials* **11**, pp. 2101443 [1–16] (2021). DOI: https://doi.org/10.21203/rs.3.rs-296909/v1
11. Yusoff, A. R. b. M., Mahata, A., Vasilopoulou, M., Ullah, H., Hu, B., Jose da Silva, W., Schneider, F. K., Gao, P., Ievlev, A. V., Liu, Y., Ovchinnikova, O. S., De Angelis, F., Nazeeruddin, M. K., Observation of large Rashba spin–orbit coupling at room temperature in compositionally engineered perovskite single crystals and application in high performance photodetectors, *Materials Today* **46**, pp. 18–27 (2021). DOI: https://doi.org/10.1016/j.mattod.2021.01.027
12. Verykios, A., Pistolis, G., Bizas, L., Tselios, C., Tsikritzis, D., Kennou, S., Chochos, C. L., Mouzakis, D. E., Skandamis, P. N., Palilis, L. C., Argitis, P., Vasilopoulou, M., Soultati, A., PEDOT: PSS: sulfonium salt composite hole injection layers for efficient organic light emitting diodes, *Organic Electronics* **93**, pp. 106155 [1–9] (2021). DOI: https://doi.org/10.1016/j.orgel.2021.106155
13. Vasilopoulou, M., Yusoff, M., Daboczi, M., Conforto, J., Gavim, A. E. X., Jose da Silva, W., Macedo, A. G., Soultati, A., Pistolis, G., Schneider, F. K., Dong, Y., Jacoutot, P., Rotas, G., Jang, J., Vougioukalakis, G. C., Chochos, C. L., Kim, J.-S., Gasparini, N., High efficiency blue organic light-emitting diodes with below-bandgap electroluminescence, *Nature Communications* **12**, Article number: 4868 (2021). DOI: https://doi.org/10.1038/s41467-021-25135-z
14. Vasilopoulou, M., Fakharuddin, A., de Arquer, F. P. G., Georgiadou, D. G., Kim, H., Yusoff, M., Gao, F., Nazeeruddin, M. K., Bolink, H. J., Sargent, E. H., Advances in solution-processed near-infrared light-emitting diodes, *Nature Photonics*, 15, pp. 656–669 (2021). DOI: https://doi.org/10.1038/s41566-021-00855-2
15. Petaroudis, C., Kostis, I., Filippatos, P.-P., Chroneos, A., Soultati, A., Vasilopoulou, M., Davazoglou, D., Influence of thermal cycling on the optical and the electrical properties of atmospheric pressure chemical vapor deposited tin oxide films grown using water and methanol vapors as oxidizers, Thin *Solid Films* **734**, pp. 138841 [1–8] (2021). DOI: https://doi.org/10.1016/j.tsf.2021.138841
16. Schmidt-Mende, L., Dyakonov, V., Olthof, S., Ünlü, F., Lê, K. M. T., Mathur, S., Karabanov, A. D., Lupascu, D. C., Herz, L. M., Hinderhofer, A., Schreiber, F., Chernikov, A., Egger, D. A., Shargaieva, O., Cocchi, C., Unger, E., Saliba, M., Byranvand, M. M., Kroll, M., Nehm, F., Leo, K., Redinger, A., Höcker, J., Kirchartz, T., Warby, J., Gutierrez-Partida, E., Neher, D., Stolterfoht, M., Würfel, U., Unmüssig, M., Herterich, J., Baretzky, C., Mohanraj, J., Thelakkat, M., Maheu, C., Jaegermann, W., Mayer, T., Rieger, J., Fauster, T., Niesner, D., Yang, F., Albrecht, S., Riedl, T., Fakharuddin, A., Vasilopoulou, M., Vaynzof, Y., Moia, D., Maier, J., Franckevičius, M., Gulbinas, V., Kerner, R. A., Zhao, L., Rand, B. P., Glück, N., Bein, T., Matteocci, F., Castriotta, L. A., Di Carlo, A., Scheffler, M., Draxl, C., Roadmap on organic–inorganic hybrid perovskite semiconductors and devices, *APL Materials* **9**, 109202 [1–82] (2021). DOI: https://doi.org/10.1063/5.0047616
17. Francone, A., Merino, S., Retolaza, A., Ramiro, J., Alves, S. A., Vieira de Castro, J., Neves, N. M., Arana, A., Marimon, J. M., Torres, C. M. S., Kehagias, N., Impact of surface topography on the bacterial attachment to micro-and nano-patterned polymer films, *Surfaces and Interfaces* **27**, pp. 101494 [1–11] (2021). DOI: https://doi.org/10.1016/j.surfin.2021.101494
18. Kabouraki, E., Melissinaki, V., Yadav, A., Melninkaitis, A., Tourlouki, K., Tachtsidis, T., Kehagias, N., D Barmparis, G. D., Papazoglou, D. G., Rafailov, E., Farsari, M., High laser induced damage threshold photoresists for nano-imprint and 3D multi-photon lithography, *Nanophotonics* **10**, pp. 3759–3768 (2021). DOI: https://doi.org/10.1515/nanoph-2021-0263
19. Perez-Gavilan, A., de Castro, J. V., Arana, A., Merino, S., Retolaza, A., Alves, S. A., Francone, A., Kehagias, N., Sotomayor-Torres, C. M., Cocina, D., Mortera, R., Crapanzano, S., Pelegrín, C. J., Garrigos, M. C., Jiménez, A., Galindo, B., Araque, M. C., Dykeman, D., Neves, N. M., Marimón, J. M., Antibacterial activity testing methods for hydrophobic patterned surfaces, *Scientific Reports* **11**, Article number: 6675 (2021). DOI: https://doi.org/10.1038/s41598-021-85995-9
20. Psochia, E., Papadopoulos, L., Gkiliopoulos, D. J., Francone, A., Grigora, M.-E., Tzetzis, D., de Castro, J. V., Neves, N. M., Triantafyllidis, K. S., Torres, C. M. S., Kehagias, N., Bikiaris, D. N., Bottom-up development of nanoimprinted plla composite films with enhanced antibacterial properties for smart packaging applications, *Macromol* **1**, pp. 49–63 (2021). DOI: https://doi.org/10.3390/macromol1010005

International Conferences Presentations (invited, oral, poster)

Katsogridakis C., Kapetanakis E., Douvas A.M., Papadokostaki K.G., Dimotikali D., Normand P., Argitis P., Ion Mobility in Photosensitive Polymeric Films Incorporated as Dielectrics in Electronic Devices and Potential Applications, *13th Hellenic Polymer Society International Conference* 12 – 16 December 2021, Athens, Greece **(invited)**

Teaching and Training Activities

1. Maria Vasilopoulou
"Spectroscopy", Winter Semester Course, Graduate Program "Applied Optoelectronics", organized by Department of Materials Science and Department of Electrical Engineering of the University of Patras and Institute of Nanoscience and Nanotechnology- NCSR Demokritos.

2. Maria Vasilopoulou and Panagiotis Argitis,
"Organic Electronics", Spring Semester Course, Graduate Program "Applied Optoelectronics", organized by Department of Materials Science and Department of Electrical Engineering of the University of Patras and Institute of Nanoscience and Nanotechnology- NCSR Demokritos.

3. Panagiotis Argitis,
Part of the course "Polymers in electronic/photonic devices and microsystems", Spring Semester, Graduate Program "Polymer Science and its Applications in Industry", Department of Chemistry, National and Kapodistrian University of Athens.

MATERIALS AND DEVICES FOR INFORMATION STORAGE & EMERGING ELECTRONICS

Project Leader: P. Normand

Permanent Research Staff: V. Ioannou-Sougleridis, P. Dimitrakis

Post Docs: F. Kalaitzakis, K. Garidis, N. Matthaiakakis

PhD candidates: N. Vasileiadis

Research Associates: E. Polydorou, K. Kariofyllis, P. Mandilas, C. Karousiotis, A. Mavropoulis

Research Collaborators: E. Kapetanakis (Adjunct Researcher), D. Skarlatos (Adjunct Researcher), Prof. I. Karafyllidis (Adjunct Researcher)

Objectives

Since 1995, our group has been committed to conducting research in the broad and multifaceted field of micro-nanoelectronics. Our research mainly focuses on exploring new materials, device design, and fabrication techniques to not only improve existing logic and memory technologies, but also advance these technologies along new, more radical paths, like in-memory and quantum computing. The last few years, particular attention was also given to electrolyte systems for flexible electronics, irradiation damage in functional materials, heterogeneous and monolithic integration, and graphene technology for electronics and sensing.

Activities and Main Results in 2021

A. Charge transport in Metal / Organic Semiconductor / Electrolyte systems

These activities are conducted in collaboration with the HM University and the INN project "Materials for Nanolithography and Organic Electronics". They are devoted to the development of Metal/Organic Semiconductor (OSC) / Electrolyte systems and associated devices (e.g., electrolyte-gated organic thin film transistors, EGOTFTs) for applications ranging from sensing (e.g., radiation detection, characterization of ionic chemical species) to low-cost logic circuits. This year we continued research on EGOTFTs stemming from in-situ photo-induced-generation of mobile ions in polymeric gate dielectrics (see previous INN annual reports). Modulation of the source-drain output current (I_{DS}) occurring with the application of gate-voltage (V_{GS}) sweeps was thoroughly examined as a function of different processing parameters. Quantities of interest like the threshold voltage and current gain factor were extracted using analytical models based on the gradual channel approximation. An empirical model has been developed for devices subject to high mobility or/and capacitance changes during $I_{DS} - V_{GS}$ measurements together with mobility degradation and contact resistance effects at high gate fields. Substantial efforts have also been put on stress experiments, where I_{DS} modulation with time was examined as a function of the applied V_{GS} and V_{DS}, OSC thickness and device channel length. These experiments revealed that I_{DS} monotonically increases with time, evolving from a superlinear power-law regime to a sublinear regime, where the contact resistance gradually dominates the total resistance of the devices as the stress time increases.

B. Processability of ALD Al_2O_3 on semiconductor substrates

In this activity we study the processing issues of ALD-Al_2O_3 films deposited on semiconductor substrates such as Si and Ge. In particular, one of the important studying issues is the post-deposition processing parameters used in the fabrication of MOS devices and how these processes influence the quality of the metal-Al_2O_3 interface as-well as dielectric-semiconductor interface. During 2021, we had examined the influence of negative lithography on Al_2O_3 films deposited on silicon, as well as the influence of post-deposition annealing parameters. This activity is conducted in collaboration with the Physics Dept. of Patras University and the Physics Dept. of Aristotle University.

C. Resistance switching mechanisms for memory cells and neuromorphic computing devices

Resistive memories are promising candidates for replacing current nonvolatile memories and realize storage class memories. Moreover, they have memristive properties, with many discrete resistance levels and implement artificial neuronal synapses. The last years researchers have demonstrated RRAM chips used as accelerators in computing,

following the new in-memory and neuromorphic computational approaches. Many different metal oxides have been used as resistance switching materials in MIM structures. Understanding of the switching mechanism is very critical for the modeling and the use of memristors in different applications. Here, we demonstrate the bipolar resistance switching of silicon nitride thin films using heavily doped Si and Cu as bottom and top electrodes respectively. Next, nitride is doped with oxygen (Fig.1 – top) in order to introduce and modify the intrinsic nitride defects. Analysis of the current-voltage characteristics reveal that under space-charge limited conditions and by setting the appropriate current compliance, the operation condition of the RRAM cells can be tuned (Fig.1 – bottom). Furthermore, resistance change can be obtained using appropriate SET/RESET pulse sequences allowing the use of the devices in computing acceleration applications. Impedance spectroscopy measurements clarify the presence of different mechanisms during SET and RESET. We prove through a customized measurement set-up and the appropriate control software that the initial charge-storage in the intrinsic nitride traps governs the resistance change.

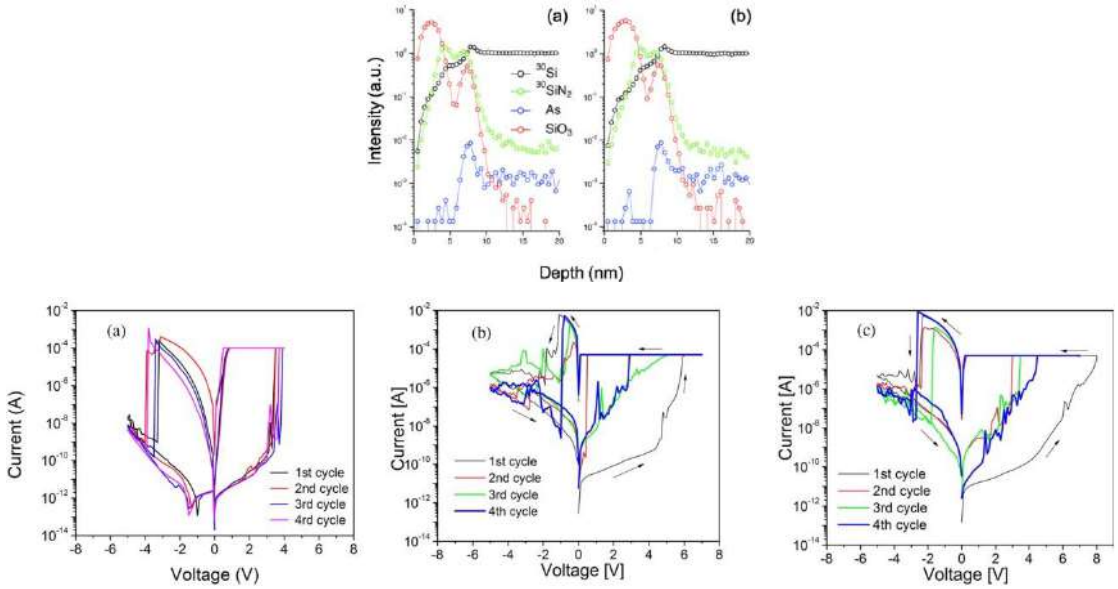


Figure 1: *(Top) ToF-SIMS measurements of plasma oxygen-doped nitride for (a) 120s and (b) 240s providing clear evidence of SiN_x oxidation and (Bottom) comparison between experimental switching I-V characteristics for samples (a) without, (b) after 120s and (c) after 240s exposure to oxygen plasma.*

D. Nano-electronic devices for Quantum Simulators

Over the last years there has been significant progress in the development of quantum computers. The use of quantum simulators is essential in developing and testing new quantum algorithms. A framework has been implemented capable of automatically generating memristor crossbar configurations that can perform quantum computations. This tool aims to simplify the investigation and the fabrication of a memristor based hardware capable of efficiently simulating a quantum computer. Taking inspiration from previous work on developing a novel quantum simulator based on memristor crossbar circuits, in this work, a framework that automates the circuit design of emulated quantum gates is presented. The proposed design framework deals with the generation and programming of memristor crossbar configuration that incorporates the desirable quantum circuit, leading to a technology agnostic design tool.

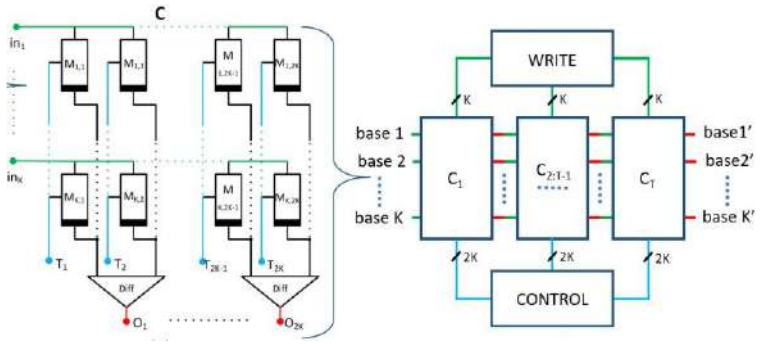


***Figure 2**. Quantum Computation implemented through Crossbar Circuit using memristors in differential crossbar architecture to realize memristor-based Quantum Circuit*

E. Studies of irradiation damage on functional materials

This activity is implemented by the Eurofusion consortium within the frame of WP JET3 ("Technological exploitation of Deuterium - Tritium operation"). The goal is to determine the radiation induced damage of high-quality materials with particular optical or insulating functionality, when exposed to high fluence of neutrons /γ-rays (14 MeV) within the JET tokamak fusion reactor. During 2021, we had extended our studies to thermally stimulated current spectroscopy using a 275 nm UV LED as excitation source. Several defect states were detected with activation energies 0.45 eV, 0.82 eV, 0.9 eV, 1 eV, 1.6 eV.

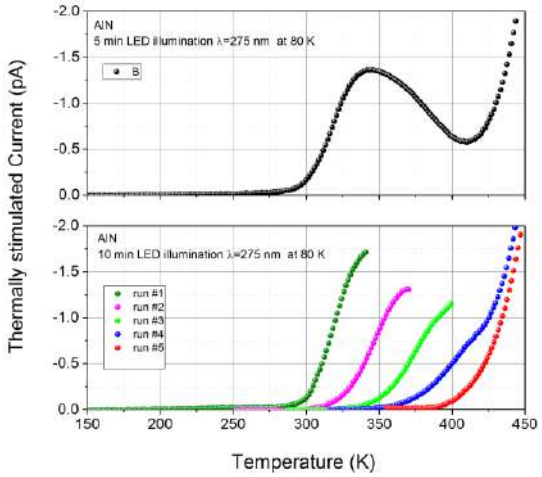


***Figure 3**: Photo-induced thermally stimulated current in AlN ceramic results in a complex relaxation peak. Fractional heating indicates that the peak is composed of several defects having activation energies within the range of 0.45 eV -1.6 eV .*

F. Heterogeneous Integration of GaN and Si interposer for heat dissipation in RF circuits

This year we continued to work on developing reconfigurable microwave power transceivers combining disruptive nanotechnology and microelectronics techniques for 2D and 3D heterogeneous integration. Focus is on the bonding of RF GaN chip modules on Si-wafer interposer for chip cooling. Main efforts were placed on eutectic bonding experiments using Al and Cu thin films (ca. 150nm) doped with Sn. The most critical parameter for successful recipes is the bonding temperature which cannot exceed 220^{o}C to preserve ohmic contacts on the GaN chip. Dry etching-based fabrication of very dense through-silicon-vias (TSVs) has been demonstrated and optimized in terms of TSV dimension accuracy, vias density and wafer stress.

G. Graphene technology for electronic devices and sensors

Graphene nanoribbons (GNRs) are the most important emerging graphene structures for nanoelectronic and sensor applications. While the electronic properties of GNRs with perfect lattices have been extensively studied, few efforts have been devoted to the more realistic case of GNRs containing lattice defects. Here, we applied the Non-Equilibrium Green's function (NEGF) method combined with tight-binding Hamiltonians to investigate the effect of lattice defects on the conductance of GNRs. We specifically studied butterfly shaped GNRs, which operate effectively as switches and have been used in CMOS-like architectures. The cases of the most usual defects, namely the single and double vacancy have been analytically examined. The effect of these vacancies was computed by placing them in different regions, namely edges, main body, contacts and narrow regions and at various densities. Our results indicate that lattice defects affect significantly the electronic properties of the devices. In general, the channel region appears to be more severely affected by defects than the contact region. Both edge and bulk channel defects reduce the maximum conductance to very low values (Fig. 4).

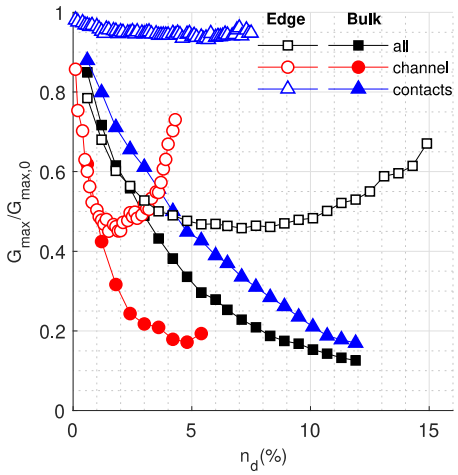


***Figure 4**. Overall comparison of the change of normalized conductance with the increase of defect density, for every examined GRN region.*

Funding

"JET3 RADA" EUROfusion- FP8 (No: 633053), 2014-2021 (~140k€), -FP9 (No: 633053), 2021-2025 (~26k€)
"ΣΕΜΘ", "Research-Create-Innovate" GSRI-NSFR (No: T1ΕΔΚ-03579) 2018-2022 (260k€)
"EINSTEIN", Greece-Russia Bilateral Research Project, GSRI-NSFR (No: T4ΔΡΩ-00031) 2018-2021 (140k€)
"RADAR", "Research-Create-Innovate" GSRI-NSFR (No: T1ΕΔΚ-00329) 2018-2022 (140k€)
"MEM-Q", Greece-Russia Bilateral Research Project, GSRI-NSFR (No: T4ΔΡΩ-00030) 2018-2021 (50k€)
"Crossbar architectures for 1D1M for neuromorphic computing", Research Group Support 2018, GSRT (No 101025) (120k€)
"3D-TOPOS", "Research-Create-Innovate" GSRI-NSFR (No. T2ΕΔΚ-00340) 2021-2023 (200 k€)

OUTPUT

Publications in International Journals

1. Vasileiadis, N., Loukas, P., Karakolis, P., Ioannou-Sougleridis, V., Normand, P., Ntinas, V., Fyrigos,I.-A., Karafyllidis, I., Sirakoulis, G.C., Dimitrakis, P., Multi-level resistance switching and random telegraph noise analysis of nitride based memristors, Chaos, Solitons and Fractals, 153, art. no. 111533, 2021. DOI: 10.1016/j.chaos.2021.111533.
2. Vasileiadis, N., Ntinas, V., Sirakoulis, G.C., Dimitrakis, P., In-memory-computing realization with a photodiode/memristor based vision sensor, Materials, 14 (18), art. no. 5223, 2021. DOI: 10.3390/ma14185223.

3. Vasileiadis, N., Karakolis, P., Mandylas, P., Ioannou-Sougleridis, V., Normand, P., Perego, M., Komninou, P., Ntinas, V., Fyrigos, I.-A., Karafyllidis, I., Sirakoulis, G.C., Dimitrakis, P., Understanding the Role of Defects in Silicon Nitride-Based Resistive Switching Memories through Oxygen Doping, IEEE Transactions on Nanotechnology, 20, art. no. 9403953, pp. 356-364, 2021. DOI: 10.1109/TNANO.2021.3072974.
4. Rallis, K., Dimitrakis, P., Karafyllidis, I.G., Rubio, A., Sirakoulis, G.C., Electronic Properties of Graphene Nanoribbons with Defects, IEEE Transactions on Nanotechnology, 20, art. no. 9337210, pp. 151-160, 2021. DOI: 10.1109/TNANO.2021.3055135.
5. Skarlatos, D., Velessiotis D., Skoulikidou, M.C., Ioannou-Sougleridis V., Vouroutzis N.Z., Stoemenos, J., Substrate damage in ion-implanted (100) germanium after extended ms flash lamp annealing: Origins and suppression, Mater. Sci. Semicond. Process. 122, 105477, 2021. DOI: 10.1016/j.mssp.2020.105477.
6. Fyrigos, I.-A., Ntinas, V., Sirakoulis, G.C., Dimitrakis, P., Karafyllidis, I.G., Quantum Mechanical Model for Filament Formation in Metal-Insulator-Metal Memristors, IEEE Transactions on Nanotechnology, 20, art. no. 9316152, 113-122, 2021. DOI: 10.1109/TNANO.2021.3049632.

Papers in Refereed Conference Proceedings

1. Vasileiadis, N., Dimitrakis, P., Ntinas, V., Sirakoulis, G.C., True random number generator based on multi-state silicon nitride memristor entropy sources combination, International Conference on Electronics, Information, and Communication, ICEIC 2021, art. no. 9369817, 2021. DOI: 10.1109/ICEIC51217.2021.9369817
2. Tsakalos, K.-A., Ntinas, V., Karamani, R.-E., Fyrigos, I.-A., Chatzinikolaou, T.P., Vasileiadis, N., Dimitrakis, P., Provata, A., Sirakoulis, G.Ch., Emergence of chimera states with re-programmable memristor crossbar arrays, Proceedings - IEEE International Symposium on Circuits and Systems, 2021-May, art. no. 9401669, 2021. DOI: 10.1109/ISCAS51556.2021.9401669
3. Fyrigos, I.-A., Chatzinikolaou, T.P., Ntinas, V., Vasileiadis, N., Dimitrakis, P., Karafyllidis, I.,Sirakoulis, G.Ch., Memristor crossbar design framework for quantum computing, Proceedings - IEEE International Symposium on Circuits and Systems, 2021-May, art. no. 9401581, 2021. DOI: 10.1109/ISCAS51556.2021.9401581
4. Vasileiadis, N., Ntinas, V., Fyrigos, I.-A., Karamani, R.-E., Ioannou-Sougleridis, V., Normand, P., Karafyllidis, I., Sirakoulis, G.Ch., Dimitrakis, P., A new 1P1R image sensor with in-memory computing properties based on silicon nitride devices, Proceedings - IEEE International Symposium on Circuits and Systems, 2021-May, art. no.9401586, 2021. DOI: 10.1109/ISCAS51556.2021.9401586

Teaching and Training Activities

Name: P. Dimitrakis
Training: Internship of University students Mr Dimitris Nikitas, Ms Evgenia Skapinaki
Location/Academic Institute: Nanotechnology and Microsystems Laboratory/INN NCSR “D”

Bachelor and Diploma Thesis

1. A. Mavropoulis, “Thin nitride films for the fabrication of memristor electronic devices”, School of Mining and metallurgical Engineering, NTUA (2021)
2. A. Spyropoulos, “Graphene gas sensors”, Physics Department, University of Athens (2021)

PHOTONIC CRYSTALS, METAMORPHIC MATERIALS AND NOVEL RF SYSTEMS

Project Leader: Harry Contopanagos

- **Objectives**

- To design, optimize and fabricate photonic crystals and frequency-agile metamaterials (metamorphic materials) in 3 dimensions and 2 dimensions (metasurfaces) for electromagnetically passive or active filters, substrates and electromagnetic lenses. Both passive and electronically controlled (smart) structures are being studied.
- Applications in novel embedded antenna architectures, scanning and smart antenna arrays, filters, waveguides and resonators operating in the microwave/mm-wave region, for integration into novel Radio Frequency (RF) transceivers. Special emphasis in Internet of Things (IoT) and 5G/6G applications.

- **Highlights / main scientific results**

An electrically small 3-D Folded Grounded Loop Antenna for omnidirectional connectivity

Electrically small antennas are of intense and increasing academic and industrial interest due to the advent of ubiquitous RFID devices and more generally within the Internet of Things (IoT) applications. For most of these applications, antennas will have to be and as small as possible, when integrated within a transceiver, while maintaining significant efficiency values. Of particular interest are antennas that can radiate omnidirectionally along a planar surface, thus establishing optimal connectivity capabilities for devices surrounding the corresponding transmitter. Such antennas are also important for energy harvesting but also for near-field wireless charging applications. In this work we describe an electrically small antenna of size $ka \approx 0.25$, where a is its effective radius and k the wave vector at operating frequency. The antenna geometry is a 3-dimensional folded meandering loop and contains its own ground, so that it becomes insensitive to the integration environment. The radiation efficiency of the antenna is 70% and it radiates as a vertically polarized dipole. The operating frequency is chosen to target RFID/IoT applications at 915 MHz and the impedance matching bandwidth, as realized, is narrow but appropriate for such applications, and may be further increased if appropriate matching networks are used. In Fig. 1 we show a photograph of the fabricated prototype. The design is all laid out in stamped metal for very inexpensive mass-fabrication, and pure Cu is the metal of choice since it has maximum conductivity.

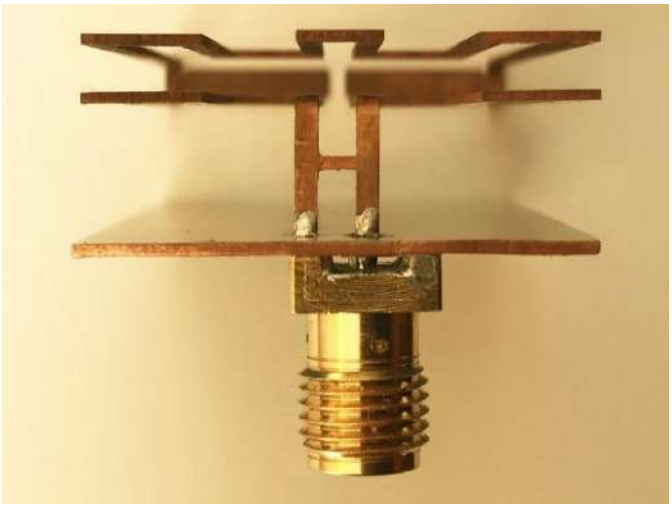


Figure 1. Photograph of the fabricated design D1 showing details of the SMA connector and feed.

In Fig. 2 we show the 3-dimensional polar plot of the simulated antenna gain, where the coordinate system has the [xy] plane parallel to the antenna ground of Fig. 1. We see that the antenna has a perfect dipole radiation pattern, with maximum gain at 0 dBi, therefore it is a perfectly omnidirectional dipole antenna. The antenna is vertically polarized, and it behaves in all respects as a dipole perpendicular to the antenna ground, even though the antenna is

fed as a grounded loop and not as a differentially fed antenna (typical dipole or loop feeds). This radiation pattern is ideal for omnidirectionally linked devices residing randomly on a planar surface, such as a table. It is important to notice here that the antenna can be quite close to that surface and yet not affected by the material of the surface, even if that were metal, because it is grounded and therefore shielded. This is not true for other small antennas, such as 2-dimensionally folded dipoles, which typically cannot be shielded by including a nearby ground, since this would short the antenna due to images induced by the nearby ground that would cancel the antenna currents. Instead, this antenna is not shorted despite the existence of its ground very near its structure.

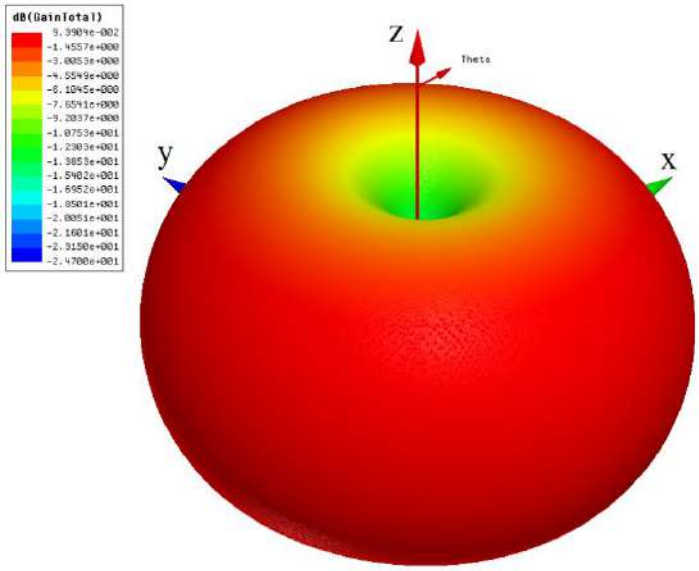


Figure 2. Total antenna gain (in dBi) at 915 MHz. The gain is due exclusively to the $\hat{\theta}$ component of the electric field (vertical polarization at θ=90°), with the cross-polarization (horizontal polarization) smaller by 25 dB.

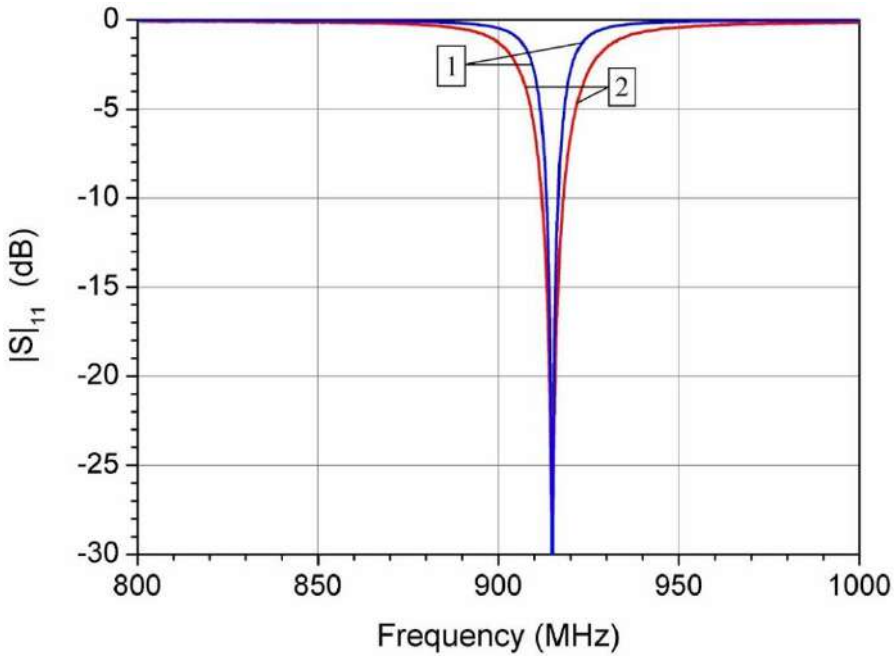


Figure 3. Theoretical (curve [1]) vs. measured (curve [2]) return loss of the antenna.

In Fig. 3 we compare the theoretical versus the measured return loss of the antenna. The -10 dB impedance matching bandwidth of the antenna is measured at about 5.7 MHz, larger than the simulated one. Fabrication inaccuracies, surface roughness as well as other distributed parasitic matching effects may cause this difference. Resonant frequencies are in excellent agreement.

In Figs. 4 a, b we compare the total gain of the antenna measured in an anechoic chamber with the corresponding simulated quantity, at 915 MHz, for the two principal cuts of the 3-dimensional radiation pattern of Fig. 2. Fig. 4a is the cut on the [yz] plane, i.e., it is the function $G_{TOT}(\theta, \phi = 90°)$, while Fig. 4b shows the corresponding comparison for the cut on the [xy] plane, hence it plots the function $G_{TOT}(\theta = 90°, \phi)$.

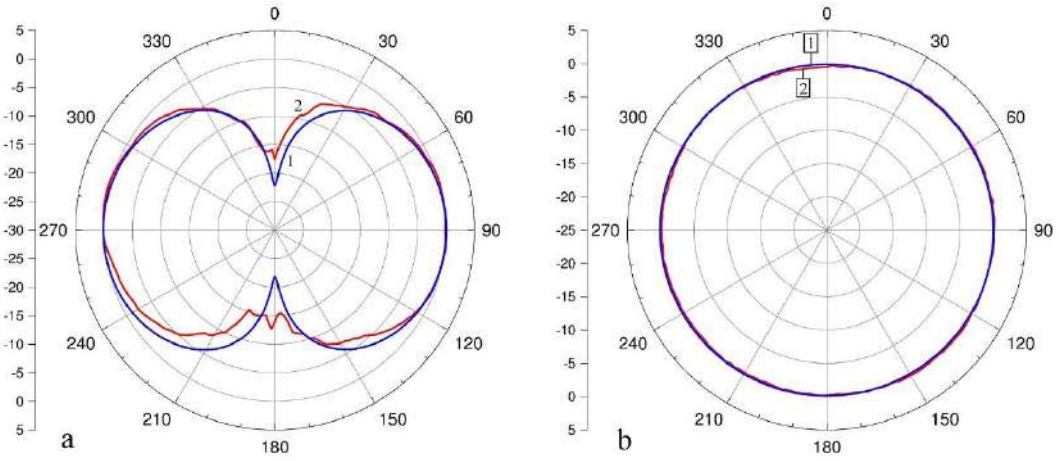


Figure 4. (a) Theoretical [1] vs. measured [2] gains at 915 MHz on the [yz] plane. (b) Theoretical [1] vs. measured [2] gains at 915 MHz on the [xy] plane.

Both measurements are in excellent agreement with the corresponding theoretical simulations and show an antenna radiating omnidirectionally as a dipole perpendicular to the [xy] plane, with a 0 dBi gain. The antenna therefore acts as a dipole, completely linearly polarized with vertical polarization relative to the plane of the antenna. The basic design constraints that have been successfully met are that the antenna has a very small electrical size, yet maintains very high radiation efficiency at the level of 70%, and further that it radiates omnidirectionally on the horizon. The stamped metal design makes it particularly inexpensive for industrial fabrication. These features make this antenna a proper candidate for industrial IoT applications where size, cost, high efficiency and omnidirectional device link between a variety of devices, in particular when spatially distributed on the same planar surface, is desired.

OUTPUT

Publications in International Journals

1. Contopanagos, H. An electrically small 3-d folded grounded loop antenna for omnidirectional connectivity. *Progress in Electromagnetics Research C* **vol 107,** pp. 245-258 (2021). DOI:10.2528/PIERC20111103

MICROFLUIDICS, LAB- AND ORGAN-ON-CHIP

Project Leader: Angeliki Tserepi

Permanent Research Staff: Evangelos Gogolides, Stavros Chatzandroulis

Research Associate: George Kokkoris

Post Docs: K. Tsougeni, K. Ellinas, M. Georgoutsou-Spyridonos, S. Ntouskas

PhD Candidates: I. Kefala, V. Papadopoulos, D. Kefallinou, P. Skaltsounis

Master Students: I. Ntovolou, K. Koutsiara, M. Savranakis, Y. Xesfyngi, D. Valadorou

Research Collaborators: D. Tsoukalas, A. Boudouvis, D.S. Mathioulakis (NTUA), S. Kakabakos, P. Petrou, D. Mastellos (INRASTES, NCSR-D), G.D. Kaprou (Luxembourg Centre for Systems Biomedicine, University of Luxembourg), D. Boumpas, M. Grigoriou (BRFAA), D. Poulikakos, A. Milionis, A. Tripathy (ETH, Zurich), Z. Ekaterinidi (Software Competitive International, S.A.), E. Mastellou (Bioanalysis Kitili, S.A.)

- **Objectives**

Our project, carried out in collaboration with the Plasma Nanotechnology project (INN) and the Immunosensors and Molecular Immunology groups of INRASTES (NCSR-D), comprises activities related to *our core technology* namely *Microfluidics Technology*, aided by *Device simulation* and its application in a large range of fields such as diagnostics for health, the environment, and the agro-food sector. These activities illustrated as the blue and violet circles in Fig. 1 enable a significant number of applications shown as the red and green circles in Fig. 1.

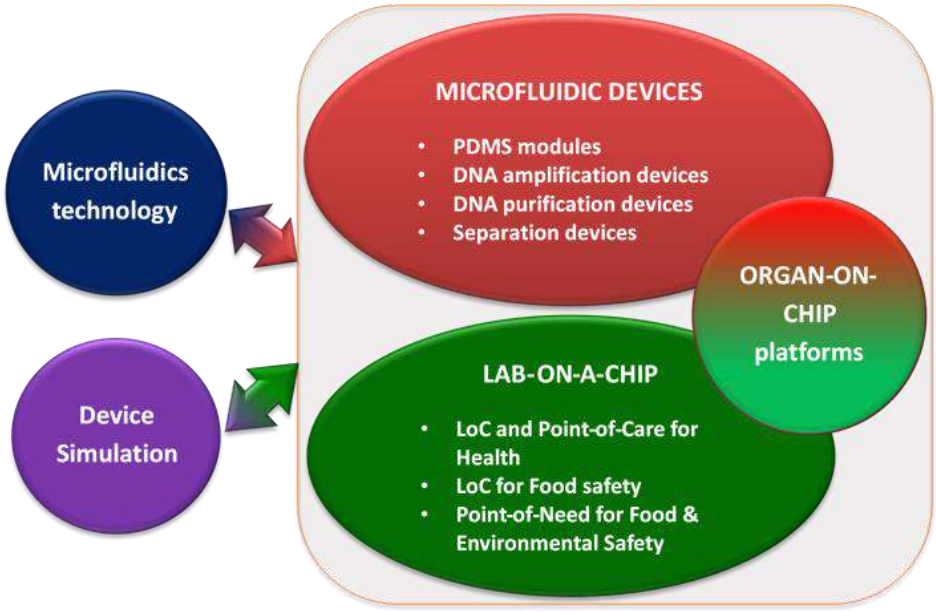


Fig. 1. Research activities of the Microfluidics, Lab- and Organ-on-Chip project

Our project objectives can be summarized as follows:

- Advance microfluidics and lab-on-a-chip technologies (section T).
- Understand and design improved microfluidic devices using modeling and simulation (section M).
- Exploit our microfluidics technology toolbox for enabling a variety of applications (section A).

