NATIONAL CENTRE FOR
SCIENTIFIC RESEARCH "DEMOKRITOS"

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INSTITUTE OF NANOSCIENCE AND NANOTECHNOLOGY

Annual Scientific Report

2020

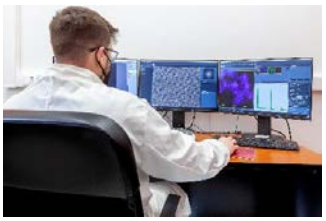
INN Institute Nanoscience Nanotechnology

Contents

PREFACE

The Institute of Nanoscience and Nanotechnology (INN) is one of the five institutes of NCSR Demokritos, by far the largest in terms of scientific personnel and research infrastructures. Its mission is to advance scientific and technological knowledge by conducting pure and applied research in a wide range of Physical, Chemical and Engineering Sciences with emphasis on Nanoscience and Nanotechnology, with research activities spanning from the study of processes to the development and characterisation of materials, devices and systems

The year 2020 has been characterised by growth in both academic output and funding, with the highlight being the installation of the new Scanning/Transmission Electron Microscope. The microscope was acquired with funds from the project “The Greek Research Infrastructure for Nanotechnology, Advanced Materials and Micro/Nanoelectronics INNOVATION-EL”, 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). This cutting-edge Thermo Scientific Talos F200i S/TEM (Field Emission Gun, 0.23 nm TEM resolution, 0.16 nm S/TEM resolution, 0.10nm Information Limit) will greatly enhance INN capacity in High Resolution TEM and S/TEM imaging, S/TEM EDS elemental mapping as well as in nanoprobe crystallography, microprobe STEM imaging/diffraction and Z-contrast imaging. These techniques will be used to study a wide range of 2-D materials, composites, oxides, semiconductors, magnetic materials, metallic and complex materials, boosting INN capabilities to develop, tailor and optimize new nanomaterials and nanostructures



During the past year two new appointments took place aiming to strengthen the institute’s agenda in the development of photonic and organic electronic devices (Nikos Kehagias, Researcher C) and in the dating of archaeological and environmental materials (Giorgos Polymeris, Researcher C). At the same time, we experienced the unexpected loss of two key members of INN with very strong scientific profiles at an international level: Dionisis Vourloumis and Androula Nassiopoulou. They both leave a substantial gap, but we feel that their colleagues and students will rise to the challenge of continuing their work. INN continued its tradition of training young scientists by supervising 83 PhD and 29 MSc funded projects as well as by employing 91 Postdoctoral fellows who work in large institutional and externally funded projects.

In terms of academic output, INN performed at its usually relatively high level with emphasis on quality. Altogether 210 papers were published in refereed journals, 87 in conference proceedings and 17 as book chapters, while INN affiliated papers had 10612 citations. Finally, during 2020 INN researchers were the scientists-in-charge in 15 Horizon 2020, 36 national and 8 externally funded projects. Furthermore, 21 contracts for service and R&D work were signed and executed at INN.

In the following pages the annual scientific report of the institute groups follows.

Vassilis Kilikoglou

Director of INN

Program 1

Nanochemistry and Nanomaterials

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, Theodoros Tsoufis, Anastasios Labropoulos, Myrsini-Kyriaki Antoniou, Diana Elena Baciu, Dimitra Giasafaki, Christina Mitzithra Charitomeni Veziri, Dionysios Karoussos, Anna Perdikaki, Evangelos Angelopoulos, Ioannis Bratsos, Antigoni Kalamara, Maria-Malvina Stathouraki, Athanassios Nikolakopoulos

Technical/Administrative Staff:

PhD Candidates: Georgios Theodorakopoulos, Christos Tampaxis, Lamprini Boutsika, Filippos Mpoukis, Ioannis Floros, Fillipo Peru, Evangelia Choleva, Eudoxia Galata, Elisavet Michailidi, Panagiotis Kastanidis, Eleni Thomou, Georgia Karataraki, Leonidas Spyrogiannopoulos, Ioannis Tournis

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.

- **Activities and Main 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.

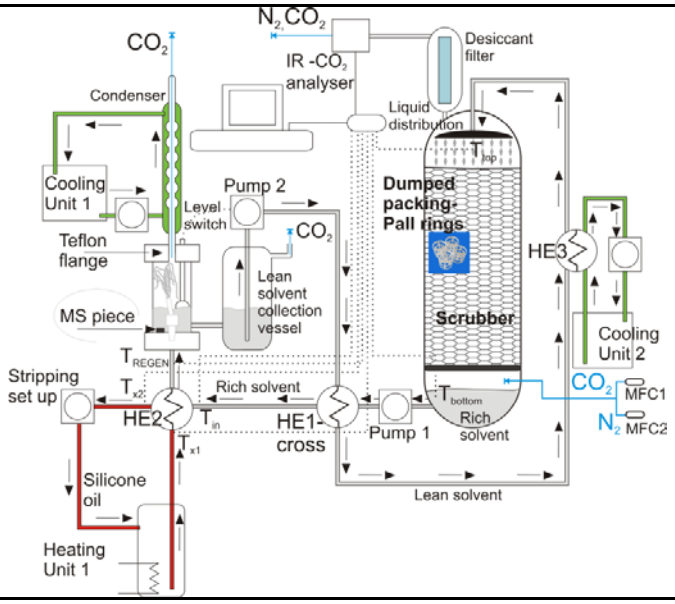
- **Pore Structure Analysis & Characterisation - Performance evaluation.**
- Pore size distribution, surface area analysis, pore volume and pore connectivity by applying techniques such as: nitrogen and mercury porosimetry, absolute and relativity gas and gas vapours permeability (single and multi-phase), 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).

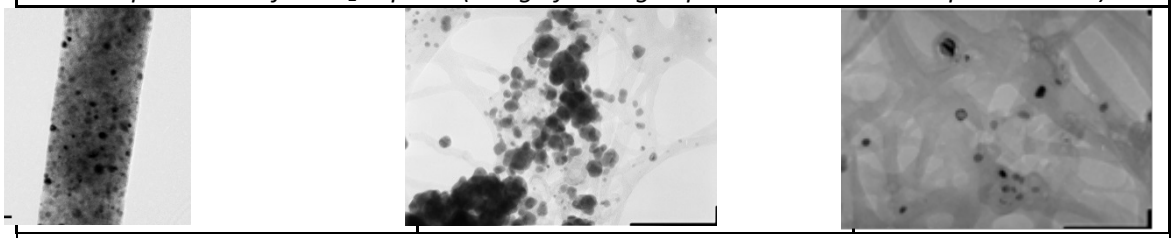
- **Applications with Industrial interest.**
- Gas Storage and separations (H_2, CH_4, CO_2, etc.)
- Membrane technology in gas (treatment and exploitation of Natural Gas and the gas streams of Oil refineries) and liquid phases (steviols separation and purification)
- Effective and sustainable water 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)

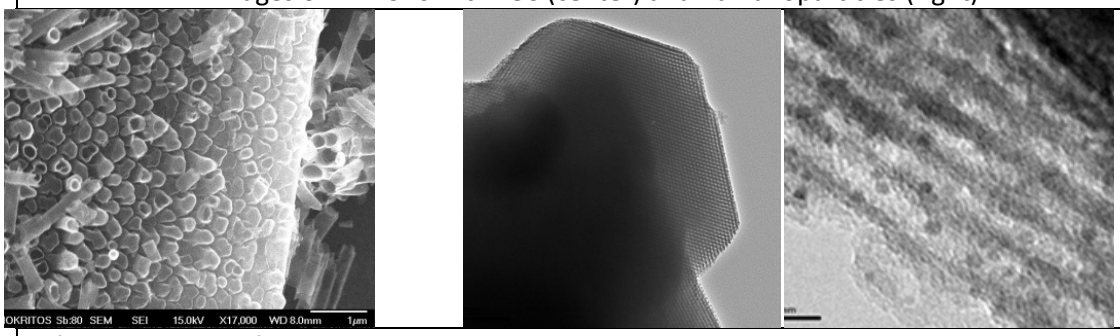
- Application of renewable/efficient energy resources in industrial applications (Solarization of cement production processes, production of Blue and Green-H2 production from fossil, CO2 conversion to fine chemicals).



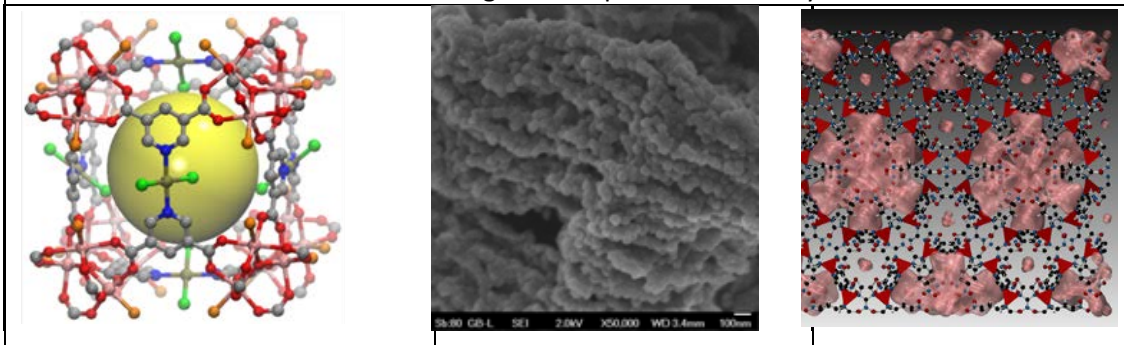
Process optimization for CO_2 capture (design for Megalopolis Public Power Corporation site)



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) 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. 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. The Research Council of Norway. CO2Hing - Carbon Membranes for CO2 Removal from High Pressure Natural Gas in Subsea Process. 01/03/2017 - 31/12/2020. Total Budget: 10,000,000 NOK, NCSRD budget: 455,860 NOK.
8. 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 – 31/01/2022 Total budget: 1,044,830, NCSRD budget 100,000 €.
9. 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 €.
10. Operational Program Competitiveness under the call Fishery and Sea, Project code: MIS 5030665 - Development of innovative non biocidal antifouling paints for aquaculture applications, 12/4/2019-12/4/2022. Total Budget: 515,628 €, NCSRD Budget: 226,271€.

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 – 10/07/2021, 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 – 03/07/2021, 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 – 27/06/2021. 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 – 30/07/2021. Total Budget: 857,787 €, NCSRD Budget 309,564 €.

15. Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE. Project code: T1EΔK-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- 30/7/2021. NCSRD subcontractor: 50,000€.
16. Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE. Project code: T2EΔK-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: T2EΔK-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. Post-Doctoral Fellows: (i) Dr. Apostolos Enotiadis & Dr Myrsini Kyriaki Antoniou in collaboration with Berling S.A., 15/9/2017 - 28/2/2021. (ii) Dr. Theodore Tsoufis in collaboration with Thrace Nonwovens & Geosynthetics S.A. (Subsidiery of Thrace Plastics Group) 01/09/2017-31/08/2020. (iii) Dr. Anastasios Lambropoulos in collaboration with SUC Hellas, 11/06/2017 - 10/05/2020, (iv) Dr. Anna Perdikaki in collaboration with JOTIS S.A., 3/7/2017-3/7/2020. Total Budget: 331,200€.
20. Industrial Research Fellowship Scheme co-funded by Stavros Niarchos Foundation and Industry. PhD students: (i) Ms. E. Choleva, Partner in collaboration with Q-Lab, 01/11/2017 – 31/10/2021 (ii) Mr. Filippos Boukis, in collaboration with Ellaktor, 01/11/2017 – 31/10/2021 (iii) Mr. I. Floros in collaboration with Ecotech, 01/10/2017 – 30/09/2021, (iv) Ms. E. Michailidi, 11/07/2017 – 10/07/2021. Total Budget: 190,400 €.

OUTPUT

Publications in International Journals

1. Gisbert-Garzarán M., Berkmann J. C., Giasafaki D., Lozano D., Spyrou K., Manzano M., Steriotis Th., Duda G. N., Schmidt-Bleek K., Charalambopoulou G., Vallet-Regí M., Engineered pH-Responsive Mesoporous Carbon Nanoparticles for Drug Delivery, *ACS Appl. Mater. Interfaces* **12**, 14946–14957 (2020). DOI: https://doi.org/10.1021/acsami.0c01786.
2. Marini S., Gjeci N., Govindaraj Sh., But A., Sportich B., Ottaviani E., Pedro García Márquez F., Bernalte Sanchez P. J., Pedersen J., Vetke Clausen C., Madricardo F., Foglini F., Bonofiglio F., Barbieri L., Antonini M., Sorani Montenegro Camacho Y., Weiss P., Nowak K., Peer M., Gobert Th., Turetta A., Chatzidouros E., Lee D., Zarras D., Steriotis Th., Charalambopoulou G., Yamas Th., Papaelias M., ENDURUNS: An Integrated and Flexible Approach for Seabed Survey Through Autonomous Mobile Vehicles, *J. Mar. Sci. Eng.* **8**, 633 (2020). DOI: https://doi.org/10.3390/jmse8090633.
3. Tampaxis Ch., Steriotis Th. A., Katsaros F. K., Sapalidis A. A., Youngs T. G. A., Bowron D. T., Stefanopoulos K. L., Enhanced densification of CO_2 confined in the pores of a carbon material: an in situ total neutron scattering study, *J. Surf. Investig.: x-ray synchrotron neutron tech.* **14,** S221-S224 (2020). DOI: https://doi.org/10.1134/S1027451020070472.
4. Stefanopoulos K.L., Tampaxis Ch., Sapalidis A.A., Katsaros F.K., Youngs T.G.A., Bowron D.T., Steriotis Th.A., Total neutron scattering study of supercooled CO_2 confined in an ordered mesoporous carbon, *Carbon* **167**, 296-306 (2020). DOI: https://doi.org/10.1016/j.carbon.2020.05.068.
5. Nguyen H. G. T., Sims C. M., Toman B., Horn J., van Zee R. D., Thommes M., Ahmad R., Denayer J. F. M., Baron G. V., Napolitano E., Bielewski M., Mangano E., Brandani S., Broom D. P., Benham M. J., Dailly A., Dreisbach F., Edubilli S., Gumma S., Möllmer J., Lange M., Tian M., Mays T. J., Shigeoka T., Yamakita S., Hakuman M., Nakada Y., Nakai K., Hwang J., Pini R., Jiang H., Ebner A. D., Nicholson M. A., Ritter J. A.,

Farrando-Pérez J., Cuadrado-Collados C., Silvestre-Albero J., Tampaxis C., Steriotis T., Řimnáčová D., Švábová M., Vorokhta M., Wang H., Bovens E., Heymans N., Weireld G. De, A reference high-pressure CH4 adsorption isotherm for zeolite Y: results of an interlaboratory study, *Adsorption* **26**, 1253–1266 (2020). DOI: https://doi.org/10.1007/s10450-020-00253-0.

6. Boffito M., Laurano R., Giasafaki D., Steriotis Th., Papadopoulos A., Tonda-Turo Ch., Cassino C., Charalambopoulou G., Ciardelli G., Embedding ordered mesoporous carbons into thermosensitive hydrogels: A cutting-edge strategy to vehiculate a cargo and control its release profile, *Nanomaterials* **10**, 2165 (2020). DOI: https://doi.org/10.3390/nano10112165.
7. Smyrnioti M., Tampaxis Ch., Steriotis Th., Ioannides Th., Study of CO2 adsorption on a commercial CuO/ZnO/Al2O3 catalyst, *Catalysis Today* **357**, 495-502 (2020). DOI: https://doi.org/10.1016/j.cattod.2019.07.024.
8. Peru F., Payandeh S., Charalambopoulou G. C., Jensen T.R., Steriotis Th. A., Hydrogen Sorption and Reversibility of the LiBH4-KBH4 Eutectic System Confined in a CMK-3 Type Carbon via Melt Infiltration, *Journal of Carbon Research* **6**(2), 19 (2020). DOI: https://doi.org/10.3390/c6020019.
9. Michailidi, E.D., Bomis, G., Varoutoglou, A., Kyzas, G.Z., Mitrikas, G., Efthimiadou, E.K., Mitropoulos, A.Ch., Favvas, E.P. Bulk nanobubbles: Production and investigation of their formation/stability mechanism, *J. Colloid Interface Sci.* **564**, 371–380 (2020). DOI: https://doi.org/10.1016/j.jcis.2019.12.093 (***On the journal cover***).
10. Floros, I., Kouvelos, E., Pilatos, G., Hadjigeorgiou, E., Gotzias, A., Favvas, E., Sapalidis, A. Enhancement of flux performance in PTFE membranes for direct contact membrane distillation. *Polymers* **12**, 345 (13) (2020). DOI: https://doi.org/10.3390/polym12020345.
11. Michalopoulou, A., Michailidi, E., Favvas, E., Maravelaki, N.-P., Kilikoglou, V., Karatasios, I. Comparative evaluation of the morphological characteristics of nanolime dispersions for the consolidation of architectural monuments. *Int. J. Archit. Herit.* **14**, 994-1007 (2020**)**. DOI: https://doi.org/10.1080/15583058.2020.1745323.
12. Barbe, S., Berger, M., Egnstler, R., Dieste, A., Clavijo, L., Favvas, E., Sapalidis, E. One-step Preparation of Bilayered Films from Kraft Lignin and Cellulose Acetate to Mimic Tree Bark. *Eur. J. Wood and Wood Prod.* **78**, 831–834 (2020). DOI: https://doi.org/10.1007/s00107-020-01537-6.
13. Vengatesan, M., Wahab, M.A., Kuppireddy, S., Kakosimos, G., Abdalla, O., Favvas, E., Reinalda, D., Geuzebroek, F., Abdala, A., Karanikolos, G. Metal-Organic Framework - Based Mixed Matrix Membranes for Carbon Dioxide Separation: Recent Advances and Future Directions. Frontier in Chemistry **8**, 534, (2020). DOI: https://doi.org/10.3389/fchem.2020.00534.
14. Sapalidis, A.A. Karantzis, P.I. Vairis, A., Barbe, S., Nitodas, S., Favvas, E.P. A study of reinforcement effect by MWCNTs into BTDA–TDI/MDI (P84) polyimide flat sheet membranes. *Polymers* **12(6)**, 1381 (2020). DOI: https://doi.org/10.3390/polym12061381.
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17. Kyzas, G.Z., Favvas, E.P., Kostoglou, M., Mitropoulos, A.C. Batch adsorption process without agitation by using bulk nanobubbles. *Colloid Surface A* **607**, 125440 (2020). DOI: https://doi.org/10.1016/j.colsurfa.2020.125440.
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artificial solar light. *Chemical Engineering Journal* **381**, 122730 (2020). DOI: https://doi.org/10.1016/j.cej.2019.122730.
20. Heliopoulos, N.S., Kouzilos, G.N., Giarmenitis, A.I., Papageorgiou, S.K., Stamatakis,K., Katsaros, F.K., Viscose Fabric Functionalized with Copper and Copper Alginate Treatment Toward Antibacterial and UV Blocking Properties. *Fibers and Polymers* **21**, 1238–1250 (2020). DOI: https://doi.org/10.1007/s12221-020-9578-4.
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23. Kontos, A. G., Romanos, G. E., Veziri, C. M., Gotzias, A., Arfanis, M. K., Kouvelos, E., Likodimos, V., Karanikolos, G. N., Falaras, P. Correlating vibrational properties with temperature and pressure dependent CO2 adsorption in zeolitic imidazolate frameworks. *Applied Surface Science* **529**, 147058 (2020). DOI: https://doi.org/10.1016/j.apsusc.2020.147058.
24. Ibrahim, I., Belessiotis, G. V., Arfanis, M. K., Athanasekou, C., Philippopoulos, A. I., Mitsopoulou, C. A., Romanos, G. E., Falaras, P. Surfactant Effects on the Synthesis of Redox Bifunctional V2O5 Photocatalysts. *Materials* (Basel) **13**(20) 1-13 (2020). DOI: https://doi.org/10.3390/ma13204665.
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26. Sapalidis, A. Porous polyvinyl alcohol membranes: preparation methods and applications. *Symmetry*, **12**, 960 (2020). DOI: https://doi.org/10.3390/sym12060960.
27. Tziveleka, L.A., Sapalidis, A., Kikionis, S., Aggelidou, E., Demiri, E., Kritis, A., Ioannou, E., Roussis, V. Hybrid Sponge-Like Scaffolds Based on Ulvan and Gelatin: Design, Characterization and Evaluation of Their Potential Use in Bone Tissue Engineering, *Materials,* **13**(7), 1763 (2020). DOI: https://doi.org/10.3390/ma13071763.
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31. Lykogianni, M., Papadopoulou, E-A, Sapalidis, A., Tsiourvas, D., Sideratou, Z., Aliferis, K. Metabolomics reveals differential mechanisms of toxicity of hyperbranched poly(ethyleneimine)-derived nanoparticles to the soil-borne fungus Verticillium dahliae Kleb, *Pesticide Biochemistry and Physiology* **165**, 104535 (2020). DOI: https://doi.org/10.1016/j.pestbp.2020.02.001.
32. Gotzias, A., Sapalidis, A. Pulling Simulations and Hydrogen Sorption Modelling on Carbon Nanotube Bundles. *Journal of Carbon Research* **6** (1), 11 (2020). DOI: https://doi.org/10.3390/c6010011.
33. Zaky A. A., Balis N., Gkini K., Athanasekou C., Kaltzoglou A., Stergiopoulos T., P Falaras. "Dye Engineered Perovskite Solar Cells under Accelerated Thermal Stress and Prolonged Light Exposure", *Chemistry Select* **5**, 4454 –4462 (2020). DOI:10.1002/slct.202000771

Books/Chapters in Books

1. Sapalidis, A., Membrane Desalination: From Nanoscale to Real World Applications, Editor, CRC Press. 2020.
2. Sapalidis, A., Kouvelos, E., Romanos, G., Kanellopoulos, N. Introduction to membrane desalination, Membrane Desalination: From Nanoscale to Real World Applications, Edited by Sapalidis, A., (1st ed.). CRC Press. Ch. 1, pp. 1-15 (2020).
3. Antoniou, M.K., Sapalidis, A., Sideratou, Z., Functionalization of Carbon-Based Additives, Membrane Desalination: From Nanoscale to Real World Applications, Edited by Sapalidis, A., (1st ed.). CRC Press. Ch. 1, pp. 67-90 (2020).
4. Kyzas G. Z., Favvas E.P., Mitropoulos A.C., Nanohybrid graphene-based materials for advanced wastewater treatment: Adsorption and membrane technology, , Membrane Desalination: From Nanoscale to Real World Applications, Edited by Sapalidis, A., (1st ed.). CRC Press. Ch. 1 (2020).
5. Theodorakopoulos, G., Athanasekou, C., Romanos, G. E., Papageorgiou, S. K. Handbook of Smart Photocatalytic Materials, Edited by Mustansar Hussain, C., Mishra, A. K., Elsevier, Ch. 8, pp. 231-264 (2020).
6. Karataraki, G., Gotzias, A., Tocci, E. Carbon Molecular Models for Desalination. Membrane Desalination: From Nanoscale to Real World Applications, Edited by Sapalidis, A., (1st ed.) CRC Press, (2020).

Other type of publications

1. Stefanopoulos, K.L., Neutron scattering methods for investigating the structural properties of porous materials and pore-confined fluids, Hellenic Neutron Association Newsletter (HENA) 6, 2-7 (2020).

International and national Conferences Presentations (invited, oral, poster)

1. Metaxa, Z.S., Favvas, E.P., Mitropoulos, A.C. Dispersing carbon nanomaterials facilitating aqueous air nanobbuble solutions for use in cement based materials. 19th International Conference on Experimental Mechanics, 5-9 July, 2020, Kraków, Poland.
2. Deze, E.G., Karousos, D.S., Sapalidis, A.A., Favvas, E.P. Mesoporous Silica based copper catalytic materials: Synthesis, Characterization & deNOx Evaluation. 17th International Conference on Nanosciences & Nanotechnologies (NN20), 7-10 July 2020, Thessaloniki, Greece.
3. Romanos, G., Innovative photocatalytic nanofiltration technology for micropollutants abatement and water reuse of Agro-industrial effluents-LIFE PureAgroH20, 1st LIFE PureAgroH2O Conference, titled "Connecting innovative water reuse technologies with the Food Industry", 17 January 2020, Athens, Greece.
4. Deze, E.G., Cuenca, E., Násner, A.M.L, Iakovlev, M., Sideri, S., Sapalidis, A., Borg, R.P., Ferrara, L. Nanocellulose containing Concretes: Evaluation of NC properties affecting UHDC & Development of mixing protocols. 17th International Conference on Nanosciences & Nanotechnologies (NN20), 7-10 July 2020, Thessaloniki, Greece.
5. Nikolakopoulos, A., Steriotis, Th., Charalambopoulou, G., Karagiannakis, G., Dimitrakis D., Konstandopoulos, A.G., Michalis, V., Katsiotis M. Solar-aided calcination of limestone: first modeling of the SOLCEMENT process, SolarPACES 2020, 28 September – 2 October 2020 (Online event).
6. Gotzias, A. Injecting Carbon Nanostructures in Living cells,11th EETN Conference on Artificial Intelligence 2020 (SETN2020 Workshops), 2-4 September 2020, Athens Greece.

Teaching and Training Activities

Conference / Workshop Organisation

1st LIFE PureAgroH2O Conference, titled "Connecting innovative water reuse technologies with the Food Industry", January 17th 2020, in Athens, Greece.

Patent

Karanikolos, G., Favvas, E.P., Heliopoulos, N.S., Papageorgiou, S.K. "MEMBRANE GAS SEPARATION UNDER MAGNETIC FIELD", *US Patent*, No: 2020/0338496 A1, 29 October 2020.

Awards/ Distinctions

K. Stefanopoulos, Member of the Facility Access Panel (FAP2 – Disordered Materials) for evaluation of neutron scattering experimental proposals at Pulsed Neutron & Muon Source, STFC Rutherford Appleton Laboratory, Oxfordshire, UK.

Th. Steriotis, Member of Task 40: Energy Storage and Conversion Based on Hydrogen, Hydrogen Technology Collaboration Programme (Hydrogen TCP), International Energy Agency.

Services

Income from services to Industrial partners: 11,923.09 €

FUNCTIONAL NANOMATERIALS OF ORGANIZED STRUCTURE

Project Leader: Tsiourvas Dimitris

Permanent Research Staff: Sideratou Zili, Arkas Michalis

Post Docs: Kaminari Archontia, Panagiotaki Katerina

PhD Candidates: Lyra Kyriaki-Marina, Eleftheriou Kleopatra, Eleni Nikoli, Michaela Papageorgiou, Eleni Gomoza

- **Objectives**
  - Dendrimers and hyperbranched polymers as targeted drug delivery nanocarriers
  - Functional liposomes as drug delivery systems
  - Functional hyperbranched polymers with antibacterial and anti-fungal properties
  - Functionalized carbon-based materials as drug delivery systems, bio-imaging systems and antibacterial agents
  - Dendritic polymer-functionalized carbon-based nanostructured composites
  - Biopolymer-nanohydroxyapatite 3D scaffolds for tissue engineering
  - Biomimetic synthesis of hybrid organic/inorganic nanoparticles
  - Novel hydrogels and xerogels as coatings for orthopedic implants.
  - Thermotropic liquid crystals and liquid crystal/nanoparticles composites

- **Activities and Main Results**
  - Dendrimers and hyperbranched polymers as targeted drug delivery nanocarriers.
    Synthesis and physicochemical characterization of functional nanomaterials, mainly hyperbranched polymers, with emphasis on their applications as targeted and controlled release drug delivery systems. Recent work on dendritic polymers includes nanocarriers for targeting either the cell nucleus or cell mitochondria as well as drug-loaded thermoresponsive drug delivery hyperbranched polymers with improved in vitro cytotoxicity.

  - Functional liposomes as drug delivery systems
    Liposomal research is currently focused on the development of novel thermoresponsive liposomal DDS employing both experimental and computational techniques that exhibit, in combination with hyperthermia, passive targeting, cell nuclei internalization and improved cytotoxicity.

  - Functional hyperbranched polymers with antibacterial and anti-fungal properties
    Hyperbranched dendritic polymers were modified with various functional groups such as N-sulfobetain, guanidinium or trimethyl ammonium groups. Their bioactivity and mechanism of action were evaluated on various types of bacteria and also on plant pathogenic fungi.

  - Functionalized carbon-based materials as drug delivery systems, bio-imaging systems and antibacterial agents
    Carbon-based materials (carbon nanotubes and carbon nanodisks) functionalized with dendritic polymers were developed. Specifically, cationic hydrophilic dendritic polymers induce, through appropriate interaction, the dispersion of nanostructured carbon-based materials in aqueous media. These nanomaterials were physicochemically characterized by a variety of physicochemical methods and subsequently were evaluated as controlled release drug delivery systems as well as antibacterial agents.
    Additionally, carbon dots have been developed and evaluated for subcellular localization and as bio-imaging agents of cancerous cells.

- Dendritic polymer-functionalized carbon-based nanostructured composites
  Advanced polymeric nanocomposite membranes were developed to meet specific water treatment applications by tuning their structure and physicochemical properties (e.g. hydrophilicity, porosity, thermal and mechanical stability) and introducing unique functionalities (e.g. antibacterial, anti-fouling, adsorptive capabilities). Specifically, carbon-based materials modified with functional dendritic polymers were used as nanofillers into polymeric matrices, i.e. poly(vinyl alcohol) and poly(vinylidene fluoride), affording nanostructured composites suitable for water treatment that demonstrated high permeability and rejection as well as excellent mechanical, anti-fouling and anti-bacterial properties.