- **Highlights / main scientific results**

Microfluidics Technology

T1. Surface functionalization of PDMS for enhanced mesenchymal stem cell growth in bone marrow-on-a-chip platforms

(D. Kefallinou, A. Tserepi, and external collaborators)

OoCs are largely constructed using poly(dimethylsiloxane) (PDMS) as their integral biomaterial. Despite its renowned advantages, PDMS is inherently hydrophobic, which compromises cell adhesion and proliferation. Extracellular matrix (ECM) protein immobilization, such as collagen or fibronectin, stands out for cell culture-related applications. Plasma treatment appears as a simple, one-step method to efficiently render the PDMS surface hydrophilic for immobilizing the ECM protein. To date however, it remains unclear in PDMS-based microfluidic devices whether plasma treatment is favorable to a stable and long-term cell-culture. We have thereby employed bone marrow-on-a-chip (BMoC) platforms, which were plasma-treated prior to type I collagen coating during the serial bonding step of their layers, and seeded with mesenchymal stem cells (MSCs). Optical observation proved enhanced MSCs adhesion, proliferation and stromal tissue surface uniformity inside the BMoC platforms, managing to successfully recapitulate the bone marrow stromal niche for 6 days (Figure 2).

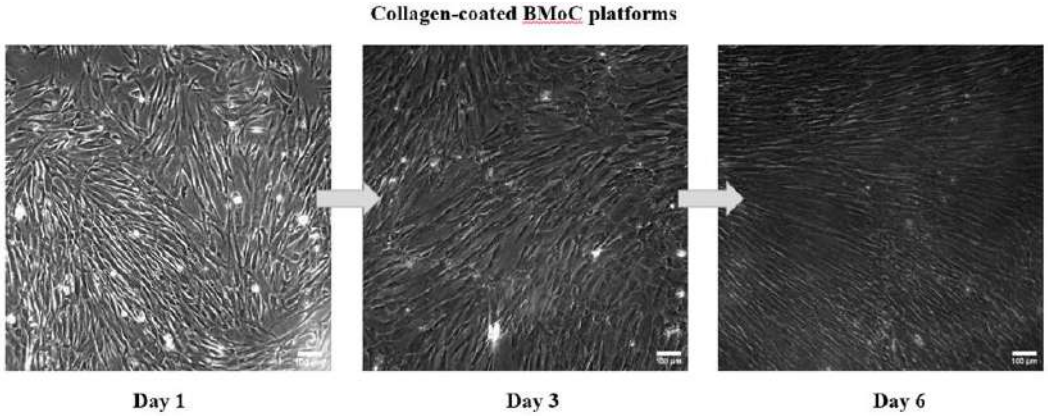
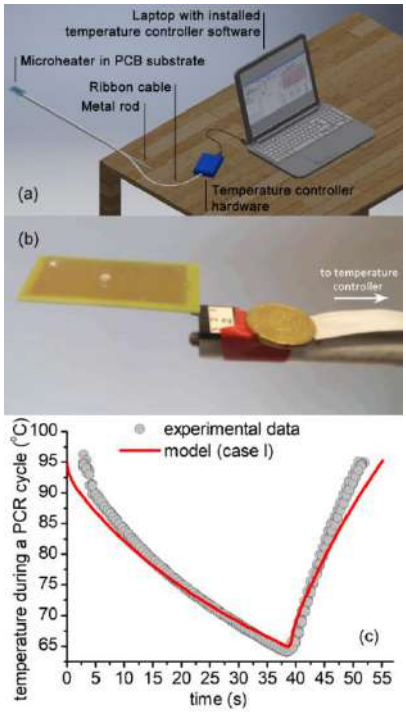


Fig. 2. MSCs seeded in oxygen-treated and collagen-coated BMoC devices for 6 days

Modeling and Simulation of Microfluidic devices



M1. Modeling heat losses in Microfluidic devices

(V. Papadopoulos, I. Kefala, A. Tserepi, G. Kokkoris, and external collaborator)

The investigation of the effect of the heat loss mechanisms and parameters on the heating and cooling rates, and the power and energy requirements through a systematic computational analysis was completed this year. The case study is a static chamber microfluidic device for DNA amplification based on PCR and the means is a detailed 3d computational framework taking into account the air flow around the microfluidic device. A new effective model for the convective heat losses is proposed, where the heat transfer coefficient (h) is a function of the surface temperature in a 2d axisymmetric geometry resembling the real geometry of the microfluidic device. The results of the new model not only compare satisfactorily with those of the detailed 3d framework, but also entail a 10-fold lower computational cost. Measurements of the temperature profile in a thermal cycle are also performed (see Fig. 3) and are in good agreement with the computational results.

Fig. 3. a) Experimental setup. b) Floating microheater in PCB. c) Measured temperature for one cycle of PCR. The simulation results for the most comprehensive model of heat losses are also shown.

M2. Design of a circular flow-through microfluidic device

(P. Skaltsounis, A. Tserepi, G. Kokkoris)

We design a novel circular flow-through microPCR with small footprint and pump-free operation, intended for fabrication on a printed circuit board (PCB).

The design of the microchip comprises two integrated meandering copper microheaters within the PCB substrate and a circular microchannel at a very close distance from the microheater, thus ensuring good heat transfer. The design of the system is based on a computational study, analyzing and optimizing various parameters, such as the geometry of the microdevice and the thermal distribution during cycles. The design of this device, on the basis of simulation and optimization analysis, appears to result in a simple, cost saving, flexible and fast method for PCR-based DNA amplification.

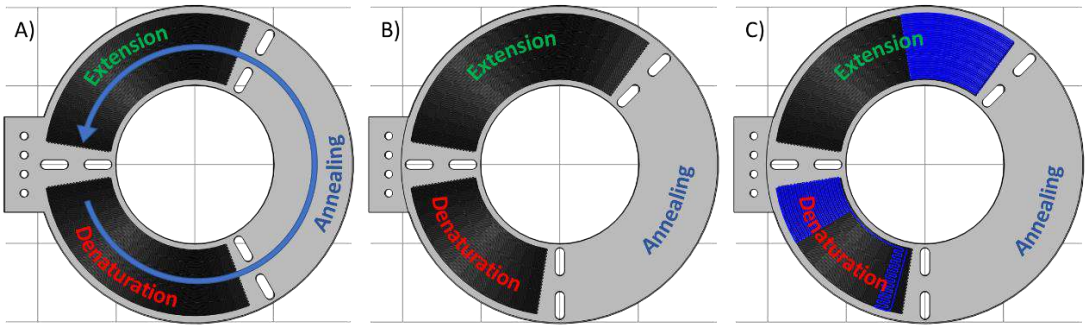
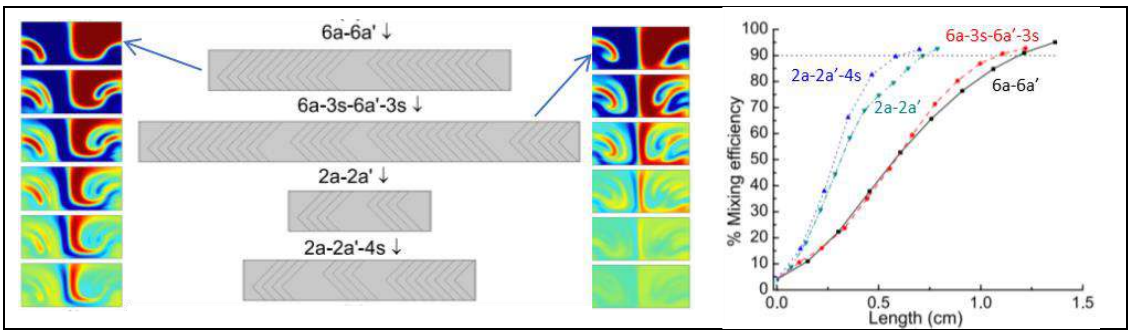


Fig. 4. Three microheater geometries were designed and evaluated through a computational study for optimizing thermal distribution

M3. Computational analysis and design of a micromixer for biomolecules' solutions

(G. Kokkoris and external collaborators)

The problem of mixing of solutions of biomolecules in the famous staggered herringbone micromixer (SHM) is revisited through a computational study with the focus on two overlooked aspects, namely the accuracy of the numerical solution and the thorough analysis of the mixing process. The study is based on the numerical solution of the continuity and Navier-Stokes equations and the mass balance of the solute. The numerical instabilities, induced by the high Peclet number (extremely low diffusion coefficient of biomolecules), are handled with stabilization methods and the accuracy is ensured by a) dense adaptive meshes constructed by an error criterion and b) systematic studies of the mesh independence of the numerical solution. The importance of the accuracy on the calculated mixing efficiency (ME) and the design of the SHM is demonstrated through a comparison with the results for non-adaptive and coarse meshes. The ME versus the length of the SHM is compared with experimental data for the first time, with the mesh independent solution in good agreement with them. The thorough analysis brings to light symmetries and periodicities in the velocity field and explains the inflection point of the ME versus the length of the SHM, observed in experimental and computational studies. Without an optimization algorithm, designs which increase the ME up to 100% are proposed.



(a) (b)

Fig. 5. a) The proposed designs of the unit cell of the SHM and concentration profiles at the outlet of successive unit cells for two of them. b) Mixing efficiency vs. the length of the SHM for the proposed designs.

Applications: Lab on a Chip for Agrofood and Life Sciences

A1. A microchip on PCB for isothermal amplification & bacteria identification in urine

(M. Georgoutsou-Spyridonos, M. Filippidou, S. Ntouskas, S. Chatzandroulis, A. Tserepi, and external collaborators)

Printed Circuit Board (PCB) technology has been recently proposed as a convenient platform for seamlessly integrating electronics and microfluidics in the same substrate, thus facilitating introduction of integrated and low-

cost microfluidics to the market, thanks to the upscaling potential of the PCB industry. Herein, a microfluidic chip, encompassing both a meandering microchannel and microheaters to accommodate recombinase polymerase amplification (RPA) was designed and commercially fabricated for the first time on PCB. The developed microchip was validated for RPA-based amplification of two *E. coli* target genes, compared to a conventional thermocycler. The RPA performance of the PCB-microchip was found to be well-comparable to that of a thermocycler, yet with a remarkably lower power consumption (0.6 W). This microchip is intended for seamless integration with biosensors in the same PCB substrate for the development of a point-of-care (POC) molecular diagnostics platform.

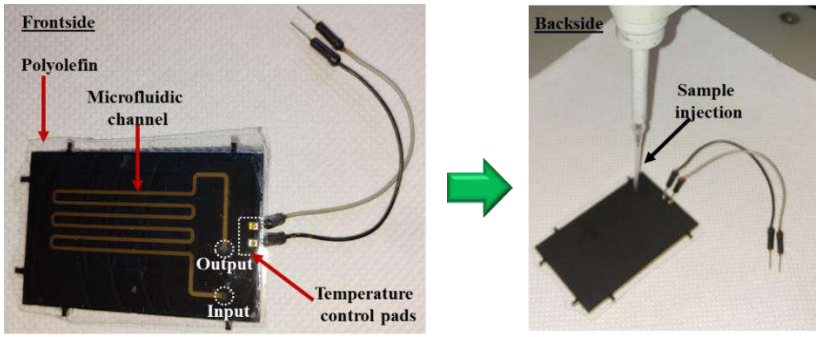


Fig. 6. Front- and back-side of the RPA-on-PCB chip ready to use. The microfluidic channel and the sealing film (polyolefin) are shown (left). Image of the backside of the device during the introduction of RPA solution in the microchannel **(**right).

A2. Rapid and Accurate Detection of Bacteria in Water using microfluidics technology

(K. Tsougeni, K. Ellinas, A. Tserepi, E. Gogolides, and external collaborators)

Very recently, *Legionella* has been identified by the World Health Organization as the highest health burden of all waterborne pathogens in the European Union. However, the low frequency sampling and the long duration of legionella cultures (up to 10 days) do not allow for prevention of legionella outbreaks. Thus, the development of more efficient water diagnostics for pathogens and faster analyses methods is recognized worldwide. Our group, leveraging the expertise acquired in the molecular testing of food-borne bacteria, in an effort led by Nanoplasmas PC, is developing a lab-on-a-chip, based on colorimetry enabling visual inspection, for ultra-rapid and easy *L. pneumophila* detection at the point of need.

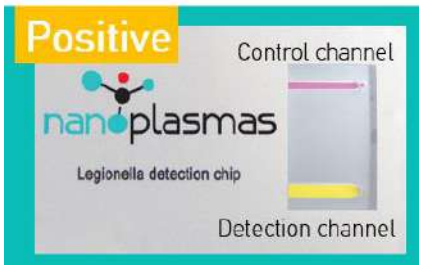


Fig. 7. Lab-on-a-Chip for accurate and fast results in the detection of *L. pneumophila*, addressed to the water analysis market. It achieves results in 70 min from sample collection to decision, instead of 10 days using standard microbiological methods. It is a molecular diagnostic technique, a nucleic acid amplification test (NAAT) with *in-situ* capture, lysis, specific DNA amplification and naked eye detection.

A3. Microfluidic devices incorporating nanostructured ZnO walls for facile on-chip cell lysis

(Y. Xesfyngi, A. Tserepi, and external collaborators)

Zinc oxide (ZnO) as a substrate material has been known for its antimicrobial activity in plenty of research studies. In this work it is being used as microfluidic wall material, studied for its ability to cause cell lysis, a necessary step for various analytical studies in molecular diagnostics. The disruption of cell membrane results in the extraction of intracellular components, such as DNA, RNA, and proteins of interest. We fabricated on ZnO substrates a microfluidic channel for bacteria lysis followed by DNA release (in collaboration with ETH, Zurich). Due to their high surface to volume ratio and chemistry, nanostructured ZnO microfluidic surfaces enhance bacteria killing and DNA release, promising potential applications.

- **Funding**

1. Contract between INN-NCSR Demokritos and Nanoplasmas for Industrial Postdoctoral Programme 01/08/2018 - 30/07/2021, total budget €82.950,00, budget for 2021 €16.129,00 (postdoctoral fellow: K. Tsougeni)
2. "DIAMOND", Research-Create-Innovate I, Contract No. MIS T1ΕΔΚ-03565, 5031222, 18/07/2018 – 17/01/2022, total budget €393.292,60, budget for 2021 €131.100,00

3. IKY PhD Fellowship, "Microfluidic devices for cell-based studies" Contract No. MIS 5000432, 01/05/2018-31/12/2022 (PhD fellow: D. Kefallinou)
4. "MICSYS", RESEARCH-CREATE-INNOVATE II, Contract No. MIS T2ΕΔΚ-02144, Oct. 2020-April 2023, budget for 2021 €16.200

OUTPUT

Publications in International Journals

1. Papadopoulos, V., Kefala, I., Kaprou, G.D., Tserepi, A., Kokkoris, G. **Modeling heat losses in microfluidic devices: the case of static chamber devices for DNA amplification**, *Int. Journal of Heat and Mass Transfer* **184**, pp. 122011 (2021, accepted). DOI: 10.1016/j.ijheatmasstransfer.2021.122011
2. Georgoutsou-Spyridonos, M., Filippidou, M., Kaprou, G.D., Mastellos, D.C., Chatzandroulis, S., Tserepi, A. **Isothermal Recombinase Polymerase Amplification (RPA) of E. coli gDNA in commercially fabricated PCB-based microfluidic platforms**, *Micromachines* **12** (11), pp. 1387 (2021). DOI: 10.3390/mi12111387
3. Hadjigeorgiou, A.G., Boudouvis, A.G., Kokkoris, G. **Thorough computational analysis of the staggered herringbone micromixer reveals transport mechanisms and enables mixing efficiency-based improved design**, Chemical Engineering Journal **414** p. 128775 (2021). DOI: 10.1016/j.cej.2021.128775

International Conferences Presentations (invited, oral, poster)

1. Skotadis E., Aslanidis E., Tserepi A., Gogolides E., Chatzandroulis S., Tsoukalas D., "Nanomaterial based flow-sensing device for microfluidic systems" (*poster*), *47th Micro and Nano Engineering conference*, 20-23 September 2021, Turin, Italy
2. Tserepi A., Tsoukalas D., Patakas K., "Rapid, timely diagnosis & monitoring of infectious diseases by means of an automated Point-of-Care system" (*oral*), *2nd Innovation Forum,* Hellenic-German Chamber of Industry & Commerce, Nov. 24, 2021, Cultural Center "Hellenic World", Athens.

Teaching and Training Activities

D. Mathioulakis, A. Tserepi, G. Kokkoris
"Microfluidic systems", Feb. 2021-June 2021, Postgraduate Program on "Microsystems and Nanodevices"
Athens, The National Technical University of Athens

Master Dissertations completed in 2021

Iliana Ntovolou
Title: Extraction of kinetics for salmonella DNA amplification from quantitative-PCR experiments
Research Supervisor at NCSR: G. Kokkoris
University where the Thesis was presented: National Technical University of Athens

Konstantina Koutsiara
Title: Algorithm for the calculation of equilibrium positions of cells in inertial microfluidic devices for cell separation
Research Supervisor at NCSR: G. Kokkoris
University where the Thesis was presented: National Technical University of Athens

Marios Savranakis
Title: Modeling and simulation of a microfluidic device for the separation of rare cells through cell-wall interactions
Research Supervisor at NCSR: G. Kokkoris
University where the Thesis was presented: National Technical University of Athens

Distinctions

Our respective publication in Micro & Nano Engineering journal has been selected for promotion by Elsevier out of thousands of other articles and an interview story was presented in *Elsevier news* (December 2021) and shared through Elsevier Computer Science social media.

MOLECULAR MATERIALS AS COMPONENTS OF ELECTRONIC DEVICES

Project Leader: N.Glezos

Permanent Research Staff: A. Kyriakis, G. Pilatos, Th. Speliotis

Post Doc Researcher: D. Velessiotis

PhD candidate: V. Lionas

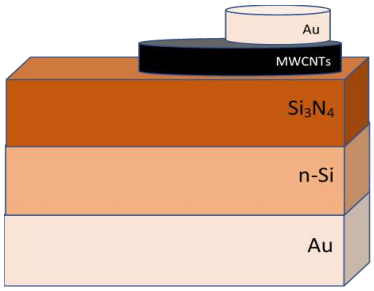
Objectives

- The fabrication of low-cost single pixel electronic detectors based on MWCNTs/semiconductor (Si) heterojunction, achieving the better possible performance when measuring radiation outside the visible spectra; more emphasis being placed towards the UV and IR radiation detection and measurement.

Main Scientific Results

Photo detector based on ordered Multi-Wall Carbon Nanotubes
Kyriakis A., Glezos N., Velessiotis D., Pilatos G., Speliotis Th., Stefanou A

Carbon nanotubes (CNTs) have attracted great interest of applications due to unique mechanical, electronic and optoelectronic properties. The advantages of the multiple wall carbon nanotubes for optoelectronic devices like photodetectors and photodiodes are the large effective photo-collector surface as well as the possibility to tune the band gap and absorbance through the growth parameters. In this work of our group, we demonstrate a hybrid Multi-Wall CNTs/Si_3N_4/n-Si photodetectors (Figure. 1) based on ordered MWCNTs and evaluate the performance in UV and visual spectrum (200nm-800nm).



Structure of the basic photodetector

The principal objective and challenge of this project is to realize novel photodetector based on dense and high length arrays (minimum of 20μm) of MWCNTs deposited directly on a silicon substrate. The nitride layer plays an important role in this device and this is manifested by electrical and optical measurements. The 'blank' device when voltage biased (top electrode positive) presents low conductance. The Chemical Vapor Deposition (CVD) is the main process technique for growth of the ordered MWCNTs layer at the top of the nitride. Two mixtures of 2 and 4g of Camphor with Ferrocene are tested to produce the CNTs. Using the CVD technique, well-ordered, high density MWCNT layers can be achieved, resulting in larger effective absorption surface. In addition, by controlling the proportions of the mixture higher structures can be fabricated. On the other hand, it requires a high thermal budget and the use of a Fe-containing catalyst which is troublesome for Si-based processing. To overcome this the investigation will focus on different process techniques such as liquid processed MWCNTs which can be deposited using drop casting or traditional printing processes.

The overall results suggest that well-ordered MWCNTs present satisfactory performance (EQE 90% @ 275nm@ 7V) for the devices, in the visual and UV part of the spectrum. The responsivity values are at the same level as those of the best performing Schottky or MSM type GaN, UV detectors. The optical responsivity values mean obtained at the UV part of the spectrum indicate that hybrid MWCNT/Si3N4/n-Si systems have a potential for UV photodetector applications. Apart from this technological goal, we investigate how Multi-Wall CNTs/Si_3N_4/n-Si heterojunction works using the well-known conduction mechanisms

During 2021 the effort was concentrated on producing devices with CNT from a liquid solution and comparison to those produced by a vapor deposition process. Devices with nitride layers with variable thickness were also fabricated. The samples which contained CNTs from a liquid solution displayed a better optical performance than those produced by the CVD method.

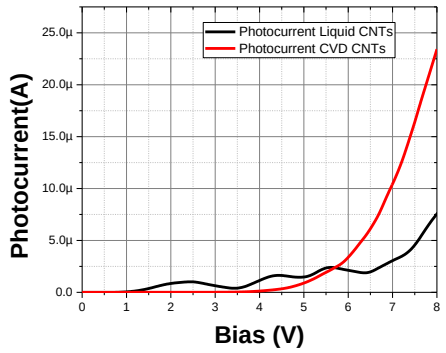


Fig 1: Comparison of the photocurrents produced for the two different types of devices. Electrode types and sizes are the same.

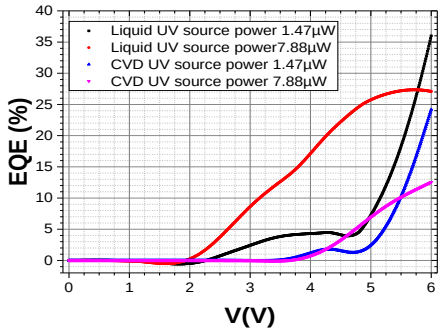


Fig 2 : Comparison of the External Quantum Efficiency for the devices under different voltage bias in reverse mode.

Funding
"Low cost carbon nanotube photodetectors" (Αισθητήρες χαμηλού κόστους με νανοσωλήνες άνθρακα) ,ȘCNTPD, starting date: 1/6/2018, ending date :31/6/2021, 180kEuro, Dimitrios Velessiotis, GSRT http://carbonphotodetectors.eu/

OUTPUT

Teaching and Training Activities

1. N.Glezos, Participation in a post graduate semester course in the subject of "Organic Electronics" (6 lectures) of the Post Graduate Course of NTUA entitled (Nanotechnology and Microsystems) , spring semester 2021

Master Dissertations completed in 2021

1. Charalampos Karakasis, "Development of a drift-diffusion transport model for a Schottky heterojunction", 2020-2021, NTUA

THEORETICAL MODELING OF WAVES IN THE MICRO AND NANO SCALE

Project Leader: N. Papanikolaou

Post Docs: E. Almpanis, G. Zisis, A. Dimitriou, L. Patsiouras

PhD Candidates: E. Panagiotidis

Master Students: J. Paschos

- **Objectives**

The group focuses on the study of wave propagation in complex micro and nano-structured media. We develop methods for solving electrodynamics problems and for the simulation of light scattering on structured surfaces and integrated photonic devices. We use multiple scattering theory which can be adapted to the study of different problems from the electronic structure of materials, to light scattering, or elastic wave propagation, and the interaction between optical, elastic and magnetic waves. Insight from the simulations is used to fabricate and characterize photonic devices, metasurfaces and other diffractive optical elements that can manipulate the light wavefront. Our activity is extended towards the development of optical sensors.

The group mission can be summarized in:

- The development of methods for the description and study of electrodynamics, spin-dynamics and elastodynamics and their interaction. One of our goals is the study of electromagnetic waves propagating through time varying media.
- Simulation and design of surfaces that can manipulate the polarization and wavefront of light.
- Demonstrate the usefulness of nanostructured surfaces in optical sensing, by addressing all the steps in the development, from the design, to the fabrication, and optical characterization to the embedding in a final device including optomechanical design and implications from bio-fuctionalization of the surfaces.

Highlights / main scientific results

- **Multiple scattering methods for electrodynamics**

There has been considerable afford on the development of the Layer Multiple Scattering method. The method was extended to deal with more complex structures that allows the design of metasurfaces. This work is in collaboration with colleagues from the Physics Department of the University of Athens. An interesting direction is the study of electromagnetic waves propagating through time varying media. Towards this end we have started extending our in-house-developed layer multiple scattering method for the solution of Maxwell's equations to structures with time varying refractive indices and geometries.

- **Optomagnonic Interaction**

Controlling the interaction of visible and infrared light with magnetization waves at the nanoscale provides impressive opportunities for developing novel efficient miniaturized devices for magnetic recording and information processing applications. In particular, there is recently growing research interest on bidirectional conversion between microwave and optical photons mediated by macroscopic collective spin excitation modes in (sub)millimeter magnetic dielectric spheres, which opens a promising route for transducing quantum information between superconducting qubits and photons. The basic obstacle towards applications is the inherently week magneto-optic interaction for near-infrared light. Our group has important contribution in the understanding of the optomagnonic interaction and E. Almpanis was the editor of a recently published book entitled "Optomagnonic Structures: Novel Architectures for Simultaneous Control of Light and Spin Waves" which summarizes the work of many groups working in the field.

We have studied magnon-mediated optical transitions in micrometer-sized axially symmetric yttrium iron garnet (YIG) particles, which act as optomagnonic cavities. Such particles exhibit high-quality-factor Mie resonances

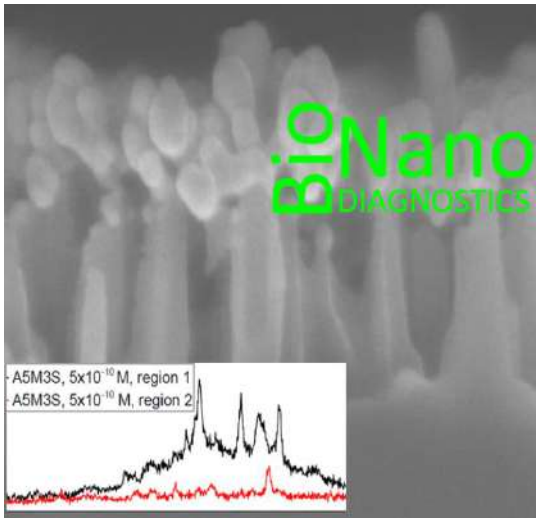
in the infrared part with separation of few gigahertz, which matches the typical frequencies of magnons. This allows for strong optical transitions mediated by spin waves, with photon-magnon coupling strengths of tens of kilohertz.

Biosensors

An accurate thickness and refractive index mapping method using reflectance spectroscopy and imaging techniques (SLICE) was developed. This is a joint venture funded by Stavros Niarchos Foundation, between ThetaMetrisis S.A. company and NCSR "Demokritos". A prototype optical setup was optimized and is currently commercialized by the industrial partner, and provides a surface analytical technique based on reflectance spectroscopy in a broad wavelength range (UV-Vis-NIR) and a variation of optical reflection microscopy.

Moreover, we proposed a new optical sensor concept using stepped-thickness transparent films on highly reflective substrates. The sensor relies on reflectivity of a light from a narrow bandwidth source, like an led, using a camera as a detector. This avoids the use of a spectrophotometer that, increases the cost of spectroscopy-based sensors.

Finally, we are also involved in the development, fabrication, optimization, and characterization of surface enhanced Raman (SERS) and Fluorescence (SEF) substrates. This continues the work of the group of A. Nassiopoulou. We have made progress concerning the repeatability and surface homogeneity of the developed substrates, but also on cost effective Raman, setups to test the sensors.



Nanostructured Ag-decorated Si nanowires as Surface Enhanced Raman scattering substrates. The substrates were fabricated using Metal Enhanced Chemical Etching of Si. Typical Raman Spectra for Rhodamine R6G at a concentration of $5x10^{-10}$ M are shown in the inset.

- **Funding**
- ISN Industrial Fellowship (G. Zisis) 6/2018- 6/2021 (46.000 Euro)
- IKY PhD Fellowship, 2018-050-0502-14583, E. Panagiotidis (22.000 Euro)
- ΕΔΚ ΙΙ, BioNanoDiagnostics T2EDK-03746, (27/8/2020-27/8/2023) Budget INN (254.000 Euro) (coordinator since 1/2021, former coordinator A. Nassiopoulou)
- 16/11/2019-15/11/2021 (E. Almpanis), 019-050-0503-17515, IKY, MIS 5033021 (26400 Euro).

OUTPUT

Publications in International Journals

1. Almpanis, E., Papanikolaou, N., Stefanou, N. Nonspherical optomagnonic resonators for enhanced magnon-mediated optical transitions, *Phys. Rev. B*, **104** (21), art. no. 214429, .(2021) DOI: 10.1103/PhysRevB.104.214429

2. Zacharatos F., Duderstadt M., Almpanis E., Patsiouras L., Kurselis K., Tsoukalas D., Reinhardt C., Papanikolaou N., Chichkov B.N., Zergioti I., Laser printing of Au nanoparticles with sub-micron resolution for the fabrication of monochromatic reflectors on stretchable substrates *Opt. Laser Tech.* **135**, 106660 (2021) DOI: 10.1016/j.optlastec.2020.106660
3. Chaitoglou S., Spachis L., Zisis G. Raptis I., Papanikolaou N., Vavouliotis A., Penedo R., Fernandes N., Dimoulas A., Layer-by-layer assembled graphene coatings on polyurethane films as He permeation barrier, *Prog. Org. Coat.* **150**, 105984 (2021). DOI: 10.1016/j.porgcoat.2020.105984
4. Almpanis, E., Zouros, G.P., Tsakmakidis, K.L. Active THz metasurfaces for compact isolation *JOSA B: Optical Physics*, **38(9)**, pp. C191–C197 (2021) DOI: 10.1364/JOSAB.430160
5. Zouros, G.P., Kolezas, G.D., Almpanis, E., Tsakmakidis, K.L. Three-Dimensional Giant Invisibility to Superscattering Enhancement Induced by Zeeman-Split Modes, *ACS Photonics,* **8(5)**, pp. 1407–1412 (2021) DOI: 10.1021/acsphotonics.1c00036

Books/Chapters in Books

1. Almpanis, E., Zouros, G.P., Papanikolaou, N., Spherical optomagnonic resonators (Book chapter) Optomagnonic Structures: Novel Architectures For Simultaneous Control Of Light And Spin Waves, 2021, pp. 243–298, (E. Almpanis Ed), World Sci.DOI: 10.1142/9789811220050_0006

International Conferences Presentations (invited, oral, poster)

1. Zouros, G.P., Almpanis, E., Katsinos, K Garnet Wires as Optomagnonic Cavities
.2021 IEEE International Conference on Microwaves, Antennas, Communications and Electronic Systems, COMCAS 2021, 2021, pp. 504–507, (oral).

2. Almpanis E., G. P. Zouros, P.-A. Pantazopoulos, K. L. Tsakmakidis, N. Papanikolaou, and N. Stefanou, Micron-sized spherical optomagnonic resonators, *Physics of Magnetism* 2021, June 28 - July 2 2021, Poznań, Poland., (oral).

Teaching and Training Activities

N. Papanikolaou
Lectures on Micro/Nanotechnology – Development of semiconductor devices/in the course Applied Optoelectronics, April-May 2021, 4 lectures, University of Patras.

N. Papanikolaou
Lectures on Semiconductor and Nanodevice Optoelectronics in the course Applied Optoelectronics, Oct-Dec 2021, 4 lectures, University of Patras

OPTICAL BIOSENSORS

Project Leader: Konstantinos Misiakos

Permanent Research Staff: Eleni Makarona

Other Staff: Alexandros Salapatas (Research Associate)

PhD Candidates: George Papageorgiou, Christina Sperantza

Master Students: Andreas Baltas, Aikaterini Ninou, Petros Katsoufis

BSc Student: Mirella Mari

Internships: Georgia Margariti, Nikolaos Stavridis, Aikaterini Kontoliou, Konstantinos Grigorakis

Research Collaborators: Dr Sotirios Kakabakos and Dr Panagiota Petrou (Immunochemistry/Immunosensors Laboratory, INRASTES), Dr Ioannis Raptis (Polymer based Sensor and Systems, Institute of Nanoscience and Nanotechnology), Dr Vasileios Psycharis (Crystallogrpahy and Coordination Chemistry of Materials, Institute of Nanoscience and Nanotechnology), Dr Andreas Karydas (XRF Laboratory, Institute of Nuclear and Particle Physics), Prof. Margarita Chatzichristidi (Chemistry Department, National and Kapodistrian University of Athens), Prof. Anastasia Pournou (Department of Conservation of Antiquities and Works of Art, University of West Attica), Prof. Constantinos Angelis (Department of Informatics & Telecommunications, University of Ioannina), Dr Maria Androulidaki (IESL, FORTH)

- **Objectives:** Development of Point-of-Need/Point-of-Care Bioanalytical Devices based on Si-based photonic sensors / Optoelectronic Devices / Multifunctional Nanostructures of Metal Oxides

- **Activities and Main Results**

I. Optical Biosensor and Immersible Photonic Chips

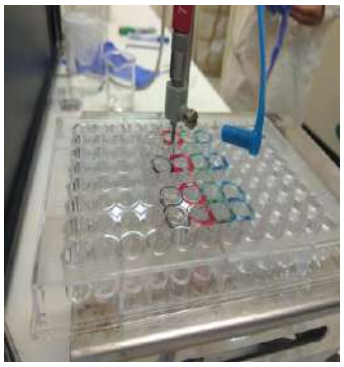


Fig.1. Photograph of the immersible photonic chips, during a biodetection experiment. As can be seen, the chips can be directly dipped into the sample wells

The Optical Biosensors Group has put a strong focus during 2020 on the development of a new concept of fully immersible silicon photonic chips. This new concept allows one to use Silicon chips containing a Photonic Integrate Circuit (PIC) as immersible probes for the label-free detection of substances simplifying the fabrication flow, facilitating the measurement process and having the ability to transform the measuring system to a portable device for Point-of-Need/Point-of-Care applications (Fig. 1).

By receiving a private funding from Athroa Innovations under a Joint Development/Sub-licensing agreement in 2020, the group continued working on the design optimization (photonic engineering) of the Integrated Photonic Circuit of the chip, the subsequent fabrication of the chips and the optimization of the reader in order for the latter to become cost-efficient, compact and autonomous. The reader became almost palm-sized and is fully powered through a USB port connected to a laptop (Fig. 2).

Fig. 2. Photograph of the portable reader with respect to the laptop that powers it up

The final system (chips and reader) was employed for the detection of SARS-CoV-2 antibodies in human sera. The chip functionalization protocol, the assay development and all validation experiments were carried out with the collaboration of the Immunochemistry/Immunosensors Labboratory, INRASTES, NCSR Demokritos (Dr S. Kakabakos and Dr P. Petrou). The results were not published during 2021 because patents were filed within the US and European Patent Offices and the applications were pending for approval. The US Patent was granted in September 2021 (US11119040B2·2021-09-14).

Concurrently, the OptoBio group started employing the bioanalytical system of the immersible photonic chips for the detection of pathogens and adulteration in raw milk under the FOODSENS project (https://www.foodsens.gr/) (nationally funded within the RESEARCH – CREATE – INNOVATE framework project code:T2ΕΔΚ-01934). The ultimate target is the creation of two versions of chips: the first format will be used for the simultaneous detection of aflatoxin M1 (AFM1) and bovine casein (adulteration) in goat milk, while the second format will be used for the simultaneous detection of two pathogens, *B. cereus and L. monocytogenes* after only 6hrs of culture of dairy-based samples. Bacteria and AFM1 are pertinent to all types of milk. Their detection above the acceptable limits automatically results in product rejection. Fighting fraud mainly concerns consumers with allergic predisposition to cow's milk and PDO products made by sheep's/goat's milk. With regard to AFM1 and adulteration, it is desirable to carry out the detection at the collection sites in order to avoid the receipt of contaminated or adulterated milk or the mixing of good-quality lots with below-standard or unsafe milk. The Optical Biosensors group apart from the development of the photonic chips was engaged in the signal analysis software, the design of the reader and the user interface.

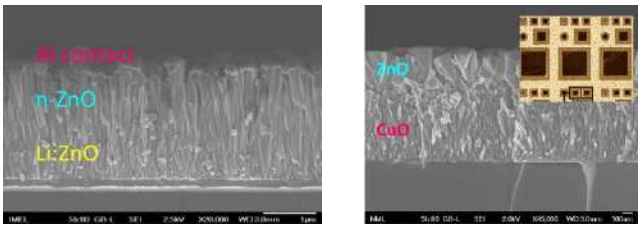
A third venue of the immersible photonic chips was their application in the determination of the nutrient content of hydroponically-cultured microgreens. A new project, named GOHydro (https://www.gohydro.org/) began in 2021 under the ICT-AGRI-FOOD framework (Grant Agreement no: 862665). Within this framework, GOhydro aims at developing a cost-efficient smart-sensing ICT platform capable of monitoring the crops' health and nutrient content of hydroponically cultivated microgreens in order to optimize the cultivation process and allow the harvest of the best possible products in any hydroponic installation. GOhydro aspires to culminate in the production of a radical platform that will be a shifting paradigm of how AI-driven technological innovation can become an affordable, accessible-by-all and user-friendly tool applicable to all forms of urban farming.

Finally, thanks to the funding from INNOVATION-EL (https://innovation-el.net/), the group developed specific fabrication protocols for Photonic Integrated Circuits that may be used as an offered service through the infrastructure.

II. Optoelectronic Devices and Multifunctional Nanostructures.

This activity of the group is separated into four parallel routes: (a) the development of optoelectronic devices (LEDs and photodiodes) based on ZnO and CuO nanostructures produced by cost-efficient chemical synthesis on Si substrates, (b) the development of micro/nanofabrication processes compatible with the chemical synthesis of Metal Oxide Nanostructures (ZnO, CuO and NiO), (c) the synthesis and exploitation of Metal Oxide Nanoparticles towards the development of novel polymer nanocomposite resists, and (d) the application of ZnO nanostructures as a cost-efficient, flexible and easy method of consolidating wooden artifacts affected by brown rot . The main incentive behind this work is the fact that these bottom-up nanofabrication chemical techniques have significant advantages over top-down approaches, such as facile implementation, low-cost and design flexibility that allows the development of a plethora of 3d nanostructures and nanoarchitectures.