- Biomimetic synthesis of hybrid organic/inorganic nanoparticles
  Hybrid organic/inorganic nanoparticles were developed employing a biomimetic silicification process in water at ambient conditions by the interaction of low cost amino functionalized hyperbranched polymers with silicic acid. Hybrid nanospheres containing biomimetically reduced metal nanoparticles, e.g., silver nanoparticles, can also be employed as bactericides or in water purification and decontamination. Additionally, the development and characterization of hybrid catalysts through three environmental friendly biomimetic routes was pursued. The catalytic properties of these materials were examined using the reduction of p-nitrophenol to p-aminophenol and p-nitroaniline to p-phenylenediamine as model reactions. The results obtained, were excellent approximating the performance of homogenous catalysis. The recovery and reuse of the catalytic compounds was also achieved. The formation of silver nanoparticles into the dendritic cavities was monitored by combined kinetics experiments (UV-Visible-DLS) and their composition was assessed by thermogravimetry.

- Biopolymer-nanoHydroxyapatite 3D scaffolds for tissue engineering
  Research is also focused on the development of hydroxyapatite nanoparticles using dendritic polymers as biomimetic templates. Hydroxyapatite nanoparticles were employed for the development of biopolymer-nanoHydroxyapatite porous 3D bio-implants of complex geometry that were found to promote Guided Bone Regeneration in rat calvarial critical-sized defects.

- Novel hydrogels and xerogels as coatings for orthopedic implants.
  Development of complex silica xerogels with dendritic polymers as biomolecule carriers loaded by gentamicin and lauryl laurate. These materials were successfully incorporated onto stainless steel orthopedic implants with titanium layers without additional chemical modification. Model orthopedic implants, coated by these hybrid materials were tested in pigs and inflammation and biofilm formation were completely suspended. One patent deriving from these successful results has been filed and two more are presently in the stage of filing.

- Thermotropic liquid crystals and liquid crystal/nanoparticles composites
  Ordering and phase transitional properties of liquid crystalline dendritic polymers and of liquid crystal composites with nanoparticles is also under investigation.

Funding

- 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.
- 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 €. Scientist in charge: Katsaros Fotios.

- Novel marine biomolecules against biofilm. Application to medical devices.(H2020 NOMORFILM - 634588). Subcontractor of Pyrogenesis SA. 2018-2010. NCSRD Budget: 30.000 Euros. Scientist in charge: Arkas Michalis.
- Medical leather manufacturing with the use of hybrid nanoparticles MEDNANOLEAT (Т6УВП-00081) Total budget: 372,490€ NCSRD budget: 67,400 €. Scientist in charge: Arkas Michalis

OUTPUT

Publications in International Journals

1. Stagni, V., Kaminari, A., Sideratou, Z., Sakellis, E., Vlahopoulos, S. A., Tsiourvas, D. Targeting breast cancer stem-like cells using chloroquine encapsulated by a triphenylphosphonium-functionalized hyperbranched polymer", *International Journal of. Pharmaceutics* **585**, 119465 (2020); DOI: 10.1016/j.ijpharm.2020.119465.
2. Lykogianni, M., Papadopoulou, E.–A., Sapalidis, A., Tsiourvas, D., Sideratou, Z., Aliferis, K. A. Metabolomics reveals differential mechanisms of toxicity of hyperbranched poly(ethyleneimine)-derived nanoparticles to the soil-borne fungus Verticillium dahliae Kleb. *Pesticide Biochemistry and Physiology*, **165**, 104535 (2020); DOI: j.pestbp.2020.02.001.
3. Kyrou, C., Tsiourvas, D., Kralj, S., Lelidis, I. Effect of superhydrophobic nanoplatelets on the phase behaviour of liquid crystals. *Journal of Molecular Liquids* **298**, 111984 (2020); DOI: 10.1016/j.molliq.2019.111984.
4. Eleftheriou, K., Kaminari, A., Panagiotaki, K. N., Sideratou, Z., Zachariadis, M., Anastassopoulou, J., Tsiourvas, D. A combination drug delivery system employing thermosensitive liposomes for enhanced cell penetration and improved in vitro efficacy. *International Journal of. Pharmaceutics* **574**, 118912 (2020); DOI:10.1016/j.ijpharm.2019.118912.
5. Chatzipetros, E., Yfanti, Z., Christopoulos, P., Donta, C., Damaskos, S., Tsiambas, E., Tsiourvas, D., Kalogirou, E.–M., Tosios, K. I., Tsiklakis, K. Imaging of nano-hydroxyapatite/chitosan scaffolds using a cone beam computed tomography device on rat calvarial defects with histological verification. *Clinical Oral Investigations* **24**, 437-446 (2020); DOI:10.1007/s00784-019-02939-4.
6. Panagiotaki, K. N., Spyrou, K., Zachariadis, M., Pratsinis, H., Kouloumpis, A., Boutsika, L. G., Enotiadis, A., Gournis, D., Giannelis, E. P., Sideratou, Z. Non-porous phosphonated ionic silica nanospheres as nanocarriers for efficient intracellular delivery of doxorubicin, *Materials Today Communications*, **23**, 100787 (2020); DOI: 10.1016/j.mtcomm.2019.100787.
7. Zygouri, P., Spyrou, K., Mitsari, E., Barrio, M., Macovez, R., Patila, M., Stamatis, H., Verginadis, I. I., Velalopoulou, A. P., Evangelou, A. M., Sideratou, Z., Gournis, D., Rudolf, P. A facile approach to hydrophilic oxidized fullerenes and their derivatives as cytotoxic agents and supports for nanobiocatalytic systems. *Scientific Reports* **10**, 8244 (2020); DOI: 10.1038/s41598-020-65117-7.
8. Heliopoulos, N. S., Kythreoti, G., Lyra, K. M., Panagiotaki, K. N., Papavasiliou, A., Sakellis, E., Papageorgiou, S., Kouloumpis, A., Gournis, D., Katsaros, F. K., Stamatakis, K., Sideratou, Z. Cytotoxicity effects of water-soluble multi-walled carbon nanotubes decorated with quaternized hyperbranched poly(ethyleneimine) derivatives on autotrophic and heterotrophic gram-negative bacteria. *Pharmaceuticals*, 13, 293 (2020); DOI:10.3390/ph13100293.

Teaching and Training Activities

1. Arkas M.
   55th Summer School of NCSR Demokritos, July 13-17, 2019/AghiaParaskevi, Greece/NCSR Demokritos.

Patents

1. Arkas, M., Vardavoulias, M., Nikoli, E. Method for chemical compound immobilization onto solid surfaces employing thermal spraying of powders / heated particles, and gel formation. Greek Patent e-Filing Number 22-0003813778-18/11/2020.
2. Arkas, M., Nikoli, E., Douloudi, M., Kythreoti, G., Arvanitopoulos, L., Arvanitopoulos, K. Hydrogel and xerogel active ingredient carriers made from dendritic polymers and silica for use as leather and textile additives. Greek Patent e-Filing Number 22-0003846572- 26/11/2020.

Awards

Arkas, M. Outstanding reviewer of the year (2020). Polymers (MDPI)

TRANSPORT OF MATTER PHENOMENA IN POLYMERS

Project Leader: Merope Sanopoulou

Permanent Research Staff: Kyriaki Papadokostaki

Post doc: Petros Oikonomou (1/1-7/8/2020 and 16/11-31/12/2020)

Master Student: Danae Koukoufilippou (November 2020-)

- **Objectives**

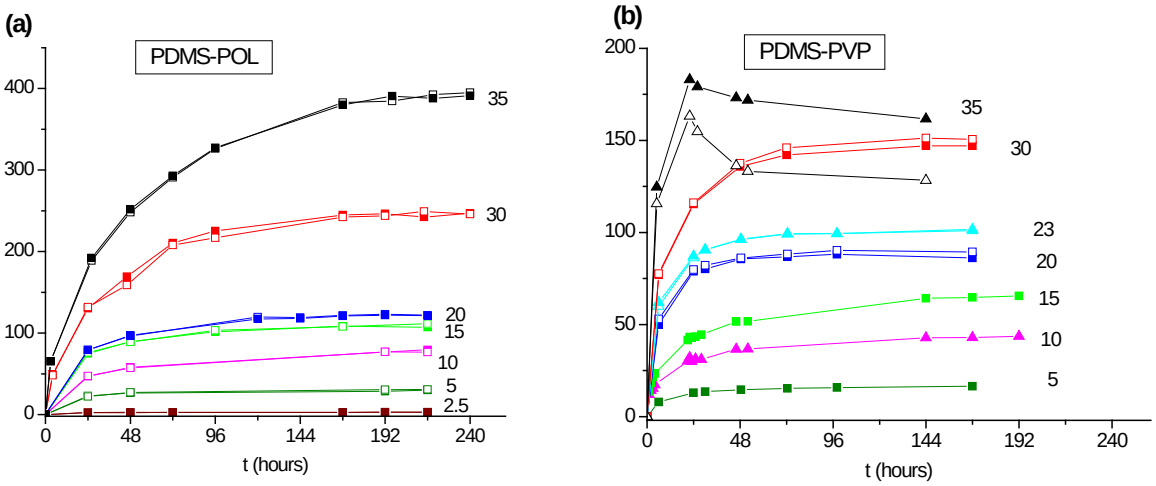
Research focuses on micromolecular sorption and transport mainly in polymeric materials by a combination of theoretical and experimental approaches. The aim of this work is to help create the basic scientific background for the optimization of the design of polymeric materials for important applications such as polymer-based controlled release systems, chemical sensors and coatings

- **Activities and Main Results**

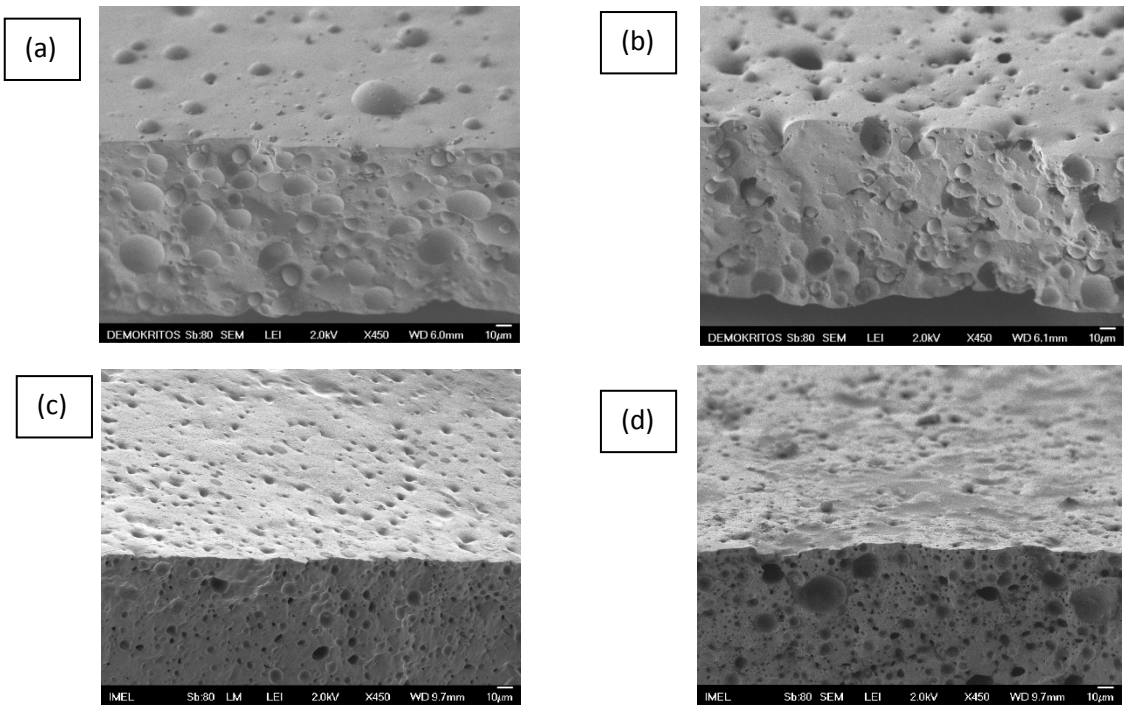
1. Polymer–based controlled release systems

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.

Current work focuses on polymer blends as matrices as for drug release or other biomedical applications. Due to the stringent specifications relating to their safety profile, research for polymeric materials to meet the needs for new applications is commonly focused on modification of existing polymers with proven safety and biocompatibility. Blending of biocompatible hydrophobic elastomers (e.g. polydimethylsiloxane, PDMS) with hydrophilic excipients (additives) is applied to enhance the affinity of the former to water. The resulting increase in the permeability of water vapor and of bioactive substances is sought in CR systems, wound dressings etc. To get insight in the underlying mechanisms for the observed increasing transport rates of slightly polar drugs with increasing excipient content, and to define the range of excipient content in the matrix where this increase is gradual (and thus can be fine-tuned) the new materials are also characterized (see figures) in terms of the physicochemical properties of the excipient, the morphological features of the matrices and the network characteristics of the elastomer phase. Recently, blends of miscible hydrophilic polymers are studied, having the advantage of environmentally friendly preparation, using water as a solvent.



Effect of blending PDMS with Poloxamer (POL) or polyvinylpyrrolidone (PVP) on water uptake kinetics in duplicate samples of (a) PDMS-POL and (b) PDMS-PVP films. The numbers next to each curve indicate the additive content in % w/w. (From Tsoka et al., *Ind. Eng. Chem. Res.* 59, 5797, 2020).

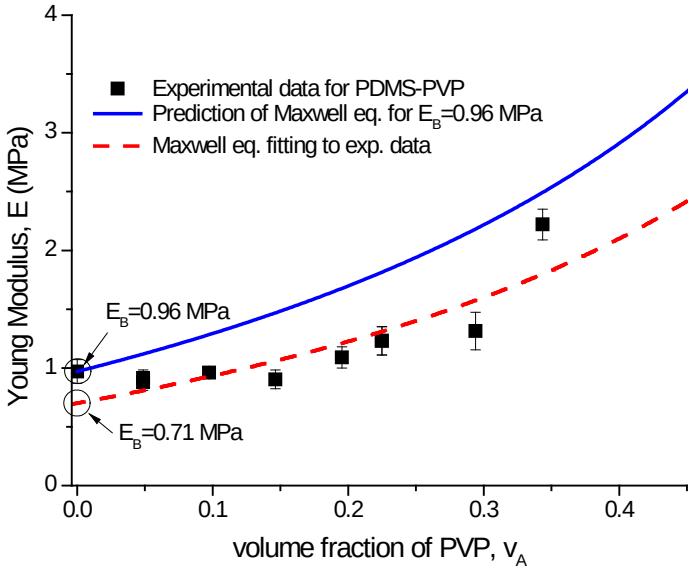


SEM images showing both the cross section and the surface of a PDMS-PVP (a, b) and a PDMS-POL film (c, d) both containing 30% w/w of additive. Left-hand images (a, c) refer to as-prepared films and right-hand ones (b, d) refer to the same films after equilibration in water and drying.

2. 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 theoretical work has focused on an analytical approach, allowing for application of the Maxwell model for two-phase systems to the practically important case of a three-phase composite medium,

where the third phase is considered to be the polymer-particle interphase, exhibiting permeability properties differing substantially from those of the bulk polymer matrix.
During the reporting period we 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. PDMS elastomers, prepared by thermal curing of prepolymer mixtures, are widely used in biomedical applications. 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.



Young modulus of composite PDMS-PVP films plotted versus the volume fraction of PVP content (squares). Solid line is the prediction of Maxwell eq. with the experimental E value for pure PDMS (E_B=0.96 MPa) and dashed line presents fitting of experimental data with output fitting parameter E_B=0.71 MPa, pointing to a looser PDMS network in the presence of PVP as compared to pure PDMS. (From Tsoka et al., *Ind. Eng. Chem. Res.* 59, 5797, 2020).

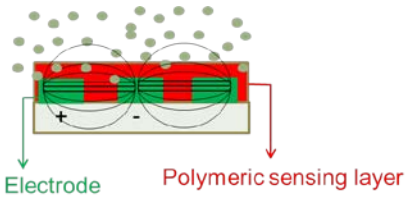
3. Thermal properties of materials for various applications

In collaboration with other laboratories we study the thermal behavior of various systems for use in different applications, e.g., phase change materials (PCM), latent heat storage applications or ceramic nanoporous membranes supporting ionic liquids for gas separation applications.

4. 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). In the reporting period, the increase in sensitivity/selectivity of chemocapacitors is sought through miniaturization and/or

modification of the geometrical configuration of the sensor's electrodes. 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) – 1/10/2018-31/9/2021, 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. 2019 Income: 560 €

OUTPUT

Publications in International Journals

1. Tsoka, M., Oikonomou, P., Papadokostaki, K.G., Sanopoulou, M. Properties of Polydimethylsiloxane Modified by Blending with Polyvinylpyrrolidone and a Poly(ethylene oxide)-Poly(propylene oxide) Triblock Copolymer. *Ind. Eng. Chem. Res.* **59**, 5797-5807 (2020). DOI: 10.1021/acs.iecr.9b06691
2. Oikonomou, P., Botsialas, A., Papanikolaou, N., Kazas, I., Ntetsikas, K., Polymeropoulos, G., Hadjichristidis, N., Raptis, I., Sanopoulou, M. Gas Sensitivity Amplification of Interdigitated Chemocapacitors through Etching. *IEEE Sensors J.* **20**, 463-470 (2020). DOI: 10.1109/JSEN.2019.2939016
3. Wang, Z., Syed, A., Bhattacharya, S., Chen, X., Buttner, U., Iordache, G., Salama, K., Ganetsos, T., Valamontes, E., Georgas, A., Raptis, I., Oikonomou, P., Botsialas, A., Sanopoulou, M. Ultra miniaturized InterDigitated electrodes platform for sensing applications. *Microelectron. Eng.* **225**, art. no. 111253 (2020). DOI: 10.1016/j.mee.2020.111253
4. Nika, A., Oikonomou, P., Manouras, T., Argitis, P., Vamvakaki, M., Sanopoulou, M., Raptis, I., Chatzichristidi, M. Reversible chemocapacitor system based on PDMAEMA polymers for fast sensing of VOCs mixtures. *Microelectron. Eng.* **227**, art. no. 111304 (2020). DOI: 10.1016/j.mee.2020.111304
5. Stathopoulos, N., Belessiotis, G., Oikonomou, P., Papanicolaou, E. Experimental investigation of thermal degradation of phase change materials for medium-temperature thermal energy storage and tightness during cycling inside metal spheres. *J. Energy Storage* **31**, art. no. 101618 (2020). DOI: 10.1016/j.est.2020.101618

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. A. Kaltzoglou (until 13.7.2020), Dr. G. Manolis, Dr. X. Vourna

PhD Candidates: G. Belessiotis, A. Chioti, E. Christopoulos, K. Gkini, D. Perganti, M. Elsenety, A. Hussien, I. Ibrahim.

Research Collaborators (emeritus or visiting): Dr. A. Kontos (Ass. Prof., NTUA), Dr. A. Kaltzoglou (Associate Researcher, National Hellenic Research Foundation, since 14.7.2020)

- **Objectives**

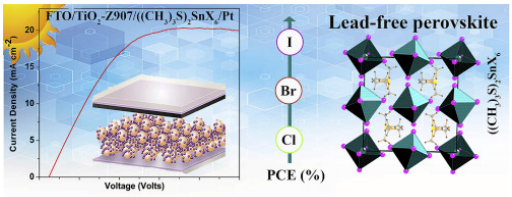
The research is focused on photoactive materials (molecular and nanostructured), the investigation of nanotechnology driven photo-induced processes and their application to the direct conversion of solar energy into electricity as well as to environmental protection and health safety, including:

- Third Generation Photovoltaics [Perovskite Solar Cells (PSCs); Dye-sensitized Solar Cells (DSCs); Quantum Dot Solar Cells (QDSCs)]
- Photocatalytic water cleaning and CO_2 conversion/storage

- **Activities and Main Results**

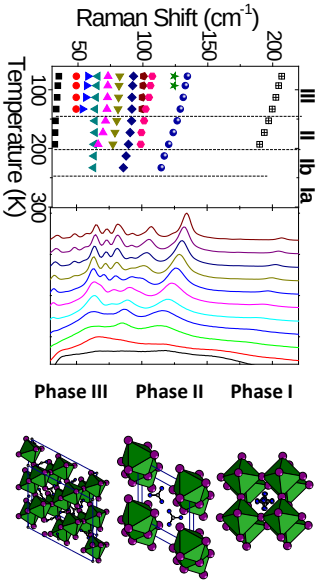
Third Generation Photovoltaics This research activity concerns the harvesting of solar irradiation by panchromatic absorbers and the sensitization of nanostructured semiconductors in efficient solution processed photovoltaic devices. Particular effort is made on developing hybrid organic-inorganic (1D, 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



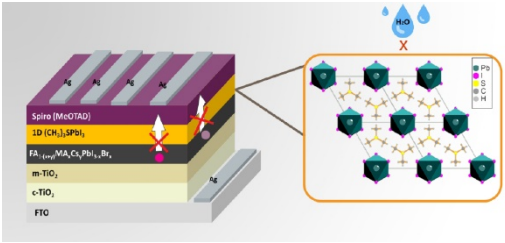
Mater. Chem. Phys. 239 (2020) 122310

New air-stable tin-based $((CH_3)_3S)_2SnI_{6-n}Cl_n$ and $((CH_3)_3S)_2SnI_{6-n}Br_n$ (n = 1, 2) defect perovskites were synthesized and their physicochemical properties were established. The lead-free Sn(IV)-based compounds were successfully incorporated as hole transporting materials (HTMs) in sensitized nanocrystalline solar cells (DSCs).



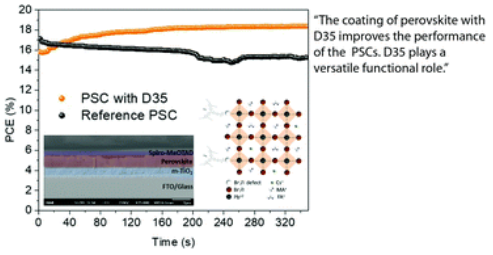
J. Phys. Chem. C, 124 (2020) 8479

Hybrid organic-inorganic $FAPbX_3$ perovskites ($FA = NH_2CHNH_2^+$, $X = Cl^-$, Br^-, I^-) are currently intensively investigated in solar cells. In this study, off-resonance Raman and far-IR absorption spectra of all single-halogen $FAPbX_3$, as well as the mixed-halogen $FAPbBr_2X$ derivatives, are reported and analyzed. Vibrations of the PbX_6 octahedra and librations of the FA cation lay at frequencies below 250 cm^{-1} while external and internal FA bands are identified above 200 cm^{-1}. Increase in the frequencies of most vibrational bands is observed upon substituting lighter and more electronegative halides for heavier ones, due to strengthening of the electrostatic interaction between X^- and the FA NH_2^+ groups. Variable temperature Raman measurements are also carried out for $FAPbBr_3$ and $FAPbCl_3$ in the 77 – 453 K range. Upon cooling, the three Pb-X Raman vibrations, characterizing the cubic structure, split into eight separate bands, signaling the transformation to the tetragonal phase at ~ 240 K and ~ 200 K for $FAPbBr_3$ and $FAPbCl_3$, respectively. At even lower temperatures, a successive phase transformation to low symmetry orthorhombic phases is evidenced.



ACS Appl. Energy Mater. 3 (2020) 2465

To restrain intrinsic volatility and ionic migration in perovskite solar cells (PSCs), a dimensionality engineering approach consisting of a (FA/MA/Cs) $PbI_{3-x}Br_x/(CH_3)_3SPbI_3$ (3D/1D) perovskite bilayer architecture was proposed. The 3D/1D bilayer structure further optimizes the corresponding absorber/hole transporting layer (HTL) interface of the PSCs, leading to significant efficiency increase and stability improvement.

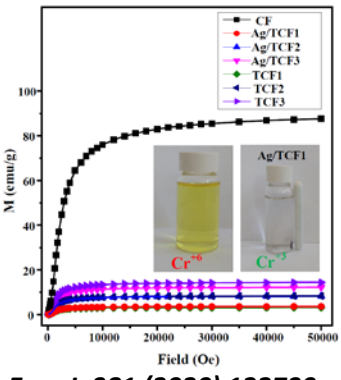


ıoscale 12 (2020) 15137

ısting perovskite nanomorphology and charge ısport properties via a functional D–π-A organic er at the absorber/hole transporter interface. organic D–π-A interlayer improves the ovskite's crystallinity and creates a smoother ovskite/HTM interface, while reducing the grain ındary defects and inducing an energy level nment with the adjacent layers. The obtained ılts consolidate the multifunctional role of anic D–π-A molecules as perovskite interface difiers towards performance enhancement and le-up fabrication of robust PSCs.

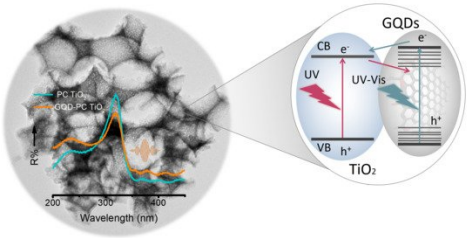
Photocatalysis Advanced oxidation and reduction processes (AOPs-ARPs) driven by photoinduced heterogeneous reactions that take place on the semiconductor surface are investigated. Special emphasis in given to the growth of innovative nanostructured titania photocatalysts and their application in the 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 and 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 and 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. 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/coatings for the construction sector. 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



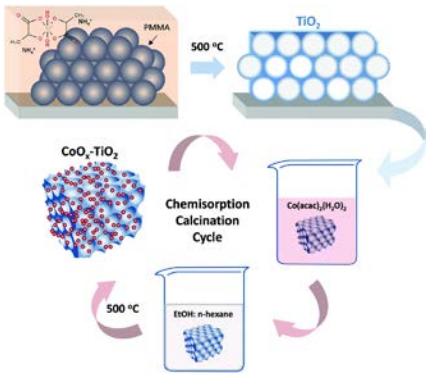
Chem. Eng. J. 381 (2020) 122730

$TiO_2/CoFe_2O_4$ composites with silver nanoparticles were synthesized and characterized. The addition of silver nanoparticles has a great contribution to the photocatalytic reduction of Cr^{+6} under UV and solar light. The reaction mechanism was studied by scavengers and spin trap experiments, revealing that photogenerated electrons were mainly responsible for the reduction of Cr^{+6} species. The magnetic $Ag/TiO_2/CoFe_2O_4$ materials were easily separated and re-used. The remarkable stability of the new photocatalysts increases their industrial potential.



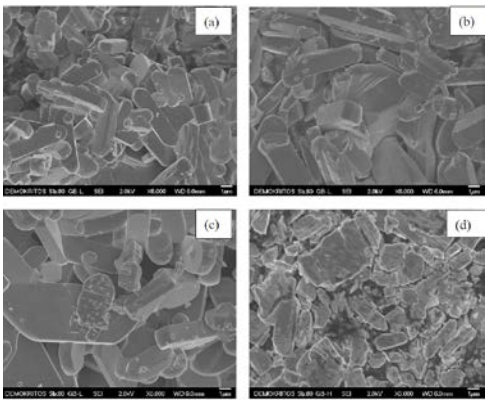
Nanomaterials 10 (2020) 2566

Surface functionalization of TiO_2 photonic crystals by blue luminescent graphene quantum dots (GQDs) was demonstrated to promote slow photon-assisted light trapping with GQD-TiO_2 interfacial electron transfer. Photonic band gap engineering by varying the inverse opal macropore size resulted in selective performance enhancement for both salicylic acid photocatalytic degradation and photocurrent generation under UV–VIS and visible light.



Materials Advances 1 (2020) 2310

face modified photonic crystals with CoO_x oclusters were fabricated using band gap ineered TiO_2 inverse opals. Fine tuning of the films' oelectronic properties by controlling the inverse l macropore size and Co oxides' loading and nposition resulted in significant enhancement of photocatalytic activity for organics decomposition ler visible light. The photocatalytic mechanism was ted to the slow-photon-assisted light harvesting by oxide nanoclusters that affect the inverse opal iodicity and texture, enabling visible light electronic orption and promoting efficient charge separation.



Materials 13 (2020) 4665

Novel bifunctional V_2O_5 photocatalysts were prepared following a wet chemical process with the addition of anionic or non-ionic surfactants into the precursor solution and further heating under reflux. Under UV light illumination, the most efficient photocatalyst (T80) based on tween 80, was capable to reduce hexavalent chromium to trivalent and showed high yields in degrading methylene blue azo-dye and tetracycline antibiotic water pollutants. This remarkably high bifunctional performance defines T80 as a promising and capable photocatalytic material for both advanced oxidation and reduction processes (AOPs-ARPs).