One PhD theses (G. Papageorgiou, Physics Department, University of Patras and one MSc thesis (A. Baltas, School of Applied Mathematics and Physical Sciences, National Technical University of Athens) were in progress during 2021. The PhD thesis studies Li-doped ZnO/ZnO homojunctions as the functional element of Light Emitting Diodes, while the MSc thesis concentrated on deriving suitable process flows for the development of CuO/ZnO heterojunctions for optoelectronic devices (Fig. 3). Both thesis exploit chemical routes for the synthesis of the metal oxide nanostructures and their integration on Si substrates.

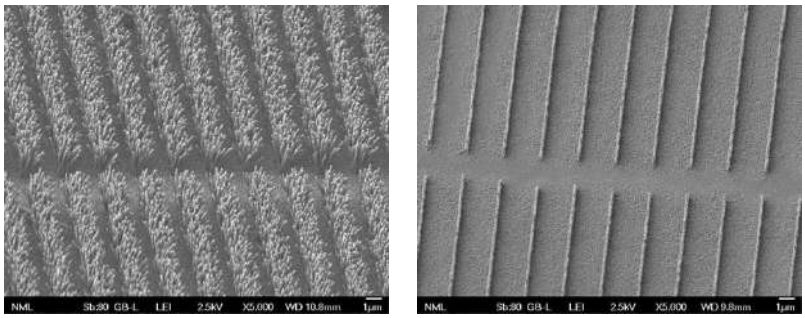


(a) **(b)**

Fig. 3. SEM images (cross-section) of (a) a Li-doped ZnO/ZnO homojunction made out of ZnO nanorods (the Al contact on top is also shown), and (b) a CuO/ZNO heterojunction (inset: optical microscope image of the device prior to the metallization step).

On the second front, the group explored the compatibility of the chemical synthesis of metal oxide nanostructures with e-beam and optical lithography. One MSc thesis (A. Ninou, Chemistry Department, National and Kapodistrian University of Athens) and one internship (Konstantinos Grigorakis, Department of Chemical Engineering, NTUA) were compelted on the subject in 2021. The thesis – supported by the intern- studied NiO nanostructure hydrothermal growth methods onto Si substrates and of their compatibility with respect to optical lithography. In parallel, the work on the hydrothermal growth of CuO and NiO nanostructures onto Si-based substrates led to a new collaboration with Dr V. Constantoudis (Plasma Group, INN). This collaboration started exploring a new idea with the intent to characterize the morphology of the aforementioned nanostructures by means of the fundamental spatial symmetry metrics and the deviation from the fully symmetrical counterparts. The focus is on the translational and scaling symmetry, which would be investigated through the mathematical tools of Fourier and (multi)fractal analysis, respectively.

Additionally, the chemical synthetic route for ZnO nanorod growth on Si and Si/SiO_2 substrates were explored with respect to e-beam lithography. This comprehensive study resulted in the combination of purely chemical, bottom-up solution-based synthesis with advanced e-beam lithography and the controllable production of hierarchical ZnO-nanostructure periodic arrays on Si substrates (Fig. 4). These structures were examined in collaboration with Dr A.G. Karydas (INP, NCSR "Demokritos") with the X-ray Fluorescence Line of the ELETTRA Synchrotron in Trieste (https://www.elettra.eu/) in July 2021 after receiving funding and beam time through the facility (Proposal No: 20205353). The concept behind this study was to develop new characterization approaches that can unravel in a non-destructive, nor preparative and insightful manner the structural details and fabrication process tolerances of more complex material architectures. This was the first time that azimuthal variable GI XRF/XRR was employed to characterize complex patterns of hierarchical nanoarchitectures , which contain within sub-micron patterns nanostructures of stochastic nature. The central goal is to fuse information of elemental, structural and morphological analyses and to determine the extent of its suitability for in depth nanometrological characterizations of three-dimensional nanoarchitectures



(a) **(b)**

Fig. 4. SEM images of two samples examined at the XRF line of the Elettra Synchrotron. The samples consist of arrays of sub-micron lines of various widths (but constant pitch of 2μm) containing ZnO nanorods hydrothermally-grown at different conditions (a) 400 nm-wide lines with 2 μm-long ZnO nanorods and (b) 100 nm-wide lines with 500nm-long ZnO nanorods.

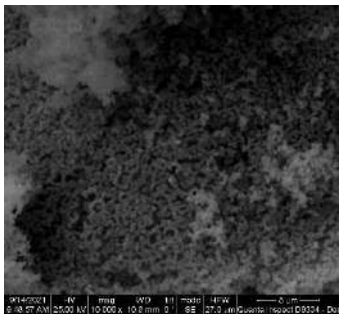


Fig. 5. NiO sub-micron nanospheres produced with microwave-assisted hydrothermal synthesis

On the third front, two interns (Nikolaos Stavridis from the Chemistry Department, NKUA and Aikaterini Kontoliou from the Department of Materials Science, University of Patras) worked on finding appropriate methods for the production of NiO nanofillers through low-cost hydrothermal or microwave-assisted solvothermal techniques (Fig. 5). The goal was to develop cost-efficient and rapid methods of NiO nanoparticles. An MSc student (Petros Katsoufis, Department of Chemistry, NKUA) will utilize these methods to produce NiO nanofillers for PMMA-based resists for e-beam lithography.

Finally, on the final front of metal oxide nanostructured materials, a PhD thesis was in progress in 2021 (Christina Sperantza, the Department of Preservation of Antiquities and Works of Art of the University of West Attica) with the assistance of an intern (Georgia Margariti, Department of Materials Science, University of Patras). The goal of this thesis is the development of ZnO nanostructures in order to consolidate wooden artifacts of cultural heritage degraded by brown rot.

The work throughout 2021 concentrated on a feasibility study of whether microwave-assisted hydrothermal growth methods can be used to grow networks of ZnO nanostructures on cellulose paper samples (key ingredient of wood) wood shavings and pine wood veneer samples. The method consists of two stages: the formation of a suitable seeding layer on the wooden substrates, and the growth of ZnO. The first stage deals with the formation of a ZnO film on the surface of the substrate through the use of a sol-gel and the second stage, the subsequent development of ZnO nanostructures through the microwave-assisted hydrothermal method. A series of different conditions (such as temperature, time, concentration of reagents, etc.) where their variation leads to morphological differences in the size and geometries of the resulting nanoparticles were examined. The experiments were successful and specific recipes for the ration wood samples with ZnO nanostructures were developed (Fig. 5).

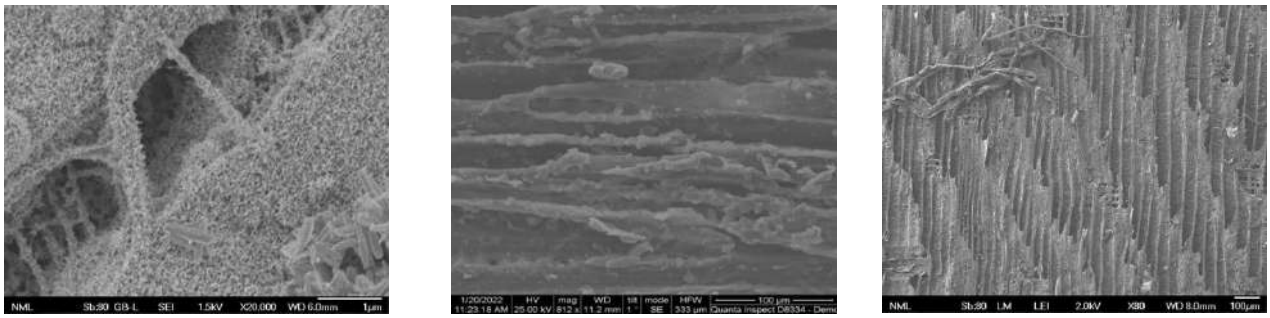


Fig. 5. SEM images of (a) cellulose paper, (b) pine wood shavings and (c) veneer decorated with ZnO nanoparticles through a microwave-assisted hydrothermal growth.

- **Funding:**

1. FOODSENS “Rapid Detection of Pathogens and Adulteration in Raw Milk via immersible photonic sensors”, ERDF of the EU and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code:Τ2ΕΔΚ-01934; duration: 29/10/2020-28/102023)
2. Athroa Innovations: under Joint Development and Sub-licensing Agreement for the development of the Photostick Technology (IP of Optical Biosensors Group)
3. INNOVATION-EL (MIS 5002772), implemented under the “Action for the Strategic Development on the Research and Technological Sector”, funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund)
4. KRIPIS II (MIS 5002567) implemented under the “Action for the Strategic Development on the Research and Technological Sector”, funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund)
5. A Preliminary Study of Grazing Angle X ray Fluorescence (GI XRF) and X ray Reflectometry (XRR) as Enabling Characterization Tools of Patterned Hierarchical Nanoarchitectures, Elettra Sincrotrone Trieste (Proposal 20205353)

OUTPUT

Publications in International Journals

1. Angelopoulou, M., Petrou, P. S., Raptis, I., Misiakos, K., Livaniou, E., Makarona, E., Kakabakos, S. Rapid detection of mozzarella and feta cheese adulteration with cow milk through a silicon photonic Immunosensor, *Analyst* **146** (2), pp. 529-537 (2021). DOI: 10.1039/D0AN01706J
2. Geka, G., Papageorgiou, G., Chatzichristidi, M., Karydas, A.G., Psycharis, V., Makarona, E. CuO/PMMA Polymer Nanocomposites as Novel Resist Materials for E-Beam Lithography, Nanomaterials, **11**(3), 762 (2021). DOI: 10.3390/nano11030762

International Conferences Presentations (invited, oral, poster)

1. Geka, G., Papageorgiou, G., Chatzichristidi, M., Karydas, A.G., Psycharis, V., Makarona. E. CuO/PMMA polymer nanocomposites as resist materials for e-beam lithography, *Athens Conference on Advances in Chemistry (ACAC) 2020*, 10-14 March, online (due to the COVID-19 pandemic); **Oral Presentation**
2. Dimou, A., Ninou, A., Chatzichristidi, M., Constantoudis, V., Makarona, E. Wet chemical synthesis of CuO and NiO nanoarchitectures and nanometrological analysis, *Athens Conference on Advances in Chemistry (ACAC) 2020*, 10-14 March, online (due to the pandemic); **Poster Presentation**
3. Papageorgiou, G.P., Psycharis, V., Androulidaki, M., Karabinaki, O., Christofilos, D., Makarona, E. Chemical Synthesis of p-type Zinc Oxide Nanostructures, *Athens Conference on Advances in Chemistry (ACAC) 2020*, 10-14 March, online (due to the pandemic); **Oral Presentation**
4. Makarona, E. "Monolithically Integrated Biosensors", *EUROPT(R)ODE XV*, November 28-December 1, 2021, Warsaw, Poland; **Invited Presentation**
5. Makarona, E. and Chatzichristidi, M. Metal Oxide/Polymer Nanocomposites and Lithographic Patterning, *13th Hellenic Polymer Society International Conference*, December 12-16, 2021 (online due to the COVID-19 pandemic)

Master Dissertations completed in 2021

Aikaterini Ninou
Compatibility study of the chemical synthesis of NiO nanostructures and polymeric lithographic materials
Eleni Makarona
Department of Chemistry, National and Kapodistrian University of Athens

Undergraduate Theses and Internships completed in 2021

1. Mirella Mari (BSc Thesis)
   Lithographic Materials with Metal Oxides
2. Eleni Makarona
   Department of Chemistry, National and Kapodistrian University of Athens
3. Nikolaos Stavridis (Internship)
   Chemical Synthesis of NiO Nanoparticles
4. Eleni Makarona
   Department of Chemistry, National and Kapodistrian University of Athens
5. Aiakterini Kontoliou (Internship)
   Chemical Synthesis of NiO nanofillers for nanocomposite lithographic resists
6. Eleni Makarona
   Department of Materials Science, University of Patras
7. Georgia Margariti (Internship)
   Chemical Synthesis of ZnO Nanoatructures on Cellulose Subsatrtes
8. Eleni Makarona
   Department of Materials Science, University of Patras
9. Konstantinos Grigorakis (Internship)
   Hydrothermal Growth of NiO Nanoarchitectures on Si Substrates
10. Eleni Makarona
    Department of Chemical Engineering, National Technical University of Athens

Patents - Technology transfer

US Patent Granted: Photonic chips with one sided optical ports self aligned to bifurcated fibers for the label free detection of biomolecular reactions through the use of integrated interferometers and resonators
US11119040B2·2021-09-14

PLASMA NANOTECHNOLOGY AND APPLICATIONS, COMPUTATIONAL NANOMETROLOGY, PROCESS ANALYSIS & SIMULATION

Project Leader: E. Gogolides
Permanent Research Staff: V. Constantoudis, A. Tserepi
Other Staff: G. Kokkoris (scientific), A. Zeniou (technical), M. Kalpouzou (administrative)
Post Docs: G. Boulousis, K. Tsougeni, K. Ellinas, A. Smyrnakis, A. Zeniou, G. Memos, E. Almpanis
PhD Candidates: D. Passaras, G. Papavieros, S. Mouchtouris, P. Sarkiris, E. Stai, D. Nioras, D. Ioannou, A. Kondi
Master Students: S. Korsak, A. Kondi, E.-M. Papia, M. Kaparelou, I. Zygouros, D. Papadopoulou, G. Tasios
Collaborators from other Projects: E. Makarona, C. Tsamis, P. Argitis, N. Kehagias
Research Collaborators: G. Lorusso (IMEC), Alessandro Vaglio Pret (KLA-Tencor), A. Papathanasiou, P. Taoukis, G. Boudouvis (NTUA), N. Vouroutzis, J. Kioseoglou (AUTH), E. Amanatides, P. Svarnas, D. Mataras (Univ. of Patras), S. Kakabakos, P. Petrou (INRASTES, NCSR-D), D. Kletsas, K. Stamatakis (IBA, NCSR-D), A. Speliotis, A. Sapalidis (INN, NCSR-D), F. Diakonos, K. Poulios, M. Chatzichristidi, A. Papathanasiou, A. Moustakas (UOA), N. Puač, Z. Petrović (IOP-Belgrade), G.P. Patsis (UOWA), G. Katsaros (HAO-DEMETER), H. Papageorgiou (ILSP, R.C. Athena), D. Papageorgiou (MIT-USA), E. Lidorikis (UOI), D. Poulikakos (ETH, Switzerland), H.-J. Butt, M. Kappl, Y. Hou (MPIP-Mainz, Germany), M.-K. Tiwari (UCL-UK), I. S. Bayer (IIT-Italy), D. Papanastasiou (Fasmatech SA), C. Vahlas (CNRS), G. Giannakopoulos (IIT, NCSR-D), K.Mavroidis, C. Pandis (BIC Violex S.A), K. Kontosis (Software Developer), B. Williams (MOXTEK), A. Mavrogonatos (HAF), D. Kontziampasis (Univ. Leeds), A. Stellas (Nanometrisis), P. Dimitrakellis (University of Delaware, USA)

- **Objectives**

The plasma Nanotechnology and Applications project comprises activities related to *our core technology* namely *Plasma Technology*, coupled with activities in *metrology* of the micro and nanostructures produced, as well as by *design and simulation* of processes. These activities illustrated as the blue and red columns in Fig. 1 enable a significant number of applications shown as the green boxes in Fig.1. Our project objectives can therefore be summarized as follows:

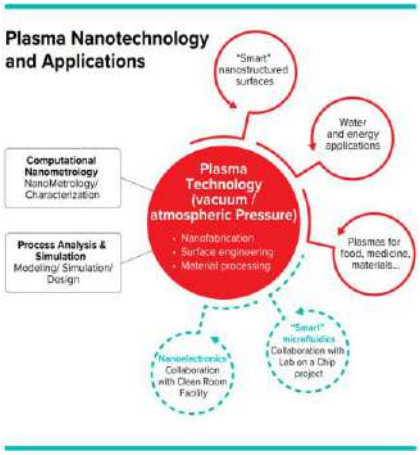


Fig.1 Schematic of project 5.11 *Plasma Nanotechnology and applications, computational nanometrology, process analysis & simulation*

- Advance **plasma nanotechnology** and nanofabrication
- Develop computational **nanometrology** for nanostructure characterization
- Understand and design improved processes using **modeling and simulation**
- Exploit our plasma technology toolbox for **enabling a variety of applications.** Applications target: (1) Surface Engineering (**"smart surfaces"**, (2) **Water Harvesting**, (3) **Plasmas for food, Agriculture medicine etc.**

For all these objectives, we work in coordination with the clean room facility, and in collaboration with several other projects within INN, institutes in NCSRD and partners in Greece and abroad.

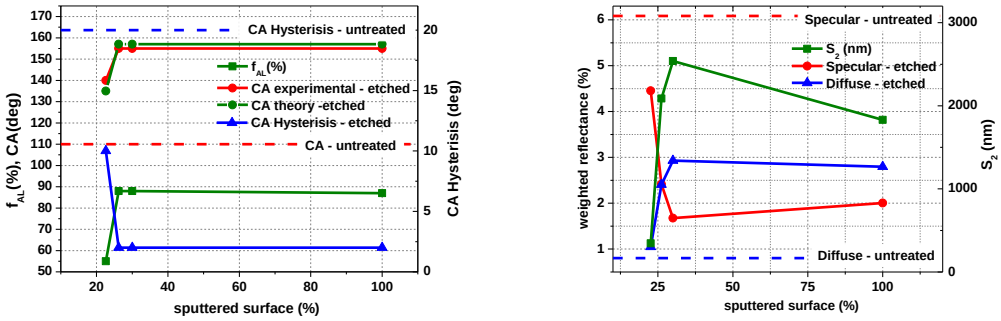
- **Highlights / main scientific results**

Plasma Nanotechnology (PT)

PT1. Controlling surface topography and functionality at will.

(A. Zeniou, G. Papavieros, A. Smyrnakis, V. Constantoudis, E. Gogolides)

Controlling micro-nano texturing at will with plasma processing (a patented process) allows control of the surface properties. The process involves anisotropic etching and co-sputtering of electrode material. This is achieved by changing the sputtered electrode surface area, thus changing the sputtered material inhibitor flux arriving on the surface being etched. During 2021 we focused on optical and wetting property control of polymeric surfaces as can be seen in Fig.2 below.



(a) (b)

Fig.2 Plasma micro-nanotexturing through the control of the inhibitors is used to create multifunctional PMMA plates. Here, wetting, and optical property control are demonstrated versus the percentage of sputtered surface. After oxygen plasma texturing, surfaces were coated with a 20nm thick plasma deposited fluorocarbon film (-CxFy-), which renders them hydrophobic to superhydrophobic, depending on their topography. Surface nanometrology parameters calculated from SEM image analysis are also plotted to show the correlation of specific functionality with specific surface metric parameter. a) Contact angle (left axis) and contact angle hysteresis (right axis) versus percentage of sputtered area, showing the transition to superhydrophobicity. The SEM image calculated air fraction fAL is also plotted (left axis), and is seen to closely follow the contact angle and hysteresis behavior. b) Weighted specular and diffuse reflectance of PMMA plates versus the percentage of sputtered electrode surface.

Computational Nanometrology (CM)

Mathematical and computational methods including Machine Learning techniques have been developed to model, enhance and characterize microscopy and scatterometry measurements of patterned and stochastic nanostructured surfaces used in the applications of plasma and other nanopatterning techniques. Also, we have elaborated a symmetry-based method for the characterization of surface complexity and disorder. Finally, this year we started an effort for the mathematical characterization of fibrous networks using stochastic geometry concepts and methods with applications in membrane metrology and nanowire-based neuromorphic computing.

CM1. Nanometrology of patterned structures

(V. Constantoudis and external collaborators from Nanometrisis (A. Stellas) and INN (E. Almpanis, N. Papanikolaou))

We trained Deep Learning (DL) models with data coming from electromagnetic simulations to a) predict the reflectivity spectrum from specific patterns and b) address the inverse problem calculating the geometrical dimensions of nanopatterns from the measurement of the reflection spectrum. It has been found that such models showed promising results performing fast predictions with reduced computational cost.

CM2. Nanometrology of open (freeform) surfaces

(E. Stai, A. Kondi, E.-M. Papia, G. Papavieros, V. Constantoudis and external collaborators from NKUA, ETH, Univ. Leeds)

a) Computational scale-enhancement of SPM (SEM/AFM) images of stochastic surfaces

A computational method has been devised to hybridize Scanning Probe Microscope (SPM) measurements of freeform stochastic surfaces obtained with different magnifications in order to output a synthesized scale-enhanced image with the highest resolution and measurement range of the input hybridized images. The method is based on the stitching of the Fourier spectra of measurements with different magnifications (Fourier Spectra Stitching-FSS-method) and has been validated in rough isotropic synthesized surfaces. Also, it has been applied in real experimental images with an example shown in Fig.3.

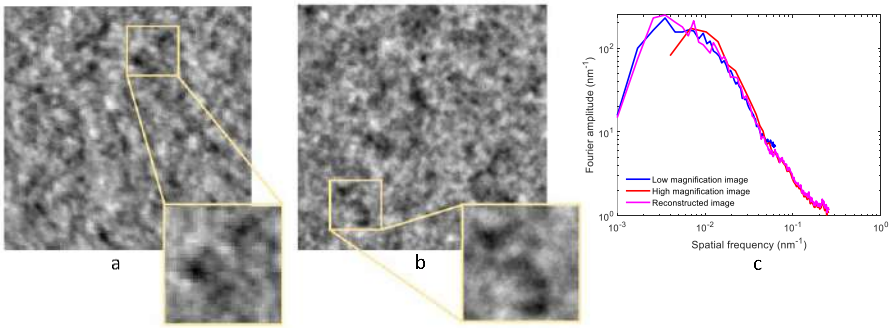


Fig.3 (a) Low magnification image of a surface of a fluorocarbon plasma-deposited film, (b) Reconstructed scale-enhanced image derived by FSS method, (c) 1D Fourier spectrum of the high and the low magnification images (red and blue curves accordingly) being compared with that of the reconstructed image (pink). Insets in two images of a) and b) show magnifications demonstrating the resolution enhancement (smaller pixel size) achieved by FSS method.

b) Theory and characterization of complex and hierarchical nanostructured surfaces

We developed further the theoretical framework for the definition and classification of hierarchical stochastic surfaces as well as the modelling algorithms for their simulation with emphasis in the cases where interaction between levels is present.

Also, we elaborated a chaos-based method for the quantification of the spatial complexity of hierarchical stochastic surfaces. The key idea is to use chaos as a dynamical microscope unfolding the surface complexity at different hierarchical scales. In particular, we consider the surface or its image as the initial condition of a chaotic discrete dynamical system and utilize the basic ingredients of chaos (stretching and folding) to quantify the complexity of S-type which maximizes between homogeneity/order and randomness. Fig.4 shows the results of the method for a spectrum of surfaces spanning from full order (left) to full randomness (right). The measured complexity is maximized in between these limits justifying the performance of chaos-based method.

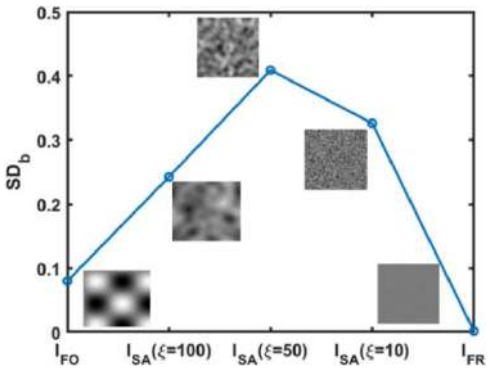


Fig.4 The diagram shows the value of SD_b (y-axis) quantifying chaos-based complexity for the surfaces shown as insets going from order (I_{FO}) to noise (I_{FR}), with I_{FO} being the 2D sinusoidal surface and I_{SA} being the surfaces with correlation lengths ξ= 100, 50 and 5 pixels and roughness exponent α= 1 respectively. I_{FR} stands for the fully noisy surface.

c) A symmetry-based approach to the characterization of surface disorder and complexity

We elaborate a symmetry-based approach for the quantitative characterization of the morphology of nanostructured surfaces. The key idea is to characterize the morphology of nanostructures by means of the fundamental spatial symmetry metrics and the deviations from the fully symmetrical counterparts. The focus of the proposed methodology is on the translational and scaling symmetry, which are investigated through the mathematical tools of Fourier and (multi)fractal analysis, respectively. The calculated metrics characterizing these symmetries are the period and the fractal dimension of surfaces while the deviations are quantified by the disorder parameter ω_d related to the FWHM of Fourier peak and by the asymmetry of the multifractal spectrum for the translational and scaling symmetry respectively. As an initial study case and in order to demonstrate its suitability, the symmetry-based methodology has been applied to nickel oxide (NiO) and copper oxide (CuO) nanostructures hydrothermally-grown on silicon substrates (see Fig.5).

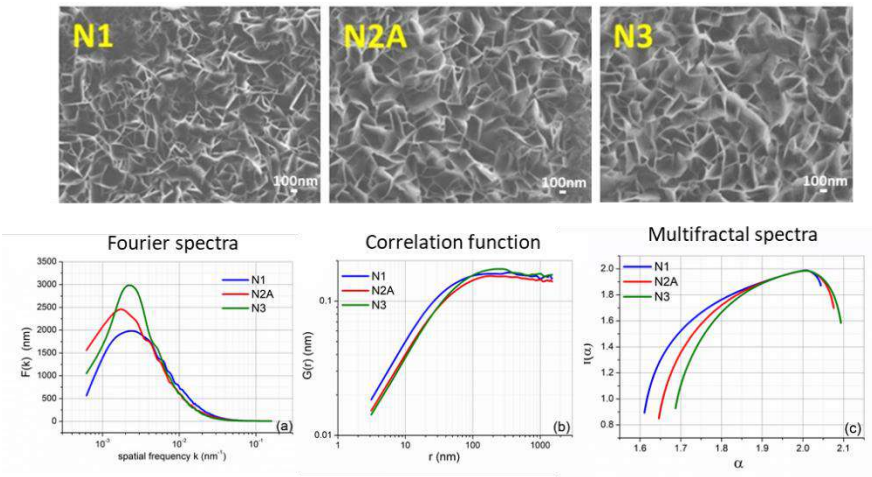


Fig.5 First row: SEM images of NiO nanostructures hydrothermally-grown on silicon substrates employing different sol-gels for the formation of the seeding layer. Second row: Fourier spectra (a), Height-Height Correlation Functions (b) and multifractal spectra (c) of all surfaces indicating the subtle differences in their deviation from full symmetries (translational and scaling).

Process Analysis & Simulation (PS)

PS1. Modeling & simulation of atmospheric pressure plasma reactors
(S. Mouchtouris, D. Passaras, G. Kokkoris & external collaborators)

A. Modeling and simulation of the kINPen plasma jet reactor

A hybrid computational framework, consisting of a detailed turbulence flow model, a global model, and a model for the calculation of the electron energy probability function, is developed to predict the density of plasma generated species along the axial direction of plasma jet reactors. The framework is applied to an Ar/O_2 plasma in a kINPen 09 reactor. It allows for a detailed description of the plasma chemistry with the low-cost global model: A reaction set of 764 reactions and 84 species is considered. The effect of different turbulence flow models, namely the detailed and high-cost large eddy simulation (LES) model and the simple and low-cost realizable k–ε model, on the densities of plasma generated species is investigated at different values of absorbed power. Although the effect is not severe on the density of the majority of the species, the differences in the densities of some species, such as $O_2(1\Sigma g)$, O^-, O_2^-, O(1D), O, and OH^- may reach an order of magnitude. The detailed LES model is a proper choice for Ar jets, and this is reinforced by the comparison of the results of the framework with atomic oxygen experimental measurements along the axial direction of the jet: the use of the LES model leads to atomic oxygen density closer to the measured one compared to (the use of) the realizable k–ε model.

B. Modeling and simulation of the COST reference plasma jet reactor

A 2D cross-field plasma fluid model (CFPM) is applied to He and He/O_2 discharges in the COST reference microplasma jet reactor to investigate the operating modes, namely *α*-, *α*-*γ*, and *γ*-mode. The model not only captures the measured spatiotemporal behavior of He excitation to He metastable but also quantitatively predicts measured power – voltage (PV) characteristics for He/O_2 discharges; although not addressed by previous studies in the literature, this is a prerequisite for the reliability of the model predictions for the critical-for-applications densities of reactive species. Through a comparison to time-averaged emission profiles and allowed by the dimensionality of the CFPM, the localized, close to the outlet of the discharge channel, onset of *γ*-mode for He discharges is predicted and justified. Criteria for the determination of the sheath boundary are proposed; model results compare well to measurements of time-averaged sheath width. Criteria for the transition between the operating modes are formulated. Finally, the sensitivity of PV characteristics on the secondary electron emission coefficients, condition of the electrode surface, and fabrication or assembly mishits of the COST jet reactor, is investigated.

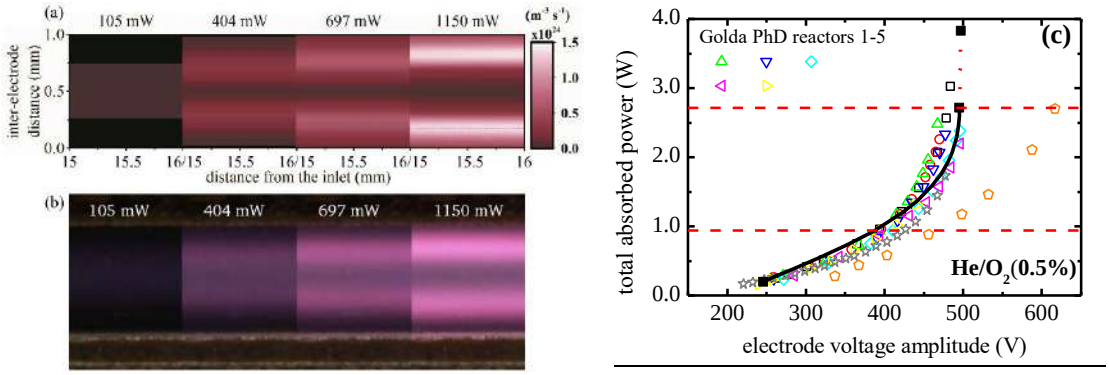


Fig.6 (a) Calculated and (b) measured time-averaged reaction rate of the electron impact excitation of He along a part of the discharge channel for a pure He discharge versus the total absorbed power. (c) Power-voltage characteristics for He with 0.5% O_2 admixture compared to five sets of measurements.

Application 1 (A1) Surface engineering for "smart" surfaces

A1.1. Optimizing razor blades using plasma processing

(K. Ellinas, E. Gogolides, and collaborators from BiC Violex Company)

This is a collaboration with the BiC Violex razor company to develop razor blade hydrophobic coatings. During the second year of this project, we have developed in collaboration with Bic Violex SA, new processes, materials and characterization methods to improve the properties of the razor blades and prepared a PCT patent application from the results of the project.

A1.2 Antibacterial Surfaces: Bactericidal Action of Plasma Micro-Nanotextured Polymeric Surfaces Enhanced by Incorporation of a Biocidal Agent

(P. Dimitrakellis, K. Ellinas, A. Tserepi, E. Gogolides, and external collaborators)

The use of antibacterial surfaces is an effective way to reduce exposure to pathogens and therefore infections. Here, a comparative study on the antibacterial properties of surfaces with different characteristics against Gram-negative bacteria (Escherichia coli) under dynamic conditions is presented, aiming to unravel the interplay among the most important factors when realizing an antibacterial surface, that is, surface morphology, wetting properties, and the use of a bactericidal agent. Significant bactericidal efficacy for the micro-nanotextured, superhydrophilic surfaces is demonstrated, possibly due to a mechanical killing induced by the interaction of bacteria with the micro-nanotopography. On the other hand, superhydrophobic surfaces without any bactericidal agent exhibit low interaction with the bacteria containing medium and therefore lower bactericidal action, whereas superhydrophobic surfaces with a bactericidal agent exhibit extreme non-wetting properties and rapid bactericidal effect through release of Cu particles. Finally, the role of the hydrophobic coating as barrier against uncontrolled release of the bactericidal agent when deposited as top layer is also showcased.

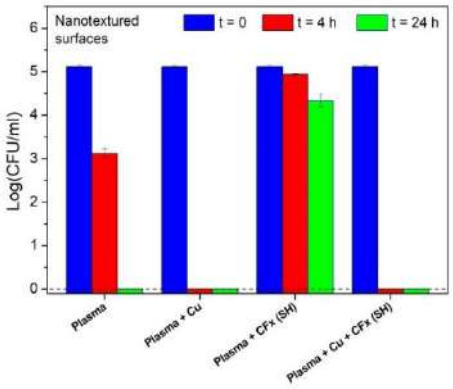
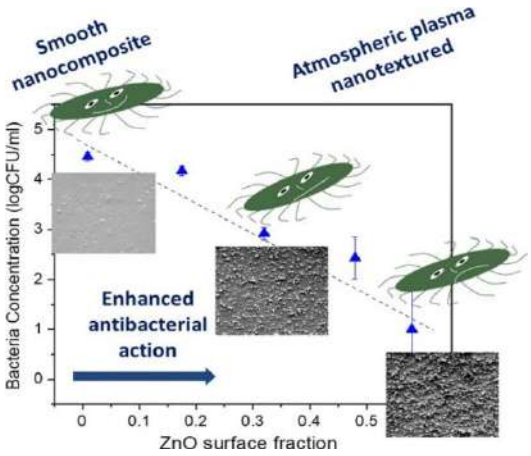


Fig.7 Bactericidal activity of plasma nanotextured (rough) surfaces against *E.Coli* after 4 and 24 h incubation under dynamic conditions.

A1.3. Antibacterial Surfaces: Enhanced antibacterial activity of ZnO-PMMA nanocomposites by selective plasma etching in atmospheric pressure



(P. Dimitrakellis, V. Constantoudis, A. Tserepi, E. Gogolides, and external collaborators)

We present an alternative route to enhance antibacterial activity of polymer matrix nanocomposites that incorporate biocidal nanomaterials, using open-air atmospheric pressure plasma etching. We applied He/O2 discharges to rapidly remove the upper organic layers of ZnO -PMMA nanocomposite coatings, thus increasing the surface concentration of ZnO. To quantify the ZnO concentration from SEM images on the surface of the

nanocomposite material, we developed and employed a new nanometrology method based on local variances of pixel luminosities and found a rapid increase of surface fraction up to 30% for the first 2 min of plasma treatment. Plasma etching resulted in enhanced antibacterial activity against Gram-negative E. coli cells after 4 h incubation under dynamic conditions. The results revealed an almost exponential drop of bacterial concentration with ZnO surface fraction, thus confirming the direct correlation of antibacterial activity with the interfacial area of the biocidal nanomaterial.

Fig.8 Antibacterial activity against E. Coli of ZnO-polymer nanocomposites by selective atmospheric pressure plasma etching.

A1.4 Antifogging surfaces (M. Tzianou, K. Ellinas, E. Gogolides)

Superhydrophobic and superhydrophilic surfaces are investigated regarding their antifogging properties. Transmittance as well as reflectance measurements under fog conditions are used to identify the surface with the optimum antifogging performance. A high impact publication was produced from the results of this thematic area. In particular, it is demonstrated that superhydrophilic surfaces with nanoscale morphology maintain their optical transmittance under fog flow for more than 20 min. This duration is one of the longest reported in the literature revealing the long-term antifogging functionality of the proposed surfaces. Finally, by tailoring the morphology and the surface wetting properties, an optically switching surface (initially “milky” which becomes “clear”) when exposed to humidity is demonstrated.

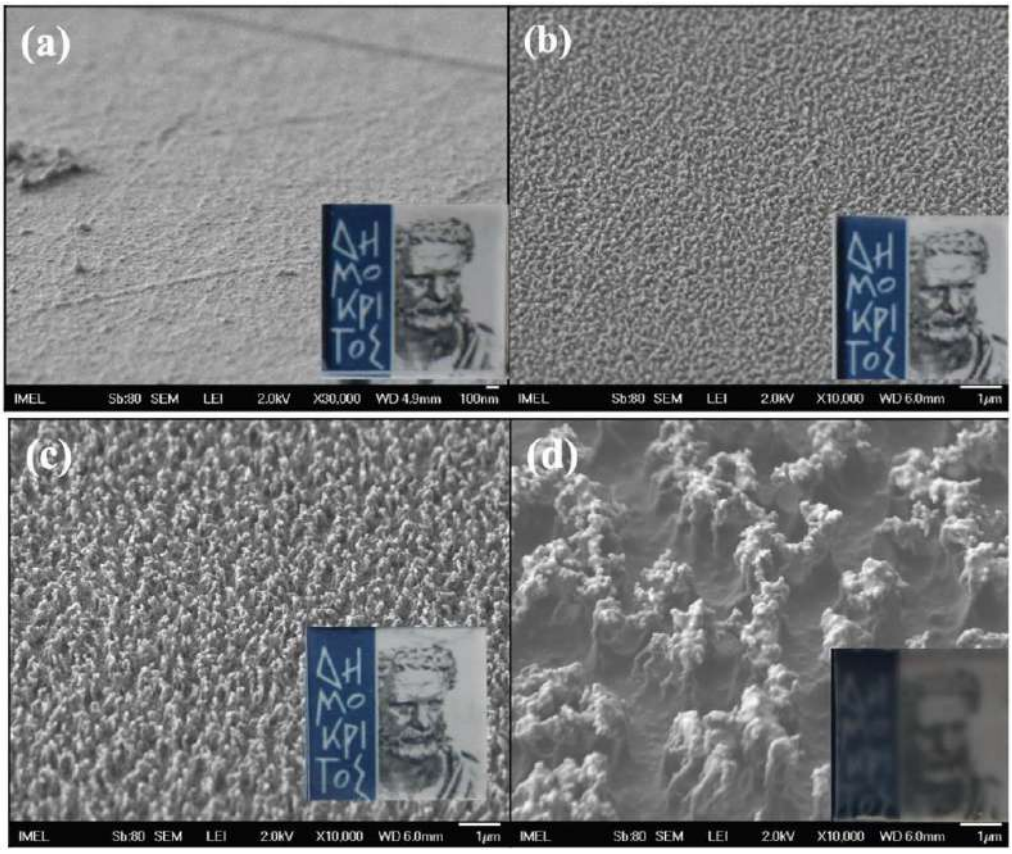


Fig.9 SEM images of the surface morphology of: (a) untreated PMMA, (b) after 1 min plasma etching, (c) after 2 min plasma etching and (d) after 5 min plasma etching. Superhydrophobic and superhydrophilic surfaces were fabricated simultaneously and therefore morphology in both cases is the same for the same etching duration. The inset shows the logo of NCSR Demokritos viewed through the surfaces in order to visualize clarity before fogging.

Application 2 (A2) Contribution to the water and energy shortage problem

Water and energy shortage will be the major two problems of our society in the decades to come. Our group has therefore started a serious effort within the EU FET project Harmonic on technologies for alleviating these problems. The group is proposing the use of micro-nanotextured superhydrophobic to face these problems.