Funding

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, T1EΔK-03547), (2018-2021) 189 K€

OUTPUT

Publications in International Journals

1. Givalou L., Tsichlis D., Zhang F., Karagianni C-S., Terrones M., Kordatos K. and Falaras P. "Transition Metal – Graphene Oxide Nanohybrid Materials as Counter Electrodes for High Efficiency Quantum Dot Solar Cells". *Catalysis Today* **355C,** 860-869 (2020). DOI: 10.1016/j.cattod.2019.03.035
2. Ibrahim I., Kaltzoglou A., Athanasekou C., Katsaros F., Devlin E., Kontos A. G., Ioannidis N., Perraki M., Tsakiridis P., Sygellou L., Antoniadou M., Falaras P. "Magnetically separable $TiO_2/CoFe_2O_4$/Ag nanocomposites for the photocatalytic reduction of hexavalent chromium pollutant under UV and artificial solar light". *Chemical Engineering Journal* **381,** 122730 (2020). DOI: 10.1016/j.cej.2019.122730
3. Balis N., Zaky A. A., Athanasekou C., Silva A. M. T., Sakellis E., Vasilopoulou M., Stergiopoulos T., Kontos A. G., Falaras P. "Investigating the Role of Reduced Graphene Oxide as a Universal Additive in Planar Perovskite Solar Cells". *Journal of Photochemistry & Photobiology A: Chemistry* **386,** 112141 (2020). DOI: 10.1016/j.jphotochem.2019.112141
4. Elsenety M. M., Antoniadou M., Kaltzoglou A., Kontos A. G., Philippopoulos A.I., Mitsopoulou C. A., Falaras P. "Synthesis, characterization of $((CH_3)_3S)_2SnI_{6-n}Cln$ and $((CH_3)_3S)_2SnI_{6-n}Br_n$ (n=1, 2) perovskites and use in dye-sensitized solar cells". *Materials Chemistry and Physics* **239**, 122310 (2020). DOI: 10.1016/j.matchemphys.2019.122310
5. Gkini K., Verykios A., Balis N., Kaltzoglou A., Papadakis M., Adamis K. S., Armadorou K.-K., Soultati A., Drivas C., Gardelis S., Petsalakis I. D., Palilis L. C., Fakharuddin A., Haider M. I., Bao X., Kennou S., Argitis P., Schmidt-Mende L., Coutsolelos A. G., Falaras P., Vasilopoulou M. "Enhanced Organic and Perovskite Solar Cell Performance through Modification of the Electron-Selective Contact with a Bodipy−Porphyrin Dyad". *ACS Appl. Mater. Interfaces* **12**, 1120-1131 (2020). DOI: 10.1021/acsami.9b17580
6. Pedrosa M., Silva E., Pastrana-Martínez L., Drazic G., Falaras P., Faria J. L., Figueiredo J. L., Silva A. M.T. "Hummers' and Brodie's graphene oxides as photocatalysts for phenol degradation". *Journal of Colloid and Interface Science* **567,** 243-255 (2020). DOI: 10.1016/j.jcis.2020.01.093
7. Elsenety M. M., Antoniadou M., Balis N., Kaltzoglou A., Sygellou L., Stergiou A., Tagmatarchis N., Falaras P., "Stability improvement and performance reproducibility enhancement of perovskite solar cells Following (FA/MA/Cs) $PbI_{3-x}Br_x/(CH_3)_3SPbI_3$ Dimensionality Engineering" *ACS Appl. Energy Mater*. **3**, 2465 – 2477 (2020). DOI: 10.1021/acsaem.9b02117
8. Zaky A. A., Balis N., Gkini K., Athanasekou C., Kaltzoglou A., Stergiopoulos T., P Falaras. "Dye Engineered Perovskite Solar Cells under Accelerated Thermal Stress and Prolonged Light Exposure", *Chemistry Select* **5**, 4454 –4462 (2020). DOI:10.1002/slct.202000771
9. Kontos A. G., Manolis G. K., Kaltzoglou A., Palles D., Kamitsos E. I., Kanatzidis M. G., Falaras P. "Halogen-NH_2^+ Interaction, Temperature Induced Phase Transitions and Ordering in $(NH_2CHNH_2)PbX_3$ (X = Cl, Br, I) Hybrid Perovskites". *J. Phys. Chem. C.* **124,** 8479–8487 (2020). DOI: 10.1021/acs.jpcc.9b11334
10. Vasilopoulou M., Fakharuddin A., Coutsolelos A. G., Falaras P., Argitis P., Yusoff A.R.M., Nazeeruddin M. K. "Molecular Materials as Interfacial Layers and Additives in Perovskite Solar Cells". *Chemical Society Reviews* **49,** 4496-4526 (2020). DOI: 10.1039/C9CS00733D
11. Soultati A. A., Verykios A., Panagiotakis S., Armadorou K.K., Haider M.I., Kaltzoglou A., Drivas C., Fakharuddin A., Bao X., Yang C., Yusoff A. R. M., Evangelou E. K., Petsalakis I., Kennou S., Falaras P., Yannakopoulou K., Pistolis G., Argitis P., Vasilopoulou M. "Suppressing the Photocatalytic Activity of Zinc Oxide Electron Transport Layer in Non-Fullerene Organic Solar Cells with a Pyrene-Bodipy Interlayer", *ACS Appl. Mater. Interfaces* **12,** 21961–21973 (2020). DOI: 10.1021/acsami.0c03147
12. Elsenety M., Stergiou A., Sygellou L., Tagmatarchis N., Balis N., Falaras P. "Boosting Perovskite Nanomorphology and Charge Transport Properties via a Functional D-π-A Organic Layer at the Absorber/Hole Transporter Interface". *Nanoscale* **12,** 15137–15149 (2020). DOI: 10.1039/d0nr02562c
13. Zaky A. A., Ibrahim M. N., Rezk H., Christopoulos E., Sehiemy R. A., Hristoforou E., Kladas A., Sergeant P., Falaras P. "Energy Efficiency Improvement of Water Pumping System Using Synchronous Reluctance Motor Fed by Perovskite Solar Cells". *International Journal of Energy Research* **44,** 11629-11642 (2020). DOI: 10.1002/er.5788

14. Kontos A. G., Romanos G. E., Veziri C. M., Gotzias A., Arfanis M. K., Kouvelos E., Likodimos V., Karanikolos G. N., Falaras P. "Correlating vibrational properties with temperature and pressure dependent CO_2 adsorption in zeolitic imidazolate frameworks". *Applied Surface Science* **529,** 147058 (2020). DOI: 10.1016/j.apsusc.2020.147058
15. Gkini K., Balis N., Papadakis M.l, Verykios A., Scoulicidou M.-C., Drivas C., Kennou S., Golomb M., Walsh A., Coutsolelos A. G., Vasilopoulou M., Falaras P. "Manganese Porphyrin Interface Engineering in Perovskite Solar Cells". *ACS Appl. Energy Mater.* **3**, 7353–7363 (2020). DOI: 10.1021/acsaem.0c00710
16. Toumazatou A., Antoniadou M., Sakellis E., Tsoutsou D., Gardelis S., Romanos G. E., Ioannidis N., Boukos N., Dimoulas A., Falaras P., and Likodimos V. "Boosting visible light har.vesting and charge separation in surface modified TiO_2 photonic crystal catalysts by CoO_x nanoclusters". *Materials Advances* **1**, 2310 – 2322 (2020). DOI: 10.1039/D0MA00510J
17. Pilidi A., Tzanis A., Helm T., Arfanis M., Falaras P., Speliotis T. "Nanometer-Thick Bismuth Nanocrystal Films for Sensoric Applications". *ACS Applied Nano Materials* **3**, 9669–9678 (2020). DOI: 10.1021/acsanm.0c01650
18. Ibrahim I., Belessiotis G., Arfanis M., Athanasekou C., Philippopoulos A., Mitsopoulou C.-A., Romanos G., Falaras P. "Surfactant Effects on the Synthesis of Efficient Bifunctional V_2O_5 Photocatalysts", *Materials* **13,** 4665 (2020). DOI: 10.3390/ma13204665
19. Antoniadou M., Balis N., Falaras P. "Novel semiconductors for energy production via electrochemical processes". *SVOA Materials Science & Technology* **2**, 76-79 (2020).
20. 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 Films for Photocatalytic Applications". *Nanomaterials* **10**, 2566 (2020). DOI: 10.3390/nano10122566
21. Belessiotis G. V., Ibrahim I., Karagianni C. S., Falaras P. "DSSCs for indoor environments: from lab scale experiments to real life applications". *SVOA Materials Science &Technology* **3,** 1-5 (2020).

International Conferences Presentations (invited, oral, poster)

1. Gkini K., Martinaiou I., Falaras P., Incorporation of graphitic carbon nitride (g-C_3N_4) within functional interfaces for highly efficient perovskite solar cells, *Perovskites for Energy Harvesting: From Fundamentals to Devices (PERENHAR)–NanoGe,* November 19-20 2020, Online Conference, Oral Presentation, Abstract ID: 019.
2. Givalou L., Christopoulos E., Gkini K., Falaras P., High Efficiency Perovskite Solar Cells Incorporating Semiconductor Quantum Dots*, Perovskites for Energy Harvesting: From Fundamentals to Devices (PERENHAR)–NanoGe*, November 19-20, 2020, Online Conference, ePoster Presentation.
3. Giasafaki D., Belessi V., Philippakopoulou T., Manolis G., Mitzithra C., Georgakilas V., Charalambopoulou G., Steriotis T., Development of Reduced Graphene Oxide Hybride - Silver Hybrid Materials for Water-Based Conductive Inks, *14th Paints Symposium*, 19-20 March 2020, Athens, Greece.
4. Falara P.P., Zourou A., Arfanis, M., Ibrahim I., Givalou L., Kordatos K., Enhanced activity of titania nanoparticles combined with nitrogen-doped carbon quantum dots for photocatalytic degradation of azo-dyes, *NANOSMAT 2020, 14th International Conference of Surfaces, Coatings and Nanostructured Materials*, 8-10 September 2020, Manchester, United Kingdom. Oral, Abstract Code: NANO-137
5. Falara P.P., Ibrahim I., Zourou A., Givalou L., Kordatos K., Photocatalytic reduction of water pollutants using innovative CQDs/TiO2 heterostructures, *NANOSMAT 2020, 14th International Conference of Surfaces, Coatings and Nanostructured Materials*, 8-10 September 2020, Manchester, United Kingdom. Oral, Abstract Code: NANO-138

Teaching and Training Activities

1. Name: Falaras P.
   Activity Title, Dates/Duration of lectures/training: Teaching Physical Chemistry
   Years: Academic Years 2019-2020 and 2020-2021
   Location/Academic Institute: Faculty of Sciences and Technology, Hellenic Open University, Athens, Greece.
2. Name: Falaras P.
   Activity Title, Dates/Duration of lectures/training: Catalysis and Environmental Protection Master Programme
   Years: Academic Years 2019-2020 and 2020-2021
   Location/Academic Institute: Hellenic Open University, Athens, Greece.
3. Name: Kaltzoglou A.
   Activity Title, Dates/Duration of lectures/training: Crystallography and Semiconducting Materials
   Years: Academic Year 2019-2020
   Location/Academic Institute: Department of Materials Science, University of Patras, Greece.

Conference / Workshop Organisation

Innovative waste treatment and water recycling technologies for the food industry; Friday 17 January 2020, Royal Olympic Hotel, Athens, Greece.

MOLECULAR THERMODYNAMICS AND MODELLING OF MATERIALS

Project Leader: Dr. Ioannis Economou (currently on leave of absence)

Permanent Research Staff: Dr. Loukas Peristeras, Researcher C,

Dr. Niki Vergadou, Researcher C

Other Staff (scientific, appointed research fellows, administrative, technical, auxiliary, etc.): Dr. Panagiotis Krokidas, Dr. Konstantinos D. Papavasileiou

Post Docs:

Dr. Christina-Anna Gatsou, Dr. Ilias Nikolaidis, Dr. Nefeli Novak, Dr. Stavros D. Peroukidis

Dr. Flora D. Tsourtou

PhD Candidates:

Matrona Panou

Diploma Students:

Aikaterini Argyropoulou, Konstantina Karanasiou, Leonidas Konstantopoulos, Dimitrios Nasikas

- **Objectives**

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. 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.

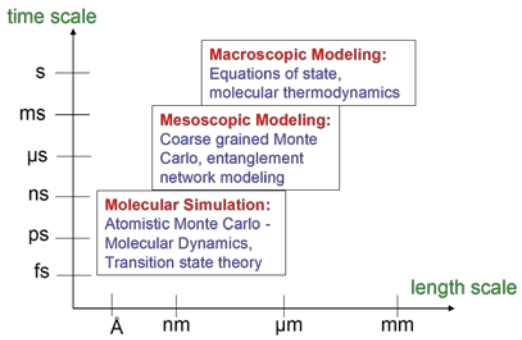


Figure 1: Hierarchical multi-scale simulation methods.

- **Activities and Main Results**

Development of multiscale models for the Gas-To-Liquids (GTL) process

The GTL process is an established, robust and economically viable technology in harnessing gas resources, such as synthetic gas for

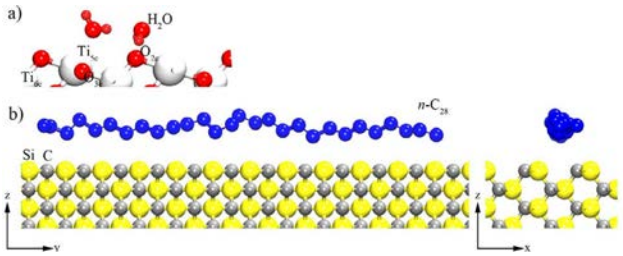


Figure 2: a) Characteristic snapshot of water monolayer molecules at the TiO_2 anatase (101) interface. b) Illustration of an n -C_{28} molecule at the SiC (220) surface, adopting a 'rod'-like conformation. Depiction of an isolated n -C 28 molecule located at the first monolayer in the SiC system.

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 investigating the effect of the presence of oxygenates and of the surface support chemistry on the wax–water mixture inside catalyst pores. To this respect, we considered a typical *n*-octacosane (*n*-C_{28}) – water mixture inside titanium dioxide (TiO_2) and silicon carbide (SiC) mesopores (Figure 2) at low-temperature FTS conditions (473.15 K), with and without the addition of small alcohols such as methanol and ethanol. Our all atom (AA) Molecular Dynamics (MD) simulations showed that inside TiO_2, *n*-C_{28} molecules occupy the pore centre with water molecules organize into two discrete layers on the TiO_2 surface; mixture phase separation is completely reversed inside the SiC pore. In both cases, alcohol addition does not influence fluid preferential distribution inside the pores. Finally, we examined the mobility of the mixture components inside the pores considered and we analysed the behaviour of the hydrogen bonds network formed between water molecules.

Artificial Intelligence-aided Coarse-Graining strategies

The broad spectra of length- and time-scales present in complex chemical systems necessitate the implementation of hierarchical multi-scale approaches. Within this scope, the development of appropriate coarse-graining schemes are often necessary. These schemes involve the substitution of groups of atoms by single interaction sites, thereby reducing the number of the system's degrees of freedom, while at the same time maintaining the ones that are important for the description of the mechanisms or processes under study. Coarse-graining approaches involve the mapping from the atomistic to a coarse-grained (CG) level and equilibration at the CG level and reverse mapping back to the atomistic representation. Systematic machine learning driven multiscale simulation schemes are currently developed for the determination of the CG mapping and of the CG interaction potentials.

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

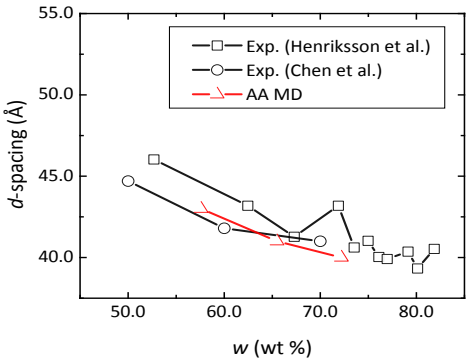


Figure 3: The prediction of the H_1 lattice spacing (d) from the AA MD simulations is in exalted agreement with the available experimental data obtained from X-Ray Diffraction measurements.

this context, we validated the performance of all atom (AA) FFs for predicting the phase diagram behaviour of these systems in the region of high concentrations. In particular, we focused on cetyltrimethylammonium chloride (CTAC) and in 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. To achieve our goal, we used Molecular Dynamic simulations and we developed a methodology that overpass the underlying problem of the poor phase space sampling. Our results are in good agreement with experiments (Figure 3) and indicate that it is possible to use MD simulation to study in detail the spontaneous L_1 to H_1 phase transition, to finely tune AA-FF based on their relevant predictions, and to explore the structural properties of the mesophase morphologies that occurred.

Properties of Intrinsically Conducting Polymers (ICPs).

ICPs also known as conjugated polymers are organic materials that combine high electrical conductivity together with excellent processability and low production cost. Due to their unique properties, they are present in a range of products and applications including, among others, displays, batteries, sensors, solar cells, organic emitting diodes, and sensors. Their end-use properties can be tuned by altering their chemistry and molecular architecture, which also affect the conformation and packing of the polymeric chains. The goal of this project is to develop methodologies for the prediction of the properties of melts and solutions of polymer systems with complex chemical constitution and chain molecular architecture. In this context, we validated the performance of available force fields in predicting the properties of the amorphous poly(3-hexylthiophene) (RR-P3HT), a representative member of the conjugated polymers materials family. Independent of the force field in use, we found that both the persistence and the effective conjugation length increase by lowering the temperature (Figure 4), due to the increasing relative population of cis- and trans- conformational states of the inter-ring torsion angles. Moreover, we prove that the probability distribution of the maximum length of the conjugated segments in a chain coincides with the theoretical distribution of the longest run of “heads” with the mean value of the former corresponding to the effective conjugation length. The result suggests that short-chain length RR P3HT chains in their bulk amorphous phase are semi flexible, but as their molecular weight increases they adopt more random coil conformations, especially at higher temperatures.

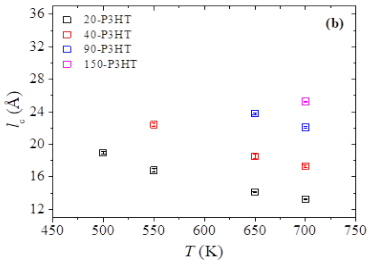


Figure 4: The effective conjugation length (l_c) for RR-P3HT of different molecular weight in the amorphous phase, as a function of temperature.

Systematic molecular simulation methods for the study of polymeric systems

Polymeric materials remain in the core of a wide range of novel applications and state-of the art membrane and barrier 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 novel polymer-based composites.

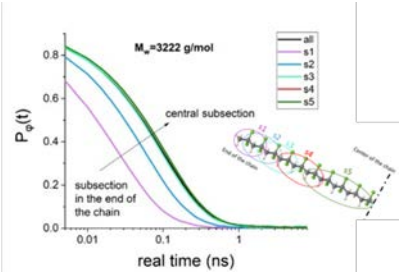


Figure 5: Second-order autocorrelation function of the backbone dihedral in different subchain sections of bulk PVDF systems

Molecular Modeling of 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. Ionic fluids inherently carry a higher degree of complexity than systems comprised of neutral species. They exhibit an exceptional combination of properties that originate primarily from their dual organic and ionic nature. A fundamental understanding of the diverse interactions and the microscopic mechanisms that give rise to the non-trivial spatial and dynamical behavior in this category of ionic fluids is required. Research work involves the implementation of systematic computational methods for the investigation of ILs as novel gas separation media and the prediction of their properties (Figure 6).

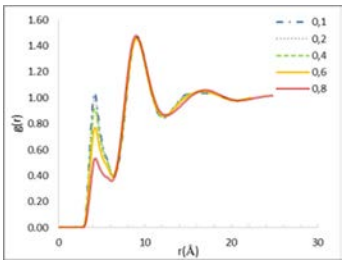


Figure 6. Effect of CO_2 concentration on the structure of [$Bmim^+$][TCM^-] IL

Funding

1. "Coarse grain modelling of polysaccharides-clay nanomaterials", *Industrial Postdoc Researcher project - Stavros Niarchos Foundation (SNF) and Scienomics SARL.* Total funding 72,000 €. Duration: October 2017 – October 2020.
2. "Mesoscale Modelling of Fischer-Tropsch Product Mixtures Confined in Graphene Nanopores", *Industrial Postdoc Researcher project - Stavros Niarchos Foundation (SNF) and Scienomics SARL.* Total funding: 72,000 €. Duration: September 1, 2017 – August 31, 2020.
3. "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.
4. "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.
5. "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 fanding: 41,500 €. Duration: April 2020 - October 2021.

OUTPUT

Publications in International Journals

1. Nikolaidis I.K., Boulougouris G.C., Peristeras L.D. and Economou I.G., "Construction of Phase Envelopes for Binary and Multicomponent Mixtures with Euler-Newton Predictor-Corrector Methods", *Fluid Phase Equil.,* **505**, 112338, pp. 1 – 18 (2020). DOI: 10.1016/j.fluid.2019.112338
2. Dawass N., Krüger P., Schnell S.K., Moultos O.A., Economou I.G., Vlugt T.J.H. and Simon J.-M., "Kirkwood-Buff Integrals Using Molecular Simulation: Estimation of Surface Effects", *Nanomaterials,* **10**(4), 771 (2020). DOI: 10.3390/nano10040771
3. Klein T., Lenahan F.D., Kerscher M., Rausch M.H., Economou I.G., Koller T.M. and Fröba A.P., "Characterization of Long Linear and Branched Alkanes and Alcohols for Temperatures up to 573 K by Surface Light Scattering and Molecular Dynamics Simulations", *J. Phys. Chem. B,* **124**(20), 4146 – 4163 (2020). DOI: 10.1021/acs.jpcb.0c01740
4. Tsimpanogiannis I.N., Michalis V.K. and Economou I.G., "Novel Methodology for the Calculation of the Enthalpy of Enclathration of Methane Hydrates using Molecular Dynamics Simulations", *Mol. Phys.,* **118**(9-10), e1711976 (2020). DOI: 10.1080/00268976.2020.1711976
5. Mohamed A.M.O., Krokidas P. and. Economou I.G., "Encapsulation of [$bmim^+$][Tf_2N^-] in Different ZIF-8 Metal Analogues and Evaluation of Their CO_2 Selectivity over CH_4 and N_2 Using Molecular Simulation", *Mol. Syst. Des. Eng.*, **5**(7), pp. 1230 – 1238 (2020). DOI: 10.1039/D0ME00021C
6. Jaubert J.-N., Le Guennec Y., Piña-Martinez A., Ramirez-Velez N., Lasala S., Schmid B., Nikolaidis I.K., Economou I.G. and Privat R., "Benchmark Database Containing Binary-System-High-Quality-Certified Data for Cross-Comparing Thermodynamic Models and Assessing their Accuracy", *Ind. Eng. Chem. Res.,* **59**(33), pp. 14981 – 15027 (2020). DOI: 10.1021/acs.iecr.0c01734
7. Papavasileiou K.D., Peristeras L.D., Chen J., van der Laan G.P., Rudra I., Kalantar A. and Economou I.G., "Molecular Dynamics Simulation of the *n*-Octacosane – Water Mixture Confined in Hydrophilic and Hydrophobic Mesopores: The Effect of Oxygenates", *Fluid Phase Equil.,* **512**, 112816 (2020). DOI: 10.1016/j.fluid.2020.112816
8. Kerscher M., Klein T., Schulz P.S., Veroutis E., Dürr S., Preuster P., Koller T.M., Rausch M.H., Economou I.G., Wasserscheid P. and Fröba A.P., "Thermophysical Properties of Diphenylmethane and Dicyclohexylmethane as a Reference Liquid Organic Hydrogen Carrier System from Experiments and Molecular Simulations", *Int. J. Hydrogen Energy,* **45** , 28903 – 28919 (2020). DOI: 10.1016/j.ijhydene.2020.07.261
9. Tsourtou, F.D., Peristeras L.D., Apostolov R., and Mavrantzas V.G., "Molecular Dynamics Simulation of Amorphous Poly(3-Hexylthiophene)." Macromolecules **53**(18), 7810–7824 (2020). DOI: 10.1021/acs.macromol.0c00454.
10. Ricci E., Vergadou N., Vogiatzis G.G., De Angelis M.G. and Theodorou D.N., "Molecular Simulations and Mechanistic Analysis of the Effect of CO_2 Sorption on Thermodynamics, Structure, and Local Dynamics of Molten Atactic Polystyrene." Macromolecules, **53**(10) 3669–3689 (2020). DOI: 10.1021/acs.macromol.0c00323

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

Konstantina Karanasiou, School of Chemical Engineering, National Technical University of Athens, Diploma Student (2019-2020) - Supervised by: Dr. N. Vergadou

Undergraduate Theses and Internships completed in 2020

Name: Leonidas Konstantopoulos
Dissertation Title: "Computational study of conformation properties of poly-ethylene melts under uniaxial elongation flow using Monte Carlo methods."
Research Supervisor at NCSR: Dr. Loukas D. Peristeras
University where the Thesis was presented: National Technical University of Athens

Name: Konstantina Karanasiou
Dissertation Title: "Molecular Simulation of Ionic Liquid – Gas Mixtures"
Research Supervisor at NCSR: Dr. Niki Vergadou
University where the Thesis was presented: National Technical University of Athens
Dimitrios Gerakinis, Internship, 2020.
Supervised by: Dr. N. Vergadou
School of Applied Mathematical and Physical Sciences, National Technical University of Athens
Dimitrios Tsagalakis, Internship, 2020.
Supervised by: Dr. N. Vergadou
School of Chemical Engineering, National Technical University of Athens
Nikolaos Theodorou, Internship, 2020.
Supervised by: Dr. N. Vergadou
School of Chemical Engineering, National Technical University of Athens
Georgios Mikaelian, Internship, 2020.
Supervised by: Dr. N. Vergadou
School of Chemical Engineering, National Technical University of Athens
Aikaterini Argyropoulou, Internship, 2020.
Supervised by: Dr. N. Vergadou
School of Chemical Engineering, National Technical University of Athens

Conference / Workshop Organization
Workshop on "Artificial Intelligence in Natural Sciences and Technology" (https://ainst.scify.org/) held within the framework of the 11th Hellenic Conference on Artificial Intelligence (SETN2020), 2 – 4 September 2020, Athens, Greece.
Organizers: Dr. G . Giannakopoulos, Dr. N. Vergadou, Dr. P. Dimitrakis, Dr. V. Constantoudis, Dr. S. Karozis.

PHOTO-CATALYTIC PROCESSES AND ENVIRONMENTAL CHEMISTRY

Project Leader: Dr. Anastasia Hiskia

Researchers: Dr. Theodoros Triantis

Post Docs: Dr Christophoros Christophoridis, Dr Sevasti-Kiriaki Zervou, Dr Maria Antonopoulou

Research Associates: Dr Triantafyllos Kaloudis

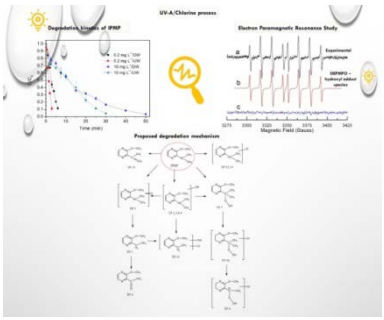
PhD Candidates: Korina Manolidi, Aikaterina Paraskevopoulou, Noura Alice Hammoud

MSc Students: Stefania Koursari, Myrto Touloupi, Maria Kehagia

Undergraduate Students: E. Klouvidaki, Maria Voumvouraki, Evagelos Sinefakis

- **Objectives**
  - Photocatalytic Processes; Evaluation of new Photocatalytic Materials
  - Advanced Oxidation Processes for Environmental Remediation; Elucidation of the Reaction Mechanisms; Identification of Transformation Products; Identification of Transient Reactive Species
  - Environmental Analytical Chemistry; Mass Spectrometry; Advanced Analytical Methods Development – Cyanotoxins, Cyanopeptides and Water Taste & Odor Compounds Analysis; Mapping of Cyanotoxins 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

- **Activities and Main 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.



Kinetic and mechanistic investigation of water taste and odor compound 2-isopropyl-3-methoxy pyrazine degradation using UV-A/Chlorine process, Science of the Total Environment 732 (2020) 138404

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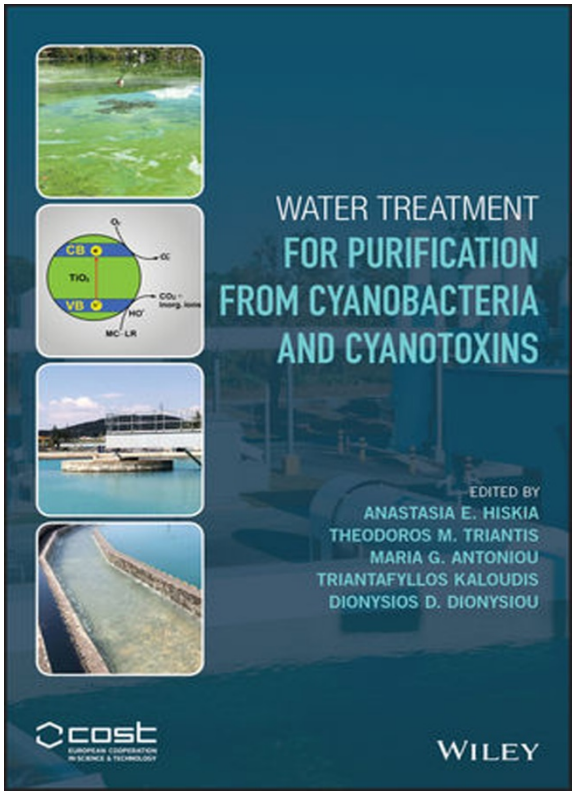
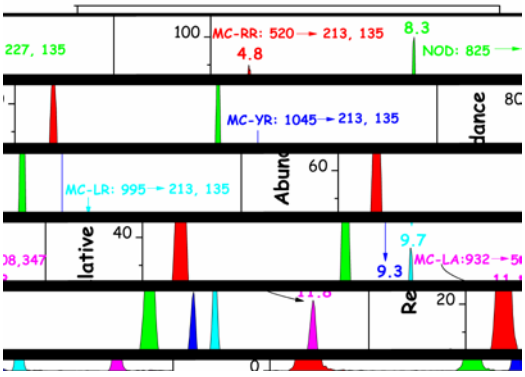
● Cyanobacteria produce structurally and biochemically diverse bioactive compounds that have been implicated in human health problems and animal fatalities. The main aim of the project is to fill current research gaps in the areas of (a) cyanotoxin analysis in environmental samples, (b) the presence of toxin producing cyanobacteria and their cyanotoxins in freshwater ecosystems and (c) advanced methods of water treatment for cyanotoxins removal. 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, 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.



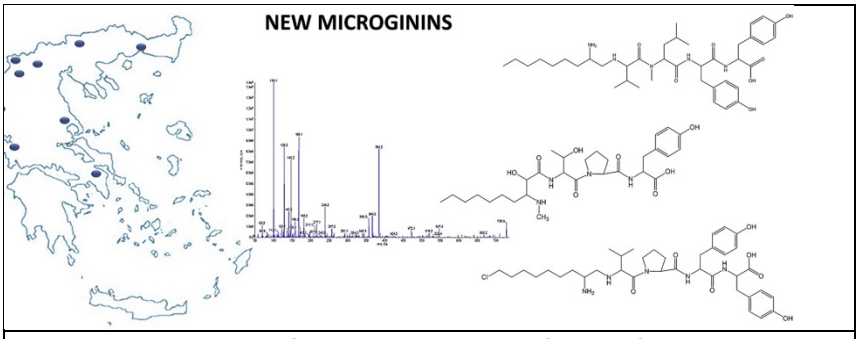
LC-MS/MS chromatogram of cyanotoxins (Environmental Analysis Laboratory: Accredited according to ISO 17025)

● 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.



A book developed in the framework of COST Action ES 1105 -CYANOCOST, describing recent advances concerning the treatment of cyanotoxins and T&O compounds in water by conventional and advanced oxidation processes

● 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.



New microginins from cyanobacteria of Greek freshwaters, Chemosphere 248 (2020) 125961

Funding

- «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€.

- "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 2019-2023. 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€.

- «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€.

- "From source to tap: risk assessment of organic pollutants in drinking water cycle of Athens", Industrial Fellowships Program – Stavros Niarchos Foundation 2017-2020:, INN-NCSR "DEMOKRITOS" in collaboration with EYDAP S.A. Research on the identification of potential threats to water quality throughout the drinking

water cycle (source, treatment, distribution network), development of a risk assessment system and providing a useful dataset of water quality data for the implementation of the Water Safety Plan. Duration: 6/2017 – 6/2020. Scientific Mentor: Dr Anastasia Hiskia, Company mentor: Dr. T. Kaloudis, Postdoc: Dr. C. Christophoridis. Group budget: 73.7 K€.

- "Evaluation of new and environmentally friendly methods for surface coating of metal alloys resistant to corrosion", funded by the Hellenic Aerospace Industry S.A. Duration 2020-2021. Project Coordinator: Dr. T. Triantis, INN, NCSR Demokritos. Budget: 19.5 K€.

- "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€.

- "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.

- "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.

- Services to the Decentralized Administration of Epirus - Western Macedonia, "Determination of cyanotoxins in water samples of Lake Vegoritida", 6.6 k€, Duration: 1/2020-12/2020.
- Services to VAPE ALTER EGO IKE, "Determination of toxic compounds in e-cigarette liquids", 20.75 k€, Duration: 1-2020 / 12-2020.

OUTPUT

Publications in International Journals

1. Antonopoulou, M., Ioannidis, N., Kaloudis, T., Triantis, T.M., Hiskia, A. "Kinetic and mechanistic investigation of water taste and odor compound 2-isopropyl-3-methoxy pyrazine degradation using UV-A/chlorine process." **Science of the Total Environment** 732**,** Art. No:138404 (2020). DOI: https://doi.org/10.1016/j.scitotenv.2020.138404
2. Vergou, Y., Touraki, M., Paraskevopoulou, A., Triantis, T.M., Hiskia, A., Gkelis, S. "β-N-Methylamino-L-alanine interferes with nitrogen assimilation in the cyanobacterium, non-BMAA producer, Synechococcus sp. TAU-MAC 0499." **Toxicon** 185, pp. 147-155 (2020). DOI: https://doi.org/10.1016/j.toxicon.2020.07.013
3. Zervou, S-K., Gkelis, S., Kaloudis, T., Hiskia, A., Mazur-Marzec, H. "New microginins from cyanobacteria of Greek freshwaters." **Chemosphere** 248, Art. No: 125961 (2020). DOI: https://doi.org/10.1016/j.chemosphere.2020.125961
4. Zervou, S-K., Gkelis, S., Kaloudis, T., Hiskia, A., Mazur-Marzec, H. "Fragmentation mass spectra dataset of linear cyanopeptides – microginins." **Data in Brief** 31, Art. No:105825 (2020). DOI: https://doi.org/10.1016/j.dib.2020.105825
5. Konstantinou D., Mavrogonatou E., Zervou S.-K., Giannogonas P., Gkelis S. "Bioprospecting Sponge-Associated Marine Cyanobacteria to Produce Bioactive Compounds" **Toxins** 12, no. 2: 73 (2020). DOI: https://doi.org/10.3390/toxins12020073

Books/Chapters in Books

1. Hiskia A,, Triantis T., Antoniou A., Kaloudis T., Dionysiou D., (Eds), *"Water treatment for purification from cyanobacteria and cyanotoxins"*, John Wiley & Sons, Ltd., Chichester, UK , pp 1-330 (2020).
2. Fotiou T., Triantis T.M., Hiskia A., Dziga D., Merel S., Edwards C., Antoniou M.G., *"Transformation products (TPs) of cyanobacterial metabolites during treatment"*, in Hiskia A,, Triantis T., Antoniou A., Kaloudis T., Dionysiou D., (Eds.), *"Water treatment for purification from cyanobacteria and cyanotoxins"* John Wiley & Sons, Ltd, Chichester, UK , Ch. 9, pg.231-305 (2020).

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

1. Dimova-Boykinova G., Kaloudis T., Akcaalan R., Devesa-Garriga R., Steinhaus M., Testai E., Hiskia A., Triantis T., Tonev R., Avagianos C., Karaolia P., Koker L., Panksep K., WaterTOP: Taste and Odor In Early Diagnosis Of Source And Drinking Water Problems *BULAQUA, Bulgarian Water Association,* 1-2, pp.32-33 (2020).

International Conferences Presentations (invited, oral, poster)

1. Touloupi M.-F., Christophoridis C., Kaloudis T., Bizani E., Thomaidis N., Hiskia A. " Degradation of cyanotoxin cylindrospermopsin in water using ultrasonication: Role of Reactive Radical Species" in Proceedings of Natural Toxins: Environmental Fate and Safe Water Supply (NaToxAq) Conference) p. 62 (2020). DOI: https://doi.org/10.5817/CZ.MUNI.P210-9659-2020.
2. Zervou S.-K., Gkelis S., Kaloudis T., Hiskia A., Mazur-Marzec H. "Characterization of new anabaenopeptins from cyanobacteria of Greek lakes" in Proceedings of Natural Toxins: Environmental Fate and Safe Water Supply (NaToxAq Conference) p. 109 (2020). DOI: https://doi.org/10.5817/CZ.MUNI.P210-9659-2020.
3. Kaloudis T., Avagianos C., Zervou S.-K., Hiskia A., van Herk M., Visser P., Gkelis S., Deftereos N., Miskaki P. "Seasonal geosmin production from benthic cyanobacteria in a freshwater canal, with implications for drinking water supplies" in SETAC Europe 30th Annual Meeting, 3-7 (2020).

Teaching and Training Activities

Theodoros Triantis

Teaching Fellow/Assistant, Department of Industrial Design and Production Engineering, University of West Attica. Graduate level course: (i) Chemistry I (laboratory) (1st semester), (ii) Chemistry II (laboratory) (2nd semester) and (iii) Thermodynamics and heat transfer (theory) (5th 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

Master Dissertations completed in 2020

Name: Koursari Stefania

Dissertation Title: Synthesis, characterization and applications of metal nanoparticles

Research Supervisor at NCSR: Dr Theodoros Triantis

University where the Thesis was presented: National and Kapodistrian University of Athens

Name: Myrto-Foteini Touloupi
Dissertation Title: Degradation of Cylindrospermopsin in water using ultrasound
Research Supervisor at NCSR: Dr Anastasia Hiskia
University where the Thesis was presented: National and Kapodistrian University of Athens

Awards
Toxins 2020 Best Paper Award for the article "Temperature Effects Explain Continental Scale Distribution of Cyanobacterial Toxins" DOI: https://doi.org/10.3390/toxins10040156

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 OIga 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.

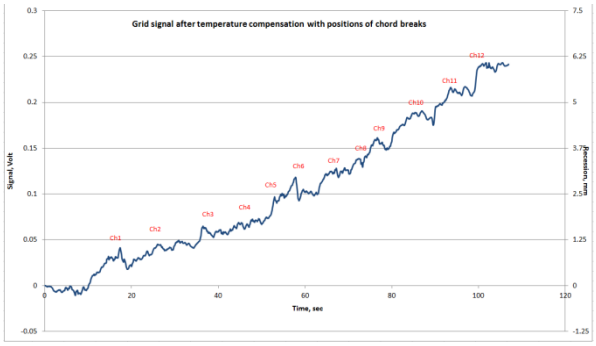


Figure 2. Ablative recession reconstruction using the ReGS-HF sensor for a phenolic-ceramic fibre material used for thermal protection of spacecraft.

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.

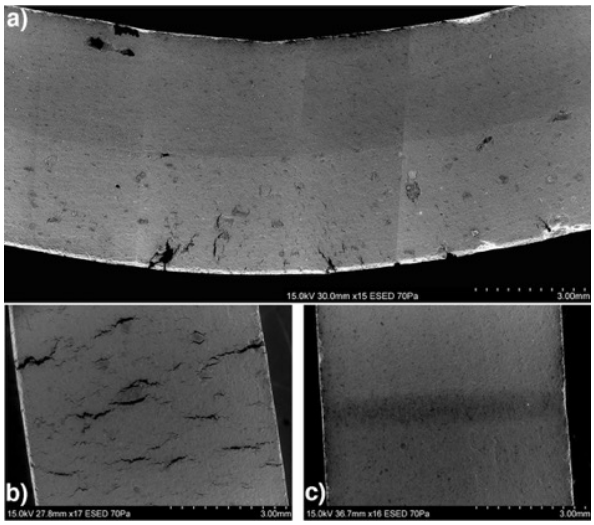


Figure 3. SEM image of a 2-layer ceramic specimen subjected to three-point flexure at 900°C

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 by 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, 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 (delayed from 2021 due to Covid-19).
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 2020: about 90000 Euro

OUTPUT

Publications in International Journals

1. Gardner, C., Müller, N.S. Vekinis, G., Freestone, I.C., Kilikoglou, V. "High-temperature performance of two-layered ceramics and the implications for Roman crucibles", *Archaeometry*, **62**, 935-951 (2020). https://doi.org/10.1111/arcm.12569
2. Kaumenova, G.N., Xanthopoulou, G., Aubakirov, Y.A., Tungatarova, S.A., Baizhumanov, T.S. "Composite materials based on Co-Al-Mg-Mn in catalytic oxidative reforming of methane", *Materials Today* **31,** 603-606 (2020). https://doi.org/10.1016/j.matpr.2020.07.530
3. Xanthopoulou, G, Karanasios, K., Tungatarova, S., Baizhumanova, T., Zhumabek, M., Kaumenova, G., Massalimova, B., Shorayeva, K. "Catalytic methane reforming into synthesis-gas over developed composite materials prepared by combustion synthesis", *Reaction Kinetics, Mechanisms, and Catalysis,* **126**, 645-661 (2020). DOI 10.1007/s11144-019-01541-9.

Other publications:

1. Kaumenova, G.N., Xanthopoulou, G., Sovetbek, Y.K,. Baizhumanova, T.S., Tungatarova, S.A., Kotov, S.O. "Co-Mg-Mn composite catalysts for partial oxidation of natural gas", *News of the Academy of Sciences of the Republic of Kazakhstan, Series Chemistry and Technology,* **4**, 64 – 72 (2020). https://doi.org/10.32014/2020.2518-1491.66
2. Talasbayeva, N., Kazhdenbek, B., Zhang, X., Kaumenova, G.N., Xanthopoulou, G., Tungatarova, S.A., Baizhumanova, T.S. "Catalytic conversion of methane into syngas and ethylene", *News of the Academy of Sciences of the Republic of Kazakhstan, Series Chemistry and Technology,* 3 (435), 6-12 (2020). https://doi.org/10.32014/2019.2518-1491.22
3. Tungatarova, S.A., Xanthopoulou, G., Kaumenova, G.N., Zhumabek, M., Baizhumanova, T.S., Grigorieva, V.P., Komashko, L.V., Begimova, G.U. "Development of composite materials by combustion synthesis method for catalytic reforming of methane to synthesis gas", *News of the Academy of Sciences of the Republic of Kazakhstan, Series Chemistry and Technology,* 6(432), 6-15 (2020). https://doi.org/10.32014/2018.2518-1491.20

Educational Activities

1. G. Vekinis, teaching 15hrs course "Advanced Ceramics" for the MSc programme on "Science and Technology of Materials, May 2020, 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 2020.
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 3 PhD students
5. G. Vekinis, Head of the Education Office of NCSR "Demokritos", many activities relating to NCSRD students (55th "Demokritos" Summer School etc) and pupils.

PhD Theses completed in 2020

1) Name: Vladislav Novikov,
Dissertation Title: "Synthesis of nanoscale Cu-Cr-O spinels using solution combustion synthesis"

Research Supervisor at NCSR: Dr Galina Xanthopoulou
University where the Thesis was presented: University of Samara, Russia

2) Name: Gulnar Kaumenova
Dissertation Title: “Development of composite materials by combustion synthesis method for catalytic reforming of methane to synthesis gas”
Research Supervisor at NCSR: Dr Galina Xanthopoulou, University where the Thesis was presented: Satbayev University, Almaty, Kazakhstan

Undergraduate Theses and Internships completed in 2020

Name: Dimitris Tzavellas
Dissertation Title: “Synthesis of nanomaterials based on Cu and FeNi3 using solution combustion synthesis”
Research Supervisor at NCSR: Dr Galina Xanthopoulou
University where the Thesis was presented: University of Ioannina

Patent
Tungatarova, S., Xanthopoulou, G., Baizhumanova, T., Zheksenbaeva, Z., Zhumabek, M., Kaumenova G. Patent N 2020/4767, Republic of Kazakhstan, “Method of preparation of catalysts for production of synthesis gas”, priority date 30.09.2019, registered 11.03. 2020**.**

Program 2

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

A point-of-care (POC) diagnostic system is developed around a lab-on-a-chip (LoC) for the detection of bacteria DNA.

Ia. Design of Lab-on-Chip for bacteria detection

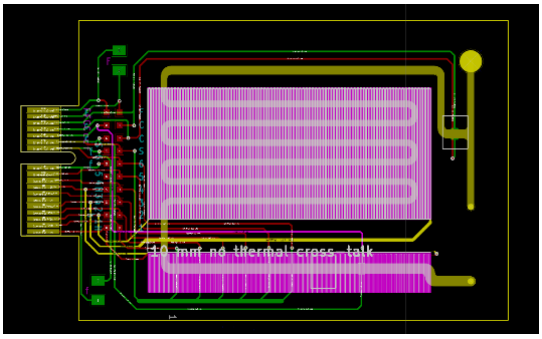


Figure 1. Layout of the LoC. Electrical connections are made fed to a PCIe edge connector.

The chip is designed so as to include a DNA amplification unit and a detection unit based on reduced graphene oxide biosensors and is going to be implemented on a Printed Circuit board thus taking advantage of the mass production amenable methods employed in the PCB industry. The microfluidic network of the chip (microchannels and microchambers) is implemented in either the top or the bottom solder mask layer of the PCB, therefore minimizing any subsequent post processing to simply depositing the rGO for the fabrication of the biosensors and the biomolecules required for the amplification and detection, plus sealing. In the current design up to 4 metal layers are taken advantage of in order to implement the heating elements for the amplification and hybridization chambers and the electronic contacting pads for the biosensors and the flow sensors. Extra considerations include dedicated fluidic inputs for inserting the sample and buffer solutions. The whole chip will be hosted and controlled by a PoC instrument currently under development.

Ib. Design of PoC Instrument

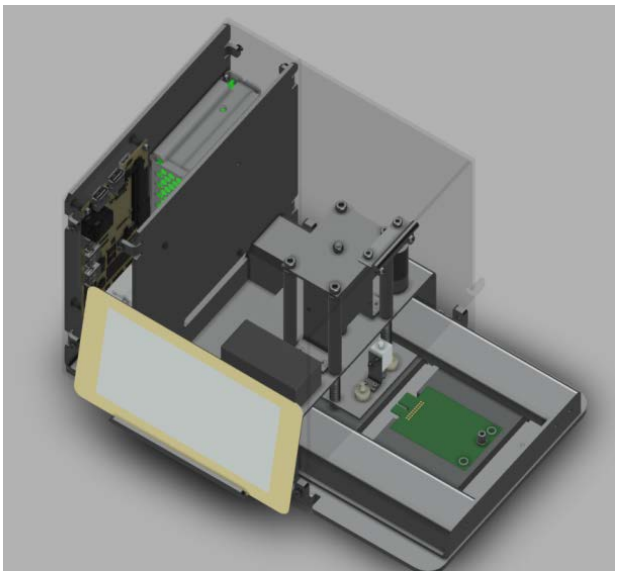


Figure 2. 3D Model of the PoC instrument

A PoC instrument able to host the Lab-on-Chip is being developed within the DIAMOND project. The instrument will provide all the microfluidic and electrical connections necessary to operate the LoC effectively. It furnishes a miniature peristaltic pump and two pinch valves to control the flow of the sample under test and the reagents necessary to perform on chip amplification and electronic detection of the biotinylated amplicons on the rGO biosensors implemented on the chip. The electronics of the instrument comprise of a computation core implemented on a raspberry Pi, a temperature controller to regulate the temperature zones of the LoC and the sensor readout circuitry. The schematic 3D view of the design is depicted in Figure 2.

II. Microsystems for obstructive sleep apnea treatment

In this activity, an automated non-invasive system for the real time monitoring and treatment via electro-stimulation (ES) of the genioglossus muscle of obstructive sleep apnea (OSA) – a common underdiagnosed disorder - is being developed. The close-loop system includes a sensor to monitor breath effort from respiratory movement, a Transcutaneous Electrical Nerve Stimulation (TENS) device, and a program that analyzes the signal of the sensor and controls the whole system. The breath effort signal is first processed and then fed to a machine learning (ML) algorithm. When an apnea event starts, the TENS device stimulates the genioglossus muscle in order to reopen the upper-airway. The final system is designed to work using resistive strain sensor patches implemented on a Polydimethylsiloxane (PDMS) substrate and using graphene nanoplatelets (GNPs). The fabrication process of the strain sensor patches utilizes PMMA substrates and drop casting of GNPs dispersions on the substrate. The GNPs are dispersed in degassed deionized (DI) water and isopropyl alcohol (IPA) in a ratio 7:3. After the evaporation of the solvents, the GNPs network can be transferred to the PDMS after drop-casting and partial curing of PDMS as described in Figure 3. The partially cured PDMS with the GNPs on it, is flipped and after making the contacts, another PDMS layer is drop-casted encapsulating the GNPs layer and part of the contacts. After a final curing, the strain sensor patch is ready for characterization. This process allows controlled fabrication of the sensor patches while minimizing material waste compared to spin-coating. It also allows modifications in the surface morphology of the sensor towards their optimization.

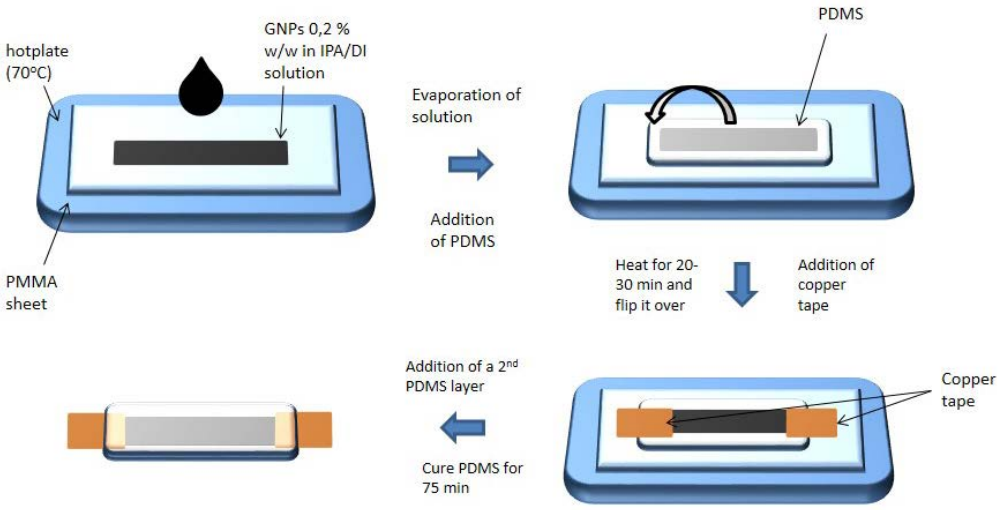


***Figure 3**. The fabrication process of the flexible strain sensor patches.*

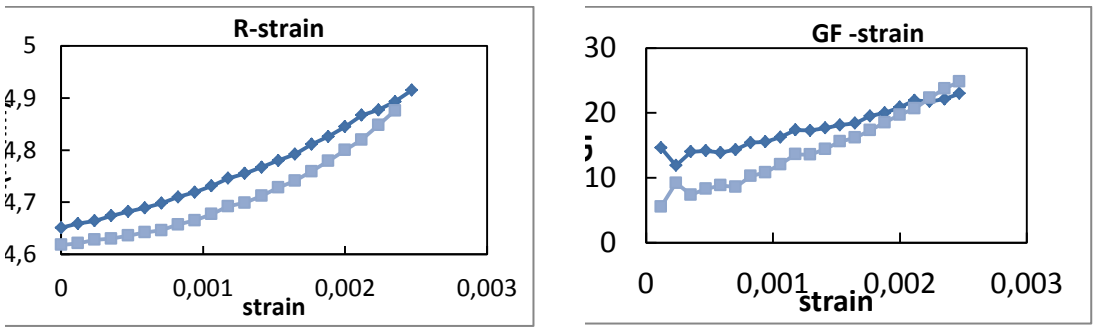


***Figure 4**. Response of a GNPs-PDMS strain sensor at low strain under a strain-release cycle.*

The fabricated strain sensor patches were evaluated using a cantilever beam setup able to apply low strain (in the millistrain range) on the sensor (Figure 4). Finally, the ability of the sensor patches in monitoring of the breath effort was also evaluated using a custom-made setup for dynamic low-strain measurements. The latter is shown in the following picture (Figure 5) and comprises a piston and a variable speed AC motor drive. The device is used to inflate/deflate a balloon on the surface of which a strain sensor patch is mounted. The small volume changes of the balloon then are used to simulate the movements of the human chest during breathing and thus effectively the breath rate.

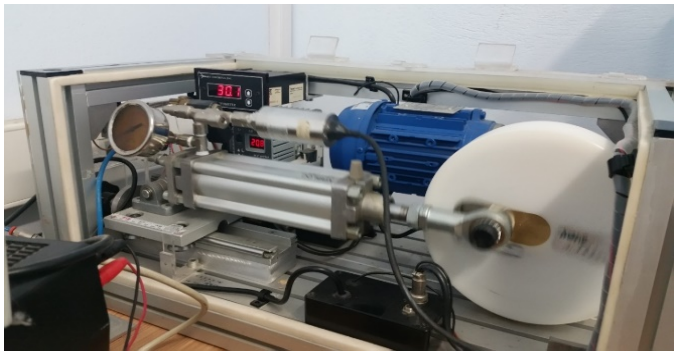


***Figure 5.**The experimental setup that is utilized as a phantom for the characterization of the flexible sensors for vital signal monitoring.*

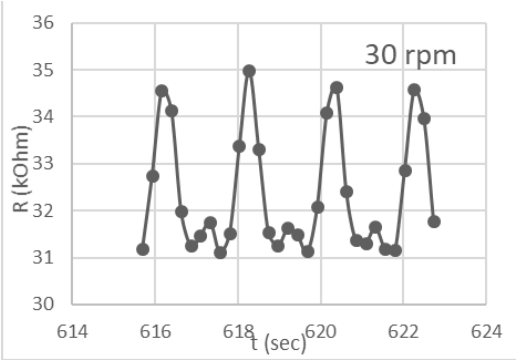


***Figure 6.** Dynamic behavior at frequencies close to breath and heart rate*

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 – 6/2020
Budget: 120.000
Budget for 2020: 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. Tsouti,V., Kanaris, AI, Tsoutis K., Chatzandroulis S., Development of an automated system for obstructive sleep apnea treatment based on machine learning and breath effort monitoring Microelectronic Engineering, **231** 111376, (2020) DOI: 10.1016/j.mee.2020.111376
2. Tsougeni K., Kaprou G., Loukas C.M., Papadakis G., Hamiot A., Eck M., Rabus D., Kokkoris G., Chatzandroulis S., Papadopoulos V., Dupuy B., Jobst G., Gizeli E., Tserepi A., Gogolides E., Lab-on-Chip platform and protocol for rapid foodborne pathogen detection comprising on-chip cell capture, lysis, DNA amplification and surface-acoustic-wave detection, Sens. Act. B, **320**, 128345, (2020), ,DOI:10.1016/j.snb.2020.128345.

International Conferences Presentations (invited, oral, poster)

1. Halkias J, Tsouti V., Kordatos K., Chatzandroulis S. Investigation of graphene based resistive strain sensors for vital signal monitoring, 17th International Conference on Nanosciences & Nanotechnologies, 7-10 July 2020, Thessaloniki, Greece (poster)

2. Filippidou M., Georgoutsou-Spyridonos M., Douskas S., Nikolakakis A., Petrou P., Mastellos,D. Chatzandroulis S., Tserepi, Nanotechnology and micro-devices for the diagnosis and treatment of infectious diseases with emphasis on Covid-19: Novel products and high TRL prototypes in Greece”, 2020, Hellenic Biocluster and the Micro Nano Scientific Society of Greece virtual conference

Teaching and Training Activities

1. Nikitas Melios Ms Thesis (started 2020, expected 2021) “Development of an epidermal, patch-type, electrochemical sensor for the detection of analytes in sweat”, NTUA/SAMPS, MSc on "Microsystems and Nanodevices"

ELECTRON MICROSCOPY AND NANOMATERIALS

Project Leader: A. Travlos

Permanent Research Staff: N. Boukos, K. Giannakopoulos

Post Docs: E. Sakellis, M. Lasithiotakis

PhD Candidates: E. Chatzigeorgiou

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

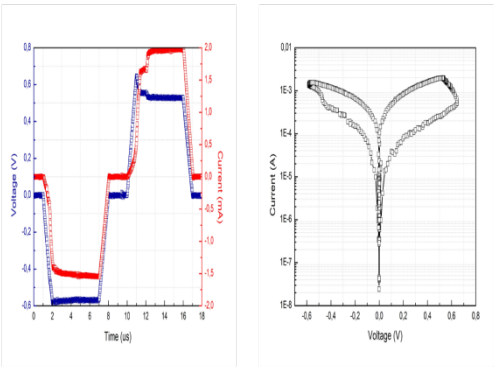
Objectives

- 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

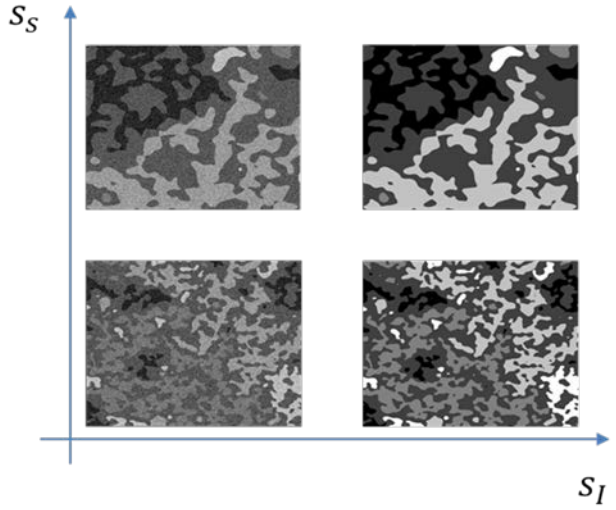
The effect of active electrode material on the resistive switching behavior of a resistive random-access memory (ReRAM) is of primary importance. The main goal was the examination of the influence of the electrode and the semiconducting layer on the conduction mechanisms that dominate the I-V characteristic curves of the device. The material used for the development of the active electrode is zinc, while the semiconducting layer is zinc oxide nanoparticles. Heterojunction diodes MSM (Metal-Semiconductor-Metal) based on Zinc Oxide nanoparticles, as the active electrode material, were fabricated, characterized electrically and studied by means of Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Photoluminescence Spectroscopy (PL), along with simulations extracted using the finite element method.



Development of a hybrid characterization method for new types of clinker combining SEM and XRD

Back-scattered electron imaging is usually utilized in the characterization of multiphase materials. In order to quantify the surface (volume) fraction of the phases present in the material segmentation methods should be additionally applied to the SEM images. A series of image acquisition parameters such as contrast, brightness, acceleration voltage etc. affect the quality of the image and hence the accuracy of segmentation

results. The calibration of these parameters in order to maximize the accuracy of segmentation results is challenging. Moreover the selection of a particular segmentation method affects the results obtained. To overcome this problem, we have proposed the concept of a segmentability index, which we define as an index that quantifies the ability of an image to be segmented accurately. Since the segmentability index is calculated from the original image data, it is invariant to the choice of the segmentation method. The validation of segmentability index has been realized with synthetic images. The synthetic back-scattered electron images were produced by a novel, non-iterative method. This method can include information extracted from real back-scattered electron images of single-phase materials but can also generate synthetic images from the scratch.



Synthetic images placed in an accenting order in respect with their spatial/intensity component of their Segmentability index (vertical axis / horizontal axis)

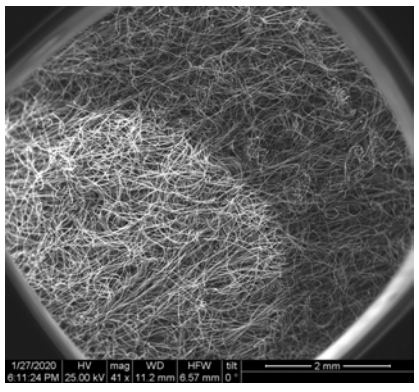
In addition, we examined the effects of contrast, dwell time, acceleration voltage and Z-contrast on the back-scattered electron images statistical moments and revealed the relation between statistical moments of back-scattered electron images with its acquisition parameters and Z-effective of the material.