A2.1 How different are fog collection and dew water harvesting on surfaces with different wetting behaviour? (D. Nioras, K. Ellinas, V. Constantoudis, E. Gogolides)

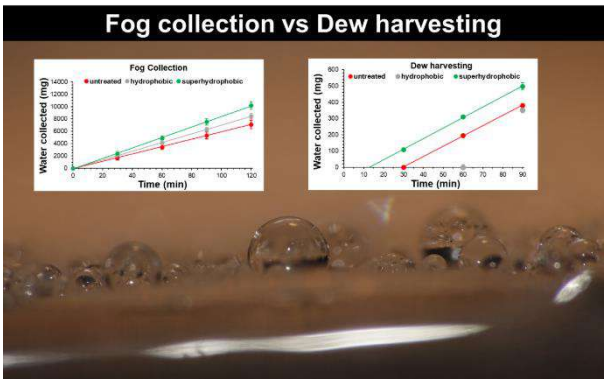


Fig.10 Dropwise water collection via fog or dew water harvesting and the amount of water collected versus time

As clean water shortage becomes a serious problem of mankind, atmospheric water harvesting emerges as a viable solution. Two main approaches to collect water from the atmosphere exist: the first is to capture it from fog, whereas the second is through condensation of vapor on surfaces with a temperature below the dew point. Our results demonstrate that drop mobility, deriving from the surface superhydrophobic properties and micro-nanotopography, is the most important factor affecting fog collection: superhydrophobic surfaces show 40 % - 65% higher fog collection rates compared to flat hydrophilic surfaces, with the more mobile among superhydrophobic surfaces (Hysteresis 2^{o}, and air-liquid fraction $f_{A\text{-}L}$>0.9) showing higher water collection. On the other hand, dew harvesting efficiency depends on the combination of drop mobility and nucleation rate, with superhydrophobic surfaces exhibiting 40% higher water collection rate compared to the flat hydrophilic or hydrophobic surfaces due to their low hysteresis as well as high surface area available for nucleation.

A2.2 Superhydrophobic plasma nanotextured membranes for enhanced membrane distillation. (D. Ioannou, K. Ellinas, E. Gogolides)

Membrane Distillation (MD) receives increasing interest as a complementary technique especially for the treatment of high salinity feedwater. Even though hydrophobicity is one of the main criteria for MD, superhydrophobicity was not always a basic requirement in membrane fabrication and modification. We introduce plasma micro-nanotexturing followed by plasma deposition as a novel, dry and green method for superhydrophobic membrane fabrication. The superhydrophobic PTFE membranes showed enhanced water flux in standard air gap membrane distillation and more stable performance compared to the commercial ones for at least 48 h continuous operation, with salt rejection >99.99 %.

A2.3 Superhydrophobic surfaces for sustainable dropwise condensation

(P. Sarkiris, V. Constantoudis, K. Ellinas, C. W. E. Lam, A. Milionis, J. Anagnostopoulos, D. Poulikakos, E. Gogolides)

Condensation control is essential for a wide range of applications that involve phase change heat transfer. An effective way to improve the heat transfer process is to induce the water vapor to condense and form highly mobile droplets on a superhydrophobic surface. In this work, superhydrophobic aluminum surfaces are prepared through etching with hydrochloric acid, followed by boehmitage process and subsequently minimization of surface energy by applying an ultra-thin hydrophobic fluorocarbon coating through C_4F_8 plasma deposition. A highly increased heat transfer coefficient was measured on such surfaces.

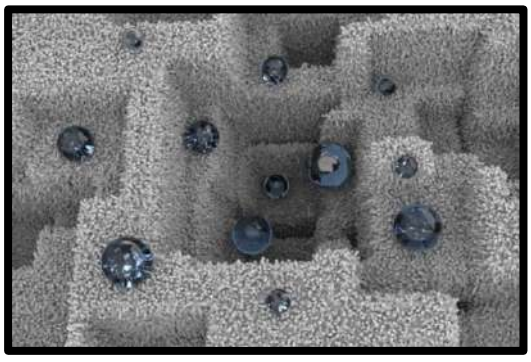


Fig.11 Computer generated image of a micro-nanotextured Aluminum surface.

- **Funding**

1. Contract with NCSR Demokritos and Fasmatech Science and Technology SA for Industrial Postdoctoral Programme "Design and development of a hyperthermal hydrogen atom gun for top-down proteomics" 14/06/2018 – 13/06/2021, total budget €82.950,00 , budget for 2021 €12.650,00

2. Contract between INN-NCSR Demokritos and Nanometrisis for Industrial Research Fellowship Program Stavros Niarchos Foundation, Computational Nanometrology with Applications in Nanoelectronics and Nanotechnology, 01/08/2017 – 30/07/2021 (PhD fellow: G Papavieros), total budget €46.200,00 , budget for 2021 €6.737,50
3. "HARMoNIC", H2020-FETOPEN-1-2016-2017, Contract No. 801229, 01/10/2018 – 31/07/2022, total budget €762.900,00 , budget for 2021 €199.017,00
4. "NOVISH", Contract No. MIS 5019170, 12/04/2019 – 11/10/2022, total budget €165.812,02 , budget for 2021 €47.375,00
5. "LagoMeal", Contract No. MIS 5067491, 27/11/2020 – 26/05/2023, total budget €68.745,00 , budget for 2021 €27.498,00
6. Hellenic Foundation for Research and Innovation (HFRI) PhD Fellowship, "Revolutionary paths of Nitrogen fixation with electrical discharges of air through computational and experimental analysis", HFRI application number: 124, 01/12/2019 - 30/11/2022 (PhD Fellow S. Mouchtouris) budget for 2021 €10.800,00
7. IKY PhD Fellowship, "Computational and experimental analysis of thin film deposition with atmospheric pressure plasma jets for controlled release of reactive substances", IKY contract No. 2018-050-0502-13687, 24/04/2018 - 23/04/2021 (PhD fellow: D. Passaras) budget for 2021 €3.250,00
8. IKY "Reinforcement of Postdoctoral Researchers—2nd Cycle" (MIS-5033021), implemented by the State Scholarships Foundation (IKY) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project Fellowship, "Superhydrophobic surfaces with ultra-low friction for interactions with liquid drops", IKY contract No. 2019-050-0503-17559, 16/11/2019-16/11/2021 (Postdoctoral fellow: K. Ellinas) budget for 2021 €11.550,00
9. "NOOSE", NATO project SPS MYP G5814, 05/04/2021-04/04/2024, total budget €56.000,00, budget for 2021 €14.000,00
10. "PlasmaForNano", H.F.R.I., 1st Call for H.F.R.I. Research Projects to Support Faculty Members & Researchers and Procure High-Value Research Equipment, 16/04/2021-15/04/2024, total budget €1.439.424,00 , budget for 2021 €339.864,00
11. "CarbyneSense", GSRT EraNet-Russia Contract No. MIS 5161208, 30/12/2021-29/06/2023, total budget €200.000,00
12. PLagri – COST Action 19110, Plasma applications for smart and sustainable agriculture, 06/10/2020 – 05/10/2024.

OUTPUT

Publications in International Journals

1. Passaras, D., Amanatides, E., Kokkoris, G., A hybrid computational framework for the simulation of atmospheric pressure plasma jets: The importance of the gas flow model. *Plasma Sources Science and Technology* **30**, art. no. 125018 (2021). DOI: 10.1088/1361-6595/ac3ba2
2. Dimitrakellis, P., Giannoglou, M., Xanthou, Z.M., Gogolides, E., Taoukis, P., Katsaros, G., Application of plasma-activated water as an antimicrobial washing agent of fresh leafy produce. *Plasma Processes and Polymers* **18**, art. no. 2100030 (2021). DOI: 10.1002/ppap.202100030
3. Dimitrakellis, P., Kaprou, G.D., Papavieros, G., Mastellos, D.C., Constantoudis, V., Tserepi, A., Gogolides, E., Enhanced antibacterial activity of ZnO-PMMA nanocomposites by selective plasma etching in atmospheric pressure. *Micro and Nano Engineering* **13**, art. no. 100098 (2021). DOI: 10.1016/j.mne.2021.100098
4. Nioras, D., Ellinas, K., Constantoudis, V., Gogolides, E., How Different Are Fog Collection and Dew Water Harvesting on Surfaces with Different Wetting Behaviors? *ACS Applied Materials and Interfaces* **13**, pp. 48322-48332 (2021). DOI: 10.1021/acsami.1c16609
5. Papavieros, G., Constantoudis, V., Vouroutzis, N., Gogolides, E., Measuring line edge roughness with pixel sizes larger than its value: A mathematical and computational approach. *Journal of Micro/Nanopatterning, Materials and Metrology* **20**, art. no. 034001 (2021). DOI: 10.1117/1.JMM.20.3.034001
6. Zeniou, A., Smyrnakis, A., Constantoudis, V., Awsiuk, K., Gogolides, E., One-step control of hierarchy and functionality of polymeric surfaces in a new plasma nanotechnology reactor. *Nanotechnology* **32**, art. no. 235305 (2021). DOI: 10.1088/1361-6528/abe6ca

7. Cheimarios, N., To, D., Kokkoris, G., Memos, G., Boudouvis, A.G., Monte Carlo and Kinetic Monte Carlo Models for Deposition Processes: A Review of Recent Works. *Frontiers in Physics* **9**, art. no. 631918 (2021). DOI: 10.3389/fphy.2021.631918
8. Ellinas, K., Dimitrakellis, P., Sarkiris, P., Gogolides, E., A review of fabrication methods, properties and applications of superhydrophobic metals. *Processes* **9**, art. no. 666 (2021). DOI: 10.3390/pr9040666
9. Dimitrakellis, P., Ellinas, K., Kaprou, G.D., Mastellos, D.C., Tserepi, A., Gogolides, E., Bactericidal Action of Smooth and Plasma Micro-Nanotextured Polymeric Surfaces with Varying Wettability, Enhanced by Incorporation of a Biocidal Agent. *Macromolecular Materials and Engineering* 306**,** art. no. 2000694 (2021). DOI: 10.1002/mame.202000694
10. Cheimarios, N., Kokkoris, G., Boudouvis, A.G., Multiscale Modeling in Chemical Vapor Deposition Processes: Models and Methodologies. *Archives of Computational Methods in Engineering* **28**, pp. 637-672 (2021). DOI: 10.1007/s11831-019-09398-w
11. Memos, G., Lidorikis, E., Gogolides, E., Kokkoris, G., A hybrid modeling framework for the investigation of surface roughening of polymers during oxygen plasma etching. *Journal of Physics D: Applied Physics* **54**, art. no. 175205 (2021). DOI: 10.1088/1361-6463/abdb0b

12. Arapis, A., Constantoudis, V., Kontziampasis, D., Milionis, A., Lam, C.W.E., Tripathy, A., Poulikakos, D., Gogolides, E., Measuring the complexity of micro and nanostructured surfaces. *Materials Today: Proceedings* **54**, pp. 63-72 (2021). DOI: 10.1016/j.matpr.2021.10.120
13. Poulios, C., Constantoudis, V., Mathematical Analysis of Nanostructured Surfaces: The Period-Scale Transform. *Mathematical Problems in Engineering*, art. no. 5533673 (2021). DOI: 10.1155/2021/5533673
14. Chanioti, S., Katsenios, N., Efthimiadou, A., Stergiou, P., Xanthou, Z.M., Giannoglou, M., Dimitrakellis, P., Gogolides, E., Katsaros, G., Pre-sowing treatment of maize seeds by cold atmospheric plasma and pulsed electromagnetic fields: Effect on plant and kernels characteristics. *Australian Journal of Crop Science* **15**, pp. 251-259 (2021). DOI: 10.21475/ajcs.21.15.02.p2932
15. Dimitrakellis, P., Giannoglou, M., Zeniou, A., Gogolides, E., Katsaros, G., Food container employing a cold atmospheric plasma source for prolonged preservation of plant and animal origin food products. *MethodsX* **8**, art. no. 101177 (2021). DOI: 10.1016/j.mex.2020.101177
16. Mouchtouris, S., Kokkoris, G., A novel plasma fluid model for fast 2D calculations in capacitively coupled atmospheric pressure plasma jets. *Plasma Sources Science and Technology* **30**, art. no. 01LT01 (2021). DOI: 10.1088/1361-6595/abccfc (letter)
17. Tzianou, M., Thomopoulos, G., Vourdas, N., Ellinas, K., Gogolides, E., Tailoring Wetting Properties at Extremes States to Obtain Antifogging Functionality. *Advanced Functional Materials* **31**, art. no. 2006687 (2021). DOI: 10.1002/adfm.202006687
18. Ellinas K., Dimitrakellis P., Sarkiris P., Gogolides E., A review of fabrication methods, properties and applications of superhydrophobic metals. *Processes* **9**, art. no. 666 (2021). DOI: 10.3390/pr9040666

International Conferences Presentations (invited, oral, poster)

1. A. Kanioura, A. Zeniou, P. Petrou, A. Papadopoulou, E. Mavrogonatou, D. Kletsas, A. Tserepi, E. Gogolides, S. Kakabakos, Effect of Micro/Nanostructured Polystyrene Substrates onto Adhesion, Viability and Differentiation of Adipose Tissue Derived Mesenchymal Stem Cells (poster), *47th Micro and Nano Engineering conference (MNE 2021)*, 20-23 September 2021, Turin, Italy
2. A. Arapis, V. Constantoudis, D. Kontziampasis, A. Milionis, Cheuk Wing Edmond Lam, A. Tripathy, D. Poulikakos, E. Gogolides, Quantifying the information content of multiscale nanostructured surfaces: an entropy-based scaling analysis (poster), *47th Micro and Nano Engineering conference (MNE 2021)*, 20-23 September 2021, Turin, Italy
3. D. Ioannou, Y. Hou, P. Shah, K. Ellinas, M. Kappl, E. Gogolides, Contribution to the clean water production via superhydrophobic, plasma nanotextured membrane distillation (oral), *47th Micro and Nano Engineering conference (MNE 2021)*, 20-23 September 2021, Turin, Italy
4. G. Papavieros, T. Kyttari, V. Constantoudis, E. Gogolides, Mathematical and computational metrology of multiscale and hierarchical surfaces (oral), *47th Micro and Nano Engineering conference (MNE 2021)*, 20-23 September 2021, Turin, Italy

5. P. Sarkiris, K. Ellinas, E. Gogolides, Superhydrophobic nanostructured metallic surfaces for enhanced heat transfer (poster), *47th Micro and Nano Engineering conference (MNE 2021)*, 20-23 September 2021, Turin, Italy
6. A. Zeniou, E. Gogolides, G. Papavieros, V. Constantoudis, Control of optical properties of polymeric surfaces via plasma processing in a new-type of plasma reactor (poster), *47th Micro and Nano Engineering conference (MNE 2021)*, 20-23 September 2021, Turin, Italy
7. A. Mavrogonatos, E.-M. Papia, P. Dimitrakellis, V. Constantoudis, Point pattern analysis of nanostructure positions: Effects of SEM image processing parameters on the Nearest Neighbour Index (poster), *47th Micro and Nano Engineering conference (MNE 2021)*, 20-23 September 2021, Turin, Italy
8. S. Mouchtouris, G. Kokkoris, Power-voltage Computations in the COST Reference Microplasma Jet (virtual poster), VIRTUAL *8th International Conference on Plasma Medicine* (online conference), 3-6 August 2021, Seoul, Republic of Korea
9. S. Mouchtouris, G. Kokkoris, A. G. Boudouvis, 3D computations in the discharge channel of the COST reference jet (virtual poster), VIRTUAL *The 74th Annual Gaseous Electronics Conference* (virtual GEC 2021), 4-8 October 2021, Huntsville, Alabama, USA
10. E. Stai, V. Constantoudis, P. Sarkiris, E. Gogolides, Computational metrology of multiscale surfaces using the Fourier stitching method (oral), *E-MRS 2021 Fall Meeting*, 20-23 September 2021, Virtual Conference

11. J.Wei, G. Cavallero, C. Xia. D. Papanastasiou, M. Kosmopoulou, A. Smyrnakis, J. Zaia, C. Costello, C. Lin, Combining ion mobility measurement with tandem mass spectrometry for in-depth glycan structural characterization, *69th ASMS Conference on Mass Spectrometry and Allied Topics*, 31 October - 4 November 2021, Philadelphia PA, USA
12. S. Chanioti, M. Giannoglou, P. Stergiou, D. Passaras, G. Kokkoris, E. Gogolides, G. Katsaros, Cold Atmospheric Plasma Activated Ice as a cooling capacitor with antimicrobial properties: case study on fish fillets preservation (poster), *35th EFFoST International Conference 2021*, 1-4 November 2021, Lausanne, Switzerland
13. E. Gogolides, Superhydrophobic self-cleaning surfaces: Principles, fabrication, characterization, durability (oral), *47th Micro and Nano Engineering conference (MNE 2021)*, 20-23 September 2021, Turin, Italy
14. V. Andreou, M. Giannoglou, M. Xanthou, D. Passaras, G. Kokkoris, A. Tserepi, E. Gogolides, G. Katsaros, Cold atmospheric plasma kinetic inactivation of Pectinmethylesterase from fresh orange juice (poster), *35th EFFoST International Conference 2021*, 1-4 November 2021, Lausanne, Switzerland
15. M. Giannoglou, M.-Z. Xanthou, S. Chanioti, P. Stergiou, P. Dimitrakellis, E. Gogolides, A. Efthimiadou, M. Christopoulos, G. Katsaros, Effect of cold atmospheric plasma and pulsed electromagnetic fields on the shelf-life of whole fresh strawberries (poster), *35th EFFoST International Conference 2021*, 1-4 November 2021, Lausanne, Switzerland
16. D. Nioras, K. Ellinas, E. Gogolides, Dew water harvesting and fog collection on biphilic, nanotextured surfaces (poster), *47th Micro and Nano Engineering conference (MNE 2021)*, 20-23 September 2021, Turin, Italy
17. G. Memos, G. Kokkoris, V. Constantoudis, A. Milionis, D. Poulikakos, E. Gogolides, Heat transfer through shadowed droplets in dropwise condensation, 8th International Symposium on Advances on Computational Heat transfer – CHT-21, Rio, Brasil, August 15 – 19, 2021. (oral)

National Conferences Presentations (invited, oral, poster)

1. E. Gogolides, "A tribute to Androula Nassiopoulou" short memorial during the welcome of the conference for the establishment of the best oral award in memory of Androula Nassiopoulou, VIRTUAL *XXXV Panhellenic Conference on Solid State Physics and Materials Science*, 26-29 September 2021, Athens, Greece
2. E. Stai, V. Constantoudis, P. Sarkiris, E. Gogolides, Hybrid metrology of multiscale surfaces using the Fourier stitching method (virtual poster), VIRTUAL *XXXV Panhellenic Conference on Solid State Physics and Materials Science*, 26-29 September 2021, Athens, Greece
3. G. Papavieros, V. Constantoudis, E. Gogolides, Computational Nanometrology in Line Edge roughness Measurements: Synthesized data and Pixelization Effects (oral), VIRTUAL *XXXV Panhellenic Conference on Solid State Physics and Materials Science*, 26-29 September 2021, Athens, Greece

Teaching and Training Activities

1. "Microelectronics and Microsystems fabrication processes", (E. Gogolides, D. Davazoglou, G. Kokkoris), Postgraduate Programs on Microsystems and Nanodevices of the National Technical University of Athens
2. "Fabrication and Characterization of nanostructures (using plasma etching and bottom up techniques)", (E. Gogolides, C. Charitidis), Postgraduate Programs on Microsystems and Nanodevices of the National Technical University of Athens
3. "Superhydrophobic surfaces, wetting theory and applications" (K. Ellinas), Postgraduate Program "Preservation of monuments of cultural heritage" University of West Attica.
4. "Mathematical modeling in Nanotechnology" (G. Kokkoris, V. Constantoudis), Postgraduate Program "Mathematical modeling in Modern Technologies and Finance", National Technical University of Athens
5. "Topics of Complex Systems" (V. Constantoudis, A. Provata, Y. Kominis, T. Bountis, M. Axenides), Postgraduate Program "Mathematical modeling in Modern Technologies and Financial Engineering", National Technical University of Athens
6. "Superhydrophobic self-cleaning surfaces: Principles, fabrication, characterization, durability" (E. Gogolides), Course during the International School of 47th Micro and Nano Engineering conference (MNE 2021), 20 September 2021, Turin, Italy

Doctoral Dissertations completed in 2021

1. Angelos Zeniou
Design and construction of new plasma sources at low and atmospheric pressure for chemical and morphological modification of polymeric materials
Thesis supervisor at NCSR: E. Gogolides, Thesis supervisor at Univ. of Patras: D. Skarlatos
University of Patras, Physics Department

2. George Memos
A hybrid modeling framework for simulating plasma-surface interactions of rough polymeric substrates
Thesis supervisor at NCSR: G. Kokkoris, Thesis supervisor at UOI: E. Lidorikis
University of Ioannina, School of Engineering, Department of Materials Science & Engineering

Master Dissertations completed in 2021

1. Sevastianos Korsak
Machine Learning based mapping of the Ising model to rough surfaces
Thesis supervisor at NCSR: Vassilios Constantoudis
Masters in Mathematical Modeling in Modern Technologies and Financial Engineering

2. Aleksandros Kondi
Image analysis with the use of discrete 2D nonlinear dynamical transformations
Thesis supervisor at NCSR: Vassilios Constantoudis
Masters in Mathematical Modeling in Modern Technologies and Financial Engineering

Patents - Technology transfer

Large Area, Uniform, Atmospheric Pressure Plasma Processing Device
Greek patent application 20150100397 – 09/09/2015, Patent grant No. 1009432
European patent application 16386016.6 – 08/09/2016, Patent grant No. EP3142467
Filed in Italy, UK, Netherlands 8/2021

Methods and systems for forming a blade of a shaving device
Christos Pandis, Konstantinos Mavroeidis, Evangelos Gogolides, Kosmas Ellinas, Dimitrios Davazoglou
PCT patent application, September 2021

POLYMER BASED SENSOR AND SYSTEMS

Project Leader: Ioannis Raptis

Permanent Research Staff: P. Petrou, S. Kakabakos

Post Docs: G. Zisis

PhD Candidates: Athanasios Botsialas

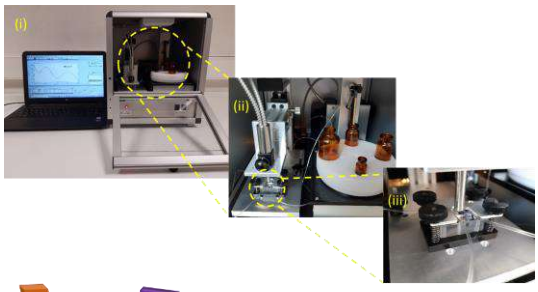
- **Objectives**
  - Development & Characterization of Optical biosensors
  - Development & Characterization of Chemocapacitive sensors

- **Highlights / main scientific results**

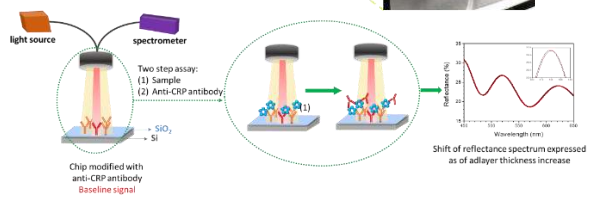
Biosensors

The development of methods and miniaturized systems for fast and reliable quantitative determinations at the Point-of-Care is a top challenge and priority in diagnostics. A compact bench-top system, based on White Light Reflectance Spectroscopy (WLRS), was introduced and evaluated in applications with high interest for human health and food safety. The WLRS platform allows for real-time monitoring of biomolecular interactions carried out a SiO_2/Si chip by transforming the shift in the reflected interference spectrum caused by the immunoreaction to effective biomolecular adlayer thickness. The system encompassed all the necessary electronic and optical components for the performance of the assay, while the dedicated software provided the sequence and duration of assay steps, the reagents flow rate, the real-time monitoring of sensor response, and data processing to deliver in short time and accurately the analyte concentration in the sample.

In the human health direction, the work was focused in the determination of C-Reactive protein (CRP) in human blood samples. The CRP assay included two steps, the first comprising the binding of sample CRP onto the chip immobilized capture antibody and the second the reaction of the surface immunosorbed CRP molecules with the detection antibody. The assay duration was 12 min and the dynamic range was from 0.05 to 200 μg/mL, covering both normal values and acute inflammation incidents. There was an excellent agreement between CRP values determined in human plasma samples using the developed device with those received for the same samples by a standard diagnostic laboratory method.



Images of the: (i) whole instrument and accompanying PC, (ii) fluidic module, and (iii) docking station

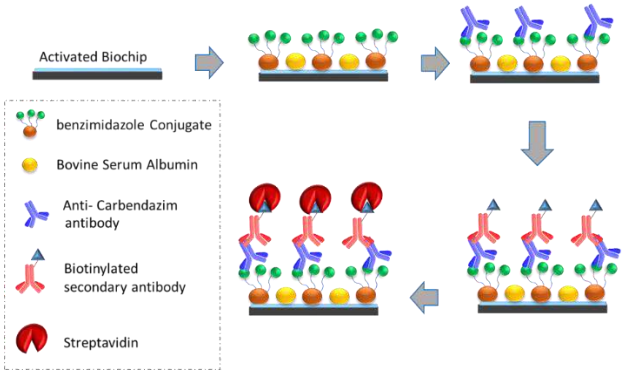


Schematic of the chip, sensing principle and two-site sandwich immunoassay procedure

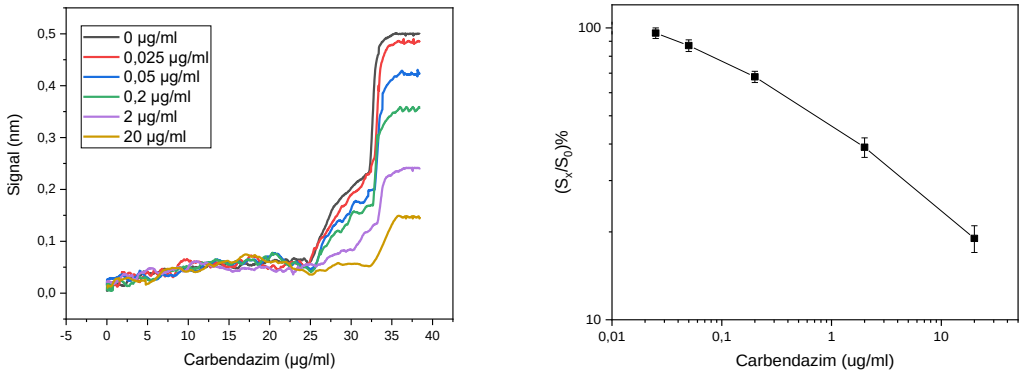
In the reporting period in the food safety direction the work was focused in the quantitative and fast determination of Carbendazim and Salmonella typhimurium. Carbendazim is a systemic benzimidazole-type fungicide with broad-spectrum activity against fungi that undermine food products safety and quality. Despite its effectiveness, carbendazim constitutes a major environmental pollutant, being hazardous to both humans and animals.

The white light reflectance spectroscopy (WLRS) biosensor was employed for the fast and sensitive determination of carbendazim in fruit juices. The transducer functionalized with a benzimidazole conjugate, and determination is based on a competitive immunoassay format. Thus, for the assay, a mixture of an in-house developed rabbit polyclonal anti-carbendazim antibody with the standards or samples is pumped over the chip, followed by

biotinylated secondary antibody and streptavidin. The sensor is able to detect 20 ng/mL of carbendazim in fruit juices with high accuracy and precision in less than 30 min, applying a simple sample treatment that alleviates any "matrix-effect" on the assay results and a 60 min preincubation step for improving assay sensitivity. Excellent analytical characteristics and short analysis time along with its small size render the proposed WLRS immunosensor ideal for future on-the-spot determination of carbendazim in food and environmental samples.



Schematic representation of assay procedure for the label-free detection of carbendazim with the WLRS biosensor.



Real-time responses obtained from biochips functionalized with a 500 μg/mL benzimidazole lysine dentrimer conjugate upon running sequentially: assay buffer; a 1:1 v/v mixture of carbendazim calibrators (0-20000 ng/mL) prepared in assay buffer with a 2 μg/mL anti-carbendazim Ab solution in the same buffer; a 1:200 diluted so-lution of biotinylated anti-rabbit IgG antibodyin assay buffer; and a 10 μg/mL streptavidin solution. (b) Typical linearized calibration curve for carbendazim.obtained with carbendazim calibrators prepared in assay buffer. Each point represents the mean value of 4 runs ± SD.

- **Funding**

HERON –Interferometric system based on a 3D structured biochip: an application to quantitative determination of hazardous substances in food" (MIS 5047824).

OUTPUT

Publications in International Journals

1. Angelopoulou M., Petrou P., Raptis I., Misiakos K., Livaniou E., Makarona E., Kakabakos S. Rapid detection of mozzarella and feta cheese adulteration with cow milk through a silicon photonic immunosensor. *Analyst* **146** pp. 529-537 (2021) DOI: 10.1039/D0AN01706J
2. Tsounidi D., Petrou P., Raptis I. Current progress on biosensors and Point-of-Care devices for sepsis diagnosis *IEEE Sensors* **21** pp. 12840-12855 (2021) DOI: 10.1109/JSEN.2021.3050887
3. Angelopoulou M., Tzialla K., Voulgari A., Dikeouli, M., Raptis I., Kakabakos S.E., Petrou P. Rapid detection of Salmonella typhimurium in drinking water by a White Light Reflectance Spectroscopy immunosensor. *Sensors* **21** pp. 2683 (2021) DOI: 10.3390/s21082683
4. Koukouvinos G., Karachaliou Ch., Raptis I., Petrou P., Livaniou E., Kakabakos S. Fast and sensitive determination of fungicide Carbendazim in fruit juices with a White Light Reflectance Spectroscopy label-free immunosensor. *Biosensors* **11** p. 153-(2021) DOI: 10.3390/bios11050153

5. Tsounidi D., Koukouvinos G., Christianidis V., Legaki E, Giogli V., Panagiotopoulou K., Taka S., Ekaterinidi Z., Kakabakos S., Raptis I., Petrou P. Development of a Point-of-Care system based on White Light Reflectance Spectroscopy: application in CRP determination. *Biosensors* **11** pp. 268 (2021) DOI: 10.3390/bios11080268

Papers in Refereed Conference Proceedings

1. Zisis G., Papageorgiou G., Anastasiadis V,. Petrou P., Papanikolaou N., Raptis I. 3D structured biochip for label-free multi-analytedeterminations at the PoN. *Micro & Nano Engineering 2023 conference*
2. Petrou P., Koukouvinos G., Mastellos D., Kakabakos S., Raptis I., Lambris J.D. Simultaneous Determination of Activated C3 Fragments and the Terminal Complement Complex C5b-9 by a Label-Free Optical Immunosensor *Europtrode XV conference*
3. Tsounidi D., Goustouridis D., Tsaousis V., Mitropoulos C., Kakabakos S., Petrou P., Raptis I. Rapid and Label-Free Determination of Three Sepsis Markers Using a White Light Reflectance *Europtrode XV conference*

ILM DEVICES FOR MICROSYSTEMS AND LARGE AREA ELECTRONICS

Project Leader: Dr. Dimitrios N. Kouvatsos

Post Docs: Dr. Georgios Papadimitropoulos, Dr. Angelika Balliou

Research Collaborators: Dr. Despina Moschou (University of Bath), Dr. Anna Regoutz (University College London), Prof. D. Tsoukalas, Prof. I. Zergioti (National Technical University of Athens), Prof. Charalambos Dimitriadis (University of Thessaloniki), Dr. Tolis Voutsas (Peratech, Inc.)

Objectives

The objectives of this group include research and development on the applications of various thin films, principally metal chalcogenides and oxides, for transistors and sensors with novel structures, including the use of hybrid materials based on molecular and low dimensional components. In particular, they are:

- Development of semiconducting transition metal chalcogenide (such as MoS_2) thin films, with evaluation of metal contacts to them, and of metal oxide films.
- Development of thin film transistor (TFT) fabrication processes at low temperatures utilizing these novel semiconductor and dielectric films and molecular liquid doping techniques for performance enhancement.
- Fabrication and characterization of various devices and microsystems, such as sensors and large area electronics, based on deposited metal chalcogenide or advanced laser annealed polycrystalline silicon thin films.

Activities and Main Results

Our recent work has focused on transition metal dichalcogenides (TMDs), specifically on thin molybdenum disulfide (MoS_2) films and TFTs and sensors based on them; MoS_2 is the most important of TMDs investigated for such applications. We are pursuing research on molecular liquid doping for TFT performance enhancement. Other TMD films are also under consideration. Dielectric films suitable for such devices like AlO_3 and Ta_2O_5 are used. Moreover, we are investigating metal oxide films suitable for sensors such as CeO_2.
TMD films obtained by many groups in single layer or a few layers exhibit high mobility, transparency and flexibility, showing promise of high performance, transparent, flexible electronics. However, their fabrication is challenging and/or expensive and/or small scale and/or poor yield.
On the other hand, amorphous bulk TMD films, especially MoS_2, are cheap and easy to obtain with large-scale techniques, but they are highly porous, exhibit large contact resistance and very low mobility, while low work function metals, n-type charge transfer dopants, high-k dielectrics or thermal anneals have only yielded incremental benefits. This means that they are highly defective, very low conductivity materials unsuitable for TFT electronics, while their high porosity, defectivity, vast internal surface show large promise for sensing applications.
The alternative path we propose, meeting the trends of inexpensive, room temperature and impurity tolerant processes, is to shape high performance hybrid (solid/liquid) MoS_2 channels inside impure low quality film precursors. This is also applicable to other low purity films. We use a processing protocol of a low thermal budget anneal forming a slightly p-type channel, followed by ionic liquid ion doping greatly enhancing it, while the liquid medium serves as gate, dielectric, ion source and passivation layer. This procedure results in low contact resistance, high mobility, self-encapsulated p-type channels formed for high performance TFTs. At the same time, we investigate as-deposited high-porosity amorphous MoS_2 films as sensors, for which they are highly suitable, for a variety of toxic gases.

Task 1: MoS_2 film characteristics and development of liquid-doping performance enhanced MoS_2 thin film transistors
TFTs are ubiquitous, increasingly used in the disposable portable electronics, displays, smartphones and wearables markets, rendering cost reduction as much of a challenge as performance improvement. Thus, processes which are energy-intensive or require expensive equipment are abandoned in favor of room temperature approaches, liquid phase deposition and colloids. Although cheaper, the latter approaches suffer from controllability, performance and large contact resistance issues, deteriorating the quality of the final product. To meet the trends without compromising performance we fabricated ionic-liquid-gated MoS_2-based field-effect transistors with dramatically higher mobility than respective back-gated counterparts and on par with some of the most competitive MoS_2 topologies.

In this task, a self-encapsulating high mobility p-type channel is shaped in a precursor matrix of amorphous MoS_2 including MoO_x and non-bound sulfur impurities, as well as an ionic liquid filler that serves simultaneously as gate dielectric, mobile carrier supplier and passivation layer for the channel. This matrix, after a low thermal budget annealing, is used as a topological ionic attractor through which positive mobile ions from the liquid phase are introduced to the channel zone and become available for FET function. To achieve this, a droplet of copper phthalocyanine / butanol (CuPc/bu) ionic liquid is placed onto the exposed channel matrix of a MoS_2 TFT with global back gate topology, as schematically depicted in Figure 1, alongside a typical transfer characteristic. A non-volatile capping layer is placed on top. The mobility enhancement, by 8 orders of magnitude, is attributed to the presence of the ionic liquid, functioning simultaneously as ionic dopant and ultrathin gating medium, effectively reducing the Schottky barrier at the MoS_2/metal S, D contacts by over 4 orders of magnitude; essential to this is that the droplet acts as both a top gate and a top dielectric through the formation of an ultrathin (1-2 μm) electric double layer that induces a large gate effect. The hybrid liquid-solid state devices exhibit p-type conductance, high ON-current of 1.5×10^4 A for holes and a competitive field effect mobility of 45.8 $cm^2V^{-1}s^{-1}$. A low contact resistance (R_c) of 2.6 kΩ·μm is achieved, competing with the values obtained for monolayer MoS_2 with engineered contacts.
These TFTs, fabricated utilizing CMOS-compatible low thermal budget impurity tolerant processes, address the unattainability of p-type conduction in MoS_2, thereby extending its pertinence to PN diodes and complementary integration logic. In addition, photo-enabled switching and memory functionality is demonstrated. Remarkably, the high mobility counteracts the presence of non-ideal channel and channel-dielectric-metal interfaces which are of high porosity, structural disorder, charged impurities, and interface roughness. The herein fabricated and evaluated architecture is, to our knowledge, the first low-cost high gain MoS_2 MOSFET based on amorphous low mobility film precursors that enables high-performance multifunctional stackable MOSFETs on any kind of processing-sensitive, plastic and/or flexible substrate. Photo switching and non-volatile memory functions, due to the fact that CuPc is an intensive UV-Visible light absorber, have also been demonstrated, as discussed in the previous report.

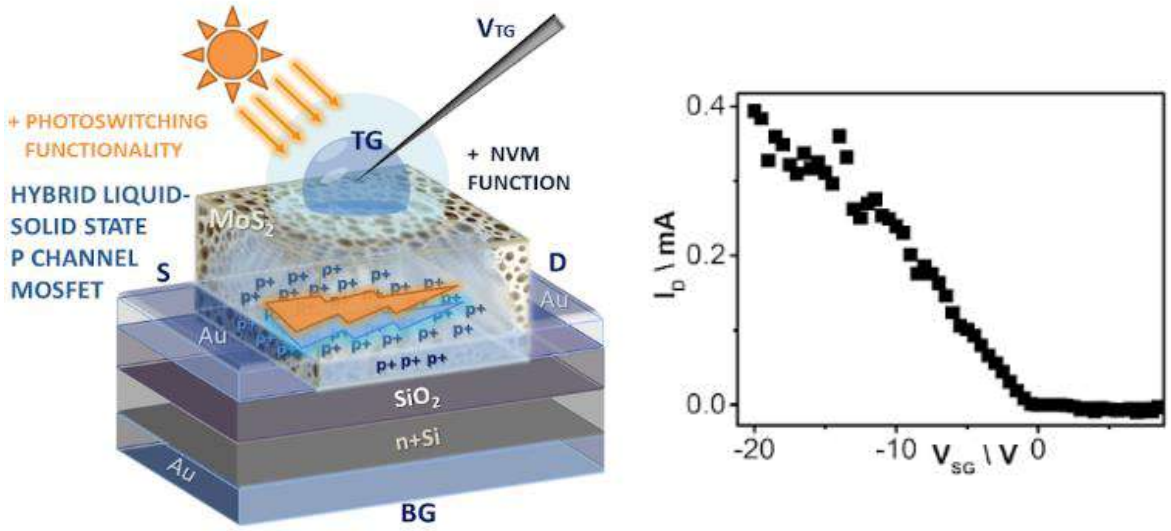


Figure 1. (left) Schematic of the liquid-doping enhanced TFT with an electric double layer. (right) Transfer characteristics of the liquid-gated p-type MoS_2 transistor.

Task 2: Development of MoS_2 thin film sensors

Metal oxides have shown the best gas sensing performance, compared to polymers, carbon nanotubes etc, in terms of time response and sensitivity. They are also cost effective and easily developed. TMDs are possible alternatives to metal oxides, with potential to improve selectivity and sensitivity. In particular, amorphous as-deposited MoS_2 is very promising, its porosity yielding vast internal surface area for gas molecules to access and be sensed. Void fraction of the order of 40%, as revealed by spectroscopic ellipsometry (possibly grains are not compact but composed of smaller grains). This is also evidenced by the SEM and AFM images of our porous hot-wire MoS_2 ($hwMoS_2$) thin films shown in Figure 2; an X-ray microanalysis plot indicating film composition is also shown. What

for TFTs is a challenge that was turned to an advantage by liquid doping after a short anneal, namely extreme porosity, for sensors is an advantage in itself.