Fabrication of Titania films for self cleaning CSP mirrors

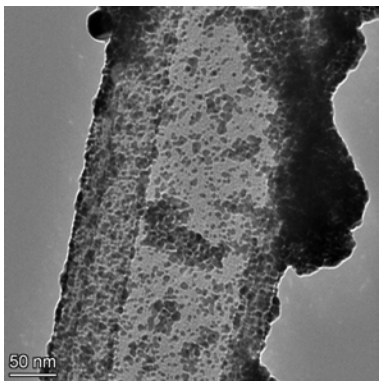
Within the framework of the Solar Eranet project Nano4CSP we have deposited a range of TiO_2 coatings on already existing Concentrated Solar Power mirrors and performed a range of processes and analyses to evaluate the stability of the films, their hydrophilicity, their phase etc. We have also studied the stability of the back side (reflective) commercial coating.

Fabrication of nanoparticles by the use of Spark Discharge method

We have performed a wide range of depositions of Au nanoparticles on fibrous substrates (carbon cloths, borosilicate glass etc) using the Spark discharge aerosol technique in collaboration with the lab for Environmental radiation of NCSR Demokritos. We employed an in situ characterisation technique (SMPS) 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.



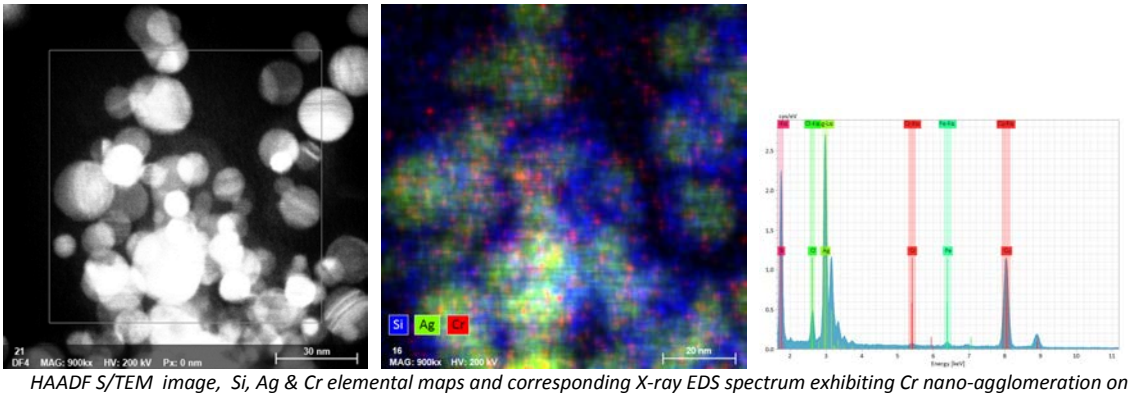
SEM image of a carbon nanoporous fibre cloth with Au nanoparticles deposited (bright area)



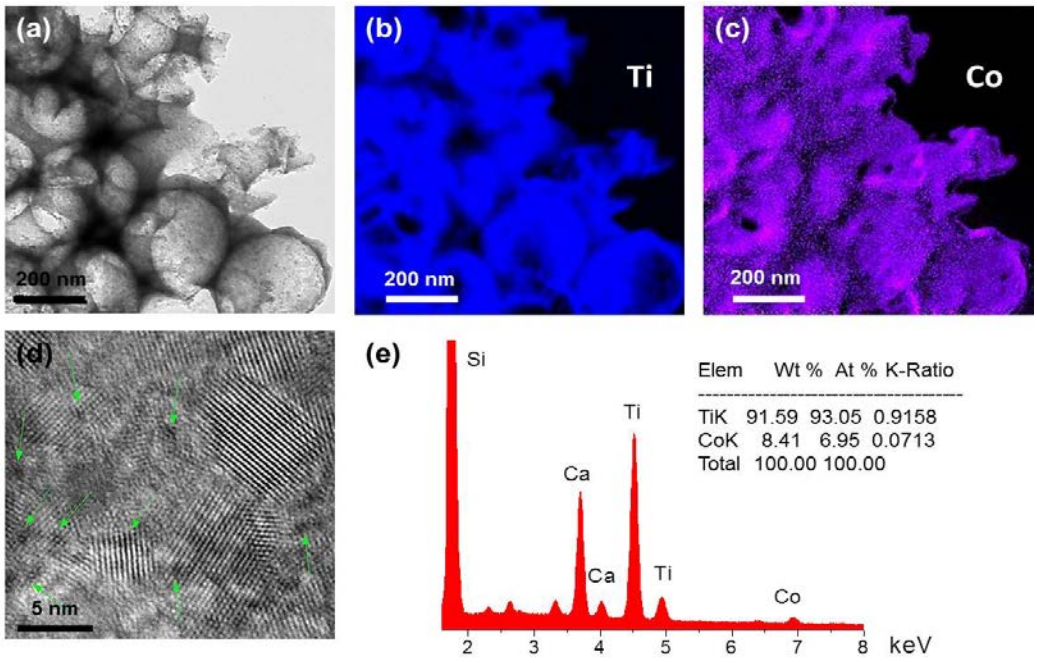
TEM image of Au nanoparticles

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, H storage, catalysis, energy and environmental applications



HAADF S/TEM image, Si, Ag & Cr elemental maps and corresponding X-ray EDS spectrum exhibiting Cr nano-agglomeration on Ag nanoparticles embedded on SiO_2 particles.



Funding

Nano4CSP: Nanomaterials for reduced maintenance costs in Concentrated Solar Power plants, Solar-ERANET, 770.000 € (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 € (Co-Supervisor)

Advanced Training Course "Spintronics Radar Detectors", NATO Science for Peace and Security, 50.000 € (Co Organiser)

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. Subrati, A., Kim, Y., Al Wahedi, Y., Tzitzios, V., Alhassan, S., Kim, H.J., Lee, S., Sakellis, E., Boukos, N., Stephen, S., Lee, S.M., Lee, J.B., Fardis, M., Papavassiliou, G., Monitoring the multiphasic evolution of bismuth telluride nanoplatelets, *CrystEngComm*, **22** (45), pp. 7918-7928. (2020*)* DOI: 10.1039/d0ce00719f

2. Basina, G., Elmutasim, O., Gaber, D.A., Gaber, S.A., Lu, X., Tzitzios, V., Vaithilingam, B.V., Baikousi, M., Asimakopoulos, G., Karakassides, M.A., Panagiotopoulos, I., Spyrou, K., Thomou, E., Sakellis, E., Boukos, N., Xu, D., Tsapatsis, M., Amoodi, N.A., Wahedi, Y.A., On the selective oxidation of H2S by heavy loaded Nanoparticles Embedded in Mesoporous Matrix (NEMMs), *Applied Catalysis B: Environmental*, **278**, art. no. 119338, (2020) DOI: 10.1016/j.apcatb.2020.119338

3. Apostolaki, M.-A., Toumazatou, A., Antoniadou, M., Sakellis, E., Xenogiannopoulou, E., Gardelis, S., Boukos, N., Falaras, P., Dimoulas, A., Likodimos, V., Graphene quantum Dot-TiO2 photonic crystal films for photocatalytic applications, *Nanomaterials*, **10** (12), art. no. 2566, pp. 1-18. (2020) DOI: 10.3390/nano10122566

4. Nikolopoulou, S.G., Boukos, N., Sakellis, E., Efthimiadou, E.K.,
Synthesis of biocompatible silver nanoparticles by a modified polyol method for theranostic applications: Studies on red blood cells, internalization ability and antibacterial activity, Journal of inorganic biochemistry, **211**, p. 111177. (2020) DOI: 10.1016/j.jinorgbio.2020.111177

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perovskite solar cells*, Journal of Photochemistry and Photobiology A: Chemistry*, **386**, art. no. 112141, (2020) DOI: 10.1016/j.jphotochem.2019.112141

10. Segkos, A., Sakellis, I., Boukos, N., Drivas, C., Kennou, S., Kordatos, K., Tsamis, C., Patterned carbon dot-based thin films for solid-state devices, *Nanoscale*, **12** (18), pp. 10254-10264. (2020) DOI: 10.1039/c9nr08904g

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14. Sagnou, M., Mavroidi, B., Kaminari, A., Boukos, N., Pelecanou, M. Novel Isatin Thiosemicarbazone Derivatives as Potent Inhibitors of β-Amyloid Peptide Aggregation and Toxicity *ACS Chemical Neuroscience*, **11** (15), pp. 2266-2276. (2020) DOI: 10.1021/acschemneuro.0c00208

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Teaching and Training Activities

N. Boukos / E. Sakellis
Nanomaterials lab, MSc course "Microsystems and Nanodevices"/Fall Semester 2020/NTUA/Athens, Greece

N. Boukos / E. Sakellis
Experimental Methods lab, MSc course "Technological Applications of Physics"/Fall Semester 2020/NTUA/Athens, Greece

K. Giannakopoulos
55th NCSR Demokritos summer school 13-17/7/2021 / Duration 30 minutes/ virtual/ NCSR Demokritos

K. Giannakopoulos
ECOWEEK MEET-UP 2020/ 16 May 2020/ Duration 1h/ Online

K. Giannakopoulos
Researcher's Night 2020. Nov 27, 2020/ Duration 3 min/ online

Awards

K. Giannakopoulos
EUvsVirus Hackathon winner under "Fast and reliable Virus tests" (Team Leader)

Services
Electron Microscopy characterization of materials and products to industrial entities in Greece.
Total income of 15.000 Euros

ENERGY HARVESTING AND AUTONOMOUS SENSORS

Project Leader: C. Tsamis

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

Objectives

- Novel materials and techniques for high efficiency energy conversion
- Design and optimization of Energy Scavengers for Autonomous Microsystems
- MEMS-based vibrational microgenerators
- Nanogenerators on Flexible Substrates
- Multifunctional Nanostructures for Smart Products & Biomedical Applications
- Low-power chemical sensors on silicon and flexible substrates for safety and security
- Carbon Quantum Dots for chemical/biochemical sensors.

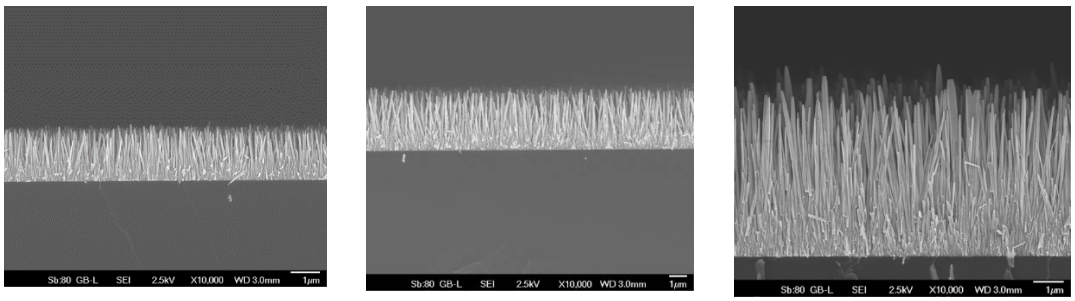
Activities and Main Results

Growth and characterization of ZnO nanostructures

A. Bardakas, C. Tsamis

During this year we expanded our activities regarding the growth ZnO nanostructures under different growth conditions. The target of this study is to investigate the influence of the growth conditions on the geometrical characteristics of ZnO nanorods. ZnO growth was performed on previously studied seeding layers grown by magnetron sputtering and spin-on sol-gel method. Growth of ZnO in aqueous solutions of zinc nitrate hexahydrate and hexamethylenetetramine (HMTA) with the addition of polyethylenimine (PEI) and ammonium hydroxide. Growth time ranged from 0.5 to 6h without solution refreshing and up to 18h with solution refreshing, at 87 C°.

The addition of ammonium hydroxide resulted in a rapid homogenous growth of ZnO particles that inhibited the heterogenous growth on the surface of the sample, creating flower-like structures in the examined ZnO powder. The effect of ammonia in an open-bath system at elevated temperatures needs further investigation. The HTMA was varied between 20 and 50mM which resulted in the reduction of the growth rate in a 2-hour window when compared to a 40mM equimolar solution. The addition of 5mM PEI in conjunction with a 40mM equimolar solution resulted in a reduction of the homogeneous growth. Using the above experimental conditions ZnO nanorods were grown for 18h with solution refreshing reaching approximately 7μm in length at a constant diameter of 50 to 70 nm (Fig 1a-c).



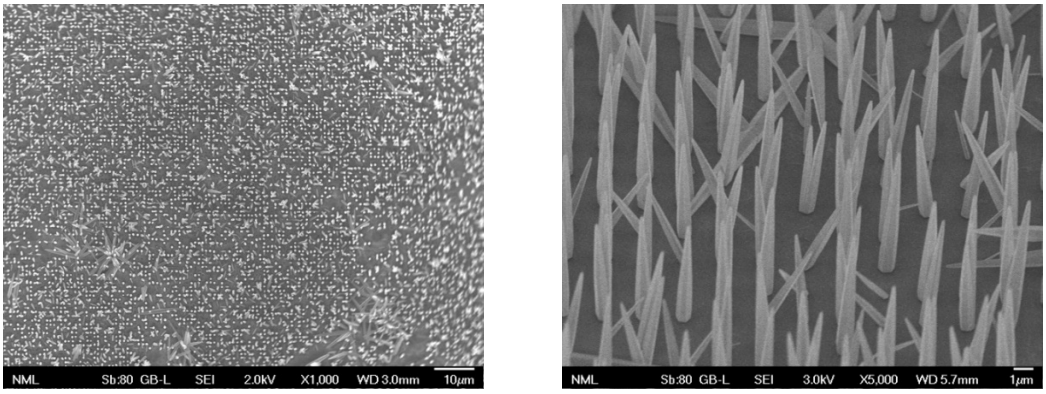
(a) (b) (c)

Figure 1. Cross section SEM images of ZnO nanorods grown with 40mM equimolar solution with 5mM of PEI for (a) 4, (b) 6 and (c) 18 hours.

Templated growth of ZnO nanorods using EBL for sensor applications

A. Bardakas, G. Papageorgiou, C. Tsamis

ZnO nanorod arrays were grown on seeded Si substrates patterned using Electron Beam Lithography (EBL). The Si substrates were seeded using magnetron sputtering resulting in 20-nm thin film annealed at 500 C° in air for 1h. For the EBL process, ARP photoresist was spin coated on top of the seeded substrates with a thickness of 300nm. A dosage study was performed in order identify the best exposure/development combination for yielding acceptable dimensional accuracy of 50 and 100nm holes. Finally, an array pattern was created consisting of 50 and 100nm apertures at 1, 2 and μm spacings (Fig 2a). Nanorod growth was performed in a 40mM equimolar solution of zinc nitrate hexahydrate and hexamethylenetetramine at 87 ^{o}C. (Fig 2b)



(a) (b)

Figure 2. (a) *SEM top view image of an area containing windows with 50nm aperture and 1μm spacing, and (b) SEM images of ZnO nanorods grown at different growth durations (4 h) for the 50nm aperture and 2μm spacing*

Study of the photoluminescence of N-doped, Carbon Dot-based nanocomposite materials from citric acid and urea

A. Segkos, E. Alexandratou[1], I. Sakellis, N. Boukos, S. Gardelis[2], K. Kordatos[3] and C. Tsamis
In collaboration with [1]Dept. of Electrical Engineering NTUA, [2]Dept. of Physics NKUA and [3]Dept. of Chemical Engineering NTUA

We studied the optical properties and underlying mechanisms of two different types of citric acid derived N-doped carbon dots (CDs). The CDs originating from open vessel (CDa) were found to be a mixture of quasi-spherical graphitic carbon dots, stacked graphene nanosheets and nanoribbons (Fig. 3a-b), while CDs obtained by the sealed vessel, high-pressure reaction (CDp) were comprised of only graphitic carbon dots (Fig. 3c). The optical studies of their solutions revealed that in CDa the formation of H-aggregates of two molecular fluorophores, HPPT and CzA derivatives, are responsible for their observed photoluminescent response, while in CDp only CzA derivatives are present and acting as active optical emitters. These molecular fluorophores were found to be parts of the carbonaceous conformations, decorating their surfaces and edges. In both samples, graphitic cores were identified as energy donors, exciting the existing fluorophores through energy transfer mechanisms. These mechanisms were found to be independent from each other, as witnessed from the pH-dependent optical studies of the dialyzed CDa fractions. Last but not least, solid-state PL studies revealed a new energy transfer mechanism in CDa samples, similar to FRET, which emerges due to spectral overlap and increased proximity of the different fluorophores after drying (Fig. 4).

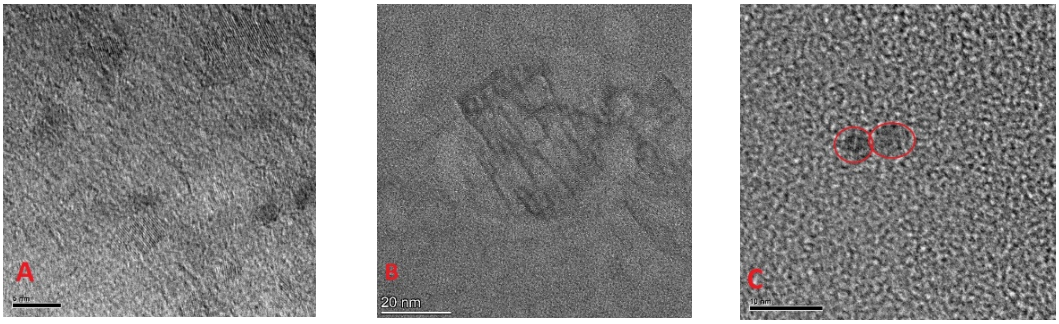


Figure 3 *TEM images of CDa (a,b) and CDp (c) at different magnifications. Scale bars are a) 5 nm, b) 20 nm and c) 10 nm.*

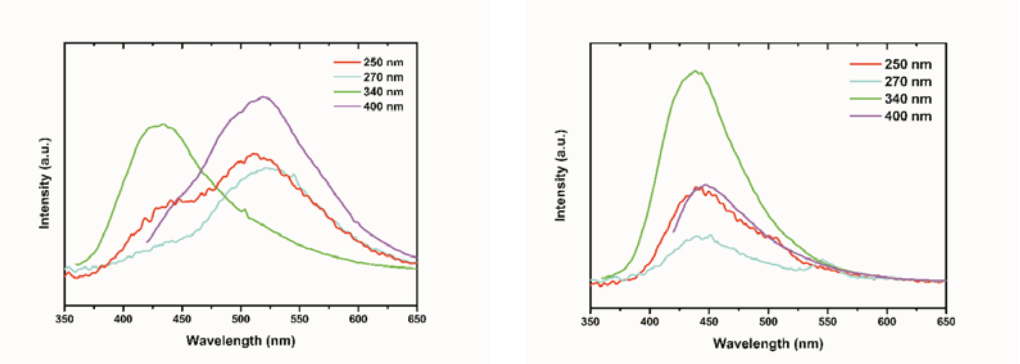


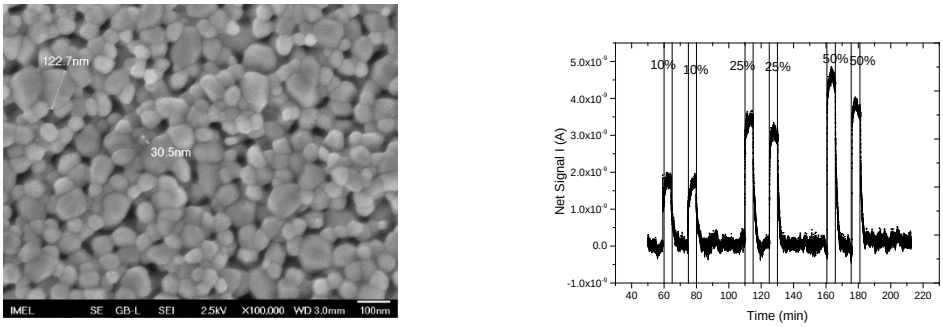
Figure 4 *Emission spectra of a) CDa and b) CDp aqueous solutions at 250 nm, 270 nm, 340 nm and 400 nm excitation.*

Fabrication of Na-doped ZnO nanostructured films for CO2 sensing at room temperature

M. Stramarkou, A. Bardakas, M. Krokida[1], C. Tsamis

In collaboration with [1]Dept. of Chemical Engineering, NTUA

2.5% Na- doped ZnO sensors, which can detect modifications in CO_2 concentration and thus indicate the quality or microbial spoilage of juice products were developed. ZnO:Na spin-coated films were deposited via sol-gel method using zinc acetate and sodium acetate as source and dopant material, respectively, 2-methoxyethanol as solvent and ethanolamine as stabilizing agent. The mixtures were magnetically stirred for 2h and aged overnight. The film deposition was conducted by 7 repetitions of spin coating (2000 rpm, 30 sec) and drying (180^{o}C, 20 min), and a final annealing of the films (500 ^{o}C, 120 min). The morphological properties of the sensors were studied through Scanning Electron Microscopy (SEM), whereas the sensing properties were determined through relative humidity (RH) and CO_2 measurements. Specifically, during the measurements, the sensors were connected to a Keithley 2400 source measure unit (SMU) and then placed in a Teflon® chamber. The RH and CO_2 content was controlled by supplying a mixture of dry air, humid air and dry air with 0,1% CO_2 through Brooks® 5800-S mass flow controllers (MFC). A 2 V constant bias was supplied using the SMU and the current of the device was measured and recorded. The study showed that after the addition of 2.5% Na, the sensors demonstrated higher particle diameter and film thickness, as shown by SEM (Fig. 5a). Finally, the sensors demonstrated enhanced CO_2 sensing properties when their response in various CO_2 contents (steps at 10%=50ppm, 25%=125 ppm and 250 ppm) was evaluated (Fig. 5b).



(a) (b)

Figure 5 *(a) Top view SEM images Na- doped ZnO films and (b) Response of Na- doped ZnO sensor at 2 V bias against various CO_2 concentrations.*

Optical characterization of inkjet-printed electronic structures based on Ag nanoparticles, PEDOT:PSS and CQDs (Carbon Quantum Dots)

D. Barmpakos, A. Segkos, C. Tsamis, G. Kaltsas[1], K. A. Rubin[2], R. Schelwald[3]

In collaboration with:

[1] *microSENSES laboratory, Dept. of Electrical and Electronic Engineering, University of West Attica*

[2] *KLA Corporation, Milpitas, CA*

[3] *Filmetrics, a KLA Company, Unterhaching, Germany*

By using 3d optical profiling, a non-contact, high resolution measurement and visualization of printed structures was performed. The examined samples consisted of inkjet-printed line of Ag nanoparticles with an overlapping area with PEDOT:PSS and PEDOT:PSS-CQDs composites on Kapton substrate (Fig. 6); such junctions play a vital role in the development of multi-material printed electronic devices; thus, information regarding topographical characteristics are considered of major importance, for assessing both the physical contact between the materials, and the printability of each material layer.

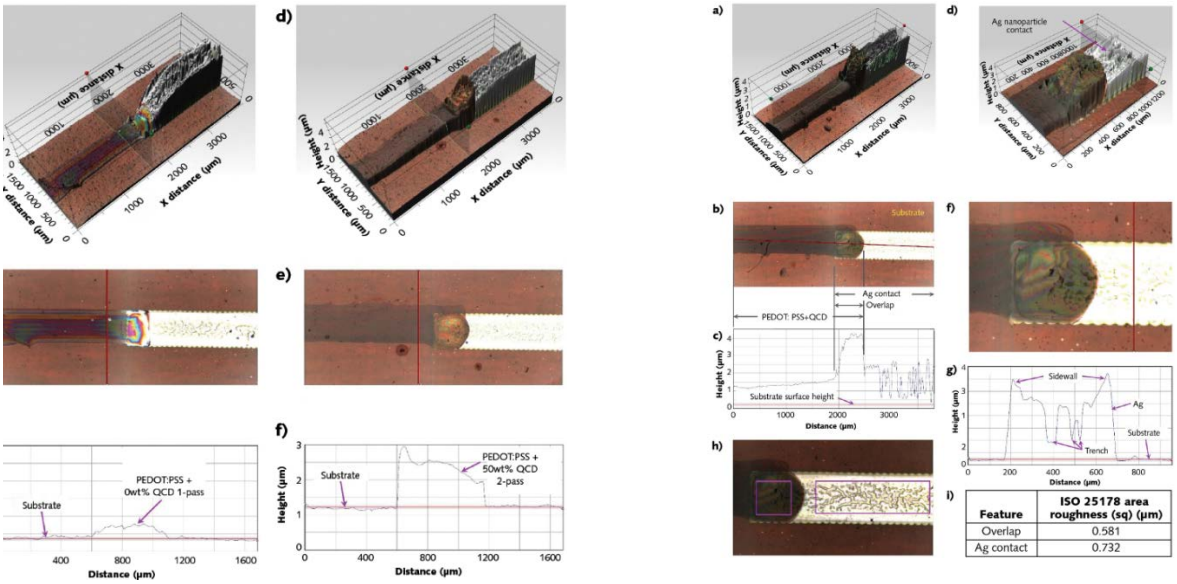


Figure 6. *3D topography of single layer printed PEDOT:PSS + 0wt% CQD and AgNPs;* ***2b.*** *two-printed pass of PEDOT:PSS + 10wt% CQD and AgNPs*

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

Publications in International Journals

1. Segkos, A., Sakellis, I., Boukos, N., Drivas, C., Kennou, S., Kordatos, K., Tsamis, C., Patterned carbon dot-based thin films for solid-state devices. *Nanoscale* **12,** pp. 10254-10264 (2020). DOI: https://doi.org/10.1039/C9NR08904G
2. Barmpakos, D., Tsamis, C., Kaltsas, G., Multi-parameter paper sensor fabricated by inkjet-printed silver nanoparticle ink and PEDOT: PSS. Microelectronic Engineering, 225, 111266 (2020)

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

1. Rubin, K., Schelwald, R., Barmpakos, D., Segkos, A., Tsamis, C., Kaltsas, G., High-performance cost-reduced optical interferometry with True Color broadens applicability of 3D optical profiling: Advancing Flexible Electronics Devices, Materials and Fabrication Processes with precise measurements. Laser Focus World (2020),

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

TWO-DIMENSIONAL MATERIALS AND GRAPHENE FOR NANOELECTRONICS

Project Leader: Dr. Athanasios Dimoulas

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

PhD Candidates: C. Zacharaki, S. Fragkos, N. Siannas, E. Symeonidou

Objectives

- 2D metal dichalcogenide materials and v.d. Waals heterostructures
- 2D monoelemental materials Xenes (bismuthene, stanene)
- HfO_2-based ferroelectrics focusing on the compatibility with Si semiconductor processing.
- Skyrmion-Topological insulators and Weyl semimetal heterostructures

Activities and Main Results

1. Topological surface states in epitaxial $(SnBi_2Te_4)_n$ $(Bi_2Te_3)_m$ natural van der Waals superlattices

We examined the structure and the electronic properties, especially those related to the TSS, of four different TI compounds and alloys, namely Bi_2Te_3, $SnBi_4Te_7$, $SnBi_2Te_4$ and $Sn_{1-x}Bi_xTe$ grown by molecular beam epitaxy on InAs(111)/Si(111) substrates. The layered structure is studied by high-resolution scanning transmission electron microscopy (STEM) revealing a layer stacking in the form of natural van der Waals superlattice. Combining first-principles calculations with in-situ and synchrotron ARPES, we confirm the presence of TSS and correlate them with magnetotransport measurements. By varying the Bi/Sn ratio and monitored by ARPES, we are able to tune the position of the Fermi level with respect to the topological surface states (TSS) and the bulk conduction band (BCB) allowing the identification of Sn composition at which the TSS contribution maximizes relative to BCB.

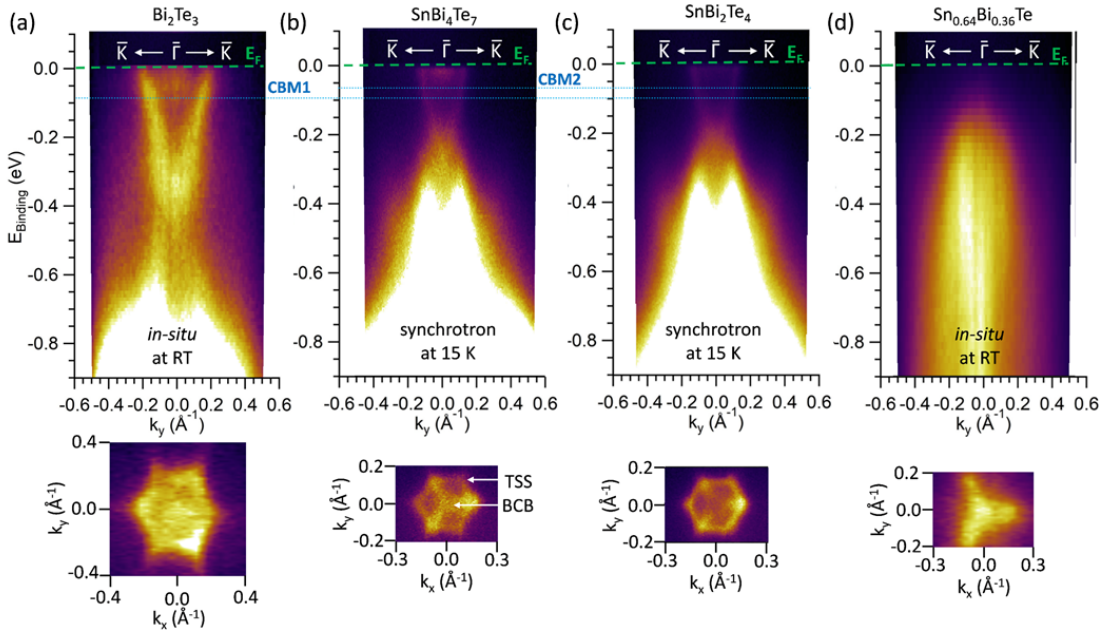


Fig. 1. *(a-d) ARPES measurements of band dispersions and their k_x-k_y Fermi surface maps for four samples with different Sn compositions recorded along $\underline{K\Gamma K}$. The shifts of the conduction band minimum are indicated with horizontal blue dotted lines. TSS and BCB in (b) denote the topological surface states and bulk conduction band respectively.*

2. Type-III Dirac fermions in $Hf_xZr_{x-1}Te_2$ topological semimetal candidate

In this paper, our first-principles calculations reveal that $HfTe_2$ and $ZrTe_2$ are type-I and type-II Dirac semimetals (DSMs), respectively, which creates the prospect that by alloying the two materials, a new $Hf_xZr_{1-x}Te_2$ type-III DSM material will emerge. After a systematic investigation of $Hf_xZr_{1-x}Te_2$ energy bands as a function of composition and strain, a type-III Dirac cone with a line-like Fermi surface is predicted to form at 20% concentration of Hf, in combination with 1% in-plane compressive strain. Furthermore, by imaging the electronic energy bands with in-situ ARPES of this layered compound at the desired composition x=0.2, grown by MBE on InAs(111) substrate, we provide experimental evidence that the top of type-III Dirac cone lies at -or very close to- the Fermi level.