In this task, the gas sensing properties of porous hwMoS_2 thin films, deposited on oxidized silicon substrates by heating a molybdenum filament in a vacuum chamber in H_2S environment, have been investigated in the 100-800 ppm range, at 100°C to 250°C. This was done by monitoring the current variations in sensing configurations caused by changes in their environment, specifically in gas flows. The samples remain at room temperature during the growth of films rendering hot-wire deposition suitable for polymeric and other sensitive substrates. The hwMoS_2 films were packed by wire bonding in dual in-line (DIL) packages. Interdigitated electrodes were formed by gold e-beam evaporation using Ti adhesion layers. The sensing properties of the samples are tested using a home-made setup consisting of a stainless-steel chamber and a heater reaching temperatures up to 500°C. The concentrations of gases (H_2, CO, moisture, acetone etc) are controlled by means of mass flow controllers, with the sensors stabilized in synthetic air before their exposure. The current changes of the sensors are measured with an electrometer connected to a personal computer. A schematic of the hwMoS_2 sensor is shown in Figure 2.

Reversible current changes were observed in hwMoS_2 films caused by the presence or removal of gases such as hydrogen (H_2) and carbon monoxide (CO). The magnitude of these changes, related to the sensitivity, was determined to depend on the concentrations of the gases and the measurement temperature. The current response time after gas exposure was found to be comparable to that needed to recover its initial value after gas removal. Response times of the order of a few seconds were measured for hwMoS_2 films while the surface of the deposited films was not activated with any catalyst, which is a common practice in most thin films used for gas sensing, rendering our process simpler and cheaper.

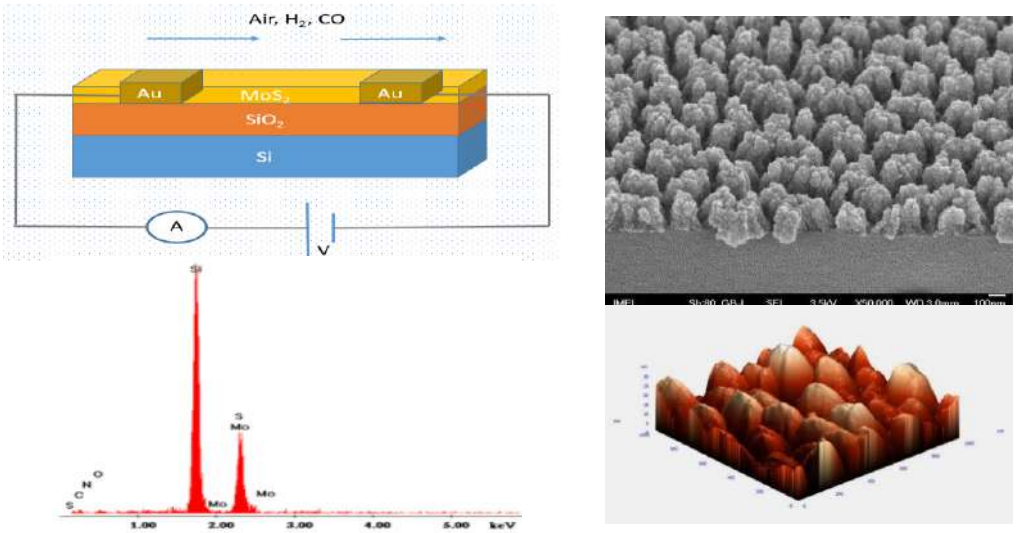


Figure 2. (left) Schematic of the MoS_2 gas sensor and X-ray microanalysis using EDX of the SEM system. (right) SEM and AFM images showing film porosity and columnar structure.

The gas sensing mechanism of the hwMoS_2 thin films likely is likely related to the fact that they consist of vertically stacked layers, comprising covalently bonded Mo-S atoms, with each neighboring layer connected to others by van der Waals forces. The relatively weak van der Waals forces enable the infiltration and diffusion of the target gas molecules between the layers. As a result, the resistance of the MoS_2 film drastically changes during the adsorption and diffusion of the gas molecules within its layers. Results for our MoS_2 sensors are shown here for CO and H_2.

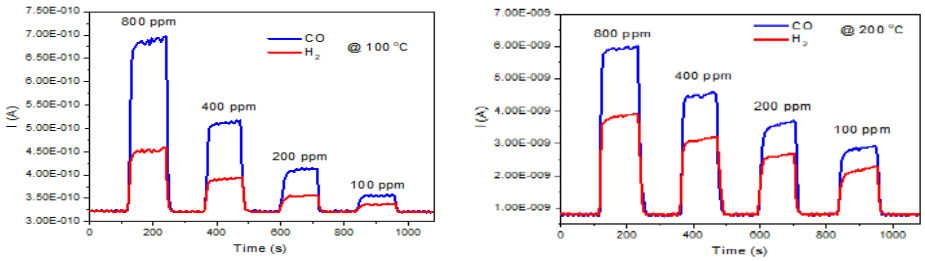
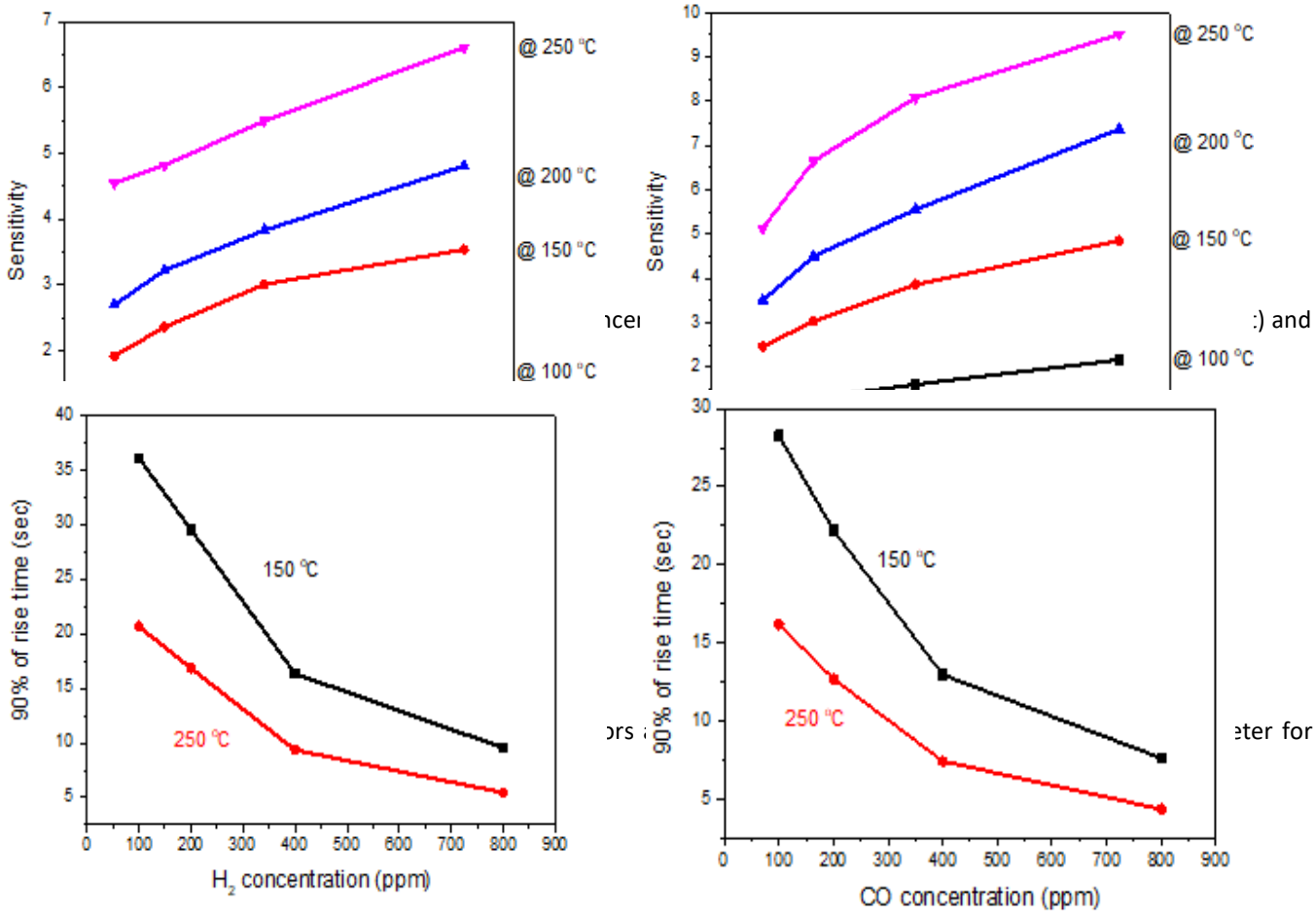


Figure 3. Temporal gas sensor response upon entry and removal of gas at 100°C (left) and 100°C (right).

Figure 3 shows the response-recovery curves, which indicate very small response and recovery times; the rapid rise and fall upon entry and exit of the gas is likely related to the high porosity of the films. These results are highly reproducible, with better sensitivity (ratio of current under test gas over current in synthetic air) observed to CO compared to H_2. The sensitivity increases with temperature and gas concentration, as shown in Figure 4; an almost linear dependence on concentration is observed. Furthermore, the 90% of rise time (time needed for the current to reach 90% of its variation) against gas concentration for CO and H_2 Is shown in Figure 5; it falls with both concentration and temperature, with CO eliciting a faster response compared to H_2. At high gas concentrations it seems that the speed of the current increase becomes less dependent on the nature of the gas and there is a saturation of the rise time. This most likely occurs due to the saturation of all MoS_2 molecules on the surface of the film.



Funding

ESPA (MIS 5047822) 2020-22, 50.050 €.

OUTPUT

Publications in International Journals

1. Papadimitropoulos, G., A. Balliou, D. Davazoglou and D.N. Kouvatsos, "Gas Sensing Investigation of Porous Hot-wire Molybdenum Disulphide Thin Films", Advanced Materials Letters 13 (1), 1689, March 2022. DOI: 10.5185/amlett.2022.011689.
2. Balliou, A., G. Papadimitropoulos, A. Regoutz, D. Davazoglou and D.N. Kouvatsos, "Low-cost high gain MoS_2 FETs from amorphous low mobility film precursors", ACS Applied Electronic Materials 4 (3), 1175-1185, March 2022. DOI: 10.1021/acsaelm.1c01253.

THIN FILMS BY CHEMICAL VAPOR AND ATOMIC LAYER DEPOSITION (CVD-ALD)

Project Leader: Dr. Dimitris Davazoglou

Permanent Research Staff: Dr. Dimitris Davazoglou

Post Docs: Dr. G. Papadimitropoulos, Dr. N. Vourdas

Ph. D. Student: Ch. Petaroudis

Research Collaborators (emeritus or visiting):): Prof. A. Iliadis (Univ. of Mairyland), Prof. N. Konofaos (Univ. of Thessaloniki), Prof. N. Stathopoulos (TEI of Pireaus), Prof. S. Savaidis (TEI of Pireaus), Prof. I. Kostis (TEI of Pireaus), Prof. D. Koudoumas (TEI of Heraklion), Prof. D. Barreca (Padova Univ.), Prof A. Gasparotto (Padova Univ.), Prof. S. Kennou (Univ. of Patras), Prof. A. Chroneos (Univ. of Coventry)

Objectives

The objectives of this group include research and development in the following:

- Development of CVD and ALD processes
- Characterization of CVD and ALD films
- Fabrication and characterization of various devices: Si Solar Cells, Hybrid Organic-Inorganic Solar Cells, Gas Sensors, large area electronics on deposited films.

Activities and Main Results

1. Hot-wire vapor deposited transition metal oxide layers used for the engineering of the energetic structure of the anode of organic photovoltaic devices

This activity is described in detail by the group of P. Argitis and M. Vasilopoulou

2. Atmospheric Pressure Chemical Vapor deposition of SnO_2 films

Depositions are carried out in an automatic APCVD system developed at the CVD-ALD laboratory of the INN shown in Fig. 3 (left image) together with the real-time graphic representation of the process (right image). For the deposition $SnCl_4$ vapors are being used as metallic precursor and water or methanol vapors as oxidizers.

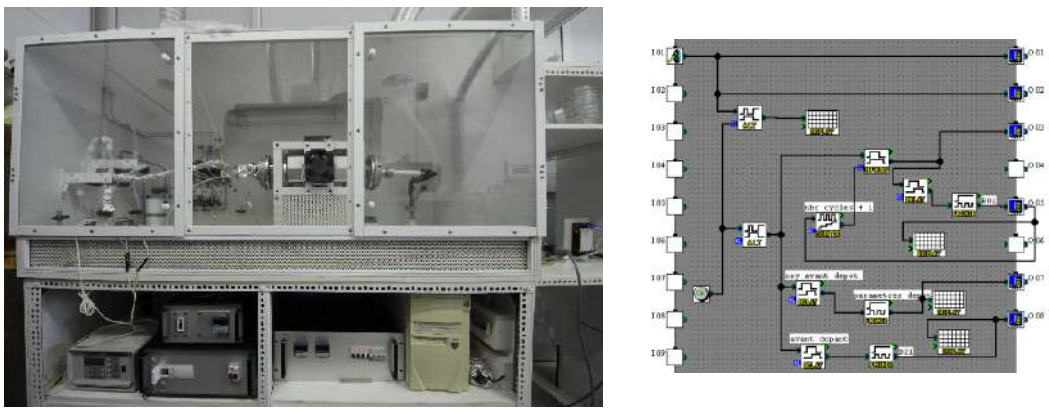


Fig. 1. The APCVD system developed for the deposition of SnO2 films (left) and the graphic representation of the process, as displayed on the screen of the personal computer that controls the process (right).

SnO2 films deposited using methanol vapors exhibit lower resistivity and higher transparency. Scanning electron microscopy images has revealed that all films exhibit a granular form, with grain sizes of 100 and 10 nm for films deposited using methanol and water vapor as oxidizer, respectively (see Fig. 4).

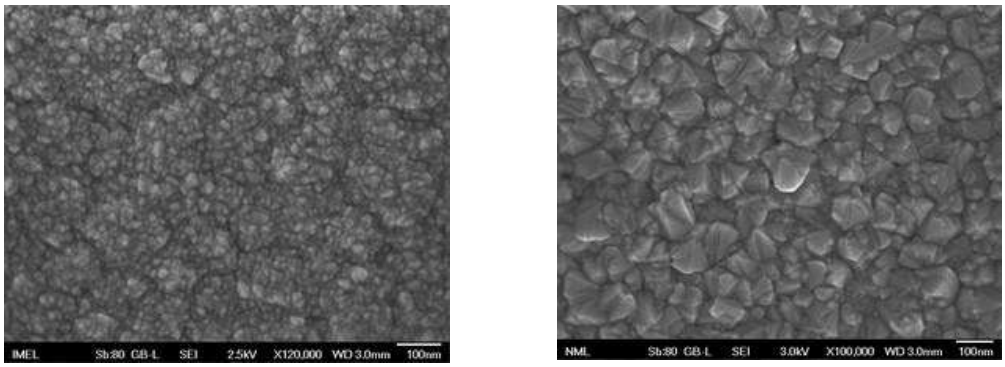


Fig. 2 SEM micrographs taken on two APCVD SnO_2 samples grown at 390 ^oC using water (a) and methanol (b) as oxidizing agents.

3 Electroluminescent displays based on ZnS

Electroluminescent (EL) displays are formed by a “sandwich” of the kind:

Substrate (glass or PET)/SnO_2/ EL material (ZnS doped with various elements)/Dielectric/Metal (Ag or Al).

The patterning may be made either by screen-printing or by lithography and etching or by lift-off. The displays are encapsulated in a usual encapsulation machine. For their operation a power supply of the order of 200 V at a frequency of 400 Hz is needed but the overall power they consume is of the order of some mW so they can be portable. Below such EL displays are shown.

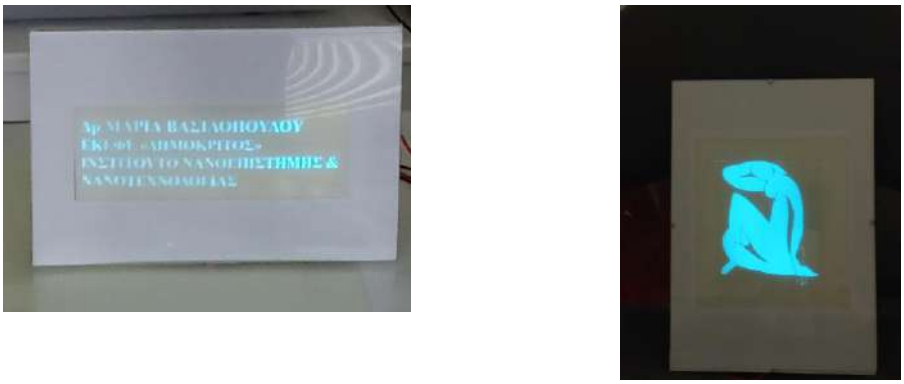


Fig. 3 Electroluminescent (EL) displays

OUTPUT

1. A. Fakharuddin, M. Vasilopoulou, A. Soultati, M. Irfan Haider, J. Briscoe, V. Fotopoulos, D. Di Girolamo, D. Davazoglou, A. Chroneos, A. R. bin Mohd Yusoff, A. Abate, L. Schmidt-Mende, M. K. Nazeeruddin Robust inorganic hole transport materials for organic and perovskite solar cells: insights into materials electronic properties and device performance}, Solar RRL, vol. 5, p 2000555 (2021)
2. P.-P. Filippatos, N. Kelaidis, M. Vasilopoulou, D. Davazoglou, A. Chroneos Structural, Electronic, and Optical Properties of Group 6 Doped Anatase TiO2: A Theoretical Approach Appl. Sci., vol. 11, p. 1657 (2021)
3. M. Vasilopoulou, H. P. Kim, B. N. Carnio, B. Ahvazi, M. Firdaus M. Noh, M. Fairuz Soh, A. Y. Elezzabi, F. Schneider, M. A. Mat Teridi, A. Soultati, P. Argitis, D. Davazoglou, J. Jang, I. Mcculloch, N. Gasparini, A. R. Mohd Yusoff, M. K. Nazeeruddin Free-standing nanopaper electrode for all-printed super-flexible perovskite solar cells Research Square (2021)
4. P.-P. Filippatos, A. Soultati, N. Kelaidis, C. Petaroudis, A.-A. Alivisatou, C. Drivas, S. Kennou, Eleni Agapaki, G. Charalampidis, A. Y., R. bin Mohd, N. N Lathiotakis, A. G Coutsolelos, D. Davazoglou, M. Vasilopoulou, A. Chroneos Preparation of hydrogen, fluorine and chlorine doped and co-doped titanium dioxide photocatalysts: a theoretical and experimental approach, Sci. Rep. Vol. 11, pp 1—12 (2021)
5. P.-P. Filippatos, N. Kelaidis, M. Vasilopoulou, D. Davazoglou, A. Chroneos Impact of boron and indium doping on the structural, electronic and optical properties of SnO2 Sci. Rep., vol. 11, pp 1—11 (2021)
6. C. Petaroudis, I. Kostis, P.-P. Filippatos, A. Chroneos, A. Soultati, M. Vasilopoulou, D. Davazoglou Influence of thermal cycling on the optical and the electrical properties of atmospheric pressure chemical vapor deposited tin oxide films grown using water and methanol vapors as oxidizers Thin Sol. Films, vol. 734, p. 38841 (2021)
7. D. G Manolesou, G. Korompili, D. Davazoglou, A. M Lazaris, D. Schizas, D. Sanoudou, T. Liakakos, C. Tsioufis, T. G Papaioannou Precision Medicine in Aortic Anastomosis: A Numerical and Experimental Study of a Novel Double-Sided Needle}, J. Personalized Medicine, Vol 11, p. 1385 (2021)

Teaching and Training Activities

Name: Dr. Dimitris Davazoglou

Activity Title, Dates/Duration of lectures/training:

1. Lectures on the “Fabrication Processes for Micro and Nanosystems and ICs”, 2013, Master Program on “Microelectronics” (common Program with the UA) and Master Program on Micro and Nanosystems (common Program with NTUA)
   Location/Academic Institute: NSCR “Demokritos”

2. Inter-Institutional Program of Graduate Students: Applied Optoelectronics (common Program with the University of Patras)
   Location/Academic Institute: NSCR “Demokritos”

Funding

ECODROPDENSER, GSRT (120 KEuros).

program 5

Nanochemistry and Nanomaterials

ADVANCED CERAMICS AND COMPOSITES LABORATORY

Project Leader: Dr George Vekinis
Permanent Research Staff: Dr Galina Xanthopoulou
Other Staff: Ms Ioanna Tsirimokou (admin), Mr Diogenis Stratidakis (technical)
Post Docs: Dr Amalia Marinou, Dr Olga Thoda

Research Objectives:

The ACCL carries out research in three main directions relating to the development of advanced ceramics and composites:

1. **Space exploration technologies**
   - materials and structures for the Thermal Protection Shield of spacecraft moving at hypervelocities through the atmosphere
   - sensors for monitoring such atmospheric transverse
2. **Combustion Synthesis of functional nano-structured materials by Solution Combustion Synthesis**
   - **catalysts for CO2 conversion**
   - **catalysts for liquid phase hydrogenation**
   - **Structural studies of SCS catalysts.**
3. **Biopolymer-ceramic composites, based on Polylactic acid**

Activities and Main Results

a) Space Exploration. Further development of the ReGS ("**Re**sistive **G**rid **S**ensor") and ReGS-HF (ReGS High Flux) sensors (figure 1, right) for in-situ monitoring of the recession of ablative composites (Figure 2) used for the thermal protection systems (TPS) used in heat shields of spacecraft when they re-enter the atmosphere at hypervelocities continued with the sensor reaching about TRL5. ArianeGroup (now owner of Airbus Space) funded the further development and testing of the sensor for sample-return missions and funding was offered for 2019-2021. The work is continuing and it is expected that the sensor will be used in a test space mission at the end of 2022. Advanced numerical methods using ANSYS/Fluent (CFD) was used for simulating the ablation of the TPS with and without embedded ReGS sensors.

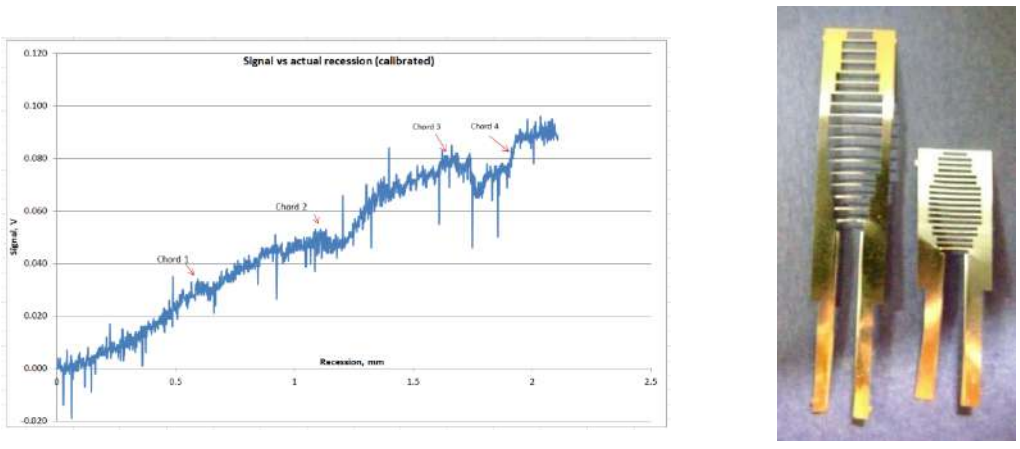


Figure 2. Ablative recession reconstruction using the ReGS-HF sensor for a phenolic-carbon fibre material used for thermal protection of spacecraft at very high thermal flux levels at a close-to- tangential incidence.

b) **Combustion Synthesis of functional nano-structured materials.** Synthesis of new catalytically-active materials is carried out in the liquid phase (Solution Combustion, SCS). Materials under development

include catalysts for hydrogenation, CO_2 reforming of methane, oxidation of CO and soot and many others.

c) **Mechanical behaviour of special structural systems**. Various systems have been studied at room and high temperatures, including 2-layer ceramics as a model material to simulate ancient Roman cooking vessels (Figure 3), microvalves for microfluidics, supporting joints for high-stress fatigue systems and others.

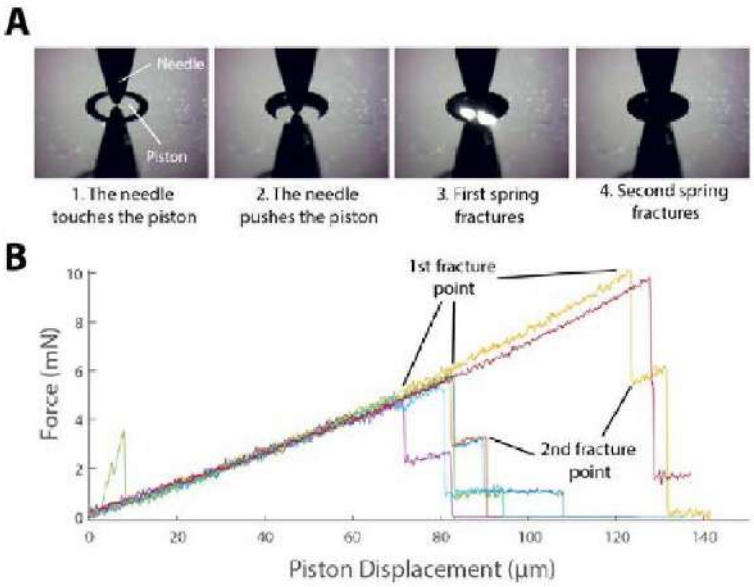


Figure 3. Micromechanical tests (A) on single microvalves in an array (B).

d) **Biopolymer-ceramic composites.** Further studies of poly-lactic acid (PLA) with ceramic and other reinforcements. PLA is the leading material globally for replacing many types of fossil-based polymers and is made from starchy plants including corn and its agricultural waste. To improve its strength and toughness we incorporate ceramic fibres and powders in the PLA matrix. In addition, we are developing a replacement for epoxy-type thermoset binder for CFRP and GFRP using lactic-acid which is polymerized in-situ by mixing two components. The work is being carried out with partial support from the Stavros Niarchos Foundation and the KRIPIS GSRT programme.

e) Technology Transfer of own Technologies and Know-how under contract.

We carry out extensive Technology Transfer activities via various industrial projects under service contracts with European or Greek industries including ArianeGroup (ex Astrium/Airbus, France), TESLA, Siemens, KORRES, 3E, ROKA Refractories, ESI (AramCo), and many others.

A notable Technology Transfer activity is the Development of a High-Flux sensor ReGS-HF for high-flux (>20MW/m^2) thermal protection systems for atmospheric entry of space capsules. This has been requested by Ariane (France) and is based on the ESA-funded research project “ReGS: A resistive grid TPS sensor”. It is expected that the new sensors will be used in a planned ESA/EU 2022 space mission for testing space-capsule re-entry systems and will be flown in Spring 2023 on a flight of the Ariane 6 rocket.

Know-how being transferred includes development and optimisation of mechanical and thermal properties of materials and products, improvement of fire-safety characteristics of chemicals and solids and many other activities.

Funding in 2021: about 50.000 Euro

OUTPUT

Publications in International Journals

1. S. A. Tungatarova, G. Xanthopoulou, G. Vekinis, T. S. Baizhumanova, M. Zhumabek, S. O. Kotov, A. Manabayeva, "Production of Hydrogen-Containing Clean Fuel from Biogas", Chemical Engineering Transactions, vol 88 (2021), 1093-1098, https://doi.org/10.3303/CET2188182
2. G. Xanthopoulou, S. Varitis, M. Zhumabek, K. Karanasios, G. Vekinis, S. A. Tungatarova, T. S. Baizhumanova, "Direct Reduction in Greenhouse Gases by Continuous Dry (CO_2) Reforming of Methane over Ni-Containing SHS Catalysts", Energies, vol 14:19(2021), 6078-6092, https://doi.org/10.3390/en14196078
3. V. Novikov, G. Xanthopoulou, A. Amosov, "Solution combustion synthesis of nanoscale Ni-Cr-O spinels: SCS mechanism, catalysts properties and activity in CO oxidation", International Journal of Self-Propagating High-Temperature Synthesis, 2021, Vol. 30, No. 4, pp. 246–250.
4. M. Zhumabek, G. Xanthopoulou, S. A. Tungatarova, T. S. Baizhumanova, G. Vekinis and D. Yu. Murzin, "Biogas Reforming over Al-Co Catalyst Prepared by Solution Combustion Synthesis Method", Catalysts **2021**, 11, 274, https://doi.org/10.3390/catal11020274

Other publications:

1. M. Zhumabek, G. Xanthopoulou, S. Tungatarova, T. Baizhumanova, D.Augaliev, A. Manabayeva, YSovetbek, R. Sarsenova, S. Kotov, "Ni-Al-Mg-Mn Composite Catalysts for Partial Oxidation of Natural Gas", UDC 542/973.7; 661.961.6, manuscript 1207,18 May 2021.
2. G. Korompili, G. Vekinis, N. Chronis, "A Self-sterilizing, Touch-Activated Microsurface for Preventing Hospital Acquired Infections", MicroTAS 2021 - 25th International Conference on Miniaturized Systems for Chemistry and Life Sciences, 2021, pp. 1255-1256

Educational Activities:

1. G. Vekinis, teaching 15hrs course "Advanced Ceramics" for the MSc programme on "Science and Technology of Materials, May 2021, Aristotelian University of Thessaloniki, Greece
2. G. Vekinis, teaching 39hrs course "Legal Issues and IP", at the Masters of Technology & Innovation Management (*MTIM*) programme of the Technical University of Crete, March 2021.
3. G. Vekinis and G. Xanthopoulou: Supervision of PhD, Masters and Bachelor students for their research projects, various universities in Greece and Kazakhstan
4. G. Xanthopoulou, visiting professor, D.V. Sokolsky Institute of Fuel, Catalysis and electrochemistry, Kazakh Al-Farabi National University, Chemistry department, Almaty, Kazakhstan, co-supervision of 8 PhD students
5. G. Vekinis, Head of the Education Office of NCSR "Demokritos", many activities relating to NCSRD students including the 56th "Demokritos" Summer School, as well as school pupils.

FUNCTIONAL NANOMATERIALS OF ORGANIZED STRUCTURE

Project Leader: Dimitris Tsiourvas

Permanent Research Staff: Zili Sideratou, Michael Arkas

Other Staff (scientific, appointed research fellows, administrative, technical, auxiliary, etc.):

Post Docs: Archontia Kaminari, Aikaterini Panagiotaki

PhD Candidates: Kleopatra Eleftheriou, Kyriaki-Marina Lyra

- **Objectives**

The group of Functional Nanomaterials of Organized Structure is focusing on the development of functional and/or multifunctional nanomaterials, mainly liposomes and dendritic polymers, giving emphasis on their biological applications. It is primarily focused on their synthesis, characterization and evaluation as targeted and controlled release drug delivery systems, or as antibacterial/antifungal agents. The group is also involved in the utilization of functionalized dendritic polymers for the development of advanced functional hybrid organic/inorganic nanoparticles, hybrid or nanocomposite carbon-based materials and nanocomposite xerogels and hydrogels exploiting their potential in several application areas including drug delivery, antimicrobial coatings, 3D tissue engineering, catalysis, and water purification.

Specifically the main research areas are:

- Dendrimers and hyperbranched polymers as targeted drug delivery nanocarriers
- Functional liposomes as drug delivery systems
- Functionalized carbon-based nanomaterials as drug delivery systems or as bioimaging agents
- Functional hyperbranched polymers with antibacterial and anti-fungal properties
- Functional carbon-based nanomaterials as antibacterial agents
- Dendritic polymer-functionalized carbon-based nanostructured coatings
- Biomimetic synthesis of hybrid organic/inorganic nanoparticles
- 3D scaffolds for tissue engineering
- Superhydrophobic and oleophobic nanoparticles
- Functional nanocomposite coatings for marine and aviation applications
- Thermotropic liquid crystals and liquid crystal-nanoparticle composites
- Composite xerogel-dendritic polymer-metal nanoparticle catalysts
- Antimicrobial and antibiofilm hydrogel and xerogel coatings
- Water purification employing dendritic polymers

- **Highlights / main scientific results**

A. Bibliometric Output[1]

	2021
Journal Publications	5
Journals Impact Factor	33.414
International conference proceedings	11
Other conferences	2
Book chapters	2
Citations	291
TOTAL	20

[1] Citations are obtained from Scopus (assessed 31/1/2021).

B. Training and Educational Activities

Lyra Kyriaki Marina, Hybrid nanomaterials based on carbon-based materials modified with functional dendritic polymers: Synthesis, characterization and applications, NTUA, 2021, Research Supervisor: Sideratou Zili

C. Undergraduate Students, Internships, and other activities

During this period 2 undergraduate students were trained in our lab, and M. Arkas was engaged heavily in Training and Educational activities targeted for the public.

Funding

The group participated in both National and International programs. An overview of the group's funding is provided in the following Table. A detailed list of each research grant is also shown below. The total funding during 2021 was 88,3 K€.

	2021
Greek Programmes (NSRF)	28300 €
EC Programmes	60000 €
Other International	
Private Funding	
Other	-
TOTAL	88300 €

Greek Programmes (NSRF)

1. Medical leather manufacturing with the use of hybrid nanoparticles MEDNANOLEAT Contract No: Т6УВП-00081 (2020-2023) Total budget: 372,490€ NCSRD budget: 67,400 €. Scientist in charge: Arkas Michael.

EC Programmes

1. Antimicrobial Nano-Functionalization of Peptide-enriched Silk Fibroin matrices to prevent bone infections and to enhance implant osseointegration in orthopaedics and dentistry", ANNAFIB (EuroNanoMed III-Joint Transnational Call-2018), Contract No: 00058 (2019-2023). Total budget: 943.500 €, NCSRD budget: 200.000 €. Scientist in charge: Sideratou Zili.
2. Development of a bifunctional hierarchically structured zeolite based nano-catalyst using 3D-technology for direct conversion of methane into aromatic hydrocarbons via methane dehydroaromatization, ZEOCAT-3D (H2020-NMBP-ST-IND-2018-2020), Grant Agreement No: 814548 (2019-2022). Total Budget: 6.764.020 €, NCSRD Budget: 423.750 €. Amount of grant for the Team: 80.000 € Scientist in charge: Katsaros Fotios.

Other International Programmes

1. Novel methods to prevent prosthetic joint infection NoMorePJI, funded by The Lundbeck Foundation, grant no. R345-2020-1674 (2021-2024). Total budget: 10.000.000 DKK, NCSRD budget: 20.000 €. Scientist in charge: Arkas Michael.

OUTPUT

Publications in International Journals

1. Papavasiliou A., Deze E.G., Papageorgiou S.K., Sideratou Z., Boukos N., Poulakis E., Philippopoulos C.J., Glisentic A., Van Everbroeck T., Cool P., Katsaros F.K., A hyperbranched polymer synthetic strategy for the efficient fixation of metal species within nanoporous structures: Application in automotive catalysis. Chem. Eng. J. 421, 129496 (2021); DOI:10.1016/j.cej.2021.129496. IF: 13.273; Citations: 3. Q1.
2. Lyra K.-M., Kaminari A., Panagiotaki K. N., Spyrou K., Papageorgiou S., Sakellis E., Katsaros F. K., Sideratou Z., Multi-Walled Carbon Nanotubes Decorated with Guanidinylated Dendritic Molecular Transporters: An Efficient Platform for the Selective Anticancer Activity of Doxorubicin. Pharmaceutics 13, 858 (2021); DOI:10.3390/pharmaceutics13060858. IF: 6.321; Citations: 0. Q1.
3. Kaminari A., Nikoli E., Athanasopoulos A., Sakellis E., Sideratou Z., Tsiourvas D., Engineering Mitochondriotropic Carbon Dots for Targeting Cancer Cells. Pharmaceuticals 14, 932 (2021); DOI: 10.3390/ph14090932. IF: 5.863; Citations: 1. Q1.
4. Douloudi M., Nikoli E., Katsika T., Vardavoulias M., Arkas M., Dendritic Polymers as Promising Additives for the Manufacturing of Hybrid Organoceramic Nanocomposites with Ameliorated Properties Suitable for an Extensive Diversity of Applications. Nanomaterials 11, 19 (2021). DOI: 10.3390/nano11010019. IF: 5.076; Citations: 2. Q1.

5. Vardavoulias M., Gkomoza P., Arkas M., Niakolas D. K., Neophytides S. G., Thermal Spray Multilayer Ceramic Structures with Potential for Solid Oxide Cell Applications. Coatings 11, 682 (2021). https://doi.org/10.3390/coatings11060682. IF: 2.881; Citations: 0. Q2.

Books/Chapters in Books

1. Antoniou M., Sapalidis A., Sideratou Z., Functionalization of Carbon-Based Additives. Chapter 3, in: *Membrane Desalination*: *From Nanoscale to Real World Applications.* A. Sapalidis (Ed.), Boca Raton: CRC Press (2021). DOI: 10.1201/9780429020254-3. \
2. Douloudi M., Nikoli E., Katsika T., Arkas M. Dendritic Polymers for Water Resources Remediation. Chapter 18, in: *Novel Materials for Environmental Remediation Applications*. D. Giannakoudakis, I. Anastopoulos, L. Meili (Ed.) Elsevier, In Press.

International Conferences Presentations (invited, oral, poster)

1. Nikoli E., Douloudi M., Fotopoulou A., Panagiotopoulos R., Arkas. M. Insights into hybrid orthosilicic acid/hyperbranched polyethylene/silver nanoparticle formation and gelation mechanisms, Conference of the European Colloid & Interface Society, 5-10 September 2021 Athens, Greece (poster).
2. Katsika T., Douloudi M., Arkas M. A rare monoclinic mesophase organization Proceedings of the 10th International Conference of the Hellenic Crystallographic Association (HeCrA), 15-17 October 2021, NCSR "Demokritos", Athens, Greece (poster).
3. Douloudi M., Nikoli E., Papageorgiou M., Arkas M., Gomoza P., Vardavoulias M., Kitsou I., Tsetsekou A., López Y., Soto S., Blirup-Plum A., Aalbæk B., Jensen H. E., Jensen L. K., Xerogel Coatings to bone implants prevent development of biofilm formation and severe osteomyelitis Athens Conference on Advances on Chemistry 10-14 March 2021, Athens, Greece (poster).
4. Lyra K.-M., Kaminari A., Panagiotaki K.N., Papavasiliou A., Sideratou Z. Carbon nanodisks decorated with guanidinylated hyperbranched polyethyleneimine derivatives with enhanced antibacterial performance, 35th Conference of the European Colloid and Interface Society (ECIS2021), 5-10 September 2021, Athens, Greece (poster).
5. Kaminari A., Nikoli E., Athanasopoulos A., Sakellis E., Sideratou Z., Tsiourvas D. Mitochondriotropic carbon dots with cell internalization specificity for cancer cells, 35th Conference of the European Colloid and Interface Society (ECIS2021), 5-10 September 2021, Athens, Greece (poster).
6. Tournis I., Tsiourvas D., Sideratou Z., Sapalidis A. Porous PVDF-based Membranes Coated with Superhydrophobic Nanoparticle for efficient Membrane Distillation, 35th Conference of the European Colloid and Interface Society (ECIS2021), 5-10 September 2021, Athens, Greece (poster).
7. Tournis I., Tsiourvas D., Sideratou Z., Sapalidis A. Superhydrophobic Nanoparticle-Coated PVDF-HFP Membranes for Increased Flux and Fouling Resistance Membrane Distillation, 17th International Conference on Environmental Science and Technology (CEST2021), 1 - 4 September 2021, Athens, Greece (poster).
8. Panagiotaki K. N., Papavasiliou A., Stamatakis K., Sideratou Z. Enhanced antimicrobial activity of N-sulfopropylated hyperbranched polyethyleneimine and its effect on photosynthesis, Advanced Nano Materials Conference 2021(ANM2021), 22 – 24 July 2021, Aveiro, Portugal (poster).
9. Tournis I., Sideratou Z., Katsaros F., Sapalidis A. Poly(vinyl alcohol) nanocomposite membranes with functionalized carbon discs for water treatment applications, Euromembrane, 28 November-02 December 2021, Copenhagen Denmark (poster).

National Conferences Presentations (invited, oral, poster)

1. Tournis I., Sapalidis A., Sideratou Z., Katsaros F. Dendritic polymer functionalized carbon nanodiscs/poly(vinyl alcohol) nanocomposite membranes for water treatment applications, Athens Conference on Advances in Chemistry, 10-14 March 2021, Athens, Greece (poster).
2. Lyra K.-M., Panagiotaki K. N., Papavasiliou A., Sideratou Z. Water-soluble multi-walled carbon nanotubes decorated with guanidinylated hyperbranched poly(ethyleneimine) derivatives with enhanced antibacterial performance, Athens Conference on Advances in Chemistry, 10-14 March 2021, Athens, Greece (poster).
3. Loukopoulos S., Sakellis E., Katsaros F., Likodimos V. Composite MoS_2-TiO_2 photonic crystals for photocatalytic applications, XXXV Panhellenic Conference on Solid State Physics and Materials Science, 26-29 September 2021, Athens, Greece (poster).

4. Tournis I., Tsiourvas D., Sideratou Z., Sapalidis A. Coating Porous PVDF-HFP Membranes with Superhydrophobic Nanoparticles improves Membrane Distillation performance, 13th Hellenic Polymer Society International Conference, 12-16 December 2021, Athens, Greece (poster).

Teaching and Training Activities

1. Michael Arkas
BASF Kids' Lab/September-November/Aghia Paraskevi "NCSR Demokritos"
2. Michael Arkas
56o Summer School, 12-16 July/ Aghia Paraskevi "NCSR Demokritos"
3. Michael Arkas
Liquid Crystal Crystallography/ 6 June/Aghia Paraskevi "NCSR Demokritos"

Undergraduate Theses and Internships completed in 2021
1.
Name: Anna Fotopoulou
Dissertation Title: Catalytic Xerogel Coatings from Silica-Hyperbranched Poly(ethylene imine)-Biomimetically Reduced Nanoparticles for Stainless Steel with micropores Induced by Thermal Spray
Research Supervisor at NCSR: Michael Arkas
University where the Thesis was presented: University of Ioannina
2.
Name: Rafael Panagiotopoulos
Dissertation Title: Catalytic Xerogel Coatings from Silica-Hyperbranched Poly(ethylene imine)-Biomimetically Reduced Nanoparticles for Stainless Steel with micropores Induced by Thermal Spray
Research Supervisor at NCSR: Michael Arkas
University where the Thesis was presented: National Technical University of Athens

Conference / Workshop Organisation

- Dimitris Tsiourvas: Organizing committee member, 35th Conference of the European Colloid and Interface Society, ECIS 2021, Athens, Greece, 5-10 September 2021.

MATERIALS & MEMBRANES FOR ENVIRONMENTAL SEPARATIONS LABORATORY

Group Leader: Theodore Steriotis

Researchers: Fotios Katsaros, Georgios Romanos, Konstantinos Stefanopoulos, Sergios Papageorgiou, Evangelos Favvas, Andreas Sapalidis, Anastasios Gotzias, Chrysoula Athanasekou, Georgios Pilatos, Evangelos Kouvelos

Research Associates: Aggeliki Papavasiliou, Diana Elena Baciu, Dimitra Giasafaki, Christina Mitzithra, Charitomeni Veziri, Dionysios Karoussos, Evangelos Angelopoulos, Ioannis Bratsos, Antigoni Kalamara, Maria-Malvina Stathouraki, Athanassios Nikolakopoulos, Panagiotis Krokidas, Iosif Scoullos

Technical/Administrative Staff: Ipek Moutafis, Aikaterina Pappa

PhD Candidates: Georgios Theodorakopoulos, Christos Tampaxis, Lamprini Boutsika, Fillipo Peru, Evangelia Choleva, Eudoxia Galata, Eleni Thomou, Leonidas Spyrogiannopoulos, Ioannis Tournis, Tallarou Chrysoula.

MSc Students: Konstantinos Mansouris

Undergraduate Students: Xristos Papanagiotou, Konstantinos Karaoulis, Maria Mamai

Objectives

The main research activities focus on the development, physicochemical characterisation and modelling of nanoporous materials, membranes and catalytic systems and their applications in advanced processes of high environmental, health, energy and industrial interest.

The research group is classified as a European leader in the S&T field of adsorption, diffusion and scattering (neutrons and X-rays) and has developed novel pore structure characterisation techniques based on application of combined adsorption/scattering or adsorption/permeability experiments.

A significant part of the activities relates to the simulation of materials and processes via Molecular Dynamics and Monte Carlo techniques. Furthermore, substantial work pertains to the development of special codes for post processing of adsorption isotherms as well as machine learning models for fast screening of materials for gas storage and/or separation processes.

Highlights / main scientific results

- **Synthesis of nanoporous materials, membranes and catalysts.**

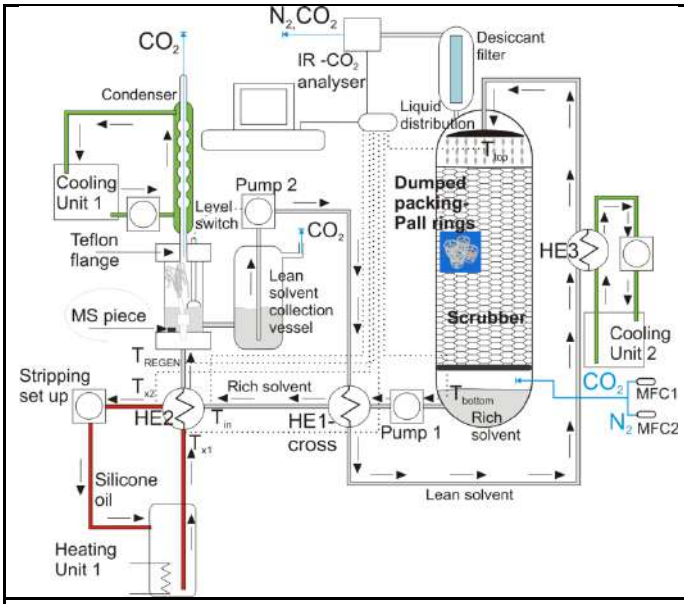
- Development and characterization of nanostructured materials for gas storage (MOFs/ZIFs, metal hydrides, metal doped nanostructured carbons and pore infiltrated complex hydrides).
- Development of ordered mesoporous silica and carbon nanoparticles for controlled release and drug delivery applications.
- Synthesis and characterisation of supported metal nanoparticles for heterogeneous catalytic applications including: deNOx, CO oxidation, CH_4, WGS reaction and HC reforming.
- Synthesis of silane modified ionic liquids and development of hybrid nanocomposite membranes and materials (Ionic Liquids / ceramic or carbon nanocomposites) for CO_2 capture and separation.
- Development of polymer/carbon and polymer/inorganic nano-composites with improved antifouling /fouling release and barrier properties, for packaging and coatings applications.
- Modification and utilisation of natural algal products and processing by-products (i.e. polysaccharides, alginic acids etc.) for the development of porous adsorbents and membranes for environmental applications and pollutant separations (i.e. heavy metal and pesticide removal from water streams, waste and brackish water treatment etc.)

- Development of multi-walled and single-walled carbon nanotubes as well as graphene oxides and graphene for diverse nanotechnology applications (e.g., desalination and gas separation membranes, conductive inks, nanocomposites with improved mechanical properties, catalysis).
- Synthesis, modification and characterisation of (e.g., carbon, AlPO4-5, ZIF, MOF) nanocomposite, mixed matrix and zeolite membranes as well as single and multi-layered hollow-fibres for gas separations and water treatment.

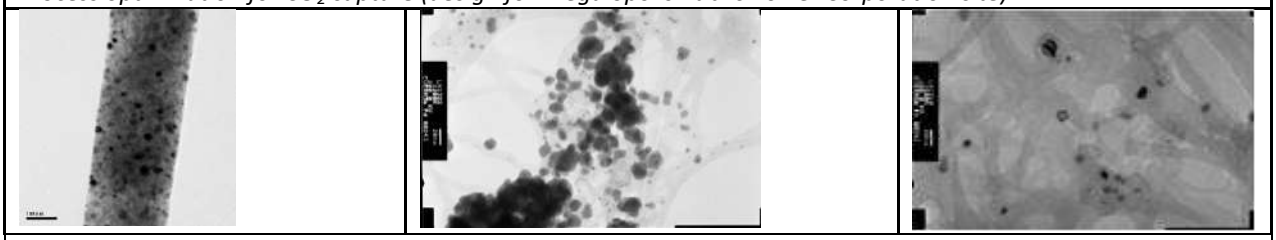
- **Pore Structure Analysis & Characterisation - Performance evaluation.**
- Pore size distribution, surface area analysis, pore volume and pore connectivity by applying techniques such as: nitrogen and mercury porosimetry, absolute and relativity gas and gas vapours permeability (single and multi-phase), adsorption in conjunction with neutron scattering experiments.
- Microscopy (Scanning Electron-Field Emission, Atomic Force)
- Spectroscopy (HPLC, GC, MS, EDAX).
- Development of techniques for characterising the surface chemistry of porous materials (adsorption /desorption of probe molecules, multiple base titrations, temperature programmed desorption – mass spectroscopy (TPD-MS).
- Characterisation, evaluation and performance validation of porous materials, membranes and catalysts under the framework of various environmental and industrial applications (separation of gaseous pollutants, gas-liquid-vapour permeability-selectivity, reverse osmosis, membrane distillation, photocatalysis, nano and ultra-filtration, heavy metal adsorption, control drug release and transcutaneous dosing systems, other biotechnological applications etc.).

- **Modelling.**
- Grand Canonical Monte Carlo (GCMC) and Molecular Dynamics (MD) methodologies for computational studies of adsorption and diffusion in porous materials and membranes.
- MD studies on the interaction of carbon nanostructures with lipid bilayers
- Design of carbon - based molecular models for ultrafiltration and water treatment.
- Study of water diffusion in Carbon Nanotubes via umbrella sampling MD.
- Post process practices on simulated adsorption isotherms.
- Free energy calculations using molecular dynamics.
- Mass transfer simulations in porous media by continuous and molecular level approaches.
- Machine learning approaches for the prediction of equilibrium and transport properties of porous solids and membranes.
- Process engineering (gPROMS, ASPEN) for gas separations based on either pressure swing adsorption or membranes as well as solar limestone calcination (cement production/CO_2 capture).

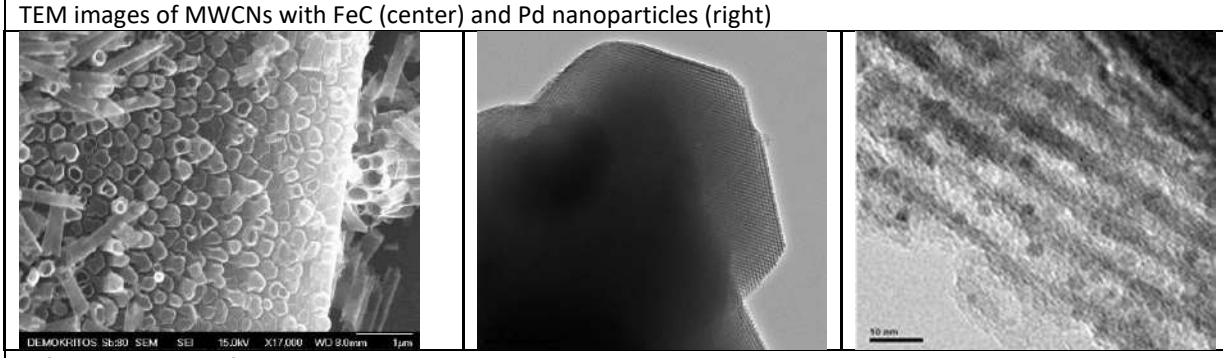
- **Applications with Industrial interest.**
- Gas Storage and separations (H_2, CH_4, CO_2, etc.)
- Membrane technology in gas (treatment and exploitation of Natural Gas and the gas streams of Oil refineries) and liquid phases (steviols separation and purification)
- Effective and sustainable water treatment processes (Nanofiltration, Membrane distillation, RO, Desalination, photocatalytic treatment).
- Smart nanocomposites (e.g., antibacterial, super-hydrophobic, conductive etc.) for specialty paints, coatings and inks.
- Process intensification (3D-printed zeolitic substrates for bioreactors, Methane dehydroaromatisation –MDA- to hydrogen and benzene.)
- Nanoporous drug carriers with controlled release properties
- Minimisation/replacement of CRM (in catalysis)
- Application of renewable/efficient energy resources in industrial applications (Solarization of cement production processes, production of Blue and Green-H2 production from fossil, CO2 conversion to fine chemicals).



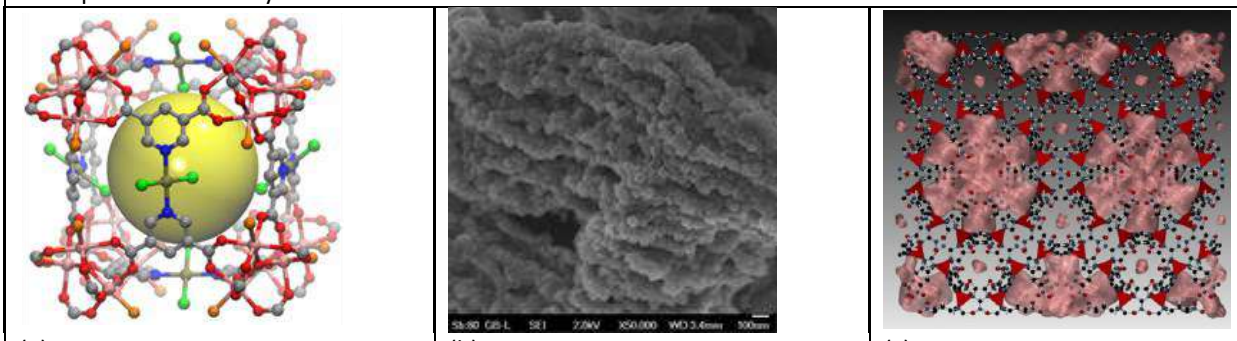
Process optimization for CO_2 capture (design for Megalopolis Public Power Corporation site)



TEM images of MWCNs with FeC (center) and Pd nanoparticles (right)



Left: SEM images of MWCTNs developed on porous substrates, Center: Order mesoporous aluminosilicate. Right: Pd doped SBA-15 catalyst



(a) (b) (c)

(a) Structure of an In-soc-MOF with Pd baring linkers (b) ZIF-8 decorated single graphene sheets and (c) GCMC simulation of Ar sorption on ZIF-8

Funding

1. H2020, IA, SPIRE-07-2020, Grant agreement: 958554. intelWATT - Intelligent Water Treatment Technologies for water preservation combined with simultaneous energy production and material recovery in energy intensive industries. 01/10/2020-31/03/2024, Total budget: € 12,515,256.25, NCSRD budget: 857,500€
2. H2020, RIA, Marie Skłodowska-Curie, Grant agreement: 894585. SmartDeZIgn - Smart Design Tool of High Performing ZIF Membranes for Important CO2-Related Separations. 01/05/2020 – 30/04/2022. NCSRD Budget: 153,085€.
3. H2020, RIA, MG-BG-01-2018, Grant agreement: 824348. ENDURUNS - Development and demonstration of a long-endurance sea surveying autonomous unmanned vehicle with gliding capability powered by hydrogen fuel cell, 01/11/2018- 31/10/2022. Total Budget: 8,747,765€, NCSRD budget: 396,250€
4. H2020, NMBP-ST-IND-2018-2020, Grant agreement: 814548. ZEOCAT-3D - Development of a bifunctional hierarchically structured zeolite based nano-catalyst using 3D-technology for direct conversion of methane into aromatic hydrocarbons via methane dehydroaromatization, 01/04/2019- 30/09/2022. Total Budget: 6,764,020 € NCSRD budget: 423,750 €
5. H2020-FETOPEN, Grant agreement: 828922. FRINGE Fluorescence and Reactive oxygen Intermediates by Neutron Generated electronic Excitation as a foundation for radically new cancer therapies. 01/05/2019-30/04/2024. Total Budget: 3,979,485 €, NCSRD budget: 719,687.50 €
6. CIRA-2019-002. Maximizing Recovery in CO2-EOR by a Holistic, Bottom-Up, and Multi-Scale Experimental and Simulation Approach involving Machine Learning Optimization, 01/07/2019-30/06/2022. Total Budget: 618,540.31€, NCSRD budget: 22,000 €
7. ERANETMED 2-72-357, IDEA - Development of a solar powered, zero liquid discharge Integrated DEsalination MembrAne system to address the needs for water of the Mediterranean region. 01/09/2017 – 31/07/2022 Total budget: 1,044,830, NCSRD budget 100,000 €.
8. Greek-German Bilateral Research and Innovation Cooperation. GG-CO2 - CO2 separations by using mixed matrix, based on nano-carbon materials, membranes. 29/05/2018 - 28/11/2021. Total Budget: 882,000 €, NCSRD budget: 277,700 €.
9. Operational Program Competitiveness under the call Fishery and Sea, Project code: MIS 5030665 - Development of innovative non biocidal antifouling paints for aquaculture applications, 12/04/2019-11/04/2022. Total Budget: 515,628 €, NCSRD Budget: 226,271€.
10. Operational Program Competitiveness - Action: Support of new researchers-II, Human Resources Development, Education and Lifelong Learning 2014–2020, MIS 5047821, “Development of nanoparticle-based catalytic membranes for NOx reduction”, 06/04/2020 – 05/11/2022, Budget: 50,050€.
11. Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE. Project code: T1EDK-02093GRAPHEIN - Development of water based conductive inks based on graphene for gravure and flexography printing, 09/07/2018 – 08/07/2022, Total Budget: 742,441 €, NCSRD Budget 176,000 €.
12. Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE, project code: T1EDK-01582. SOLCEMENT - Use of concentrated SOLar radiation in the CEMENT industry: Design of a suitable, integrated and low carbon footprint process for limestone calcination, 04/07/2018 – 03/12/2022, Total Budget: 900,841 €, NCSRD Budget 207,935 €.
13. Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE, project code: T1EDK-02992. PUREHY - Development of a biogas reformer using stand-alone membrane systems for the production and recovery of high purity hydrogen, 28/06/2018 – 27/12/2022. Total Budget: 851,578 €, NCSRD Budget 280,629 €.
14. Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE, project code: T1EDK-00770. PUREGAS - Application of Novel Porous Materials in Industrially Relevant Gas Separation/Purification Processes, 31/07/2018 – 30/10/2022. Total Budget: 857,787 €, NCSRD Budget 309,564 €.

15. Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE. Project code: T1ΕΔΚ-00235 TasteSTEVIA - Holistic Approach along the production cycle of Stevia Rebaudiana plant cultivated in Greece, via combined application of innovative methods of Precision Agriculture and bitter aftertaste removal techniques, 31/7/2018- 28/2/2022. NCSRD subcontractor: 93,000€.
16. Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE. Project code: T2ΕΔΚ-00362 3D-BIOFILM- 3D printing technology of bioreactor material, 12/05/2020 - 12/11/2022. NCSRD subcontractor: 35,000€.
17. Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE. Project code: T2ΕΔΚ-04043 - PHOTOsan - Development and Integration of a Rehabilitation System for Anaerobic Waste Digestion Plants using Photocatalytic Membranes, 12/05/2020 - 12/11/2022. NCSRD subcontractor: 50,000€.
18. Industrial Research Fellowship Scheme funded by Stavros Niarchos Foundation and Industry. Adjunct Researcher: Dr. E.S. Angelopoulos, 12/06/2017 – 11/06/2021. Budget 122,000 €.
19. Industrial Research Fellowship Scheme co-funded by Stavros Niarchos Foundation and Industry. PhD student: Ms. E. Choleva, Partner in collaboration with Q-Lab, 01/11/2017 – 31/10/2021 Budget 47,600 €.

OUTPUT

Publications in International Journals

1. Lyra K.-M., Kaminari A., Panagiotaki K.N., Spyrou K., Papageorgiou S., Sakellis E., Katsaros F.K., Sideratou Z. Multi-Walled Carbon Nanotubes Decorated with Guanidinylated Dendritic Molecular Transporters: An Efficient Platform for the Selective Anticancer Activity of Doxorubicin, *Pharmaceutics* **13**, Art No 858 (2021) DOI: https://doi.org/10.3390/pharmaceutics13060858. **IF: 6.321, Citations: 0**
2. Gotzias, A. Binding free energy calculations of bilayer graphenes using molecular dynamics. Journal of Chemical Information and Modeling, 61(3):1164–1171, 2021**. IF 4.956 cited By 1**
3. Gotzias, A., E. Tocci, and A. Sapalidis. On the consistency of the exfoliation free energy of graphenes by molecular simulations. International Journal of Molecular Sciences, 22(15), 2021**. IF 5.924 cited By 0**
4. Papavasiliou A., Deze E.G., Papageorgiou S.K., Sideratou Z., Boukos N., Poulakis E., Philippopoulos C.J., Glisenti A., Van Everbroeck T., Cool P., Katsaros F.K., A hyperbranched polymer synthetic strategy for the efficient fixation of metal species within nanoporous structures: Application in automotive catalysis, *Chemical Engineering Journal* **421,** Article number 129496 (2021). DOI: https://doi.org/10.1016/j.cej.2021.129496. **IF**: **13.273, Citations: 3**
5. Theodorakopoulos G.V., Romanos G.E., Katsaros F.K., Papageorgiou S.K., Kontos A.G., Spyrou K., Beazi-Katsioti M., Falaras P., Structuring efficient photocatalysts into bespoke fiber shaped systems for applied water treatment, *Chemosphere* **277,** Article number 130253 (2021). DOI: https://doi.org/10.1016/j.chemosphere.2021.130253. **IF**: **7.086, Citations: 1**
6. Esser, T., Wolf, T., Schubert, T., Benra, J., Forero, S., Maistros, G., Barbe, S., Theodorakopoulos, G.V., Karousos, D.S., Sapalidis A.A., Favvas, E.P., CNTs based cellulose acetate membranes: an optimization study of the filler materials dispersion method and its investigation by using impedance spectroscopy, Nanomaterials 11(2), 280 (2021). DOI: https://doi.org/10.3390/nano11020280 **IF: 5.076, Citations: 1**
7. Metaxa, Z.S., Tolkou, A., Efstathiou, S., Rahdar, A., Favvas, E.P., Mitropoulos, A.C., Kyzas, G.Z., Nanomaterials in cementitious composites: An update, Molecules 26, 1430 (2021). DOI: https://doi.org/10.3390/molecules26051430 **IF: 4.411**, **Citations: 4**
8. Gotzias A., Sapalidis A., Favvas E. Hydrogen Adsorption Simulations in Isomorphous Borohydride and Imidazolate Frameworks: Evaluations using Interpolation, *Int. J. Hydrog. Energy* **46**, 19778–19787 (2021). https://doi.org/10.1016/j.ijhydene.2021.02.212 **IF: 5.816, Citations: 1**
9. Kummar K.V., Ramisetty K.A., Devi K.R., Krishna G.R, Heffernan, C., Stewart, A., Guo, J., Gadipelli, S., Brett, D., Favvas, E.P., Rasmuson, A., Pure curcumin spherulites from impure solution via non-classical crystallization, *ACS Omega* 6, 23884–23900 (2021). https://doi.org/10.1021/acsomega.1c02794 **IF: 3.512, Citations: 4**
10. Favvas E.P., Kyzas G.Z., Efthimiadou E.K., Mitropoulos A.Ch. Production methods of Bulk NBs, stability mechanisms and applications, (Invited Review Article) *Curr. Opin. Colloid Interface Sci.* **54**, 101455 (2021). https://doi.org/10.1016/j.cocis.2021.101455. **IF: 6.05 , Citations: 8**
11. Singh S., Varghese A. M., Reddy K. S. K., Romanos G. E., Karanikolos G.N., Polysulfone Mixed-Matrix Membranes Comprising Poly(ethylene glycol)-Grafted Carbon Nanotubes: Mechanical Properties and CO2 Separation

Performance, *Ind. Eng. Chem. Res.* **60** (30), 11289-11308 (2021). DOI: https://doi.org/10.1021/acs.iecr.1c02040, **IF: 3.72, Citations: 3**

12. Thomou E., Sakavitsi V, Angeli G.K., Spyrou K., Froudas K.G., Diamanti E.K., Romanos G.E., Karanikolos G.N., Trikalitis P.N., Gournis D., Rudolf P., A diamino-functionalized silsesquioxane pillared graphene oxide for CO2 capture, *RSC Advances* **11** (23), 13743-13750 (2021). DOI: https://doi.org/10.1039/d1ra00777g, **IF: 3.245 Citations: 0**
13. Karanikolos G.N., Romanos G.E., Vega L.F. Editorial: Chemical Modification of Adsorbents for Enhanced Carbon Capture Performance, *Frontiers in Chemistry* **9,** art_number 657669 (2021). DOI: https://doi.org/10.3389/fchem.2021.657669, **IF: 5.221, Citations: 1**
14. Athanasekou C.P., Pedrosa M.F., Silva A.M.T., Psycharis V.P., Romanos G.E. Mild temperature-gas separation performance of graphene oxide membranes for extended period: micropore to meso- and macropore readjustments and the fate of membranes under the influence of dynamic graphene oxide changes, *Chemical Engineering Journal Advances* **5,** 100066, (2021). DOI: https://doi.org/10.1016/j.ceja.2020.100066, **IF: N/A, Citations: 3**
15. Mamai M., Giasafaki D., Salvanou E.-A., Charalambopoulou G., Steriotis T., Bouziotis P., Biodistribution of mesoporous carbon nanoparticles via technetium-99m radiolabelling after oral administration to mice, *Nanomaterials* **11**, 3260 (2021). DOI: https://doi.org/10.3390/nano11123260. **IF: 4.921, Citations: 0**
16. Björk E.M., Atakan A., Wu P.-H., Bari A., Pontremoli C., Zheng K., Giasafaki D., Iviglia G., Torre E., Cassinelli C., Morra M., Steriotis T., Charalambopoulou G., Boccaccini A.R., Fiorilli S., Vitale-Brovarone C., Robertsson F., Odén M., A shelf-life study of silica- and carbon-based mesoporous materials, *Journal of Industrial and Engineering Chemistry* **101**, 205-213 (2021). DOI: https://doi.org/10.1016/j.jiec.2021.06.011. **IF: 5.278, Citations: 2**
17. Christoforidou, T., Giasafaki, D., Andriotis, E.G., Bouropoulos N., Theodoroula N.F., Vizirianakis I.S., Steriotis T., Charalambopoulou, G., Fatouros, D.G., Oral drug delivery systems based on ordered mesoporous silica nanoparticles for modulating the release of aprepitant, *International Journal of Molecular Sciences* **22**(4), 1896 (2021). DOI: https://doi.org/10.3390/ijms22041896. **IF: 5.923, Citations: 7**
18. Kostoglou, N., Liao, C.-W., Wang, C.-Y., Kondo J.N., Tampaxis C., Steriotis T., Giannakopoulos K., Kontos A.G., Hinder S., Baker M., Bousser E., Matthews A., Rebholz, C., Mitterer, C., Effect of Pt nanoparticle decoration on the H2 storage performance of plasma-derived nanoporous graphene, *Carbon* **171**, 294-305 (2021). DOI: https://doi.org/10.1016/j.carbon.2020.08.061. **IF: 9.594, Citations: 4**
19. Giannakopoulou T., Pilatos G., Todorova N., Boukos N., Vaimakis T., Karatasios I., Trapalis C., Effect of processing temperature on growing bamboo-like carbon nanotubes by chemical vapor deposition, *Materials Today Chemistry* **19**, 100388 (2021). DOI: https://doi.org/10.1016/j.mtchem.2020.100388. **IF: 8.301**

Papers in Refereed Conference Proceedings

1. Deze, E.G., Bareka, M.D., Karousos, D.S., Sapalidis, A.A., Favvas, E.P., Mesoporous silica based copper catalytic materials for potential deNOx application: synthesis and characterization, Materials Today: Proceedings, 2021, https://doi.org/10.1016/j.matpr.2021.02.548. **IF: 1.24**, Citations: -
2. Deze, E.G., Cuenca E., Násner A., Iakovlev M, Sideri S., Sapalidis A. Nanocellulose enriched mortars: Evaluation of nanocellulose properties affecting microstructure, strength and development of mixing protocols, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2021.09.511
3. Bhoria N. Pokhrel J., Anastasiou S., Reddy K.S.K., Romanos G., Karanikolos G.N. Composite porous nanostructures as multi-action adsorbents and membrane fillers for carbon dioxide separation: Comparative performance of metal organic framework – graphene oxide hybrids, *Materials Today: Proceedings* **37,** 4044-4048 (2021). DOI: https://doi.org/10.1016/j.matpr.2020.07.466, **IF: 1.24, Citations: 3**

Books/Chapters in Books

1. Favvas E.P., Kaldis S.P., He X. Chapter 6: "Carbon membranes for natural gas sweetening", in book entitled "Carbon Dioxide Separation/Capture by Using Membranes", Eds: X. He and I. Kumakiri, 1st Edition, pp. 79–113, ISBN 9781138333376, CRC publisher, 2021, Abington, UK.

Other type of publications

International and national Conferences Presentations (invited, oral, poster)

1. Tournis I., Sideratou Z., Katsaros F., Sapalidis A. Poly(vinyl alcohol) nanocomposite membranes with functionalized carbon discs for water treatment applications, Euromembrane, 28 November – 2 December 2021, Copenhagen, Denmark (poster)
2. Tournis I., Tsiourvas D., Sideratou Z., Sapalidis A. Superhydrophobic Nanoparticle-Coated Porous PVDF Membranes for Efficient Membrane Distillation Coating Porous PVDF Membranes with Superhydrophobic Nanoparticle enhances Membrane Distillation performance Porous PVDF-based Membranes Coated with Superhydrophobic Nanoparticle for efficient Membrane Distillation. 35th ECIS 2021 - Conference of the European Colloid & Interface Society 5-10 September 2021, Athens – Greece
3. Scoullos I.M., Kouvelos E., Sapalidis A. The effect of membrane hydrophobicity on biofouling. International Conference On Water And Energy ICWE'21 25-27 May 2021, Chlef, Algeria - online (Oral)
4. Thomou E., Diamanti E., Enotiadis A., Spyrou K., Mitsari E., Boutsika L., Sapalidis A., Alfonsín E., De Luca O., Gournis D., Rudolf P., "New Porous Heterostructures Based on Organo-Modified Graphene Oxide for CO2 Capture" 15th International conference on materials chemistry (MC15) 12 - 15 July 2021 – online
5. Tournis I., Lyra M-K., Katsaros F.K, Sideratou Z., Sapalidis A. Nanocomposite membranes of poly(vinyl alcohol) with functionalized carbon nanodiscs for water treatment applications. Advanced Nano Materials. 17th Edition ANM2021 (www.advanced-nanomaterials-conference.com), 22-24 July 2021, Aveiro, Portugal
6. Tournis I., Sapalidis A., Sideratou Z., Katsaros F. "Dendritic polymer functionalized carbon nanodiscs/poly(vinyl alcohol) nanocomposite membranes for water treatment applications", Athens Conference on Advances in Chemistry (acac2020), online March 10 to 14, 2021.
7. Theodorakopoulos G., Katsaros F., Papageorgiou S., Romanos G. Kinetics study of the MO adsorption and photocatalytic degradation using an engineering efficient HF photocatalyst, 17th International Conference on Environmental Science and Technology, 1-4 September 2021, Athens, Greece (oral)
8. Veziri C.M., Romanos G.E., Kouvelos E., Katsaros F. Synthesis of hierarchical zeolites structures for methane valorization", Advanced Nanomaterials Conference (ANM2021), 22-24 July, Aveiro, Portugal (Oral).
9. Tournis I., Tsiourvas D. Sideratou Z. and Sapalidis A. "Superhydrophobic Nanoparticle-Coated PVDF-HFP Membranes for Increased Flux and Fouling Resistance Membrane Distillation" 17th International Conference on Environmental Science and Technology, CEST2021, 1-4 September 2021, Athens, Greece
10. Mansouris, K., Theodorakopoulos, G., Karousos, D., Sapalidis, A.A., Efthimiadou, E., Favvas, E.P. Ternary phase diagrams of polyimide/solvent/non-solvent systems. Athens Conference on Advances in Chemistry (ACAC2020), 10 -14 March, 2021, Athens, Greece (oral).
11. Pahoulis, M., Sapalidis, A.A., Kouvelos, E.P., Mitropoulos, A.Ch., Kyzas, G.K., Favvas, E.P. Study of Cu+2 and dyes removal by palygorskite in batch and continuous flow processes, International conference on water and energy (ICWE'2021), 25–27 May 2021, Chlef, Algeria (oral).
12. Theodorakopoulos, G.V., Karousos, D.S., Sapalidis, A.A., Forero, S., Schubert, T., Favvas, E.P. Pebax/Polyimide dual-layer hollow fiber membranes for gas separation applications, Euromembrane 2021, 28 November – 02 December, Copenhagen, Denmark (poster).
13. Favvas, E.P., Sapalidis, A.A., Kouvelos, E.P., Kyzas, G.K., Mitropoulos, A.C. Nanobubbles' effect on Desalination via Direct Contact Membrane Distillation, Euromembrane 2021, 28 November – 02 December, Copenhagen, Denmark (poster).
14. Theodorakopoulos, G.V., Karousos, D.S., Sapalidis, A.A., Forero, S., Schubert, T., Favvas, E.P. Towards green chemistry: comparative study of effective composite hollow fiber membranes preparation for CO2/CH4 separation, Euromembrane 2021, 28 November-02 December, 2021, Copenhagen, Denmark (poster).
15. Kalamara, A., Grigalavicius, M., Savva, M.I., Vasilopoulou, T., Lagoyannis, A., Stefanopoulos, K.L., Theodossiou, T., Stamatelatos, I.E. Fast Neutron Beam Dosimetry Characterization for Biomedical Sample Irradiations. 29th Symposium of the Hellenic Nuclear Physics Society (HNPS-2021), 24-25 September 2021, NCSR Demokritos, Athens, Greece.
16. Stefanopoulos, K.L. Neutron Scattering from Porous Materials and Confined Fluids: Applications to CO2 Sequestration and Oil Recovery. 29th Symposium of the Hellenic Nuclear Physics Society (HNPS-2021), 24-25 September 2021, NCSR Demokritos, Athens, Greece.
17. Arfanis, K. M., Theodorakopoulos, G., Anagnostopoulos, C., Georgaki, E., Liapis, K., Romanos, Em. G., Markellou, E. and Falaras, P. Photocatalytic Removal of Pesticides Present in Agro-industrial Water Effluents. 17th

International Conference on Environmental Science and Technology (CEST2021), Athens, Greece, 1 to 4 September 2021,

18. Ibrahim, I., Belessiotis, G. V., Kaltzoglou, A., Katsaros, F., Salama, T. M., Falaras, P. Silver decorated TiO2/g-C3N4 nanocomposites for photocatalytic elimination of water pollutants under UV and artificial solar light. 17th International Conference on Environmental Science and Technology, (CEST2021), Athens, Greece, 1 to 4 September 2021, paper accepted for presentation.
19. Theodorakopoulos, G. V., Katsaros, F. K., Sapalidis, A. A., Papageorgiou, S. K., Romanos, G. Em. Engineering efficient photocatalysts tailored bead shaped systems for applied water treatment. International conference on water and energy ICWE'21 25-26 May 2021, University of Chlef, Algeria.
20. Thomou, E., Sakavitsi, V., Angeli, G. K., Spyrou, K., Froudas, K. G., Diamanti, E. K., Romanos, G. Em., Karanikolos, G. N., Trikalitis, P. N., Gournis. D., and Rudolf, P. A diamino-functionalized silsesquioxane pillared graphene oxide for CO2 capture. 5th EuChemS Conference on Green and Sustainable Chemistry, virtual event, September 26-29, 2021.
21. Koutsonikolas D., Pantoleontos G., Boutsika L., Charalambopoulou G., Steriotis Th., Karagiannakis G., Optimal design configuration of membrane cascade schemes for high purity H2 production, World Online Conference on Sustainable Technologies (WOCMP), 17-19 March, 2021, Online Conference.
22. Gotzias, A. Umbrella sampling and Decoupling dynamics to compute the exfoliation free energy of Graphenes, November 2021-IAS Twitter Poster Conference 2
23. Koutsioukis A., Philippakopoulou Th., Anastasopoulou M., Giasafaki D., Mitzithra C., Steriotis Th., Charalambopoulou G., Georgakilas V., Belessi V., Carbon Black and reduced Graphene Oxide water-based conductive inks, IARIGAI 2021: 47th iarigai and 52nd International Circle Conference, 19-24 September, 2021, Athens-Greece (oral).
24. Nikolakopoulos A., Steriotis Th., Charalambopoulou G., Karagiannakis G., Dimitrakis D., Konstandopoulos A. G., Michalis V., Katsiotis M., Solar-Aided Limestone Calcination in Tandem with Thermochemical Energy Storage and CO2 Capture, SolarPACES 2021, 27 September – 01 October, 2021, Online Conference.
25. Belessi V., Philippakopoulou Th., Koutsioukis A., Mandis D., Charalambopoulou G., Steriotis Th., Georgakilas V., Environmental Aspects of water based conductive inks based on graphene for gravure and flexography printing, 6th CIDAG "Go Green for 2030 - Sustainable and Green Design for the Future", International Digital Conference in Design and Graphic Arts, 20-22 October, 2021, Lisbon, Portugal (oral).
26. Mitzithra C., Giasafaki D., Belessi V., Steriotis Th., Charalambopoulou G., Electrical and Despersibility Properties of New rGO/AgNPs Hybrid Systems, NANOCON 2021, 20-22 October 2021, Brno - Czech Rebublic (poster).
27. Giasafaki D., Mitzithra C., Belessi V., Charalambopoulou G., Steriotis Th., Development of Conductive and Hydrophilic rGO/AgNWs Composites for Electronic Applications, NANOCON 2021, 20-22 October 2021, Brno - Czech Rebublic (poster).
28. Boutsika L., Bratsos I., Charalambopoulou G., Steriotis Th., CO2 separation via Zr-MOFs/Pebax mixed matrix membranes, EUROMEMBRANE 2021, 28 November - 2 December, 2021, Copenhagen - Denmark (poster).
29. Krokidas P., Karozis S., Giannakopoulos G., Kainourgiakis M., Economou I., Steriotis Th., Design of Highly Selective Zeolitic-imidazolate Frameworks with a Novel Machine Learning Model, 4th European Conference on Metal Organic Frameworks and Porous Polymers, 10-15 September, 2021, Kraków, Poland (oral).
30. Krokidas P., Karozis S., Kainourgiakis M., Steriotis T., Economou I. Physics Driven Machine Learning Model for the Design of Highly Selective Zeolitic-imidazolate Frameworks, 31st European Symposium on Applied Thermodynamics, 5-9 July, 2021, Paris - France (oral).
31. Krokidas P., Karozis S., Giannakopoulos G., Kainourgiakis M., Steriotis Th., Economou I., A Novel Machine Learning Model for the Accurate Design of Highly Selective Zeolitic-Imidazolate Frameworks, AIChE Annual Meeting, 7-19 November, 2021, Boston, USA (oral).