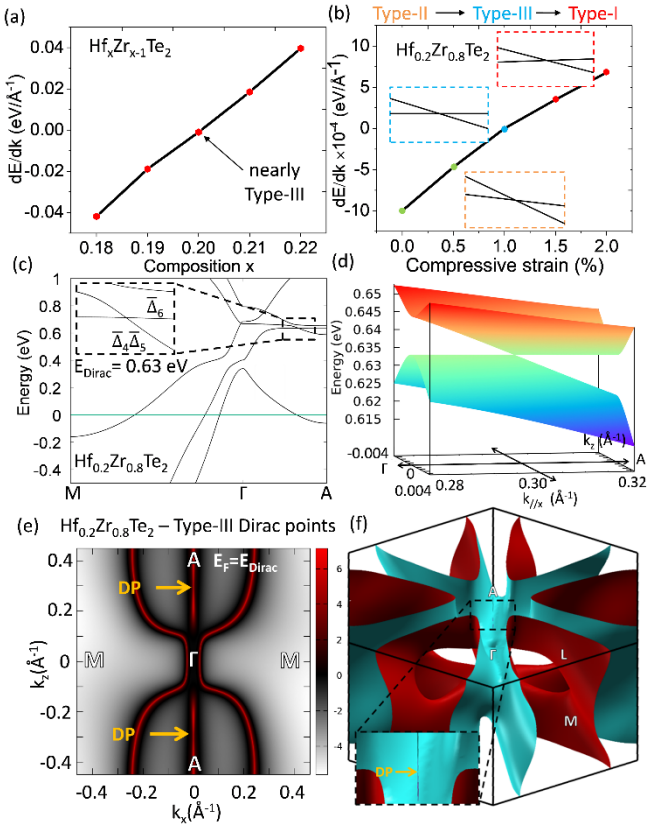


Fig. 2. *(a) Systematic investigation of $Hf_xZr_{1-x}Te_2$ energy bands as a function of composition and (b) of compressive strain, where the green, blue and red insets show the evolution of the Dirac cone (type-II, type-III, and type-I respectively). (c) Electronic band structure of $Hf_{0.2}Zr_{0.8}Te_2$ with 1% in-plane compressive strain along the M-Γ-A direction. The inset indicates the type-III band crossing between valence and conduction bands featuring a line-like Fermi surface. (d) The 3D band structure near the crossing point. (e) and (f) the 2D and 3D Fermi surfaces of $Hf_{0.2}Zr_{0.8}Te_2$, respectively.*

3. 2D crystalline thin films with non-trivial topology

Among ultrathin Monoelemental 2D Materials (ME2DMs), bismuthene, the single layer of heavier group-VA element bismuth (Bi), has been predicted to have large non trivial gap. We demonstrated the growth of Bi films by molecular beam epitaxy (MBE) on 2D-HfTe2 template. At the initial stage of Bi deposition (1-2 bilayers, BL), both the pseudocubic Bi(110) and the hexagonal Bi(111) phases are formed. When reaching 3 BL Bi, a transformation to pure hexagonal Bi(111) occurs. The electronic band structure of 3BL Bi(111) films was measured by Angle-Resolved Photoemission Spectroscopy (ARPES) showing very good matching with the Density Functional Theory (DFT) band structure calculations of 3BL free standing Bi(111). The grown Bi(111) thin film was capped with a protective Al2O3 layer and its stability under ambient conditions, necessary for practical applications and device fabrication, was confirmed by XPS and Raman spectroscopy

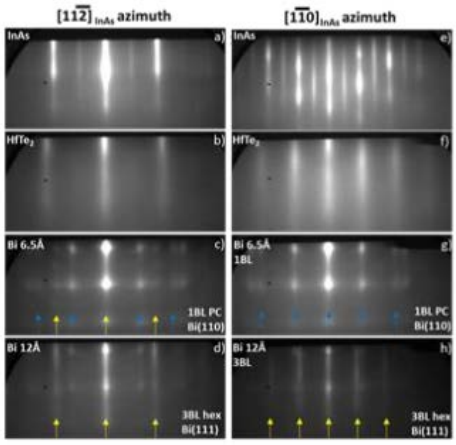
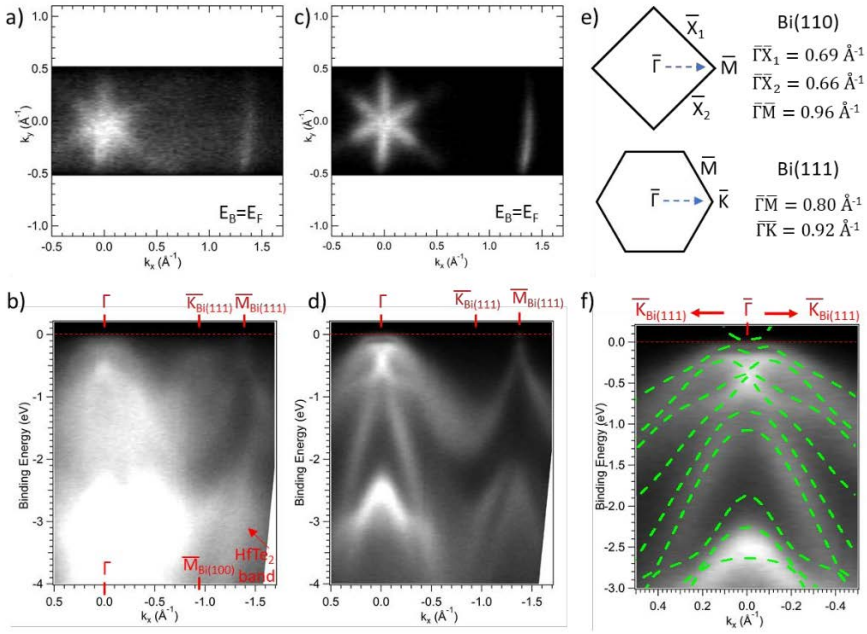


Fig. 3. RHEED pattern of Bi deposition on InAs/HfTe2 templates. (a, e) Two different azimuths of (a, e) InAs(111) substrate and (b, f) 2 ML HfTe 2 on InAs(111) are shown for comparison. (c, g) 6.5 Å of Bi deposited on HfTe 2 and (d, h) 12 Å of Bi deposited on HfTe 2 . Bleu arrows indicate the main streaks of Bi(110) with tetragonal symmetry and the yellow arrows show the Bi(111) streaks with hexagonal symmetry.



***4**. ARPES data, measured with He I (21.22 eV) radiation at RT. Fermi surface & energy ersion along Γ-K-M direction of Bi(111) for: (a, b) Bi mixed (6.5 Å) PC-hexagonal phase and l) 3BL Bi(111) (12 Å), respectively. (e) Surface Brillouin zone of PC and hexagonal structures, Calculated band structure of 3 BL free standing Bi(111) overlaid on measured ARPES data of Bi(111) (12 Å) showing very good agreement.*

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)O_2) 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.

OUTPUT

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: 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: 10.1103/PhysRevMaterials.5.014203
3. Zacharaki C., Tsipas P., Chaitoglou S., Evangelou E.K. , Istrate C.M., Pintilie L., Dimoulas A., Depletion induced depolarization field in Hf1-xZrxO metal-ferroelectric-semiconductor capacitors on germanium, Applied Physics Letters, 116, 182904, (2020), DOI: 10.1063/5.0007111
4. Zacharaki C., Tsipas P., Chaitoglou S., Bégon-Lours L., Halter M., Dimoulas A., Reliability aspects of ferroelectric TiN/Hf0.5Zr0.5O2/Ge capacitors grown by plasma assisted atomic oxygen deposition, Applied Physics Letters, 117, 212905, (2020), DOI: 10.1063/5.0029657

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

1. Fragkos S., Tsipas P., Tsoutsou D., Sant R., Alvarez C., Renaud G., Okuno H., Dimoulas A., Epitaxial growth and characterization of topological semimetals from the 2D transition metal dichalcogenides family, *APS March Meeting 2020*, March 2–6 2020, Denver Colorado

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

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

Objectives

Since 1995, our group has contributed to the broad and multi-faceted area of Micro/Nanoelectronics with particular focus on low-dimensional materials and devices for information storage and processing. Along the years, we have gained from our experience in facing difficult scientific and technological challenges, while keeping in mind the following objectives: (1) Development of dielectrics and nanostructures for inorganic and organic electronics, (2) Integration of new materials into micro- & nanoelectronics technologies, (3) Design, fabrication and testing of electronic devices with emphasis on non-volatile memory cells and, (4) Technology transfer to industry.

Activities and Main Results in 2020

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. Particular efforts are placed on identifying and understanding the physicochemical processes taking place at the interfaces and in the bulk, including how and to what extent they affect the performance of the devices. Much of this year's focus was on developing and evaluating p-type OTFTs using polymeric gate dielectrics with embedded triphenyl sulfonium (TPS) salts. UV irradiation of the TPS salts produces strong Brønsted acid resulting in the formation of anions (X^-) and cations (H^+). Device operation is highly sensitive to the amount of generated anions and their ability to migrate throughout the gate dielectric as shown in Fig. 1 for the particular case of hexafluoro antimonate $[SbF_6]^-$ counter anions. Simple tractable models taking into account the dependence of the gate capacitance and hole mobility on the magnitude and duration of the applied gate voltage have been developed. Output-current modulation is currently examined as a function of the polymer electrolyte baking temperature and the thickness of the OSC layer for getting more insight into the effect of ion mobility on device operation and the issue of whether electrochemical doping occurs in the bulk of the OSC.

B. Processability of ALD Al_2O_3 on semiconductor substrates

Here, focus is on the processability of Al_2O_3 films formed on semiconductor substrates using the atomic-layer-deposition (ALD) technique. To which extend the post-deposition processing parameters used in the fabrication of MOS devices affect the quality of the metal-Al_2O_3 interface and the properties of the dielectric-semiconductor interface is examined. During 2020, an attempt was made study the influence of negative lithography on Al_2O_3 films deposited on Si, which allows a direct comparison with the effects that take place in the case of Ge substrates (see INN previous activity report). This activity is conducted in collaboration with the Physics Dept. of Patras University and the Physics Dept. of Aristotle University.

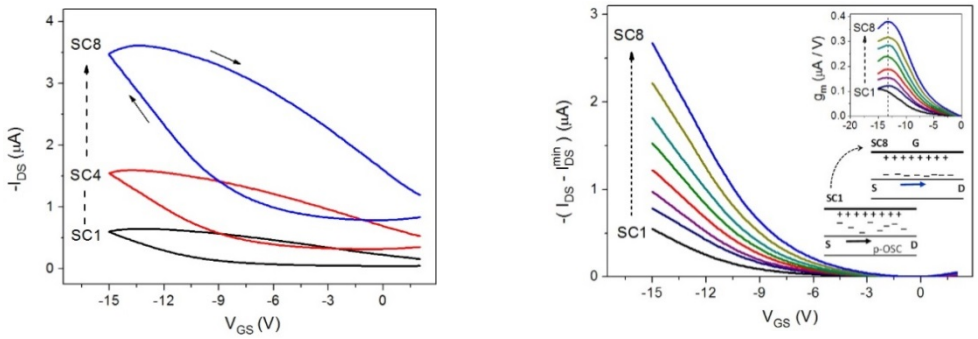


***Figure 1**: I_{DS}-V_{GS} (left) and (I_{DS} - I_{min})-V_{GS} (right) characteristics of a p-type (P3HT) OTFT using a gate dielectric made of PMMA with embedded triphenyl sulfonium (TPS) salts. Measurements were performed after UV irradiation for eight successive V_{GS} round sweep cycles (SCs). Inset graph (right fig.): transconductance (g_m = dI_{DS}/dV_{GS}) vs V_{GS} plots. Accumulation of anions (SbF_6^-) at the dielectric/P3HT interface with the applied SC moves the transfer curves towards higher drain currents and enhances the gain factor of the transistor, but does not affect the location of the transconductance peak.*

C. <u>Processing issues in Ge CMOS technology</u>

This activity is conducted in collaboration with the Physics Dept. of Patras University (Greece) and Aristotle University of Thessaloniki (Greece). The main task is the fabrication of ultra-shallow and highly activated n+/p junctions for advanced n-channel Ge MOSFETs. This year the research was focused on the Ge substrate damage induced by ion implantation and subsequent thermal processing, where a variety of defect surface morphologies was observed and explained.

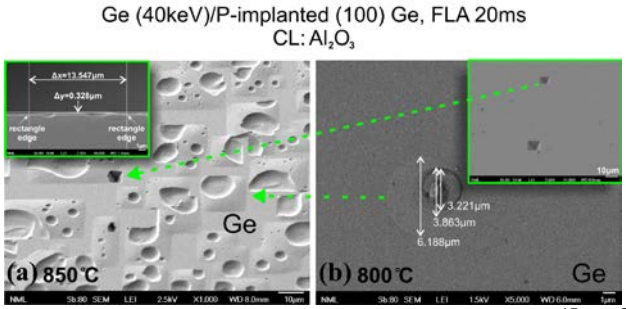


***Figure 2**: Representative SEM images of Ge/P [40keV/$10^{15}cm^{-2}$ and 11keV/$10^{15}cm^{-2}$ respectively] co- implanted (100) Ge, capped with 30 nm Al_2O_3, after preheating at 450°C for 4min and FLA at (a) 850°C for 20ms and (b) 800°C for 20ms. Images have been taken at 40° tilt after removing the capping layer. Note the formation of inverted pyramids in the Ge substrate.*

D. <u>Resistance switching mechanisms for memory cells and neuromorphic computing devices</u>

A novel quantum-based model for filamentary resistive switching nanodevices (RSN), like MOxBF based RSN, was introduced. A quantum random walk-based algorithm was developed to model the evolution of the conductive filament, while in each step of the filament evolution the conductance of the device is calculated by the NEGF method (Fig. 3(a)). The simulation results provide clear identification of the robustness of the model for a number of retention energies for both dielectric and metal. Furthermore, as a single proof of concept, data were used from prototype RSNs, namely planar MIM devices made of 30nm Cu (active electrode) on a 40nm-thick deposited SiO_2 and 100nm thick Pt (counter electrode), and were compared with the model's output. The results showed a fair qualitative and quantitative agreement between the experimental and simulated data (Fig.3(b)). As further step, more parameters like temperature distribution, electron mobility and ion concentration of the under-study devices will be considered.

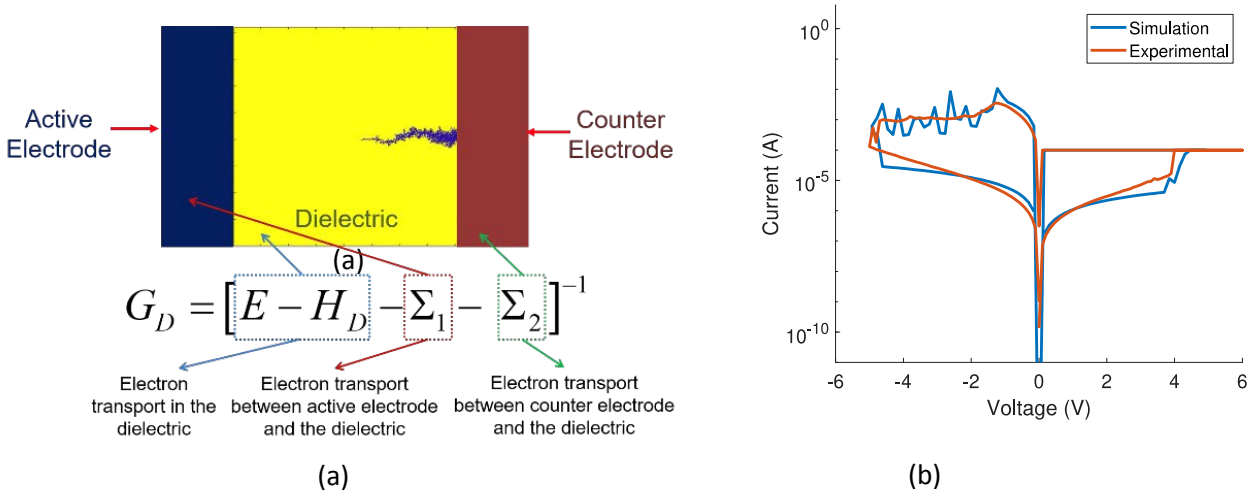


Figure 3: *(a) The parts of the matrix equation for retarded Green's function G_D that describe the active electrode, the dielectric containing metallic ions and the counter electrode and (b) comparison between experimental data and simulation output.*

E. <u>Studies of irradiation damage on functional materials</u>

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 2020 neutron irradiated experiments were performed on polycrystalline alumina materials at relatively low doses. Subsequent measurements revealed that the technique of diffuse reflectance spectroscopy is able to detect the absorption bands generated in the material during neutron irradiation.

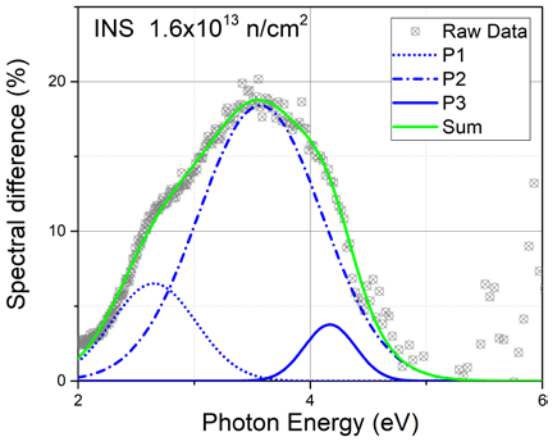


Figure 4*: Spectral difference of the apparent absorption spectra before and after irradiation as a function of the photon energy of illumination light for the case of the polycrystalline alumina with purity 99.9 %. This spectral difference reveals the absorption bands which are generated by the irradiation which are shown as individual peaks.*

F. Nano-electronic devices for Quantum Simulators

An approach to emulate quantum gates utilizing reprogrammable memristor (MR) crossbars was investigated. More specifically, given that for quantum computing (QC), the matrix- vector multiplication (Fig.5) is the dominant algebraic operation, we utilized the unprecedented characteristics of memristive grids to implement circuit-level QC. Hadamard and CCNOT, which comprise a universal quantum set for real probability amplitudes, were mapped successfully on MR crossbars and their correct operation was demonstrated. Our simulation results enable further exploration of the original idea of using MR devices for hardware acceleration of QC.

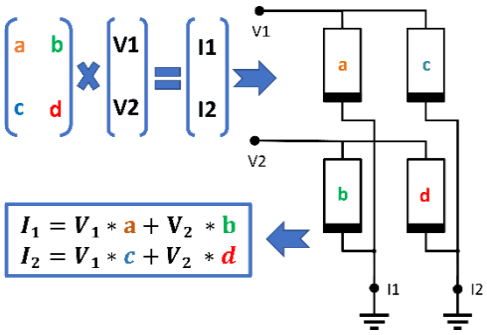


***Figure 5**. Crossbar Vector-Matrix Multiplication example using memristors*

G. 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°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.

H. Graphene technology for electronic devices and sensors

Graphene is a promising material for bioelectronic and biomedical applications. Highly desirable would be the fabrication of graphene logic nanocircuits that could be incorporated in living tissue to perform computations locally. This would provide new possibilities for monitoring and controlling biochemical processes that involve ion transport. Graphene nanoribbons are the most important emerging Graphene structures for nanoelectronics and sensors. This year, we presented the design and simulation of a Majority graphene gate, using tight-binding Hamiltonians and the NEGF method. The structure of the gate combined with applied top-gate potentials results in effective conductance modulation and accurate execution of the Majority gate truth table without using back-gates. The absence of back-gates leaves the graphene layer free to be incorporated with biological substrates. The universality of the Majority gate and the density of the graphene sheet combined with its biocompatibility hold great promise for graphene circuit technology-based biological and biomedical applications (Fig. 6).

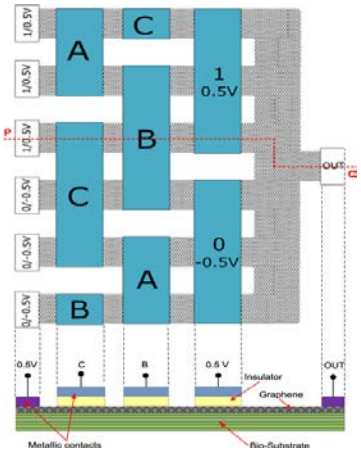


***Figure 6**.* Up: Top view of the graphene Majority gate. Down: Cross section of the graphene Majority gate along the (red) PQ dashed line.

Funding

- "JET3 RADA" 2014-2020 (~120k€)
- "ΣΕΜΘ", "Research-Create-Innovate" GSRT-NSFR (No: T1ΕΔΚ-03579) 2018-2020 (260k€)
- "EINSTEIN", Greece-Russia Bilateral Research Project, GSRT-NSFR (No: Τ4ΔΡΩ-00031) 2017-2018 (140k€)

- “RADAR”, “Research-Create-Innovate” GSRT-NSFR (No: T1ΕΔΚ-00329) 2018-2020 (140k€)
- “MEM-Q”, Greece-Russia Bilateral Research Project, GSRT-NSFR (No: Τ4ΔΡΩ-00030) 2017-2018 (80k€)

OUTPUT

Publications in International Journals

1. Kapetanakis, E., Katsogridakis, C., Dimotikali, D., Argitis, P., Normand, P., Ion-Activated Greatly Enhanced Conductivity of Thin Organic Semiconducting Films in Two-Terminal Devices, Advanced Electronic Materials, 2000238 (2020). doi:10.1002/aelm.202000238
2. Ioannou-Sougleridis, V., Alafakis, S., Vouroutzis, N. Z., Mergia, K., Speliotis, A., Skarlatos, D., Degradation of Pt-Al2O3-Ge Metal Oxide Semiconductor Structures due to Pt-Al2O3 Induced Reactions, ECS J. Solid State Sci. Technol. 9 024003 (2020). doi.org/10.1149/2162-8777/ab682e

Papers in Refereed Conference Proceedings

1. Ntinas, V., Karamani, R.E., Fyrigos, I.A., Vasileiadis, N., Stathis, D., Vourkas, I. , Dimitrakis, P., Karafyllidis, I, Sirakoulis, G., Cellular Automata coupled with Memristor devices: A fine unconventional computing paradigm, in Proceedings of International Conference on Electronics, Information, and Communication (ICEIC) 2020, 19-22 Jan. 2020, Barcelona, Spain DOI: 10.1109/ICEIC49074.2020.9051236
2. Ntinas, V., Karakolis, P., Sirakoulis, G.C., Dimitrakis, P., Neuromorphic circuits on segmented crossbar architectures with enhanced properties, in Proceedings of ECCTD 2020 - 24th IEEE European Conference on Circuit Theory and Design, art. no. 9218289, (2020). DOI: 10.1109/ECCTD49232.2020.9218289

International Conferences Presentations (invited, oral, poster)

1. Karakolis, P, Vasileiadis, N, Normand, P., Dimitrakis, P., Ntinas, V., Fyrigos, I.A., Karafyllidis, I., Sirakoulis, G., Silicon Nitride RRAM Technology, International Conference on Electronics, Information, and Communication (ICEIC) 2020, 19-22 Jan. 2020, Barcelona, Spain (oral)

Conference / Workshop Organization

Teaching and Training Activities

Name: P. Dimitrakis
Training: Internship of NTUA students Mr Mavropoulis Alexandros, Ms Georgopoulou Despina
Location/Academic Institute: Nanotechnology and Microsystems Laboratory/INN NCSR “D”

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. Marinos Tountas, Dr. Dimitra Niakoula

PhD Candidates: Ermioni Polydorou, Apostolis Verykios, Charis Katsogridakis, Anastasia Nika, Varvara Marazioti, Petros-Panagis Filippatos

Research Collaborators : Prof. Nikos Vainos, Prof. Dimitris Alexandropoulos, Prof. Stamatios Boyatzis, Prof. Georgios Fakorellis, Prof. Dimitris Tsoukalas, Prof. Margarita Chatzichristidi, Prof. Stella Kennou, Prof. Leonidas Palilis, Prof. Athanassios Coutsolelos, Dr. Ioannis Petsalakis, Prof. Maria Vamvakaki, Dr. Theodoros Manouras, Prof. Alexander Chroneos

Objectives

- Research on materials for organic 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

Main research activities

- Interfacial Layers and Nanostructure Issues in Organic Optoelectronic Devices (Organic Photovoltaics and Organic Light Emitting Diodes).
- Development of nanostructured materials with emphasis on hybrid materials and metal oxides/polyoxometalates (POMs) for applications in organic electronic devices and photocatalysis.
- Porphyrin compounds as charge transfer mediators in organic optoelectronics.
- Proton Conducting Polymeric Materials as Composite Dielectrics in Sensors and Memory Devices.
- Polymeric Materials for Nanopatterning and Light-Induced Processes Aiming at Applications in Optical Storage, MEMs, bio-MEMs and Drug Delivery.
- 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.
- Physicochemical investigation of porphyrin sensitizers in solution and in solid state for photocatalytic applications.
- Physicochemical investigation of photolithographic materials based on POMs for the fabrication of micro-structured bio-systems.
- Physicochemical research on the characterization, pathology and removal of spray-paints from contemporary mural surfaces.
- Polymeric Materials for Multilayer Coatings of Advanced Performance.
- Organic and/or inorganic polymer resist materials with tailored properties for multi-functional applications

Main Results

(A) Efficient colloidal quantum dot light-emitting diodes operating in the second near-infrared biological window

A colloidal quantum dot (CQD) light-emitting diode (LED) with a peak emission at 1,397nm, an EQE of 16.98 % and an ultra-high radiance of 83.93 W sr^{-1} m^{-2} was fabricated. The device efficiency surpasses that of any previously reported CQD NIR-I and NIR-II LEDs and is the highest reported to date for any solution-processable NIR-II LED. These achievements rely on the effective modification of both the emissive layer, by using CQDs with outstanding emission properties well dispersed in a mobile and defect-less triple cation perovskite matrix, and of the hole-injecting contact, through insertion of an appropriate porphyrin interlayer. With this approach a high PLQE of 84% for the hybrid CQD-in-perovskite film and a charge balance close to unity for the hybrid LED were achieved, resulting in the enhanced device performance. The synthesis of CQDs and fabrication of CQD-in-perovskite films and LEDs are presented in Figure 1.

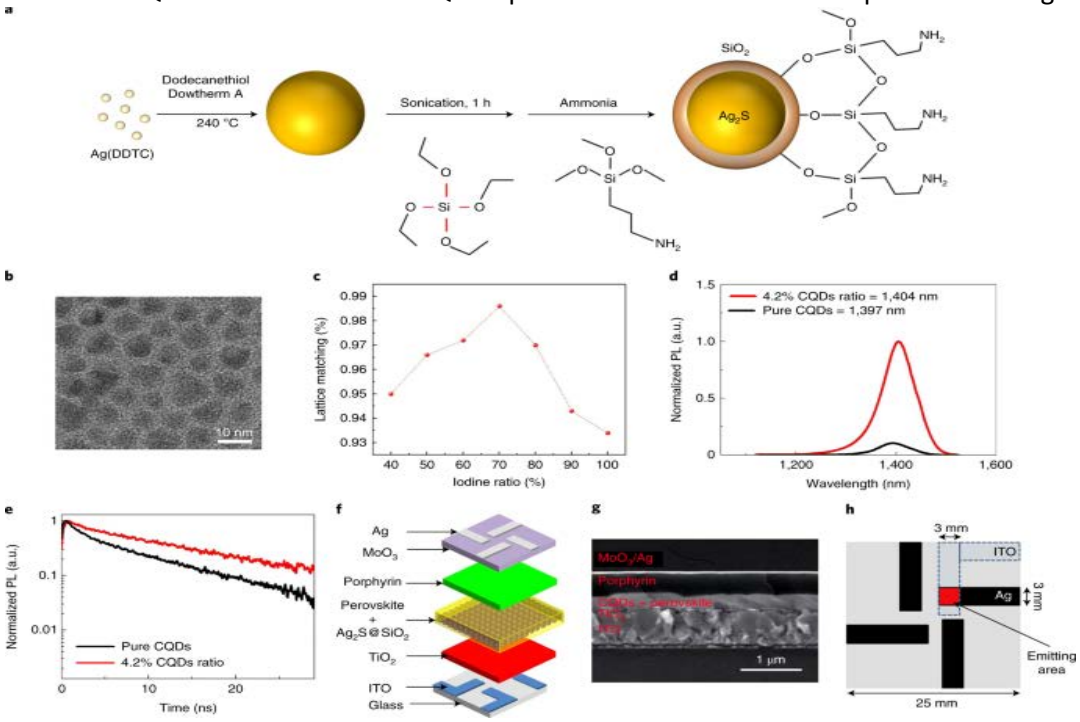


Figure 1. Syntesis of CQDs and fabrication of CQD-based LEDs.

(B) A carbon-doped tantalum dioxyfluoride as a superior electron transport material for high performance organic optoelectronics

The design and development of novel materials with superior charge transport capabilities plays an essential role for advancing the performance of electronic devices. Ternary and doped oxides can be potentially explored because of their tailored electronic energy levels, exceptional physical properties, high electrical conductivity, excellent robustness and enhanced chemical stability. In this work, a route for improving metal oxide characteristics is proposed by preparing a novel ternary oxide, namely, carbon-doped tantalum dioxyfluoride (TaO_2FC_x) through a straightforward synthetic route and exploring its effectiveness as an electron transport material in optoelectronic devices based on organic semiconductors. Among other devices, we fabricated fluorescent green organic light emitting diodes with current efficiencies of 16.53 cd/A (Figure 3) and single-junction non-fullerene organic solar cells reaching power conversion efficiencies of 14.14% when using the novel oxide as electron transport material (Figure 3). Our devices also exhibited the additional advantage of high operational and temporal stability. Non-fullerene OSCs based on the novel compound showed unprecedented stability when exposed to UV light in air due to the non-defective nature of TaO_2FC_x. We employed a tank of experiments combined with theoretical calculations to unravel the performance merits of this novel compound. This study reveals that properly engineered ternary oxides, in particular, TaO_2FC_x or analogous materials can enable efficient electron transport in organic optoelectronics and are

proposed as an attractive route for the broader field of optoelectronic devices including metal-organic perovskite, colloidal quantum dot and silicon optoelectronics.

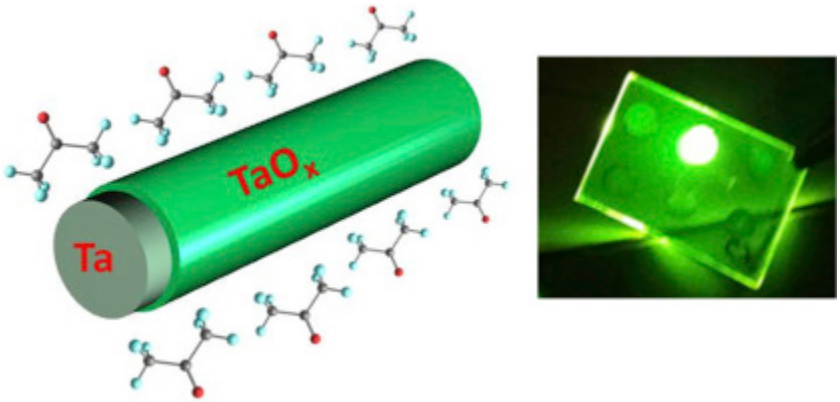


Figure 2. *Image of the fabricated OLED based on the TaO_2FC_x.*

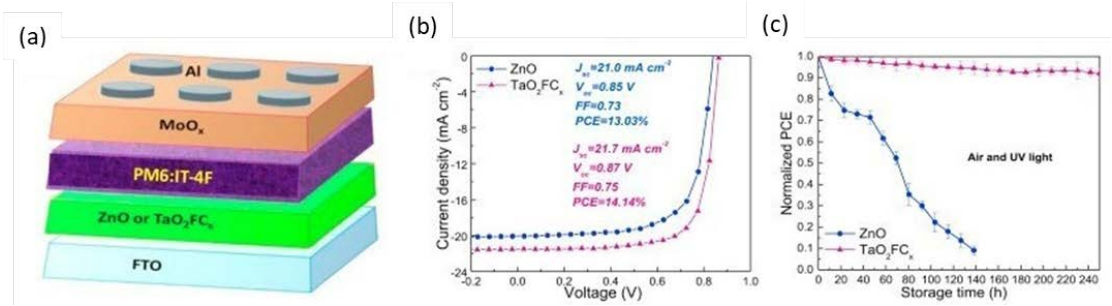


Figure 3*. (a) The inverted OSC architecture based on TaO_2FC_x ETL, (b) J-V under 1.5 A.M. illumination of the devices shown in (a) and (c) the variation of PCE of unencapsulated inverted devices versus time in air under UV illumination.*

(C) Bottom-Up Development of Nanoimprinted PLLA Composite Films with Enhanced Antibacterial Properties for Smart Packaging Applications

Successful production of nanocomposite PLLA films, which exhibited improved mechanical and thermal properties compared to the pristine material, as well as notable antibacterial activity have been developed setting a new groundwork for the potential development of bio-based smart packaging materials.

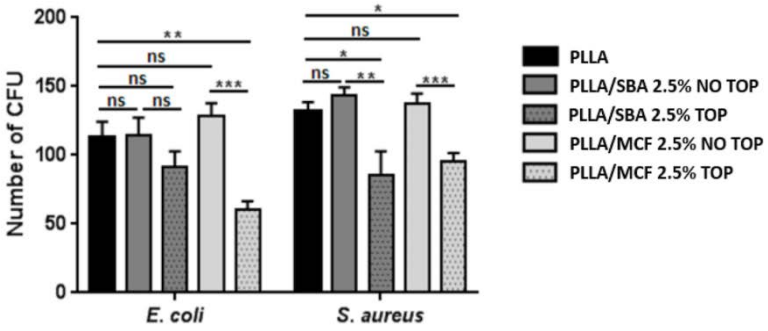


*Fig. 4. Number of CFU formed on the surface of the films prepared in this work (ns; non susceptible, *; low CFU number, **; high CFU number, ***; very high CFU number).*

(D) Process development for the realisation of nano scale patterns on silica aerogel material dried with high temperature methanol supercritical drying.

Rainbow holographic surfaces were fabricated by an alternative nanomanufacturing technique namely nanoimprint lithography (NIL). NIL with its apparent simplicity is a high throughput low cost and inexpensive replication technology engaged and demonstrated in multidisciplinary applications. For the generation of holographic coloring of the aerogel material we used a thin (2 μm) hybrid resist layer which was gravure coated on a 36μm PET foil. Ultraviolet light nanoimprint lithography was utilized to replicate the negative relief of 200 nm – 600 nm nano scale grating structures within the hybrid resist layer.

Funding

1. IKY, Post-Doctoral Researchers (MIS 5033021)): Anastasia Soultati, "Novel organic and perovskite solar cells of high efficiency using porphyrins as transport layers and/or molecular liknkers", Total Budget : 26,400 Euros, 2020 Budget : 11,000.
2. IKY, Post-Doctoral Researchers (MIS 5033021)): Marinos Tountas, "Colloidal quantum dot-in-perovskie light emitting diodes with high efficiency in the second near-infrared window", Total Budget : 26,400 Euros, 2020 Budget : 11,000
3. Stavros Niarchos Foundation, Industrial Adjunct Researcher in collaboration with the abrasive coatings company "Smirdex" : Dimitra Niakoula, "Adhesive polymeric materials and non-destructive characterization methods for abrasive coatings", Total Budget : ~ 112. 000. Budget for 2020 : ~ 28 000.
4. Greek Russian Project on Quantum Technologies, 2018-2020, NCSR D Funding 90,000, in collaboration with Dr. P. Dimitrakis, Dr. D. Davazoglou.
5. GSRT, Heliokeramos, Industrial Materials Project for OPV incorporation in Buildings (OPV Tiles), 2020- 2023, NCSRD Funding 200, 000 Euros, Cooperation with Dr. V. Kilikoglou and Dr. I Karatasios
6. GSRT, NanoMet, Industrial Materials Project on Nanofabrication and Nanometrology, 2020- 2023, NCSRD Funding ~90, 000 Euros, Cooperation with Dr. V. Constantoudis and Dr. N. Papanikolaou
7. ELIDEK, iPHOTO-PACK - Basic Research on Organic Photonics for Sensing and Packaging, 2019-2023, NCSR D funding ~80,000 Euros, Collaboration with Agricultural University of Athens, Principal Investigator, Prof. Panagiotis N. Skandamis
8. GSRT, OLED-LUMIN-PACK, Ereynw Kainotomw - Industrial collaboration project for Food Packaging, 2020-2023 NCSR D Funding ~200,000

OUTPUT

Publications in International Journals

1. Nika, A. , Oikonomou, P., Manouras, T., Argitis, P., Vamvakaki, M., Sanopoulou, M., Raptis, I., Chatzichristidi, M., Reversible chemocapacitor system based on PDMAEMA polymers for fast sensing of VOCs mixtures, *Microelectronic Engineering*, **227**, 111304 (2020). https://doi.org/10.1016/j.mee.2020.111304
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5. Balis, N., Zaky, A.A., Athanasekou, C., Silva, A.M.T., Sakellis, E., Vasilopoulou, M., Stergiopoulos, T., Kontos, A.G., Falaras, P., Investigating the role of reduced graphene oxide as a universal additive in planar perovskite solar cells, *Journal of Photochemistry and Photobiology A*, **386**, 112141 (2020). https://doi.org/10.1016/j.jphotochem.2019.112141
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9. Vasilopoulou, M., Kuganathan, N., Bao, X., Verykios, A., Polydorou, E., Armadorou, K.-K., Soultati, A., Papadimitropoulos, G., Haider, M.I., Fakharuddin, A., Palilis, L.C., Kennou, S., Chroneos, A., Argitis, P., Davazoglou, D., A carbon-doped tantalum dioxyfluoride as a superior electron transport material for high performance organic optoelectronics, *Nano Energy*, **70**, 104508 (2020). https://doi.org/10.1016/j.nanoen.2020.104508
10. Soultati, A., Verykios, A., Armadorou, K.-K., Tountas, M., Vidali, V.P., Ladomenou, L., Palilis, L., Davazoglou, D., Coutsolelos, A.G., Argitis, P., Vasilopoulou, M., Interfacial engineering for organic and perovskite solar cells using molecular materials, *Journal of Physics D: Applied Physics,* **53** (26), 263001 (2020). https://doi.org/10.1088/1361-6463/ab7f73
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International Conferences Presentations

1. Soultati, A., Papadimitropoulos, G., Dimogerontaki, N., Kaminaris, S., Davazoglou, D., Argitis, P., Vasilopoulou, M., Highly-efficient and stable organic photovoltaics using a zinc molybdate-mixed ZnO electron transport layer, ISFOE 2020, 6 – 9 July 2020, Thessaloniki, Greece,

Teaching and Training Activities

1. M. Vasilopoulou, "Spectroscopy", Winter Semester Course and M. Vasilopoulou, P. Argitis, "Organic Electronics", Spring Semester Course, Graduate Program "Applied Optoelectronics", organized by Department of Materials Science, University of Patras.
2. P. 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.

Doctoral Dissertations completed in 2020

1. Anastasia Nika
Polymeric Materials for Lithography via Light Guided Processes (top-down) and Self-Assembling (bottom-up)
Research Supervisor at NCSRD: Panagiotis Argitis
Department of Chemistry, National and Kapodistrian Univesity of Athens, June 2020, Advisory Committee : Prof. M. Chatzichristidi, Prof. M. Vamvakaki, Dr. P. Argitis

2. Ermioni Polydorou
Study of molecular oxides and transition metal oxides as interfacial layers for highly efficient organic solar cells
Research Supervisor at NCSRD: Maria Vasilopoulou
Department of Physics, University of Patras December 2020, Advisory Committee: Dr. Maria Vasilopoulou, Prof. Leonidas Palilis, Prof. Michalis Fakis.

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

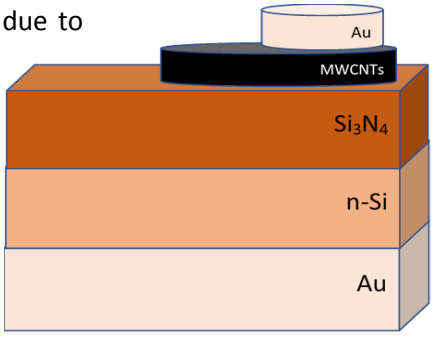
Objectives

- 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.

Activities and Main Results

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

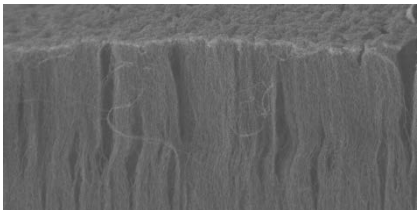
Carbon nanotubes (CNTs) have attracted great interest of applications due to unique mechanical, electronic and optoelectronic properties. The advantages of the multiple wall carbon nanotubes for optoelectronic devices like photodetectors and photodiodes are the large effective photo-collector surface 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).



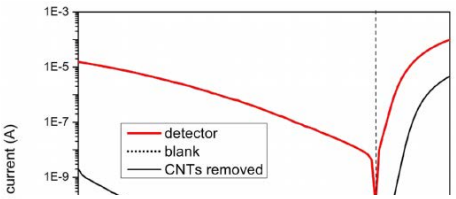
Structure of the basic photodetector

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.

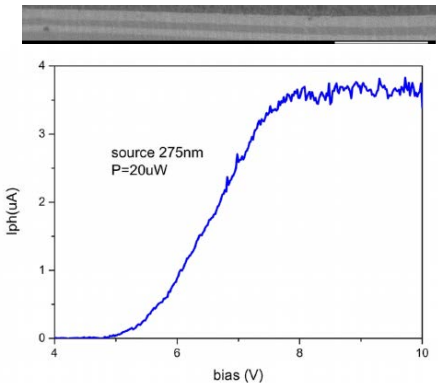
The overall results suggest that well-ordered MWCNTs present satisfactory performance (EQE 90% @ 275nm@ 7V) for the devices, in the visual and UV part of the spectrum. The responsivity values are at the same level as those of the best performing Schottky or MSM type GaN, UV detectors. The optical responsivity 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



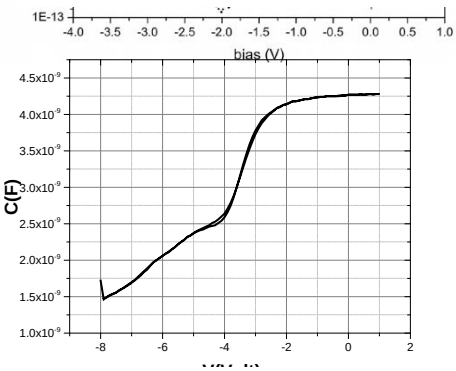
SEM picture of the MWCNTs produced



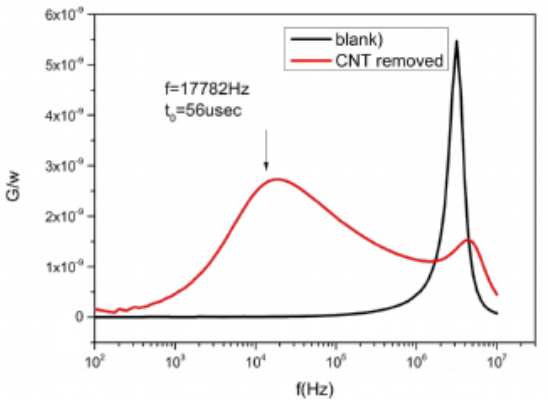
The current /voltage characteristic of the detector compared to reference samples



UV response of the device vs bias voltage



Capacitance vs voltage measurements -Influence of the Fe traps at the inversion region



The CNT formation procedure requires the presence of Fe catalyst. This is blocked by the Si3N4 layer resulting in donor/acceptor traps with a characteristic time of 56sec

OUTPUT

Publications

- Kyriakis A., Glezos N., Velessiotis D., Pilatos G., Speliotis Th., Stefanou A. A UV photodetector based on ordered free standing MWCNT, Journal of Instrumentation 2020 C0101515 (1)

Acknowledgements

This project has received funding from the Hellenic Foundation for Research and Innovation (HFRI) and the General Secretariat for Research and Technology (GSRT), under grant agreement No 157446/I2/21-9-2018

OPTICAL BIOSENSORS

Project Leader: Konstantinos Misiakos

Permanent Research Staff: Eleni Makarona

Other Staff: Alexandros Salapatas (Research Associate)

PhD Candidates: George Papageorgiou, Christina Sperantza, Spyridon Ntouvalis

Master Students: Georgia Geka, Anthi Dimou, Andreas Baltas, Aikaterini Ninou

Undergraduate Student: Zinovia Samioti

Research Collaborators: Dr Sotirios Kakabakos and Dr Panagiota Petrou (Immunochemistry/Immunosensors Labboratory, 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 bioanalytical lab-on-a-chip devices based on interferometric monolithic optoelectronic transducers (bioactivated optocouplers) for highly sensitive and label free assays suitable for Point of Care applications / 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, which can be used either as immersible probes or by simple drop casting of the liquid sample*

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, the group focused on the optimization of the design (photonic engineering) of the Integrated Photonic Circuit of the chip, the subsequent fabrication of the chips, the optimization of the optomechanical coupling of the chips to a suitable portable reader, the design of the portable reader as well as the software development for both the real-time signal analysis and user interface. The final system (chips and reader) was employed for the detection of SARS-CoV-2 antibodies. 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 2020 because patents were filed within the US and European Patent Offices and the applications were pending for approval.

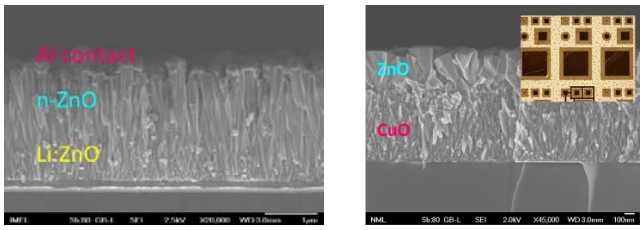
At the end of 2020, the group received additional funding from the RESEARCH – CREATE – INNOVATE framework through the FOODSENS project (code:T2EΔK-01934; duration: 29/10/2020-28/102023). The new project that started right at the end of the year targets at using the immersible photonic probes for the detection of pathogens and adulteration in raw milk. The chips are envisioned to be developed in two formats; 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. The Optical Biosensors group apart from the development of the photonic chips will be engaged in the signal analysis software, the design of the reader and the user interface.

Moreover, building upon previous experience of the group on optical biosensing and in particular surface modification of silicon nitride waveguides three articles were prepared and published in relevant journals in the field of biochemical sensing.

Finally, thanks to the funding from INNOVATION-EL, 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 three 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), and (c) the synthesis and exploitation of Metal Oxide Nanoparticles towards the development of novel polymer nanocomposite resists for e-beam lithography. 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. Two PhD theses (G. Papageorgiou, Physics Department, University of Patras and S. Ntouvalis, Department of Informatics & Telecommunications, University of Ioannina) and one MSc thesis (A. Baltas, School of Applied Mathematics and Physical Sciences, National Technical University of Athens) were in progress during 2020. The two PhD theses study in depth 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. 2). Both thesis exploit chemical routes for the synthesis of the metal oxide nanostructures and their integration on Si substrates.



(a) **(b)**

Fig. 2. *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 and on BSc thesis were completed (A. Dimou and Z. Samioti, respectively, Chemistry Department, National and Kapodistrian University of Athens) pertaining with the study of CuO nanostructure hydrothermal growth methods onto Si substrates and of their compatibility with respect to optical lithography. One more Msc thesis started in 2020 (A. Ninou, Chemistry Department, National and Kapodistrian University of Athens) which in an analogous way to the study of NiO nanostructure hydrothermal growth methods onto Si substrates and of their compatibility with respect to optical lithography. The study of these fabrication methods led to the realization that the created CuO and NiO nanostructures are morphologically and hierarchically complex with no apparent way of appropriately describing their features in a quantifiable and methodological way. As a result, the group in collaboration with Dr V. Constantoudis started exploring a new idea with the intent is 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. The preliminary results were included as part of two conference presentations. 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 ZnO-nanostructure periodic arrays on Si and SiO_2 substrates (Fig. 3). The study was complemented with micro-X-ray fluorescence (μ-XRF) spectroscopy demonstrating the latter's great potential to leverage the development of novel nanofabrication processes (in collaboration with Dr A.G. Karydas, INP, NCSR "Demokritos"). The study was presented in a relevant publication.

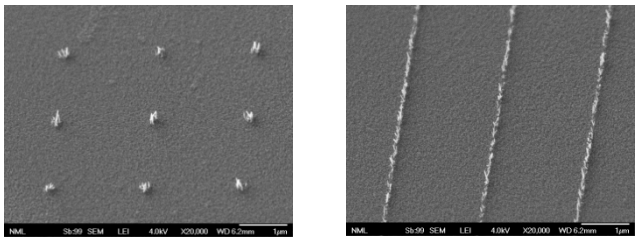


Fig. 3 *SEM images of arrays containing ZnO nanorods produced by the developed combinatorial method of bottom-up ZnO hydrothermal growth and e-beam lithography (a) array of 100nm circles (b) array of 50nm-wide and 200μm-long lines.*

Finally, on the third front a MSc thesis (G. Geka, Chemistry Department, National and Kapodistrian University of Athens) was completed which focused on the synthesis of CuO nanoparticles that were used as nanofillers for the production of PMMA-based polymer nanocomposite resists for e-beam lithography. Several nanofiller loadings, spin coating conditions and two solvents (acetone and methyl ethyl ketone) were explored and assessed with regards to their effect on producing CuO/PMMA nanocomposite resists. The films were patterned with EBL and contrast curve data and resolution analysis were used to evaluate their performance as a resist material. μ-XRF was employed as an alternative non-destructive technique in order to investigate the uniform dispersion of the nanofillers within the polymer matrix and to assist in the selection of the optimum preparation conditions. This study revealed that it is possible to produce low-cost CuO/PMMA resist material without resorting to complicated preparation techniques

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:T2ΕΔΚ-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)

OUTPUT

Publications in International Journals

1. Stavra, E., Petrou, P.S., Koukouvinos, G, Economou, A., Goustouridis, D., Misiakos, K., Raptis, I., Kakabakos, S.E., Fast, sensitive and selective determination of herbicide glyphosate in water samples with a White Light Reflectance Spectroscopy Immunosensor, *Talanta,* **214**, 120854 (2020), https://doi.org/10.1016/j.talanta.2020.120854
2. Korompili, G., Misiakos, K., Chronis, N., An optoelectronic chip with integrated epi-illumination source and collection optics for imaging applications, *Sensors and Actuators A: Physical,* **312**, 112082 (2020), https://doi.org/10.1016/j.apsusc.2019.145002
3. Gajos, K., Budkowski, A., Petrou, P., Awsiuk, K., Misiakos, K., Raptis, I., Kakabakos, S., Spatially selective biomolecules immobilization on silicon nitride waveguides through contact printing onto plasma treated photolithographic micropattern: Step-by-step analysis with TOF-SIMS chemical imaging, *Applied Surface Science*, **506**, 145002 (2020), https://doi.org/10.1016/j.sna.2020.112082
4. Papageorgiou, G.P, Karydas, A.G., Papageorgiou, G., Kantarelou, V., Makarona, E., Controlled synthesis of periodic arrays of ZnO nanostructures combining e-beam lithography and solution-based processes leveraged by micro X-ray fluorescence spectroscopy, *Micro and Nano Engineering,***8**, 100063 (2020). DOI: https://doi.org/10.1016/j.mne.2020.100063

Books/Chapters in Books

1. Makarona E., Kavoura A., Immunity Passports and Entrepreneurial Opportunities in the COVID-19 Era, *Strategic Innovative Marketing and Tourism in the COVID-19 Era,*Edited by Kavoura A., Havlovic S. J, Totskaya N., Springer Proceedings in Business and Economics, Ch. 21, pp. 187-198 (2020). DOI: https://doi.org/10.1007/978-3-030-66154-0_21

International Conferences Presentations (invited, oral, poster)

1. Makarona E., Immunity Passports in the COVID-19 Era: Facts, Fiction and Perspectives, *International Conference on Strategic Innovative Marketing and Tourism 2020, ICSIMAT 2020*, September 26-28, 2020 (on-line) – oral

2. Constantoudis V., Arapis A., Chatzigeorgiou M, Makarona E., Milionis A., Lam C. W. E., Poulikakos, D., Gogolides E., The challenge of nanocomplexity, *NANOTEXNOLOGY 2020: International Conferences & Exhibition on Nanotechnologies - Organic Electronics & Nanomedicine*, July 4-11, 2020, Thessaloniki, Greece - oral

Master Dissertations completed in 2020

Anthi Dimou
Development of hydrothermal growth methods fro Copper Oxide nanoarchitectures compatible with optical photolithography techniques and microelectronic fabrication processes
Eleni Makarona
National and Kapodistrian University of Athens

Georgia Geka
Study of CuO/PMMA polymer nanocomposites as novel resists for electron beam lithography
Eleni Makarona
National and Kapodistrian University of Athens

Undergraduate Theses and Internships completed in 2020

Zinovia Samioti (BSc Thesis)
Synthesis of Copper Oxide Nanostructures with Green Chemistry Methods

Eleni Makarona
National and Kapodistrian University of Athens

Other
Eleni Makarona: Managing Guest Editor of the Virtual Special Issue “Nanofabrication” of the Micro and Nano Engineering journal (Elsevier); Editorial Board Member, *Sensors* (MDPI);.

MICROFLUIDICS, LAB AND ORGAN-ON-CHIP

Project Leader: A. Tserepi

Permanent Research Staff: E. Gogolides, S. Chatzandroulis

Research associate: G. Kokkoris

Post Docs: K. Tsougeni, K. Ellinas, M. Georgoutsou-Spyridonos, G. Boulousis

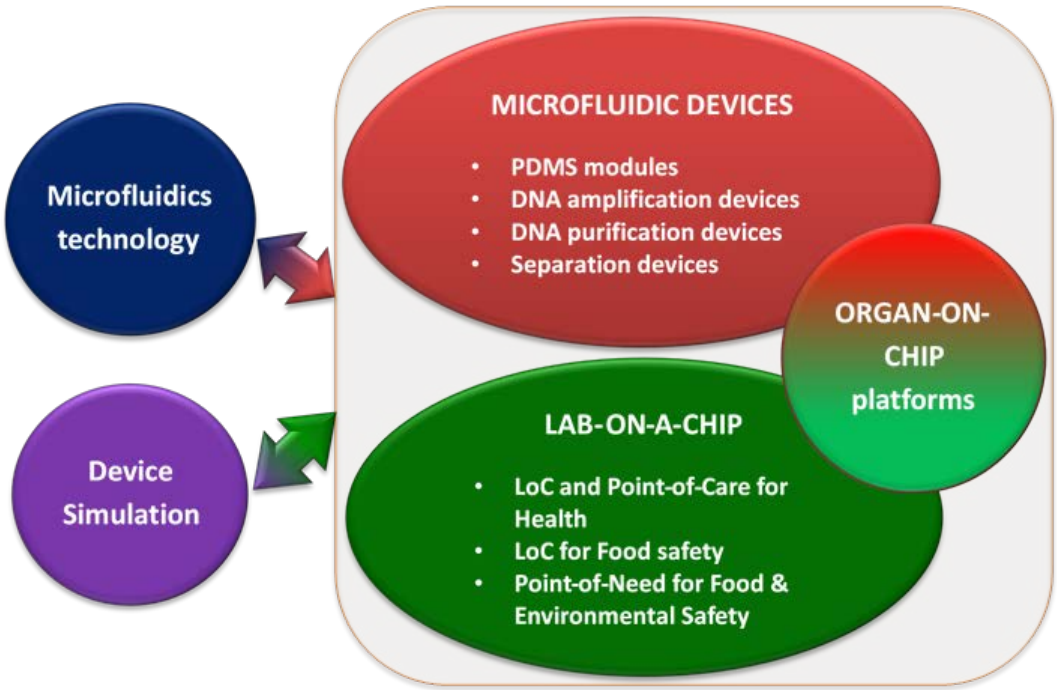
PhD Candidates: I. Kefala, V. Papadopoulos, D. Kefallinou, S. Ntouskas, P. Skaltsounis

Master Students: P. Skaltsounis, K. Koutsiara, M. Savranakis, I. Ntovolou, Y. Xesfyngi

Research Collaborators (emeritus or visiting): D. Tsoukalas, D.S. Mathioulakis (NTUA), S. Kakabakos, P. Petrou, D. Mastellos (INRASTES, NCSR-D), B. Dupuy (Inst. Pasteur), E. Gizeli, G. Papadakis (FORTH, UOC), G. Jobst (Jobst Tech), G.D. Kaprou (Univ. of León, Spain), D. Boumpas, M. Grigoriou (BRFAA), C.M. Loukas (Fast Track Diagnostics S.à.r.l., Luxembourg), Z. Ekaterinidi (Software Competitive International, S.A.), E. Mastellou (Bioanalysis Kitili, S.A.), A.S. Kastania

- **Objectives**

In 2019, it was decided to separate the two programs of Plasma Nanotechnology and Lab on-a-Chip, in order to boost the visibility of the Lab on a Chip and related activities. We continue as usual the strong collaboration between the two programs but we report the activities separately. Our project 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. Our project objectives can therefore be summarized as follows:



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

- 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**).

- **Activities and Main Results**

Microfluidics Technology

T1. Fabrication of a 3D microfluidic device with a porous membrane for cell culturing

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

Microfluidic technology has revealed *organs-on-chips* as the epitome of biomimetic systems, outweighing conventional static cell culture methods. These novel 3D microfluidic cell culture devices allow for faithful mimicry of the *in vivo* cellular microenvironment, thereby constituting a successful *in vitro* replica of a vital human organ unit. Our aim being to develop a purely *in vitro* and scaffold-free *bone marrow-on-a-chip*, as a prognostic and therapeutic platform of Systemic Lupus Erythematosus (SLE), 3D microfluidic cell culture chambers have been fabricated and injected with *mesenchymal stem cells* (MSCs), resulting in the successful growth of bone marrow tissue for 8 days.