Teaching and Training Activities

Conference / Workshop Organisation

1. A. Sapalidis, Organizing and scientific committee International Conference On Water And Energy ICWE'21 25-27 May 2021, Chlef, Algeria - online

Services

Income from services to Industrial partners: 5.899,09 €

MOLECULAR THERMODYNAMICS AND MODELLING OF MATERIALS LABORATORY

Project Leader: Dr. Ioannis Economou (on leave of absence until 31 Dec 2021, then resigned)

Permanent Research Staff: Dr. Loukas Peristeras, Researcher C
Dr. Niki Vergadou, Researcher C

Other Staff (scientific, appointed research fellows, administrative, technical, auxiliary, etc.):

Dr. Konstantinos D. Papavasileiou

Dr. Panagiotis Krokidas

Post Docs:

Dr. Eleonora Ricci, Dr. Ilias Nikolaidis, Dr. Nefeli Novak, Dr. Stavros D. Peroukidis, Dr. Flora D. Tsourtou

PhD Candidates: Matrona Panou,

Diploma Students: Dimitrios Nasikas, Aikaterini Argyropoulou

- **Objectives**
- **Highlights / main scientific results**

Development of multiscale models for the Gas-To-Liquids (GTL) process

Research work in the Molecular Thermodynamics and Modelling of Materials Laboratory (MTMML) focuses on the development and implementation of novel hierarchical methods and algorithms for the computer modelling and calculation of advanced material properties at the molecular, mesoscopic and macroscopic levels (Figure 1). Through this work, quantitative links are established between chemical constitution, processing conditions, and physical (thermal, mechanical, rheological, transport, interfacial, optical, dielectric) properties, which are critical for the optimal design of industrial processes and also govern the end-use performance of commercial products. In parallel, the molecular mechanisms underlying structure - property - processing - performance relations are elucidated with the objective of designing new, tailor-made materials.

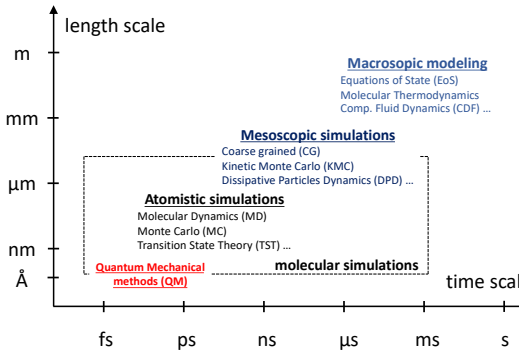


Figure 3: Hierarchical multi-scale simulation

The hierarchical approaches developed and implemented at MTMML start with atomistic simulations addressing length scales on the order of tens of nanometers and time scales on the order of tens of nanoseconds (e.g., Monte Carlo, molecular dynamics, transition-state theory analysis of infrequent events) and proceed with mesoscopic methods (e.g., entanglement network modelling, kinetic Monte Carlo simulation, self-consistent field theory of inhomogeneous systems) to address longer time- and length scale phenomena. Finally, for the efficient design of novel processes mainly for the chemical, polymer and pharmaceutical industry, accurate macroscopic models, mostly in the form of equations of state (eos), are developed for phase equilibria and other thermodynamic properties of multicomponent mixtures. These eos are rooted to statistical mechanics and can be safely extrapolated to conditions where limited or no experimental data exist.

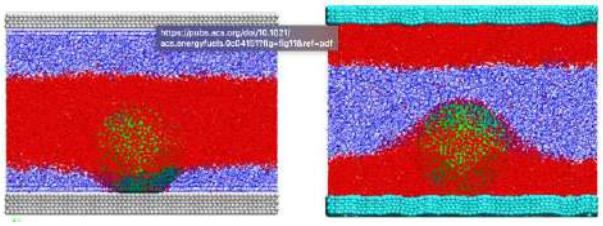


Figure 2: Characteristic snapshots of equilibrated conformations of Co Np emerged in *n-C_{28} mixture inside G (left) and GO (right) slit pore.*

The GTL process is an established, robust and economically viable technology in harnessing gas resources, such as synthetic gas for the efficient production of cleaner and high-quality transportation fuels by the petrochemical industry. The Fischer-Tropsch (FT) reaction is fundamental to the fuel production process and its performance is controlled by several factors, such as operating conditions, the choice of the metal catalyst and its support material. This project aims at the utilization of mesoscale molecular simulation methodologies using the MARTINI force field in order to address a number of fundamental questions raised by the GTL industry. Within this context, our efforts focused on simulating using atomistic (AA) and coarse-grained (CG) molecular dynamics (MD) simulations the n-octacosane (*n*-C_{28})– H_2O mixture inside graphene (G) and graphene oxide (GO) mesopores under low-temperature FTS conditions (473.15K) with the inclusion of a Co Nanoparticle (NP). We also evaluated the presence of long-chain alcohols such as dodecan-1-ol at 7 wt % on the phase behavior of the mixture. Both AA and CG simulations accurately capture the mobility of the components as a function of the distance from the G and GO pore centers. Dodecan-1-ol is mostly located at the *n*-C_{28} interface showing a higher preference toward paraffin, slightly reducing the mobility of water. Finally, with DFT-derived parameters for Co NP, we studied the mixture's behavior in its presence finding that the Co NP does not affect the phase separation of the *n*-C_{28} mixture inside the pores.

Machine Learning-aided Molecular Simulation Strategies

Due to the wide range of time- and length scales that are present in complex chemical systems, hierarchical multiscale strategies are required, that are usually elaborate and system-specific. These schemes could be generalized and streamlined by the application of Machine Learning (ML) methods. Machine learning is having increasing impact in the physical sciences, engineering and technology, addressing research problems that range from molecular reaction mechanisms to high-throughput screening of functional materials. A main advantage of ML models in the context of molecular simulations is that they are not constrained to a predefined mathematical function, therefore they are endowed with higher flexibility and expressive character compared to traditional coarse-grained (CG) models, thus they are potentially capable of accurately capturing many-body interactions and enable larger and longer scale simulations, which are necessary to study macromolecular systems. Our research work involves the investigation of ML schemes for the construction of CG mapping models (Figure 3) and the utilization of neural network methods to develop CG force fields.

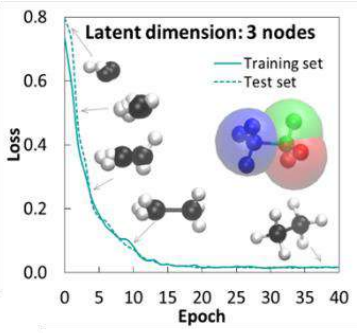


Figure 3: Loss over the training and test sets along with reconstructed molecules during training of a Variational Autoencoder for the ethane molecule with three latent nodes.

Hierarchical modelling for the optimum design of personal hygiene products

The ability of surfactants to reduce the interfacial tension between fluids renders them essential ingredients in a wide range of products and applications including, among others, health and personal care products. This project aims to create a coarse grain (CG) force field (FF), able to predict the properties of surfactants' aqueous solution for a range of concentrations. Within this context, we developed a methodology for validating the performance of all-atom (AA) FFs in predicting the phase diagram behavior of these systems in the region of high concentrations. In particular, we used cetyltrimethylammonium chloride (CTAC) as a model system to study the region of its phase diagram where the transition from the micellar (L_1) phase to hexagonal liquid crystal (H_1) phase occurs according to the published experimental studies. Central to our approach is the ability to examine the spontaneous occurrence of the H1 phase by testing a number of plausible values for the linear density (molecules per unit length) along the cylindrical columns formed in the simulation cell. Starting from random initial configurations, the MD simulations demonstrate that the micellar phase occurs for concentrations up to 50.0 wt%, with CTAC molecules self-assembling into a mixture of spherical and rod-like micelles. A detailed analysis of the size, shape, and structure of the micelles as a function of the concentration was carried out by an in house developed software tool based on Voronoi tessellation for the identification of the assemblies. At even higher concentrations, the system self-organizes into the H_1 phase in accordance with the available experimental data.

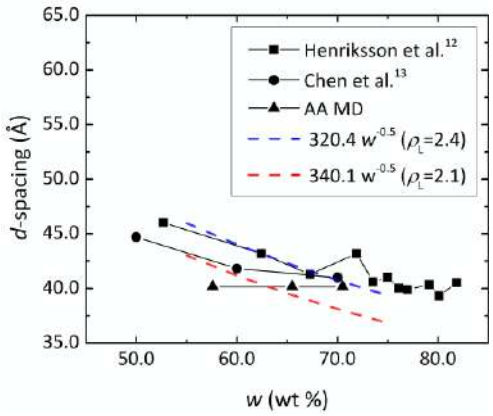


Figure 4: The prediction of the H_1 lattice spacing (d) from the AA MD simulations is in exalted agreement with the available experimental data obtained from X-Ray Diffraction measurements.

Systematic molecular simulation methods for the study of polymers and polymer-based systems

Polymeric materials remain in the core of a wide range of novel applications and state-of the art membrane and barrie technologies, from energy and environmental engineering such as in gas separations and water purification, to biomedical engineering and packaging applications. The wide range of time scales that are involved in the relaxation of their various modes of motion, render the prediction of their properties a very challenging task. Systematic molecular simulation methods are applied to generate realistic initial structures, predict a wide range of properties (Figure 5) and unravel the underlying microscopic mechanisms of polymer systems and polymer-based composites.

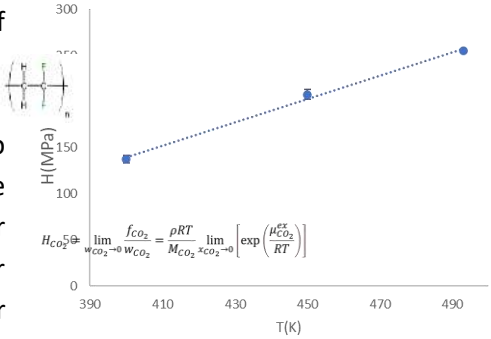


Figure 5: Solubility in the infinite dilution regime of CO_2 in 50-mer polyvinylidene difluoride as a function of temperature.

Molecular Modeling of Ionic Liquids

Ionic liquids (ILs) are identified as innovative designer solvents and advanced materials that can be utilized in a wide range of cutting-edge green processes and industrial applications. They exhibit an exceptional combination of properties that

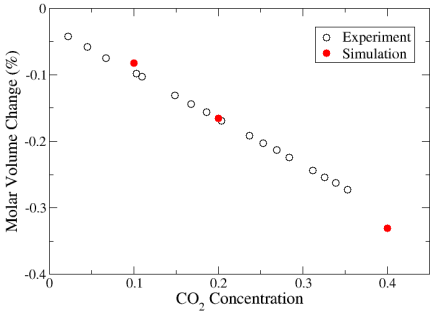


Figure 6: Molar volume change as a function of CO_2 concentration in [C_4mim$^+$][TCM$^-$] IL at 298K

originate primarily from their dual organic and ionic nature. Molecular simulation methods have been developed and implemented for the study of their complex microscopic behavior and the prediction of a wide range of properties (Figure 6) (thermodynamic, dynamic, transport, sorption, permeability, selectivity) of pure systems and their mixtures with gases.

- **Funding**

1. "Research and Development Project for Integrated Workflows for Materials Design", *Contract Research Agreement, Scienomics SARL, Paris, France.* Total funding: 700,000 €. Duration: August 1, 2019 – December 31, 2022.
2. "New Paradigm in Electrolyte Thermodynamics", *European Research Council Advanced Grant.* Lead Principal Investigator: Prof. G.M. Kontogeorgis, Technical University of Denmark. Total funding: 2,500,000 €. Funding for MTMML: 230,000 €. Duration: September 1, 2019 – August 31, 2024.
3. "Hierarchical Modelling for the optimum design of personal hygiene products (HygiMod)" (MIS: 5047819) – Greece and European Union (European Social Fund- ESF), Operational Programme «Human Resources Development, Education and Lifelong Learning 2014-2020». Total funding: 41,500 €. Duration: April 2020 - October 2021.
4. "Machine Learning-Aided Multiscale Modelling Framework For Polymer Membranes (ML-MULTIMEM), *European Commission, Horizon 2020 Programme - Marie Skłodowska-Curie Actions (Grant agreement ID: 101030668), in collaboration with Institute of Informatics and Telecommunications of NCSRD,* Marie Skłodowska-Curie Postdoctoral Fellow: Dr. Eleonora Ricci**,** Funding: 153,085 €. Duration: November 2021 – November 2023.

Publications in International Journals

1. Papavasileiou K.D., Peristeras L.D., Bick A., Economou I.G., Molecular Dynamics Simulation of the n - Octacosane–Water Mixture Confined in Graphene Mesopores: Comparison of Atomistic and Coarse-Grained Calculations and the Effect of Catalyst Nanoparticle, *Energy Fuels*., **35**, pp. 4313-4332 (2021). DOI: 10.1016/j.fluid.2020.112816
2. Piña-Martinez A., Privat R., Nikolaidis I.K., Economou I.G., Jaubert J.-N., What Is the Optimal Activity Coefficient Model to Be Combined with the translated- consistent Peng-Robinson Equation of State through Advanced Mixing Rules? Cross-Comparison and Grading of the Wilson, UNIQUAC, and NRTL aE Models against a Benchmark Database Involving 200 Binary Systems, *Ind. Eng. Chem. Res.*, **60**, pp. 17228–17247 (2021). DOI: 10.1021/acs.iecr.1c03003
3. Novak N., Kontogeorgis G.M., Castier M., Economou I.G., Water-Hydrocarbon Phase Equilibria with SAFT-VR Mie Equation of State, *Ind. Eng. Chem. Res.,* **60**, pp. 5278–5299 (2021). DOI: 10.1021/acs.iecr.1c00480
4. Novak N., Kontogeorgis G.M., M. Castier, Economou I.G., Modeling of Gas Solubility in Aqueous Electrolyte Solutions with the eSAFT-VR Mie Equation of State, *Ind. Eng. Chem. Res.,* **60** pp. 15327–15342 (2021). DOI: 10.1021/acs.iecr.1c02923
5. Nikolaidis I.K., Privat R., Jaubert J.-N., Economou I.G., Assessment of the Perturbed Chain-Statistical Associating Fluid Theory Equation of State against a Benchmark Database of High-Quality Binary-System Data, *Ind. Eng. Chem. Res.,* **60**, pp. 8935–8946 (2021). DOI: 10.1021/acs.iecr.1c01234
6. Hillman F., Hamid M.R.A., Krokidas P., Moncho S., Brothers E.N., Economou I.G., Jeong H.-K., Delayed Linker Addition (DLA) Synthesis for Hybrid SOD ZIFs with Unsubstituted Imidazolate Linkers for Propylene/Propane and n-Butane/i-Butane Separations, *Angewandte Chemie International Edition,* **60**, pp. 10103–10111 (2021). DOI: 10.1002/ange.202015635
7. G.M. Kontogeorgis, R. Dohrn, I.G. Economou, J.-C. de Hemptinne, A. ten Kate, S. Kuitunen, M. Mooijer, L.F. Žilnik and V. Vesovic, "Industrial Requirements for Thermodynamic and Transport Properties: 2020", *Ind. Eng. Chem. Res.*, **60**(13), 4987 – 5013 (2021). ACS Editors' Choice.

Books/Chapters in Books

1. Romanos G., Vergadou N., Economou I.G., "Ionic Liquids in Carbon Capture" in Sustainable Carbon Capture: Technologies and Application, Suleman H. ,Loldrup Fosbøl P., Nasir R., Ameen M., CRC Press, Taylor & Francis Group (in press).

International Conferences Presentations (invited, oral, poster)

1. Papavasileiou K.D., Peristeras L.D., Bick A. and Economou I.G., "Mesoscale Modeling of Fischer-Tropsch Product Mixtures Confined in Graphene Nanopores", *31st European Symposium on Applied Thermodynamics,* France (2021), virtual. Oral
2. Novak N., Kontogeorgis G.K., Castier M. and Economou I.G., "Modeling of Water – Hydrocarbon Phase Equilibria with the SAFT-VR Mie Equation of State", *31st European Symposium on Applied Thermodynamics,* France (2021), virtual. Oral
3. Krokidas P. and Economou I.G., "Physics-driven Machine Learning Model for the Design of Highly Selectivity Zeolitic-Imidazolate Frameworks", *31st European Symposium on Applied Thermodynamics,* France (2021), virtual. Oral
4. Economou I.G., Papavasileiou K.D., Peristeras L.D. and Bick A., "Clean, High Quality Low Emission Fuels with Fischer-Tropsch Synthesis: A Multiscale Study of Transport Properties in Confined Systems", *9th International Symposium on Molecular Thermodynamics and Molecular Simulation,* Japan (2021). Keynote Lecture, virtual. Oral
5. Economou I.G., "Computational Engineering for Environment-Friendly Industrial Processes and Materials Design", *International Conference on New Trends in Science and Applications* (2021). Keynote Lecture, virtual. Oral
6. Economou I.G., Krokidas P., Karozis S., Giannakopoulos G., Kainourgiakis M. and Steriotis T., "A Novel Machine Learning Model for the Accurate Design of Highly Selective Zeolitic-Imidazolate Frameworks", Session 51c, *AIChE Annual Meeting,* Boston, Massachusetts, USA (2021). Oral
7. Economou I.G., Papavasileiou K.D., Peristeras L.D. and Bick A., "Clean, High Quality Low Emission Transportation Fuels with Fischer-Tropsch Synthesis: A Mesoscale Study of Transport Processes in Confined Systems", Session 342bd, *AIChE Annual Meeting,* Boston, Massachusetts, USA (2021). Oral
8. Tsourtou F.D., Peroukidis S.D., Peristeras L.D., "Mesophase behavior of Cetyltrimethylammonium chloride: insights from all-atom Molecular Dynamics simulation", Session 3b, Athens Conference on Advances in Chemistry, Greece (2021). Oral
9. 35th Panhellenic Conference on Solid State Physics and Materials Science: K. Karanasiou, M. Panou, N. Vergadou, "Computational Study of Ionic Liquids as Carbon Capture Media", September 26- 29, Athens, Greece (2021). Oral
10. 35th Panhellenic Conference on Solid State Physics and Materials Science, M. Panou, A. Argyropoulou, N. Vergadou, "Molecular Dynamics Simulation of Poly(vinylidene fluoride)", September 26- 29, Athens, Greece (2021). Poster
11. Athens Conference on Advances in Chemistry: K. Karanasiou, N. Vergadou, "Molecular Modelling of Ionic Liquid – CO2 Mixtures", March 10-14, Athens, Greece (2021). Oral
12. Athens Conference on Advances in Chemistry: M. Panou, N. Vergadou, "Molecular Dynamics Simulation of Poly(vinylidene fluoride)", March 10-14, Athens, Greece (2021). Oral

Teaching and Training Activities

Dimitrios Nasikas, School of Chemical Engineering, National Technical University of Athens, Diploma Student (2020-2021) - Supervised by: Dr. N. Vergadou

Aikaterini Argyropoulou, School of Chemical Engineering, National Technical University of Athens, Diploma Student (2020-2021) - Supervised by: Dr. N. Vergadou

Undergraduate Theses and Internships completed in 2021

Name: Dimitrios Nasikas
Dissertation Title: "Development of Coarse-Grained Molecular Simulation Models Using Machine Learning Techniques"
Research Supervisor at NCSR: Dr. Niki Vergadou
University where the Thesis was presented: National Technical University of Athens

Dimos Aslanis, Internship, 2021.
Supervised by: Dr. N. Vergadou
School of Chemical Engineering, National Technical University of Athens

Dimitrios Sipsis, Internship, 2021.
Supervised by: Dr. N. Vergadou
School of Chemical Engineering, National Technical University of Athens

PHOTO- CATALYTIC PROCESSES AND ENVIRONMENTAL CHEMISTRY

Project Leader: Dr. Anastasia Hiskia

Permanent Research Staff: Dr. Theodoros Triantis

Other Staff (scientific, appointed research fellows, administrative, technical, auxiliary, etc.): Irini Dousi

Post Docs: Dr Sevasti-Kiriaki Zervou, Dr Maria Antonopoulou

PhD Candidates: Korina Manolidi, Aikaterina Paraskevopoulou, Sofia Iliakopoulou

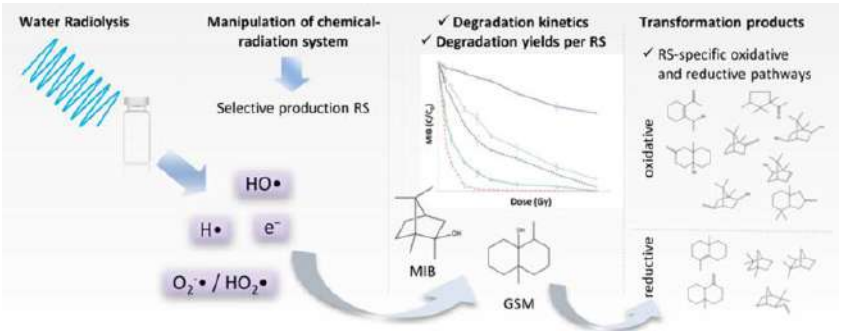
Undergraduate Students: Efstathia Karampela, Ioannis Raptis

Research Collaborators (emeritus or visiting): Dr Triantafyllos Kaloudis, Dr Christophoros Christophoridis

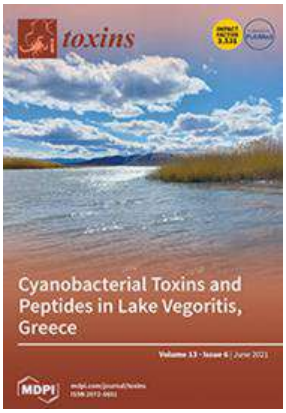
Objectives

- Photocatalytic Processes; Evaluation of new Photocatalytic Materials
- Advanced Oxidation/Reduction Processes (AOPs/ARPs) for Environmental Remediation; Elucidation of the Reaction Mechanisms; Identification of Transformation Products; Identification of Transient Reactive Species
- Environmental Analytical Chemistry; High resolution mass spectrometry; Advanced analytical methods development – Cyanotoxins, cyanopeptides and water taste & odor compounds analysis; Construction of MS2 spectra libraries for cyanometabolites; Mapping of cyanotoxins/cyanopeptides in Greek water bodies
- New Categories of Bioactive Compounds from Cyanobacterial Biomass; Extraction, Isolation and Identification of Cyanobacterial Metabolites; Bio-activity Studies
- Quality Control and Accreditation Activities

Highlights / main scientific results



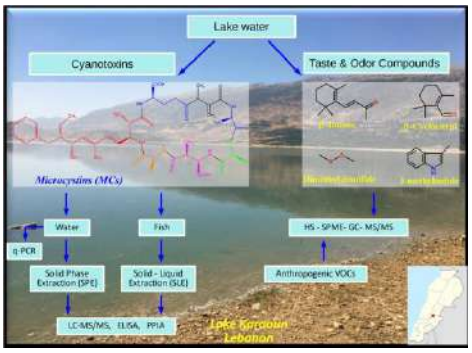
• Photocatalytic reactions for solar energy utilization, environmental detoxification and environmentally friendly processes. Aggregates of metal oxides, mainly TiO2, and polyoxometallates (POM) are used in thermal and photochemical reactions for: (a) non-selective oxidation (photodegradation-mineralization) of organic pollutants to CO2, H2O and inorganic anions, (b) reduction-removal of metallic ions, (c) synthesis of metal nanoparticles, (d) development of a standard procedure for assessing the photocatalytic activity of materials with regards to water purification.



Advanced oxidation process (AOPs) such as UV-based processes, sonolysis and γ-irradiation for environmental detoxification. Focus is given on: (a) novel approaches for understanding the molecular-level interactions and pathways of ROS-driven oxidation of less studied, emerging pollutants (cyanotoxins, water taste& odors), (b) assessment of transformation products generation and toxicity after application of different ROS-producing technologies for water treatment,(c) novel technological knowledge of the efficiency of ROS-producing treatments to degrade target pollutants in water.

Toxins from cyanobacteria (cyanotoxins, CTs) are nowadays considered as major threats for water quality, public health and aquatic ecosystems. Apart from CTs there is a plethora of bioactive compounds such as cyanopeptides that are also produced as

secondary metabolites from cyanobacteria (cyanometabolites, CMs) while studies focusing on their occurrence and fate in the environment are missing. The multitude of compounds and the lack of commercially reference materials and databases present research challenges. The main objectives of our group in the area of environmental analytical chemistry are focused on (a) the development of advanced analytical procedures for the targeted/untargered identification of multiclass CTs and cyanopeptides, (b) the generation of analytical fingerprints (MS spectral library) that will facilitate future studies of the research community, (c) the understanding of their fate in the aquatic environment and the identification of structure of their transformation products (TPs), d) the assessment of cyanobacterial metabolites bioactivity as well as of their TPs with a set of in vitro assays. To overcome the challenges, an integrated approach with innovative workflows, instrumentation of technological peak (HRMS and tandem MS) and valid methods are used.



Contamination of water supplies with organic pollutants such as cyanotoxins, PAHs, PCBs, pesticides, pharmaceuticals and endocrine disruptors is one of the most important global problems. Recent EU Directives propose the determination of these target pollutants in drinking and surface water and set their maximum concentration. Resulting from the above, it is mandatory to monitor these analytes using appropriate methods. The development of new advanced analytical methods can give rise to sensitive and reliable determinations even at the ppt level. Our contribution to this area of research can be summarized into the following: (a) Development of advanced analytical methods for the determination of trace organic/emerging pollutants in waters, food and environmental samples (e.g. cyanotoxins, cyanobacterial metabolites, compounds that give taste and odor in water etc.). Accreditation (according to ISO 17025) for the determination of cyanotoxins in water and biomass, (b) Development and accreditation (according to ISO 17025) of advanced analytical method for the identification and quantitative determination of polycyclic aromatic hydrocarbons (PAHs) in waters using LC-APPI-MS/MS. Photo-Catalytic Processes and Environmental Chemistry Laboratory is the first research laboratory in Greece to be involved in cyanotoxins research since 2005 and currently the only research group in Greece in the field with significant contributions through published papers and collaborations in Greece, Europe and USA. It has also established itself as the national laboratory for cyanotoxin analysis in water and biomass, by extending its scope of accreditation (ISO 17025) as well as a national focal point for cyanotoxins research, with the research team being internationally recognized as pioneers and experts in the field of cyanotoxins analysis.

In the field of cyanotoxin analysis, several sensitive and fast targeted-screening analytical methods using advanced analytical instrumentation have been facilitated for the determination of a wide range of cyanotoxins, i.e. MCs, CYN, ATX-a, SXTs and BMAA. However, there are several other cyanobacterial metabolite chemical groups that have not been thoroughly studied. Identification of new cyanotoxins (CTs) and novel cyanobacteria (CB) metabolites as well as assessment of their biological activities presents a research challenge. In this framework, a new research activity has been initiated by our research group which focused on the development of novel analytical workflows based on mass spectrometric methods (LC/MS-MS and HRMS) for screening of new CTs and CB bioactive compounds produced by culture collections of CB strains isolated from Greek sites as well as in natural samples (cyanobacterial biomass, water) from Greek Lakes known for their history in forming cyanobacterial harmful algae blooms. In addition, appropriate protocols for the extraction / fractionation of bioactive compounds from cyanobacteria biomass (e.g. Arthrospira sp.) are under development and further investigation of hazardous or beneficial properties of bioactive molecules will be performed. "Hit" compounds will be studied further to elucidate their mechanism of action and characterize them using LC-MS/MS or HRMS techniques. Project results are expected to have a significant impact on the economy by attracting the interest of different market sectors like natural pharmaceuticals, cosmetic ingredients and functional foods triggered by the increasing demand of consumers for high added value “green” products with unique properties.

Funding

1. «Bioconversion of CO_2 into High-added Value Bioproducts through Sustainable Microalgae Cultivation Processes - CO_2-BioProducts» (E-12257), co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation (NSRF 2014-2020), under the call

RESEARCH – CREATE - INNOVATE (project code: T1EΔK-02681). Duration 2018-2022. Project Coordinator: Prof. C. Kiparissides. NCSR-D Principal Investigator: Dr. T. Triantis. NCSR-D Budget: 100 K€.

2. "Taste and Odor in early diagnosis of source and drinking Water Problems –WATERTOP" (E-12368), COST Action CA 18225 funded by COST – European Cooperation in Science and Technology. The main aim of WATERTOP project is to increase capabilities and capacities in Europe for managing water T&O problems, by creating the first European network of multi-disciplinary experts, end-users and stakeholders in the field. Duration 2019-2024. Dr. A. Hiskia: WG4 Leader; Dr. T. Kaloudis: MC Chair; Dr. T. Triantis: Management Committee (MC) member; Action Grant Holder and Scientific representative of NCSR "Demokritos", Budget per year 140 K€.
3. "Evaluation of new and environmentally friendly methods for surface coating of metal alloys resistant to corrosion", 2020-2021. The purpose of this project was to compare old and new methods and materials in terms of their resistance to corrosion. Conventional and new light Al-LI alloys coated with known and new anti-corrosion protection methods (containing or free of chromium, respectively). The project funded by the Hellenic Aerospace Industry S.A. Project Coordinator: T. Triantis, Budget: 19.5 K€.
4. «National Nanotechnology, Advanced Materials and Micro/Nanoelectronics Infrastructure» INNOVATION-EL (E-12193) (MIS 5002772), which is implemented under the Action "Support of Research and Innovation Infrastructure", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund). Duration 2018-2021: Project Coordinator: Dr. V. Kilikoglou, INN, NCSR Demokritos. Group budget: 20 K€.
5. "National Network on Climate Change and its Impacts—Climpact" Action, which is implemented under the sub-project 3 of the project "Infrastructure of national research networks in the fields of Precision Medicine, Quantum Technology and Climate Change", funded by the Public Investment Program of Greece, General Secretary of Research and Technology/Ministry of Development and Investments. Research topic "Investigation of harmful algal blooms (HABs) in freshwater bodies and their correlation with climate change". Duration: 10/2019 - 8/2021. Participants: Dr. Anastasia Hiskia, Dr. Theodoros Triantis and Dr. Sevasti-Kiriaki Zervou. Group budget: 27.5 K€.
6. "Identification of bioactive cyanopeptides from Greek lakes", post-doctoral fellowship by State Scholarships Foundation (IKY), Greece. Duration: 11/2019 – 11/2021. Scientific Mentor: Dr. Anastasia Hiskia, Post-doctoral researcher: Dr. Sevasti-Kiriaki Zervou.
7. "Advanced Oxidation Processes for the removal of taste and odor compounds in drinking water", post-doctoral fellowship by State Scholarships Foundation (IKY), Greece. Duration: 11/2019 – 2/2021. Scientific Mentor: Dr. Anastasia Hiskia, Post-doctoral researcher: Dr. Maria Antonopoulou.
8. Services to the Decentralized Administration of Epirus - Western Macedonia, "Determination of cyanotoxins in water samples of Lake Vegoritida", 12.3 k€, Duration: 1/2021-12/2021.
9. Services to VAPE ALTER EGO IKE, "Determination of toxic compounds in e-cigarette liquids", 12.72 k€, Duration: 1-2021 / 12-2021.
10. Other services, 2.6 k€, Duration: 1-2021 / 12-2021.

Publications in International Journals

1. Christophoridis, C., Pestana, C.J., Kaloudis, T., Lawton, L.A., Triantis, T.M., Hiskia, A. Radiolytic degradation of 2-methylisoborneol and geosmin in water: Reactive radical species and transformation pathways. *Chemical Engineering Journal Advances* **8**, Art No 100196 (2021). DOI: https://doi.org/10.1016/j.ceja.2021.100196. **IF:**, **Citations:**

2. Donis, D., , Mantzouki, E., … Triantis, T., …., Ibelings, B.W. Stratification strength and light climate explain variation in chlorophyll a at the continental scale in a European multilake survey in a heatwave summer. *Limnology and Oceanography* **66** 4314–4333 (2021). DOI: https://doi.org/10.1002/lno.11963. **IF:**4.745, **Citations**: 6

3. Hammoud, N.A., Zervou, S.-K., Kaloudis, T., Christophoridis, C., Paraskevopoulou, A., Triantis, T.M., Slim, K., Szpunar, J., Fadel, A., Lobinski, R., Hiskia, A. ***I***nvestigation of the Occurrence of Cyanotoxins in Lake Karaoun

(Lebanon) by Mass Spectrometry, Bioassays and Molecular Methods. *Toxins* **13(10)** 716 (2021). DOI: https://doi.org/10.3390/toxins13100716. **IF:**4.086, **Citations:**3

4. Zervou, S.-K., Moschandreou, K., Paraskevopoulou, A., Christophoridis, C., Grigoriadou, E., Kaloudis, T., Triantis, T.M., Tsiaoussi, V., Hiskia, A. Cyanobacterial toxins and peptides in Lake Vegoritis, Greece. *Toxins* **13(6)** 394 (2021). DOI: https://doi.org/10.3390/toxins13100716. **IF:**4.086, **Citations:**10

Books/Chapters in Books

1. Antonopoulou M., Hiskia A., Nano-photocatalysts for water remediation: treatment of industrial wastewater in M. Litter, A. Ahmad (Eds.), *Industrial Applications of Nanoparticles- A Prospective Overview*, CRC Press. (Accepted).

International Conferences Presentations (invited, oral, poster)

1. Paraskevopoulou A., Kaloudis T., Hiskia A., Triantis T.M., Determination of volatile compounds in Spirulina food supplements using HS-SPME– GC/MS, *12th International Conference on "Instrumental Methods of Analysis" (IMA-2021), Organized by AUTH & NTUA*, 20-23 September 2021 (Abstract published in Applied Sciences 11 (2021) 11767) Virtual conference (Oral)
2. Paraskevopoulou A., Kaloudis T., Hiskia A., Triantis T.M., Optimized methods for the extraction of C-phycocyanin and b-carotene from *Arthrospira spp.* (Spirulina) and their application to microalgae isolated from freshwaters of Greece, *12th International Conference on "Instrumental Methods of Analysis" (IMA-2021), Organized by AUTH & NTUA*, 20-23 September 2021 (Abstract published in Applied Sciences 11 (2021) 11767) Virtual conference (poster)
3. Hammoud N.A., Zervou S.-K., Kaloudis T., Paraskevopoulou A., Christophoridis C., Triantis T.M., Hiskia A., Szpunar J., Slim K., Lobinski R., Investigation on the occurrence of cyanobacterial secondary metabolites in Lebanese lake Karaoun using mass spectrometry and molecular techniques, *31st Annual Meeting of the Society of Environmental Toxicology and Chemistry- Europe (SETAC Europe)*, May 3-6, 2021, Virtual conference (oral)
4. Zervou S.-K., Hammoud N. A., Godin S., Kaloudis T., Hiskia A., Szpunar J., Lobinski R., Untargeted analysis of cyanobacterial metabolites in lake Karaoun, Lebanon, by LC-HRMS with CyanoMetDB, *12th International Conference on "Instrumental Methods of Analysis" (IMA-2021), Organized by AUTH & NTUA*, 20-23 September 2021 (Abstract published in Applied Sciences 11 (2021) 11767) Virtual conference (oral)
5. Kaloudis T., T&O with negative effects on water quality; from detection to treatment, Istanbul University, 11 May 21, online (oral)
6. Kaloudis T., Cyanobacterial metabolites with relevance to water quality; cyanotoxins, cyanopeptides and volatiles. European Algae Biomass Association, 8 July 21, online (oral)
7. Kaloudis T., Cyanobacterial metabolites with negative effects on water quality; cyanotoxins and T&O, Seminar Series "The Engineer in Society", University of Cyprus, 14 April 21, online (oral)

Editorial Activities

1. Special Issue "Cyanotoxins in Bloom: Ever-Increasing Occurrence and Global Distribution of Freshwater Cyanotoxins from Planktic and Benthic Cyanobacteria", *Toxins* (2020-2021) Guest Editors: Triantafyllos Kaloudis, Anastasia Hiskia, Theodoros Triantis.
2. Special Issue "Water taste and odour (T&O): challenges, gaps and solutions", Chemical Engineering Journal Advances (2020-2021), Guest Editors: Triantafyllos Kaloudis, Andrea Dietrich, Arash Zamyadi, Tsair-Fuh Lin, Ana Rita Lado Ribeiro.
3. Special Issue "Water Quality Optimization", *Water* (2020-2021), Guest Editors: G. Besseris, T. Kaloudis.
4. Special Issue "Advances in Water Quality Monitoring and Assessment of Aquatic Toxicity", *International Journal of Environmental Research and Public Health* (2020-2021), Guest Editors: Magdalena Toporowska, Agnieszka Budzyńska, Triantafyllos Kaloudis.
5. T. Kaloudis, Editorial Board Member, *Toxins (MDPI)*, Section: Marine and Freshwater Toxins.

Teaching and Training Activities

Theodoros Triantis
Teaching Fellow/Assistant, Department of Industrial Design and Production Engineering, University of West Attica. Graduate level course: Chemistry II (laboratory) (2nd semester).

Maria Antonopoulou
Teaching, Course: Environmental Pollution Control, Duration: 36 hours, Department of Environmental and Natural Resources Management, University of Patras
Teaching, Course: Catalytic processes, Safety & Environment, Duration: 36 hours, Department of Environmental and Natural Resources Management, University of Patras

Doctoral Dissertations completed in 2021

Name: Korina Manolidi
Dissertation Title: Development of analytical methods for the determination of cyanotoxins in water, plant and animal tissues using liquid chromatography coupled to tandem mass spectrometry
Research Supervisor at NCSR: Dr A. Hiskia
University where the Thesis was presented: National and Kapodistrian University of Athens,
Department of Chemistry.

Conference / Workshop Organisation

Taste and Odor in early diagnosis of source and drinking Water Problems, Editorial meeting of the COST Action CA18225 (WATERTOP) organized by T. Triantis, T. Kaloudis, A. Hiskia, 27-30 September 2021, Nafplio, Greece

Patents - Technology transfer

Constant partnership with EYDAP S.A. since 2006 in Emerging pollutants and treatment processes in water. Transfer of know-how and technological expertise through (a) co-coordination of COST Networks (WATERTOP CA 18225 & CYANOCOST ES1105); (b) Application of hydrogen peroxide (H2O2) (mesocosm studies) to control harmful algal Blooms; (c) Control of cyanotoxins in water reservoirs of Athens: (the only ISO 17025-Accredited lab in Europe)

Awards/ Academy memberships/Networking activities

- **Our article:** Zervou, S.-K., Moschandreou, K., Paraskevopoulou, A., Christophoridis, C., Grigoriadou, E., Kaloudis, T., Triantis, T.M., Tsiaoussi, V., Hiskia, A. Cyanobacterial toxins and peptides in Lake Vegoritis, Greece. *Toxins* **13(6)** 394 (2021) has been selected as journal issue cover and Editor's choice article.
- **Hiskia:** (a) Leader of WG4 "Advances in water treatment for removal of taste and odor (T&O) compounds" of the WATERTOP COST Action CA18225 (2019 – 2023); Web link: https://www.cost.eu/actions/CA18225/#tabs|Name:overview ; (b) Member of ISO/TC 147 "Water Quality"/SC 2 "Physical, chemical and biochemical methods" (2018-2021).Web links: https://www.iso.org/standard/72563.html?browse=tc
- **T. Triantis:** Management Committee Member and Scientific Representative (SR) of the Grant Holder Institution (NCSR-D) of the WATERTOP COST Action. Web link: https://www.cost.eu/actions/CA18225/#tabs|Name:overview
- **T. Kaloudis:** Management Committee Chair of the WATERTOP COST Action. Web link: https://www.cost.eu/actions/CA18225/#tabs|Name:overview

TRANSPORT OF MATTER PHENOMENA IN POLYMERS

Project Leader: Kyriaki Papadokostaki

Post doc: Petros Oikonomou (1/1-15/4/2021 and 5/5-4/8/2021)

Master Student: Danai Koukoufilippou

Research Collaborators (emeritus): Merope Sanopoulou

Objectives

Research focuses on micromolecular sorption and transport mainly in polymeric materials by a combination of theoretical and experimental approaches. The aim of this work is to help create the basic scientific background for the optimization of the design of polymeric materials for important applications such as polymer-based controlled release systems, chemical sensors and coatings.

Highlights / main scientific results

1. Polymer-based controlled release systems

The development of polymer-based controlled release (CR) devices constitutes a significant progress towards the efficient and safe drug therapy and is continuously evolving to new therapeutic approaches. Our work focuses on systems where diffusive transport through a polymeric medium plays an important role in the release process, with emphasis to matrix systems, which are relatively simple to manufacture, and safe against dose dumping. They are also challenging in respect to the main requirement of a CR device to deliver the drug load at a uniform rate within the therapeutic window of the drug. Matrix-based pharmaceutical products are used for broad spectra of pathological conditions and duration of treatment, include subcutaneous and ophthalmic implants, transdermal patches and drug eluting stents. Our research in this area aims at the optimization of the design of matrix-type controlled release devices by (i) development and validation of advanced models simulating their release performance and (ii) experimental work on complex mechanisms of release kinetics from hydrogels, elastomers and their composites. Recent work focused on modification of polymer matrices through physical or chemical methods in order to facilitate the release or stabilize the release rate.

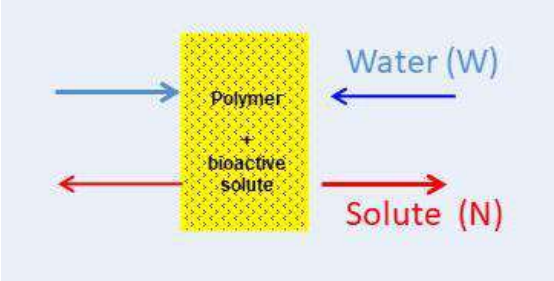


Fig. 1. *Matrix-type controlled release (MCR) devices consist of a polymer matrix incorporating the bioactive solute and are activated by the ingress of water when placed in aqueous biological environment*

2. Transport and related physicochemical properties of polymer blends for biomedical applications

The use of polymer mixtures is a widespread strategy to improve and/or combine the properties of the parent polymers. Blending of existing, well characterized polymers in order to meet the demand of new structures for specific applications is also economically advantageous in comparison to synthesis of new polymers. The properties of the blend, such as transport, mechanical and thermal properties, depend primarily on those of the parent homopolymers, the blend composition and the miscibility state of the blend. Our work mainly concerns polymer blends for biomedical applications. Due to stringent safety specifications, research for polymeric materials for new biomedical uses is commonly focused on modification of existing polymers with proven safety and biocompatibility. We focus on

(i) Modification of hydrophobic elastomers through blending with hydrophilic polymers in order to enhance the affinity of the former to water. The resulting increase in the permeability of water vapor and of bioactive substances (drugs, proteins) is sought in controlled release systems, wound dressings, transdermal patches, etc. The elastomer–hydrophilic polymer blends possess a two-phase morphology due to the immiscibility of its components. Detailed

work has been performed on blends of PDMS, a widely used thermosetting polymer for biomedical uses, with hydrophilic polymers, namely PEG, PVP, Poloxamer and we defined the range of additive content that ensures a gradual and thus controllable increase of drug permeability.

(ii) Blends of miscible hydrophilic polymers, which have the advantage of environmentally friendly preparation, using water as a solvent. In this case, due to the hydrophilicity of both parent polymers, blends absorb readily water when exposed to external humidity (Fig. 1a). The plasticizing effect of even small amounts of sorbed water results in depression of the glass transition temperature of the blend and affects the material's performance, especially in applications such as functional films and protective coatings. Eventually with increasing humidity and amount of sorbed water, a point is reached where the glass to rubbery transition occurs at ambient temperatures (see Fig 1b). The water content of each blend necessary to reach this point is of critical importance for the performance of the material at practical external conditions, as many properties undergo a drastic change at that point (e.g. permeation, diffusion and rheological properties, and mechanical strength, stiffness and ductility (Fig 1c, d)). Highlights of this work include

- establishment of inter property relations between the degree of hydration and the thermal and mechanical properties
- theoretical analysis of water-induced depression of the glass transition of the blends.

3. Permeability and mechanical properties of composite polymeric materials

The proper theoretical description of the permeability or analogous properties (thermal and electrical conductivity, electrical or magnetic permittivity, elastic modulus, etc.) of composite polymeric materials is of great interest, particularly in view of the growing technological importance of these materials and the significant improvement of their properties when the dispersed particle phase is of the nanoscale. Recent work has focused on the solute permeability and mechanical properties of elastomeric films containing dispersed swellable hydrophilic particles. This subject is related to various biomedical applications, as for example controlled release systems, where the hydrophilic additive swells upon immersion of the composite matrix in aqueous environment, and facilitates the release of the embedded bioactive substance. The permeability, as well as mechanical, properties of PDMS materials modified by blending with hydrophilic additives are studied in relation to blend composition, physicochemical properties of the additive and the morphology of the blend.

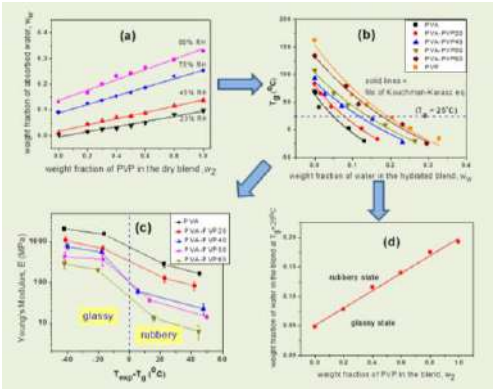


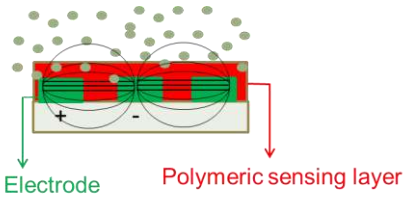
Fig. 1. Interrelation between the degree of hydration and thermal and mechanical properties of PVA-PVP blends. (a) Effect of PVP content on moisture sorption of the blends at various RHs. (b) T_g depression of blends vs amount of absorbed water in the blends. Fits to Couchman-Karasz eq. are shown as solid lines. (c) Young's modulus data plotted vs $T_{exp}-T_g$, where T_{exp} (=25 °C) is the experimental temperature of the strain−stress tests and T_g refers to the glass transition temperature determined for each sample at the humidity that the test was performed. (d) Minimum weight fraction of sorbed water, needed to convert the initially dry glassy blend to a rubbery material at an ambient temperature of 25 °C vs the weight fraction of PVP in the dry blend.

4. Thermal properties of materials for various applications

In collaboration with other laboratories we study the thermal behavior of various systems for use in different applications, e.g., phase change materials (PCM) for latent heat storage applications, ceramic nanoporous membranes supporting ionic liquids for gas separation applications or materials to be used in solar cells and luminescent devices.

5. Polymer-based chemical sensors

Our collaboration with the laboratory of Polymer-based Sensors and Systems at INN, concerns the performance, evaluation and simulation of capacitive-type sensors, developed at the above laboratory, for VOCs detection and monitoring in real complex vapor environments. The operation of the low cost, low energy consumption chemocapacitors is based on changes in the dielectric properties of the polymer layer due to sorption of the vapour analyte. For a particular geometrical design of a capacitive sensor, sorption properties determine not only the sensitivity of the sensor to a particular VOC but also its selectivity for the target VOC in real complex environments. Our collaboration includes development and evaluation of (i) optical methodologies for fast screening the sorption properties of polymeric materials for gas sensor applications (ii) simulation methodologies for the prediction of chemocapacitors performance and (iii) sensor arrays, developed at the laboratory of Polymer based sensors and systems, for specific applications concerning the detection and continuous monitoring of VOCs and/or moisture in complex vapor environments (e.g. industrial installations using solvents). More details can be found under the heading "Polymer based sensors and Systems" in the "Nanoelectronics, Photonics and Microsystems" section of this report.



Funding

1. "Transport mechanisms in Polymeric membranes for Biomedical and Electronic Applications" Internal NCSR "Demokritos" project (code 11958) – 1/10/2018-31/9/2024, total budget 24000 euro
2. Participation at the *KRIPIS* project "Development of Materials and Devices for Industrial, Health, Environmental and Cultural Applications" (MIS 5002567), "Action for the Strategic Development on the Research and Technological Sector", NSRF 2014-2020, starting date: 1/11/2017
3. Participation at the *Innovation-el* project "National Infrastructure in Nanotechnology, Advanced Materials and Micro-/Nanoelectronics" (MIS 5002772) Action "Reinforcement of the Research and Innovation Infrastructure", NSRF 2014-2020, starting date: 1/4/2018
4. Services Thermal analysis of drug formulations from Pharmaceutical Industry. 2021 Income: 320 €

OUTPUT

Publications in International Journals

1. Oikonomou, P., Sanopoulou, M., Papadokostaki, K.G. Blends of Poly(vinyl alcohol) and Poly(vinyl pyrrolidone): Interrelation between the Degree of Hydration and Thermal and Mechanical Properties, *Ind. Eng. Chem. Res.* 60, 14203–14212 (**2021**). DOI: 10.1021/acs.iecr.1c02650

International Conferences Presentations

1. Oikonomou P., Sanopoulou M., Papadokostaki K., Effect of humidity level on the thermal and mechanical properties of poly(vinyl alcohol) and poly(vinyl pyrrolidone) blend films, 13th Hellenic Polymer Society International Conference, 12 – 16 December 2021, Athens, book of Abstracts, Poster No 48.

NANOTECHNOLOGY PROCESSES FOR SOLAR ENERGY CONVERSION AND ENVIRONMENTAL PROTECTION

Project Leader: Dr. P. Falaras (Researcher A')
Other Staff (scientific, appointed research fellows, administrative, technical, auxiliary, etc.):
Post Docs: Dr. M. Antoniadou, Dr. M. Arfanis, Dr. N. Balis, Dr. L. Givalou, Dr. G. Manolis, Dr. X. Vourna
PhD Candidates: G. Belessiotis, A. Chioti, E. Christopoulos, K. Gkini, D. Perganti, M. Elsenety, A. Hussien, I. Ibrahim.
Undergraduate Students: E. Mpompoli, A. Tzavara-Roussi
Research Collaborators (emeritus or visiting): Dr. A. Kontos (Assist. Prof., NTUA), Dr. A. Kaltzoglou (Associate Researcher, National Hellenic Research Foundation), Dr. Nasikas Nektarios

- **Objectives**

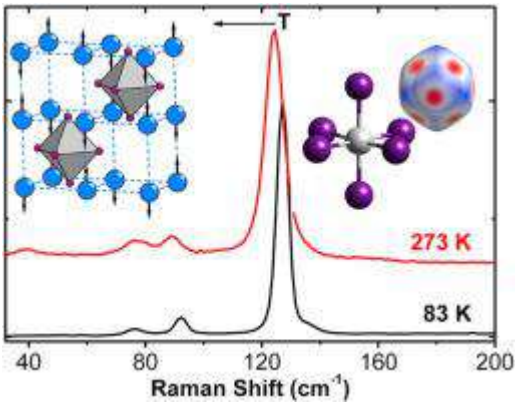
Following a holistic approach including photoactive materials (molecular and nanostructured) design/synthesis/characterization, reaction mechanisms elucidation, process engineering and device fabrication/optimization), the mission of the NPSECEP group is to perform original and high level fundamental and applied research in solar energy conversion, environmental protection and health safety.
The research focuses on the interaction of the light with the matter at molecular scale and nanoscale, the investigation of nanotechnology driven light induced processes and the development of third generation photovoltaics [Perovskite Solar Cells (PSCs); Dye-sensitized Solar Cells (DSCs); Quantum Dot Solar Cells (QDSCs)] and photocatalytic applications (including photocatalytic water cleaning, removal of emerging contaminants/microorganisms/cancer cells, water splitting and photocatalytic membrane reactors and CO2 conversion/storage).

- **Activities and Main Results**

Third Generation Photovoltaics This research activity concerns the harvesting of solar irradiation by panchromatic absorbers and the sensitization of nanostructured semiconductors in efficient solution processed photovoltaic devices. Particular effort is made on developing hybrid organic-inorganic (1D, 2D and 3D) perovskite (lead-based and lead-free) halides with powerful absorption in the visible spectrum and enhanced hole mobility, nanocomposite materials (powders, colloidal solutions) and thin films with optimum morphological characteristics (mainly high surface area) is searched via sol-gel chemistry. The research further aims at the manufacture and optimization of robust electrodes (photoactive and counter-) using various deposition techniques (screen-printing, doctor-blade, spin-coating, dip-coating) as well as the synthesis of new sensitizers (organic dyes, quantum dots). State of the art characterization is performed by combining microscopy (SEM, AFM), spectroscopy (micro-Raman, photoluminescence) and electrochemical techniques (EIS, IMPS, IMVS). Applied research is undertaken in collaboration with leading companies in the field on the development and optimization of the corresponding solar cells (Perovskite, Dye-sensitized, Quantum-dot) in terms of efficiency, stability and life-time, including process engineering, interface tuning and accelerated aging stress tests.

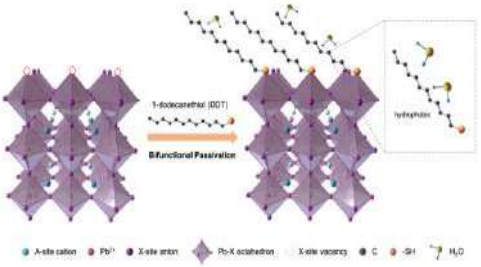
Synthesis/Characterization of Perovskite Halides for DSCs and PSCs

Temperature effects on the vibrational properties of the Cs2SnX6 'defect' perovskites
Mat. Chem. Phys. 267 (2021) 124679
A comprehensive Raman investigation of air-stable, vacancy-ordered double Cs2SnX6 (X = Cl, Br, I) perovskites is performed over an extended temperature range of 83–433 K in order to provide insight to their lattice dynamics. Substitution of the lighter and more electronegative Cl halogen with the heavier bromide and iodide ones resulted in the decrease of the frequencies for all Raman modes comprising the internal vibrations in the SnX6 octahedra and the vL(F2g) mode due to Cs vibrations against SnX6 in the rigid lattice. Blue shift, narrowing of the SnX6 stretching and bands bending were



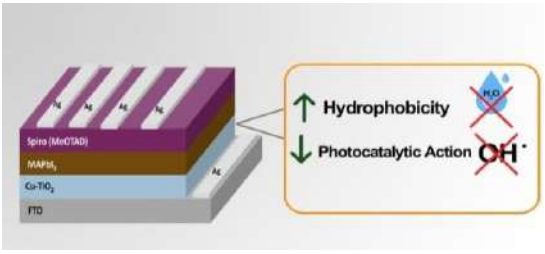
invariably observed for all halogen analogues with temperature decrease, evidencing the presence of lattice anharmonicity. The elusive vL(F2g) phonon was only observed for Cs2SnCl6 for all temperatures, complying with the predictions of Hirshfeld surface analysis for the enhanced Cs–SnCl6 interactions. The latter mode emerged for Cs2SnI6 only above room temperature, indicating that combination of anharmonic lattice dynamics with the increased Cs–SnI6 oscillation energy upon increasing temperature may activate this specific "lattice mode", which in the limit of very weak Cs–I interaction approaches the "rattling'' Cs vibrations in the cuboctahedral cage. Strong lattice anharmonicity for the chemically stable Cs2SnX6 compounds can be accordingly inferred, which is a key aspect for their performance in future optoelectronic and thermoelectric applications.

Defect passivation and humidity protection for perovskite solar cells enabled by 1-dodecanethiol
J. Mater. Chem. C 9 (2021) 9584



A surface hydrophobic modifier, 1-dodecanethiol (DDT) was introduced in perovskite solar cells to repair defects and enhance the moisture resistance of perovskite films. We found that defect repair by the thiol group in DDT can reduce trap density, inhibit non-radiative recombination, and improve charge carrier transportation and extraction performance. In addition, benefiting from the excellent hydrophobicity of the dodecyl alkyl chain in DDT, both device efficiency and stability are significantly improved. The device post-treated with DDT delivered champion power conversion efficiency (PCE) of 20.89%, accompanied by outstanding long-range stability that exceeded 90% of its initial PCE after 1000 hours at a relatively high humidity (85%) and without any encapsulation.

Enhancing efficiency and decreasing photocatalytic degradation of perovskite solar cells using a hydrophobic copper-modified titania electron transport layer
Appl. Cat. B Environ. 284 (2021) 119714



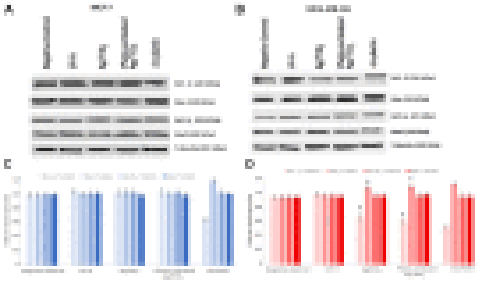
A novel interface engineering approach was adopted and Cu-modified TiO_2 was incorporated in planar perovskite solar cells in order to improve ETL/perovskite interface. The Cu-TiO_2 solution was obtained by blending Cu (NO3)2.3H2O with the TiO2 precursor solution. The presence of copper significantly advanced the quality of the TiO2 compact ETL by mitigating its photocatalytic action, increasing its conductivity and improving the adjacent interface with the perovskite layer. XPS analysis revealed the presence of copper in the form of oxide Cu2O, J–V measurements for modified electron-only devices indicated improved electron mobility and conductivity, PL spectroscopy evidenced the advanced electron transport at the Cu-ETL/perovskite interface, while trap density measurements implied the suppression of surface perovskite trap states. Therefore, PSCs with higher open circuit voltage (Voc) of 1.12 V, higher short circuit current density (Jsc) of 23.15 mA cm−2 and a higher fill factor (FF) of 73 % were obtained after copper addition, resulting in a champion PCE of 18.15 %. Improved results against reference devices were also obtained for mesoporous PSCs when copper was added in the mesoporous titania scaffold, indicating the universality of our approach. The findings of this study showed that PSCs performance can be directly enhanced by modifying TiO2 ETL with Cu cations.

Photocatalysis Advanced oxidation and reduction processes (AOPs-ARPs) driven by photoinduced heterogeneous reactions that take place on the semiconductor surface are investigated. Special emphasis is given to the growth of innovative nanostructured titania photocatalysts and their application in the re-establishment of the environment (water, air) and the protection of health. Efficiency of the photocatalytic activity is improved via: a) control of the

photocatalytic materials properties in the nano-scale level, b) increase of the photocatalyst effective surface area c) efficient separation of the photoinduced electron and hole carriers d) shift of the photocatalytic response in the visible by metal/non-metal doping and heterostructuring e) judicious balance of the photocatalytic and superhydrophilic properties in films which inherent self-cleaning functionality and f) immobilization of the nanocatalyst powders in complex photocatalytic films with controlled morphology (nanoparticulate, nanotubular) and increased chemical/mechanic stability. This research also includes the development of advanced antipollution technology (AAT) and its application in the photochemical decomposition of harmful organics of emerging concern in water as well as photocatalytic treatment of cancer cells. Thus, we develop innovative composite photocatalytic nanomaterials with parallel design, optimization, modeling and scale up of photocatalytic membrane reactors for water treatment as well as photocatalytic self-cleaning materials for buildings and antifouling coatings for corrosion protection in marine environments. Innovative titania nanomaterials and devices are also employed for CO_2 conversion (photoinduced reduction path) to useful chemicals (e.g. hydrocarbons). In parallel, carbon functionalization is performed and nanotechnology based modified electrodes and spectro-/electro- chemical sensors are developed for direct monitoring of harmful pollutants in water.

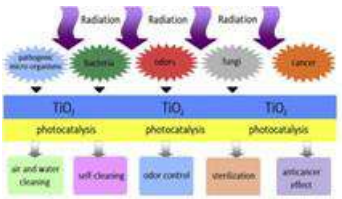
New Materials with high efficiencies in photocatalytic and catalytic reactions

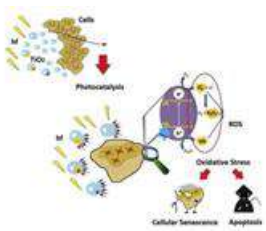
Biological effect of silver-modified nanostructured titanium dioxide in cancer
***Cancer Genomics and Proteomics* 18 (2021) 425**



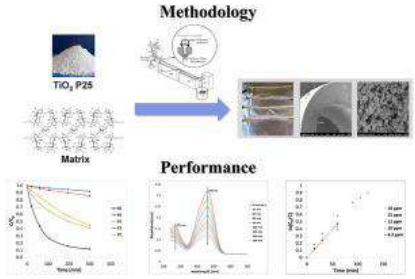
Nanostructured Ag/modified TiO2 was synthesized and characterized in order to be used for the investigation of their cytotoxicity on MCF-7 and MDA-MB-231 cells. An inhibition of cell proliferation on MDA-MB-231 cells was observed, while MCF-7 were unaffected. Our findings show that the TiO2 nanoparticle cytotoxicity can upregulate the proapoptotic Bax expression, downregulating the antiapoptotic Bcl-2 expression. DNA damage and caspase-mediated PARP cleavage are also associated phenomena, and this means that cell apoptosis is the prevalent mechanism of cytotoxicity.
The design and development of an alternative photodynamic cancer therapy that can be activated upon visible light irradiation, in parallel with a drug delivery approach, using smart polymers that might allow the controllable release of the catalyst in the biological system, maintaining the photo-induced activity of the smart composite. Our promising results show that photoexcited Ag/TiO2 might be considered as an anticancer agent. Hence, an alternative approach based on the use of nanomaterials might be very intriguing, if we consider that multidrug-resistance of tumor cells is a common major obstacle to the success of chemotherapy in addition to undesirable side effects.

Photo-activated nanostructured titanium dioxide, as a promising anticancer agent
Pharmacology & Therapeutics, 222 (2021) 107795
The multivariate condition of cancer disease has been approached in various ways. Recent studies focus on individualized treatments, minimizing the undesirable consequences of the conventional methods, but the development of an alternative effective therapeutic scheme remains to be held.
Nanomedicine could provide a solution, filling this gap, exploiting the unique properties of innovative nanostructured materials. This work provides insights into the field of nanomedicine and particularly into the wide context of TiO_2-NP-mediated anticancer effect, shedding light on the achievements of nanotechnology and proposing this nanostructured material as a promising anticancer photosensitizer. Due to its biocompatibility, it has also a great number of biomedical applications. It is now clear that photo-excited TiO_2 nanoparticles induce generation of pairs of electrons and holes which react with water and oxygen to yield reactive oxygen species (ROS) that have been proven to damage cancer cells, triggering controlled cellular processes.





Ceramic hollow fiber photocatalysts for application in industrial wastewater processes
Chemosphere 277 (2021) 130253



Innovative photocatalytic systems were successfully developed based on Alginate molds and a wet-spinning/cross-linking technique, yielding commercial photocatalyst (Degussa P25) in the form of all-ceramic hollow fibers (HFs). Taking advantage of alginate's exceptional sorption properties, copper augmented hollow fibers (HFs) were also developed. Synthesis and heat treatment parameters were found to affect the fibers' properties, allowing their optimization. Treatment at 600 °C under Ar was found to produce the best performing photocatalysts in terms of mechanical stability, resistance to attrition and photocatalytic performance. Ca-Alginate precursors led to structures with increased mechanical stability, while Cu-Alginate decorated the surface of the photocatalyst with highly dispersed copper nanoparticles, in the state of metallic and CuO. The developed materials were photo-catalytically active, while the copper decorated ceramic HFs exhibited the highest MO adsorption and photocatalytic degradation performance, reaching a MO removal of 73.4%. The synergetic effect of adsorption on the MO degradation performance was also noticed. Moreover, the copper addition facilitated the photocatalytic process by improving the electron-hole separation and inhibiting the recombination effects. The presence of carbon residue was also beneficial, enhancing the MO sorption on the photocatalysts. It is noteworthy that the structured photocatalysts retained their efficiency for at least four photocatalytic cycles. The prepared ceramic HFs exhibited enhanced mechanical properties and excellent resistance to attrition after subsequent cycles, rendering them excellent candidates for application in industrial wastewater processes.

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1. MAESTRO-Making Perovskites Truly Exploitable, H2020-MSCA-ITN-2017 Project number: 764787, (2017-2021) 273K€
2. LIFE PureAgroH2O-Pollutant Photo-NF remediation of Agro-Water, LIFE17 ENV/GR/000387, (2018-2021) 785K€
3. NEROPHOS-Hydrogen and electricity production via water splitting in a tandem photoelectrochemical-perovskite solar cell, HFRI (ELIDEK), (coordinator: Dr M. Antoniadou), (2018-2021) 180 K€
4. SELAS-Autonomous system for the non-intermittent generation and storage of electricity using photovoltaics on motorways (ESPA, MIS 5033815, T1ΕΔΚ-03547), (2018-2021) 189 K€
5. DRAstiC- Industrial research for the development of robust, lightweight and low drag hull coatings of high antifouling performance, having multiple applications. «ΕΡΕΥΝΩ-ΔΗΜΙΟΥΡΓΩ-ΚΑΙΝΟΤΟΜΩ», (Τ2ΕΔΚ-00868), 172.065,00 €
6. Functional interfaces in perovskite photovoltaic cells of high efficiency and increased stability (ΟΠΣ ΕΣΠΑ 14-20, MIS: 5047816), 41.500,00 €
7. Advanced Materials for stable Perovskite Solar Cells, HFRI (ELIDEK), (coordinator: Dr A. Kaltzoglou), (2018-2021)
8. Photovoltaic devices based on perovskite quantum dots, IKY Fellowship to Dr. L. Givalou
9. Innovative method of developing oriented films of hybrid perovskite semiconductors with application to photovoltaic devices, IKY Fellowship to Dr.G. Manolis

OUTPUT

Publications in International Journals

1. Zaky A.A., Christopoulos E., Gkini K., Arfanis M.K., Sygellou L., Kaltzoglou A., Stergiou A., Tagmatarchis N., Balis N. and Falaras P. "Enhancing efficiency and decreasing photocatalytic degradation of perovskite solar cells using a hydrophobic copper-modified titania electron transport layer". *Applied Catalysis B Environmental* **284,** 119714 (2021). DOI: 10.1016/j.apcatb.2020.119714

2. Lagopati N., Evangelou K., Falaras P., Tsilibary E-P.C. , Vasileiou P.V.S. , Havaki S., Angelopoulou A., Pavlatou E.A. and Gorgoulis V.G. "Nanomedicine: Photo-activated nanostructured titanium dioxide, as a promising anticancer agent". *Pharmacology & Therapeutics* **222**, 107795 (2021). DOI: 10.1016/j.pharmthera.2020.107795

3. Theodorakopoulos G.V., Romanos G.E., Katsaros F.K., Papageorgiou S.K., Kontos A.G., Beazi-Katsioti M. and Falaras P. "Structuring efficient photocatalysts into bespoke fiber shaped systems for applied water treatment". *Chemosphere* **277,** 130253 (2021). DOI: 10.1016/j.chemosphere.2021.130253

4. Gkini K., Martinaiou I. and Falaras P. "A Review on Emerging Efficient and Stable Perovskite Solar Cells Based on g-C_3N_4 Nanostructures". *Materials* **14**, 1679 (2021). DOI: 10.3390/ma14071679

5. Belessiotis G.V., Arfanis M., Kaltzoglou A., Likodimos V., Raptis Y.S., Falaras P. and Kontos A.G. "Temperature effects on the vibrational properties of the Cs_2SnX_6 'defect' perovskites (X = I, Br, Cl)". *Materials Chemistry and Physics* **267**, 124679 (2021). DOI: 10.1016/j.matchemphys.2021.124679

6. Lagopati N., Kotsinas A., Veroutis D., Evangelou K., Papaspyropoulos A., Arfanis M.K., Falaras P., Kitsiou P.V., Pateras I., Bergonzini A., Frisan T., Kyriazis S., Tsoukleris D.S., Tsilibary E-P.C., Gazouli M., Pavlatou E.A. and Gorgoulis

V.G. "Biological effect of silver-modified nanostructured titanium dioxide in cancer". *Cancer Genomics and Proteomics* **18**, 425-439 (2021). DOI: 10.21873/cgp.20269
7. He D., Xu X., Liang Z., Niu Y., Sun Y., Tulloch G., Falaras P. and Hu L. "Defect passivation and humidity protection for perovskite solar cells enabled by 1-dodecanethiol". *Journal of Materials Chemistry C* **9**, 9584-9591 (2021). DOI:10.1039/d1tc01720a
8. Kaltzoglou A. and Falaras P. "Recent developments on hybrid perovskite materials for solar energy conversion and environmental protection". *Current Opinion in Chemical Engineering* **1,** 100708 (2021). DOI: 10.1016/j.coche.2021.100708
9. Kochylas I., Gardelis S., Likodimos V., Giannakopoulos K.P., Falaras P. and Nassiopoulou A.G. "Improved Surface-Enhanced-Raman Scattering Sensitivity Using Si Nanowires/Silver Nanostructures by a Single Step Metal-Assisted Chemical Etching". *Nanomaterials* **11**, 1760 (2021). DOI: 10.3390/nano11071760
10. Zaky A.A., Fathy A., Rezk H., Gkini K., Falaras P. and Abaza A. "A Modified Triple-diode Model Parameters Identification for Perovskite Solar Cells via Nature Inspired Search Optimization Algorithms". *Sustainability* **13**, 12969 (2021). DOI: 10.3390/su132312969
11. Kostoglou, N., Liao, C.-W., Wang, C.-Y., Kondo, J.N., Tampaxis, C., Steriotis, T., Giannakopoulos, K., Kontos, A.G., Hinder, S., Baker, M., Bousser, E., Matthews, A., Rebholz, C., Mitterer, C. "Effect of Pt nanoparticle decoration on the H_2 storage performance of plasma-derived nanoporous graphene", *Carbon* **171**, 294-305 (2021). DOI: 10.1016/j.carbon.2020.08.061

International Conferences Presentations (invited, oral, poster)

1. Arfanis M.K., Theodorakopoulos G., Anagnostopoulos C., Georgaki E., Liapis K., Romanos G.Em., Markellou E., Falaras P., Photocatalytic Removal of Pesticides Present in Agro-industrial Water Effluents, *17th International Conference on Environmental Science and Technology-CEST 2021,* 1 to 4 September 2021, Athens, Greece, Flash and Poster Presentation, cest2021_00432.
2. Ibrahim I., Belessiotis G.V., Kaltzoglou A., Katsaros F., Salama T.M., Falaras P., Silver decorated TiO_2/g-C_3N_4 nanocomposites for photocatalytic elimination of water pollutants under UV and artificial solar light, *17th International Conference on Environmental Science and Technology-CEST 2021, 1 to 4 September 2021*, Athens, Greece, Flash and Poster Presentation, cest2021_00151.
3. Kossyvakis D.N., Christopoulos E., Raptis V., Christoforou E.V., Falaras P., Kaltzoglou A., Incorporation of Peltier coolers on perovskite solar cells, 1*4th International Symposium on Flexible Organic Electronics (ISFOE21), Workshop on OPVs & Perovskite PVs* 2, 5-8 July 2021, Thessaloniki, Greece, Book of Abstracts, page 60.
4. Belessiotis G.V., Arfanis M., Kaltzoglou A., Likodimos V., Raptis Y.S., Falaras P., Kontos A.G., Temperature dependence of Vibrational and Emission characteristics in the 0D vacancy ordered Cs_2SnI_6 double perovskite, *18th International Conference on Nanosciences & Nanotechnologies (NN21)*, 6-9 July 2021, Thessaloniki, Greece, Book of Abstracts, P. 157.
5. Raptis V., Kaltzoglou A., Falaras P., A study of halide perovskite structures combining Hirshfeld analysis with theoretical considerations, *18th International Conference on Nanosciences & Nanotechnologies (NN21)*, 6-9 July 2021, Thessaloniki, Greece, Book of Abstracts, p. 168.
6. Manolis G. K., Kaltzoglou A., Falaras P., Manipulating the preferred orientation of $(CH_3)_3SPbI_3$ hybrid perovskite, *XXXV Panhellenic Conference on Solid State Physics and Materials Science*, Virtual Conference, September 26-29 2021, Athens, Greece, P1.9, Book of Abstracts, pages 77-78.
7. Theofylaktos L., Christopoulos E., Falaras P., Stergiopoulos T., Enhanced photoluminescence of lead halide perovskite films through surface functionalization with SCN--containing ionic liquids, *XXXV Panhellenic Conference on Solid State Physics and Materials Science*, Virtual Conference, September 26-29 2021, Athens, Greece, P1.10, Book of Abstracts, pages 79-80.
8. Karnachoriti M., Kontos A.G, Bounos G., Stoumpos C.C., Tsetseris L., Kaltzoglou A., Guo X., Lü X., Falaras P., Kanatzidis M.G, Raptis Y.S., Structural Transformations in Cs_2SnI_6 Defect Perovskite under High Pressure, *XXXV Panhellenic Conference on Solid State Physics and Materials Science*, Virtual Conference, September 26-29 2021, Athens, Greece, T2A.1, Book of Abstracts, pages 161-162.
9. Raptis V., Falaras P., Kaltzoglou A., Hirshfeld surface analysis and graph-theoretical considerations in the study of halide perovskite compounds and their structure-property relations, *XXXV Panhellenic Conference on Solid State*

Physics and Materials Science, Virtual Conference, September 26-29 2021,Athens, Greece, T2A.2, Book of Abstracts, pages 163-164.

10. Kochylas I., Likodimos V., Gardelis S., Falaras P., Nassiopoulou A.G., Si Nanowires/Ag nanostructures fabricated by a single step MACE process for improved detection by SERS and Photoluminescence, *XXXV Panhellenic Conference on Solid State Physics and Materials Science*, Virtual Conference, September 26-29 2021, Athens, Greece, T2A.6, Book of Abstracts, pages 171-172.

11. Apostolaki M.A., Toumazatou A., Antoniadou M., Sakellis E., Xenogiannopoulou E., Gardelis S., Boukos N., Falaras P., Dimoulas A., Likodimos V., Graphene quantum dot-TiO_2 photonic crystal photocatalysts, *XXXV Panhellenic Conference on Solid State Physics and Materials Science*, Virtual Conference, September 26-29 2021, Athens, Greece, T2B.1 Book of Abstracts, pages 173-174.

12. Givalou L., Christopoulos E., Falaras P., Incorporation of Semiconductor Quantum Dots and Perovskite for High Efficiency Perovskite Solar Cells, *XXXV Panhellenic Conference on Solid State Physics and Materials Science*, Virtual Conference, September 26-29 2021, Athens, Greece,. P2.28, Book of Abstracts, pages 262-263.

13. Falara P.P., Arfanis M.K., Kordatos K., Photocatalytic degradation of antibiotic pharmaceuticals using nitrogen-modified TiO_2 nanostructures, *12th International Conference on Instrumental Methods of Analysis – IMA-2021*, September 20th-23th 2021, Virtual Event, Book of Abstracts, page 177.

Other type of publications (non-refereed Conference Proceedings, magazine, etc)

1. Hussein A.A.Z., Perovskite Solar Cells as an Alternative for Silicon Ones (Hopes and Challenges), *1st online meeting of postgraduate students*, January 21 2021, Institute of Nanoscience and Nanotechnology, NCSR Demokritos, Athens, Greece.

2. Elsenety, M.M.T., Development of Inorganic and Hybrid Perovskite Materials and their Application in Photovoltaic Devices, *1st online meeting of postgraduate students*, January 21 2021, Institute of Nanoscience and Nanotechnology, NCSR Demokritos, Athens, Greece.

International Conferences Presentations (invited, oral, poster)

1. Falaras, P., Scale up and demonstration of innovative photocatalytic nanofiltration technology for pollutants removal and water recovery, *9th International Conference on Water Resources and Arid Environments (ICWRAE),* March 29-31, 2021, King Saud University (virtual), Saudi Arabia, *invited*.

Teaching and Training Activities

1. Name: Falaras Polycarpos
   Activity Title, Dates/Duration of lectures/training: Teaching Physical Chemistry
   Years: Academic Years 2020-2021 and 2021-2022
   Location/Academic Institute: Faculty of Sciences and Technology, Hellenic Open University, Athens, Greece
2. Name: Falaras Polycarpos
   Activity Title, Dates/Duration of lectures/training: Catalysis and Environmental Protection Master Programme
   Years: Academic Years 2020-2021 and 2021-2022
   Location/Academic Institute: Hellenic Open University, Athens, Greece
3. Name: Antoniadou Maria
   Activity Title, Dates/Duration of lectures/training: Environmental Protection and antipollution technologies
   Years: Academic Year 2021-2022
   Location/Academic Institute: School of Pedagogical and Technological Education (ASPETE), Department of Mechanical Engineering Educators, Athens, Greece

Doctoral Dissertations completed in 2021

1. Name: Mohamed Mahmoud Taha Elsenety
   Dissertation Title: Development of Inorganic and Hybrid Perovskite Materials and their Application in Photovoltaic Devices
   Research Supervisor at NCSR: Dr. Polycarpos Falaras

University where the Thesis was presented: National and Kapodistrian University of Athens, Department of Chemistry

2. Name: Alaa Ahmed Zaky Hussein
Dissertation Title: Development of New Photovoltaic Devices based on Perovskite Cells and Application in Electric Power Systems
Research Supervisor at NCSR: Dr. Polycarpos Falaras
University where the Thesis was presented: National Technical University of Athens, School of Electrical and Computer Engineering

Undergraduate Theses and Internships completed in 2021

1. Name: Elpiniki Mpompoli
Dissertation Title: Innovative materials for nanocrystalline solar cells
Research Supervisor at NCSR: Dr. Polycarpos Falaras
University where the Thesis was presented: University of Ioannina, Department of Physics
2. Name: Athina Tzavara-Roussi
Dissertation Title: Nanostructured materials in photoinduced processes
Research Supervisor at NCSR: Dr. Polycarpos Falaras
University where the Thesis was presented: National Technical University of Athens, School of Chemical Engineering