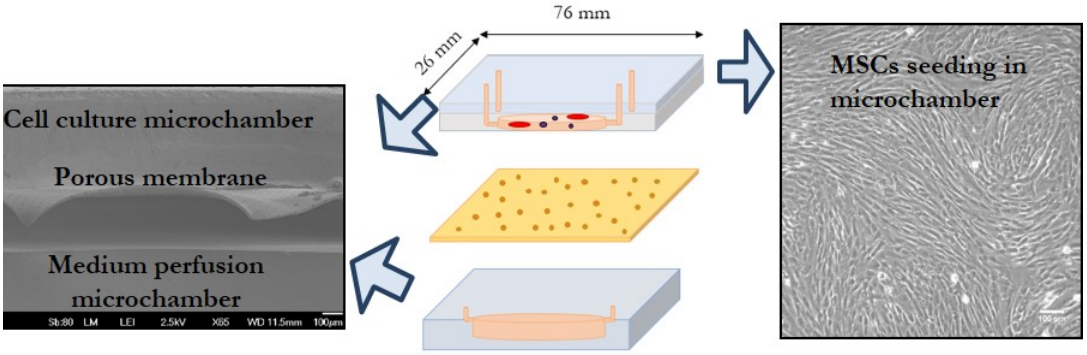


Fig. 2. *Exploded 3D illustration of the bone marrow-on-a-chip (center), with SEM image of a cross section of it (left), including the cell culture and medium perfusion microchambers conveying via the intermediate porous membrane. MSCs static culture inside 3D cell culture microchambers in day 5 building up bone marrow stromal tissue (right).*

Modeling and Simulation of Microfluidic devices

M1. Modeling heat losses in Microfluidic devices

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

Most of the functions integrated in lab-on-chip systems require the heating and cooling of samples in order to activate specific reactions. In such cases, the speed of operation and the power and energy consumption are influenced by the heat losses to the ambient. We investigate 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. 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.

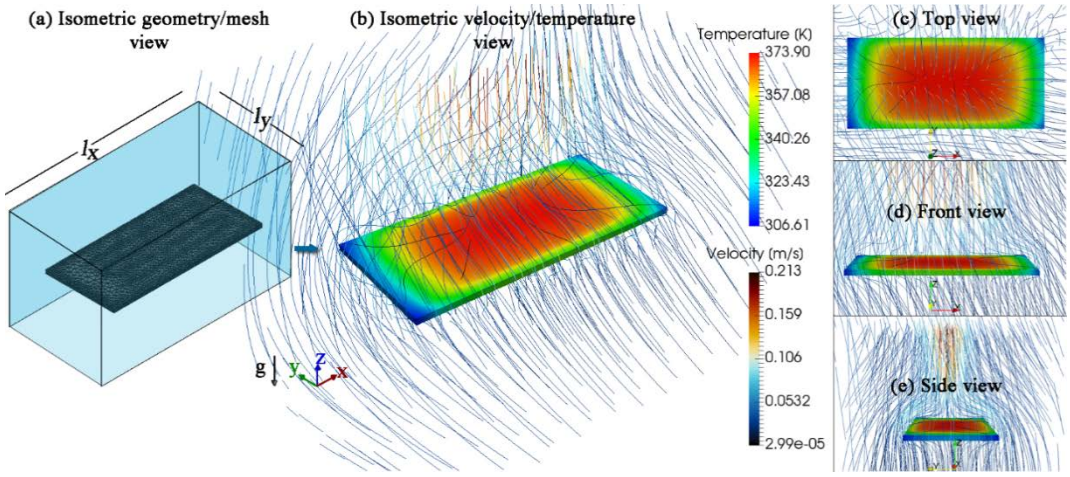


Fig. 3. *Snapshots of the temperature and the streamlines of the velocity in the surrounding medium (air) from isometric, (c) top, (d) front and (e) side view, extracted when the temperature at the boundaries of the μPCR device is 373.15 K.*

M2. Design of a circular flow-through microfluidic device

(S. 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, the flow velocity and the thermal distribution during cycles (see figure 3). 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.

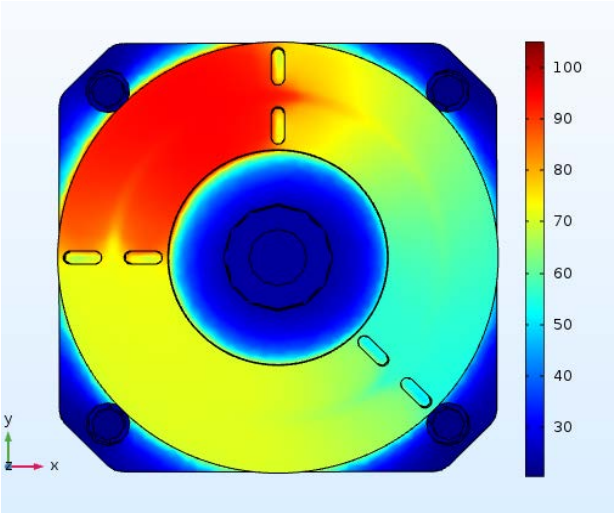


Fig. 4. *Temperature distribution on a slice in the middle of the channel height, indicating a thermal cross-talk between thermal ones due to the fluid flow*

<u>Applications: Lab on a Chip for Agrofood and Life Sciences</u>

A1. Lab-on-a-chip for food pathogen analysis

(K. Tsougeni, G.D. Kaprou, C.M. Loukas, G. Kokkoris, S. Chatzandroulis, A. Tserepi, E. Gogolides, and external collaborators)

We developed an integrated, compact, lab on a chip (LoC) platform and protocol for rapid pathogen analysis in food samples. The proposed LoC was based on an oxygen plasma nanotextured polymeric chip combining in one microfluidic chamber bacteria immunoaffinity capturing on the chip surface, chemical lysis and DNA isothermal amplification, followed by label-free detection with a Surface Acoustic Wave (SAW) biosensor. The proposed operation protocol included: 1) a short (3h) off-chip pre-culturing step, starting from 1-5 CFUs in only 25ml of spiked fresh or pasteurized milk, followed by a brief centrifugation step for concentration of the 25ml down to 100μl, and, 2) injection of the preconcentrated sample on chip for automated bacterial capture, lysis, DNA amplification and acoustic detection. The sample-to-answer analysis time was less than 4.5h, which is at least 5-times faster compared to conventional methods. Label-free detection of four different bacteria *Salmonella*, *B. Cereus*, *Listeria* and *E. coli* in milk was demonstrated with minimal off chip handling and record fast analysis time.

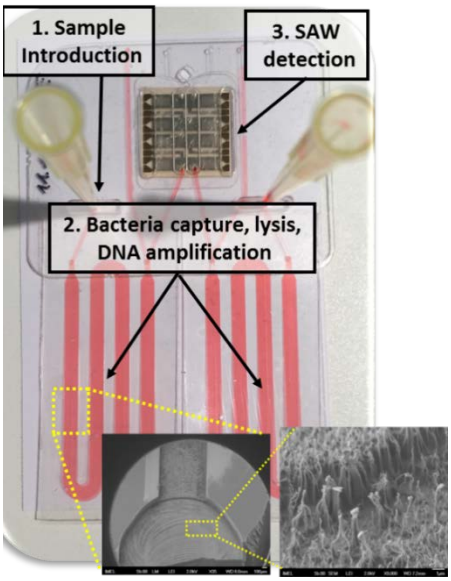


Fig. 5. Compact, disposable, plastic credit card sized chip, hosting 2 chambers allowing for bacteria capture, lysis, DNA amplification and detection, for 2 samples analyzed sequentially. Sample loading is achieved by aspiration with downstream-placed peristaltic micropumps out of regular disposable pipette tips preventing cross-sample contamination. The polymeric microfluidic chip is O_2 plasma nanotextured (inset). The selected chip comprises two meandering microchannels, each being 2.5 mm wide, ~150 μm deep. The total volume of each microchannel is ~ 60 μl.

A2. DNA amplification microdevices

(G.D. Kaprou, V. Papadopoulos, I. Kefala, C-M. Loukas, G. Kokkoris, A. Tserepi, and collaborators)

In recent years, printed circuit board (PCB)-based microfluidics have been explored as a means to achieve standardization, seamless integration, and large-scale manufacturing of microfluidics, thus paving the way for widespread commercialization of developed prototypes. In this work, static micro polymerase chain reaction (microPCR) devices comprising resistive microheaters integrated on PCBs are introduced as miniaturized thermocyclers for efficient DNA amplification. Their performance is compared to that of conventional thermocyclers, in terms of amplification efficiency, power consumption and duration. Exhibiting similar efficiency to conventional thermocyclers, PCB-based miniaturized thermocycling achieves faster DNA amplification, with significantly smaller power consumption. Simulations guide the design of such devices and propose means for further improvement of their performance.

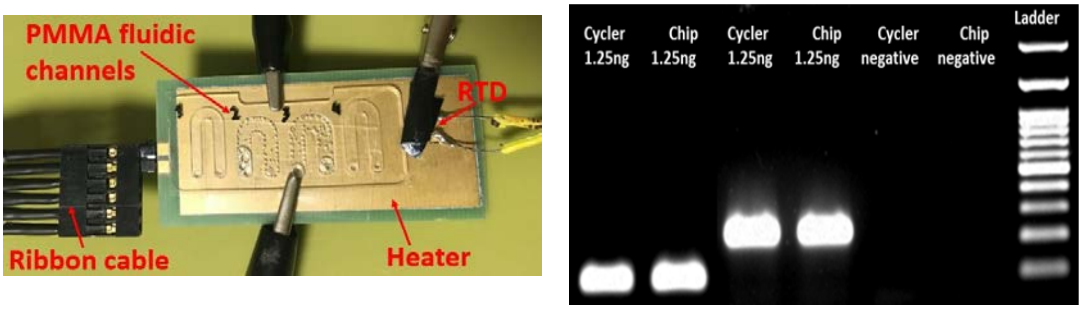


Fig. 6. *(a) PMMA fluidic chip with 4 u-shaped chambers on a PCB-based microheater, connected for thermocycling. (b) Gel electrophoresis image of PCR-based amplification for purified genomic Salmonella DNA using 1.25 ng of DNA/25 μl PCR reaction on the static chamber microfluidic chip and comparison with PCR on conventional thermocycler*

A3. DNA purification in microfluidics

(A.S. Kastania, P.S. Petrou, C.-M. Loukas, E. Gogolides)

We developed a disposable polymeric microfluidic device capable of reversibly binding and purifying *Salmonella* DNA through solid phase extraction (SPE). The microfluidic channels are first oxygen plasma treated and simultaneously micro-nanotextured, and then functionalized with amine groups via modification with L-histidine or poly-L-histidine. L-Histidine and poly-L-histidine bind on the plasma treated chip surface, and are not detached when rinsing with DNA purification protocol buffers. A pH-dependent protocol is applied on-chip to purify *Salmonella* DNA. Using the chip modified with poly-L-histidine, high recovery efficiency of at least 550 ng of isolated *Salmonella* DNA as well as DNA purification from *Salmonella* cell lysates corresponding to less than 5000 cells or 0.026 ng of *Salmonella* DNA was achieved. The protocol developed does not require ethanol or chaotropic solutions typically used in DNA purification, which are known inhibitors for downstream operations such as polymerase chain reactions (PCR) and which can also attack some polymeric microfluidic materials.

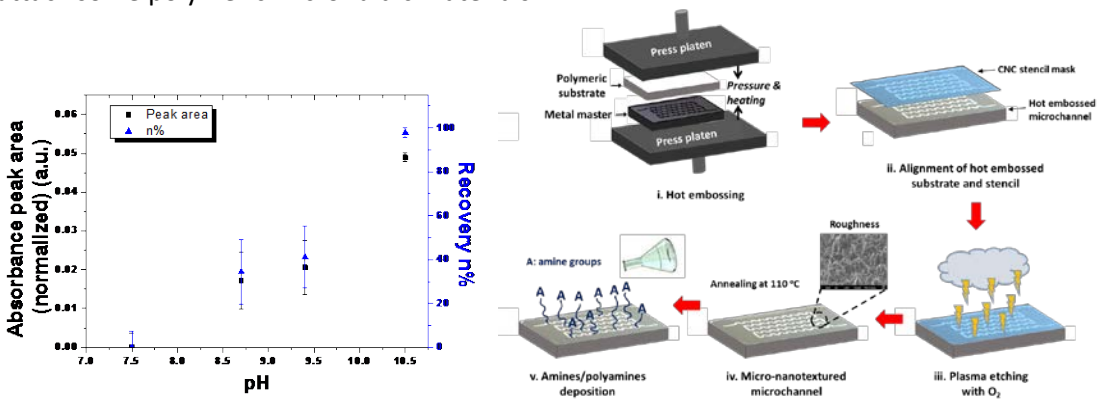


Fig. 7. (Left) Absorbance of eluted purified DNA peak as a function of pH and extent of recovery of purified from unpurified DNA. (Right) Fabrication process of the microfluidic chip for DNA purification.

A4. Enrichment and separation of cancer cells on plasma micro-nanotextured microfluidics

(A. Kanioura, V. Constantoudis, P. Petrou, A. Tserepi, E. Gogolides, S. Kakabakos and collaborators)

We study cell-surface interactions, using oxygen plasma micro-nanostructured commercial PMMA plates on the adhesion, morphology and proliferation of normal skin fibroblasts and A431 skin cancer cells. It was found that the adhesion and proliferation of normal skin fibroblasts was significantly inhibited, while their morphology and focal points formation were seriously impaired on plasma treated surfaces with peak-to-valley height≥5μm, as compared to the untreated ones. On the other hand, the adhesion of cancer cells was 2.5–3 times higher in all rough surfaces as compared to the untreated ones, whereas their proliferation rate was considerably improved on the rough surfaces prepared through plasma treatment for 5 and 10 min. Moreover, the enhanced adhesion of cancer cells with respect to normal ones onto plasma micro/nanostructured surfaces was investigated under flow conditions using micro-channels with micro-nanostructured bottom. In this case, an enrichment ratio of cancer to normal cells of 1.5 was determined compared to 0.5 obtained for the untreated PMMA after 1-h culture with the surface.

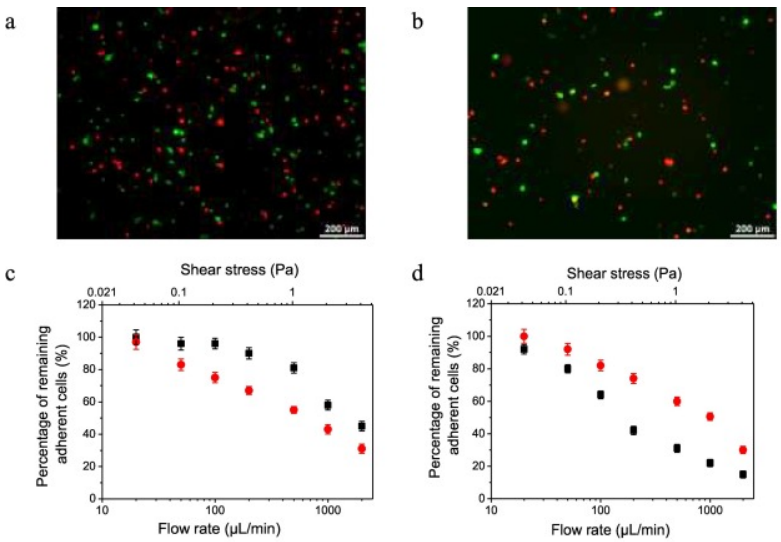
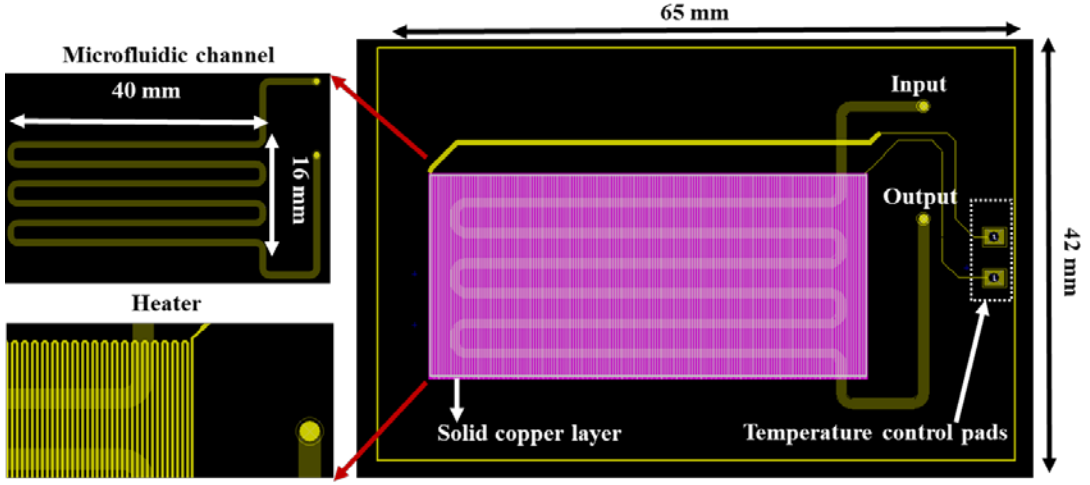


Fig. 8. (a, b) Characteristic fluorescence microscope images of adherent A431 cancer cells (red) and skin fibroblasts (green) on oxygen plasma treated PMMA surfaces (a) prior to and (b) after washing with PBS at a flow rate up to 500 μL/min for 1 min. The scale bar is 200 μm in all cases. (c, d) Percentage of remaining adherent A431 cancer cells (black squares) and skin fibroblasts (red circles) on (c) oxygen plasma micro-nanostructured or (d) untreated PMMA surfaces after each washing step. Each point is the mean of 3 measurements ± SD.

A5. Lab-on-a-chip platform and protocol for bacteria identification in urine

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

We designed and realized a Lab-on-a-Chip (LoC) device integrating bacterial DNA amplification and detection, seamlessly fabricated on a printed circuit board (PCB) substrate for the detection of *E-coli*.



9. *Design of the **RPA**-on-PCB chip for bacteria DNA amplification*

The proposed LoPCB integrates recombinase polymerase isothermal DNA amplification (RPA) method with a reduced graphene oxide (rGO) biosensor in a single PCB substrate. The use of graphene oxide biosensors allows for sensitive electrical detection, alleviating the need for cumbersome optical setups, thus promoting compact design. The novelty of the proposed concept lies in the seamless fabrication of the proposed chip, which is completely compatible with the established PCB industry allowing for increased manufacturability at a low cost, thus tackling the commercialization bottle-neck of bioMEMS. During 2020, the biological assays

for bacteria culturing and RPA-based DNA amplification were developed and finalized, while the RPA-on-PCB chip was designed (see Fig. 9).

A6. Rapid and Accurate Detection of Bacteria in Water using microfluidics technology
(K. Tsougeni, K. Ellinas, A. Tserepi, E. Gogolides, and external collaborators)

Many water-borne infections are commonly caused by bacteria. 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 and in collaboration with Nanoplasmas PC, is developing a lab-on-a-chip based on colorimetric detection (visual inspection) for ultra-rapid and easy L. *pneumophila* detection at the point of need.

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 2020 €27.650,00 (postdoctoral fellow: K. Tsougeni)
2. "DIAMOND", T1EΔK-03565, Contract No. MIS 5031222, 18/07/2018 – 17/01/2022, total budget €393.292,60, budget for 2020 €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)

OUTPUT

Publications in International Journals

1. Kefallinou, D., Grigoriou, M., Boumpas, D.T., Gogolides, E., Tserepi, A., Fabrication of a 3D microfluidic cell culture device for bone marrow-on-a-chip, *Micro & Nano Engineering* **9**, 100075 (2020). DOI: 10.1016/j.mne.2020.100075
2. Tsougeni, K., Kaprou, G., Loukas, C.M., Papadakis, G., Hamiot, A., Eck, M., Rabus, D., Kokkoris, G., Chatzandroulis, S., Papadopoulos, V., Dupuy, B., Jobst, G., Gizeli, E., Tserepi, A., Gogolides, E., Lab-on-Chip platform and protocol for rapid foodborne pathogen detection comprising on-chip cell capture, lysis, DNA amplification and surface-acoustic-wave detection, *Sensors and Actuators, B: Chemical* **320**, 128345 (2020). DOI: 10.1016/j.snb.2020.128345
3. Kastania, A.S., Petrou, P.S., Loukas, C.-M., Gogolides, E., Poly-L-histidine coated microfluidic devices for bacterial DNA purification without chaotropic solutions, *Biomedical Microdevices* **22** (3) 44 (2020). DOI: 10.1007/s10544-020-00497-1
4. Kaprou, G.D., Papadopoulos, V., Loukas, C.-M., Kokkoris, G., Tserepi, A., Towards PCB-Based Miniaturized Thermocyclers for DNA Amplification, *Micromachines* **11** (3), 258 (2020). DOI: 10.3390/mi11030258

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

1. Filippidou M.K., Georgoutsou M., Douskas S., Nikolakakis A., Petrou P., Mastellos D., Chatzandroulis S., Tserepi A., A point-of-care platform for rapid detection of urinary tract infections (oral), *1st Nanotechnology Webinar "Nanotechnology & Microdevices for the diagnosis and treatment of infectious diseases with emphasis on COVID-19: Novel products and high TRL prototypes in Greece"*, Oct. 2, 2020 (virtual event

Teaching and Training Activities

1. “Microfluidic systems”, (G. Kokkoris, I. Anagnostopoulos, A. Tserepi), Postgraduate Program on Microsystems and Nanodevices of the National Technical University of Athens

Master Dissertations completed in 2020

Panagiotis Skaltsounis
Closed-loop microfluidic device for DNA amplification
Research Supervisor at NCSR: G. Kokkoris, A. Tserepi
Interdepartmental Programme "Microsystems and Nanodevices", National Technical University of Athens

Undergraduate Theses and Internships completed in 2020

Alkmini Tsami
Microfluidic devices for DNA amplification and application in bacteria identification
Research Supervisor at NCSR: A. Tserepi
Internship in collaboration with NTUA

Patents

“Methods for ultrasonic fabrication and sealing of microfluidic or other microdevices” Evangelos Gogolides, Kosmas Ellinas, Georgios Boulousis, European Patent Application No. 20 211 850.1, 04 December 2020.

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

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Technical Staff: A. Zeniou

Administrative Staff: M. Kalpouzou

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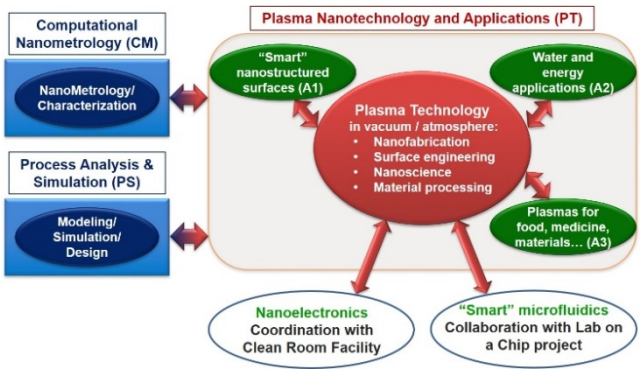
A) Historical evolution of the group

In 2019 the Group Leaders Evangelos Gogolides and Angeliki Tserepi have decided to separate the two programs of Plasma Nanotechnology and Lab on a Chip in order to make reporting manageable and to boost the visibility of the Lab on a Chip activity. We continue as usual the strong collaboration between the two programs but we report the activities separately.

B) 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:



1 *Schematic of project 5.11 Plasma Nanotechnology and applications, computational nanometrology, process simulation*

- Advance **plasma nanotechnology** and nanofabrication (section **PT**).
- Develop computational **nanometrology** for nanostructure characterization (section **CM**).
- Understand and design improved processes using **modeling and simulation** (section **PS)**.
- Exploit our plasma technology toolbox for **enabling a variety of applications.** Applications target: (1) Surface Engineering (**"smart surfaces"** section **A1**), (2) **Water Harvesting** (section **A2**), (3) **Plasmas for food, Agriculture medicine etc.**

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

Activities and Main Results

Plasma Nanotechnology (PT)

PT1. Plasma Nanoinhibit process. Controlling surface morphology at will.

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

Hierarchical micro-nanostructured surfaces are key components for "smart" multifunctional materials, being used for controlling the wetting, adhesion, tactile, friction, optical, antifogging, antibacterial, and many more surface properties. We proposed a key idea of the new "nanoinhibit" technology, as well as a new plasma reactor with the ability to control the simultaneous flux of etchants and inhibitors on the surfaces being etched. Inhibitors are sputtered electrode atoms. Therefore, the idea of controlling the inhibitor flux boils down to our ability to control the electrode surface being sputtered. To achieve this, we have constructed a variable electrode shield, i.e. a variable grounded surface, placed above the electrode. Ions shielded from the electrode shield do not sputter the electrode, thus reducing the inhibitor flux. These ions also do not sputter the shield material either, since the shield is grounded and not negatively biased as the electrode. The new "nanoinhibit" plasma reactor design is shown in Fig.PT1.

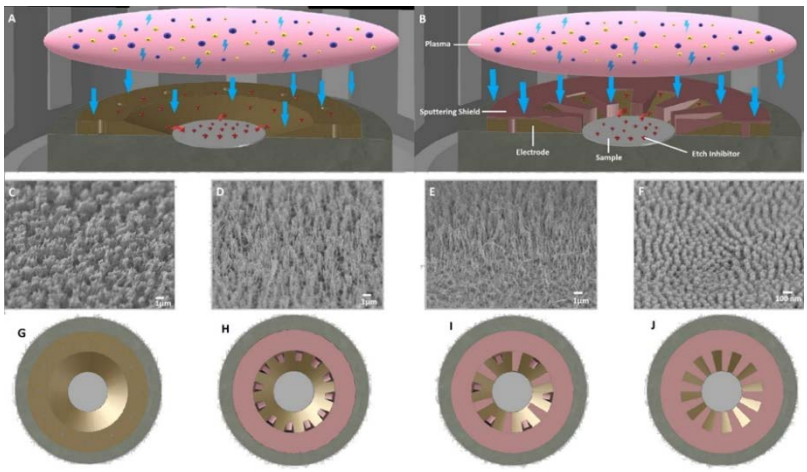


Fig.PT1 *The "nanoinhibit" new plasma reactor with controlled flux of inhibitors. (A) Classical Plasma reactor with unshielded Electrode. (B) The new plasma reactor with shielded electrode, in which the "nanoinhibit" process is materialized. (C)-(F) Control of surface* topography of Oxygen plasma-etched PMMA plates. (G)-(J) Shielding positions for controlling the exposed sputtered surface thus controlling the etch inhibitor flux from fully *sputtered (G: 100%) to partially sputtered (J: 22,6%) in order to obtain the desired topography*

PT2. Design and development of a low-pressure hydrogen plasma source

(A. Smyrnakis, E. Gogolides, and collaborators from Fasmatech Science and Technology SA)

In this project we work in close collaboration with a company manufacturing mass spectrometry and ion mobility instrumentation for protein analysis. The objective of the project is to develop new techniques for the coordinated dissociation of gas phase ions, extending the complete top-down characterization of proteins and antibodies. In addition to ionization by electrons, further protein fragmentation by hydrogen atoms and ions is desirable. Thus, hydrogen plasma source is needed. During the second year of this project, the mechanical design of the pulsed plasma source was finalized, assembled, and successfully connected to the Omnitrap (Fasmatech) linear ion trap and the Orbitrap mass spectrometer (ThermoFisher Scientific). Two source variants were constructed, the one involving a neutralization mechanism and the other not, to study the interaction of proteins in the trap with both neutral hydrogen atoms and hydrogen ions, respectively. The electronics needed to drive the new source were designed and manufactured, and debugging tests were performed on the new control software for both the plasma source and the Omnitrap. Hydrogen ion current measurements were employed to characterize the source, and protein (ubiquitin, cytochrome C) as well as antibody (trastuzumab) fragmentation experiments were successfully performed by hydrogen ion bombardment, resulting in significant protein sequence coverage.

Computational Nanometrology (CM)

CM1. Nanometrology of patterned structures

(G. Papavieros, V. Constantoudis and external collaborators from AUTH, MOXTEK, ICN2)

(a) Pixelization effects on SEM-based nanometrology: One of the great challenges of the SEM-based metrology of nanopatterns is the pixel size of acquired images which limits the accuracy of obtained measurements. The pixelization effects are very critical in the measurement of the Line Edge Roughness (LER) of line/space patterns (gratings) used abundantly in nanoelectronic and nanophotonic devices where the targeted values to be measured is of the order of pixel size (~1nm). In order to investigate further these effects and correct their bias on LER measurement, we performed a thorough mathematical analysis and derived a sound mathematical result enabling the correction of the pixelization bias in the measurement of the LER even when the pixel size of SEM images is much larger than its rms value (see Fig.CM1a). This result emphasizes *the power of mathematical and computational methods to enhance the metrological output of SEM images in deep nanometer scale*.

(b) Characterization of defects in nanopatterns: We proposed a methodology for the mathematical and quantitative characterization of the deviation of rough line/space patterns from their ideal smooth shape to identify defects related to line mass and shape. The methodology has been applied in real AFM images of line/space patterns while a modelling framework is elaborated for the generation of rough line/space patterns with controlled top and sidewall roughness and size variations. We also explored the consequences of the proposed methodology in the metrology of LER and its relation to 3D patterns. (see Fig.CM1b).

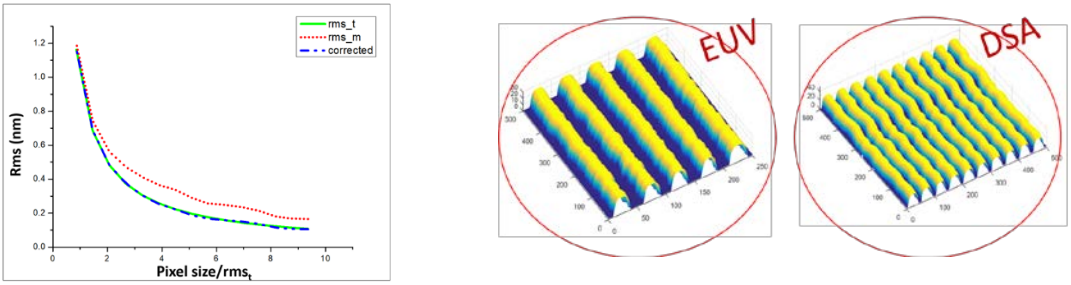


Fig.CM1 *(a) The rms value of the LER of synthesized SEM images vs. normalized pixel size before (red dotted line) and after correction (blue dashed-dotted line) with respect to the true value (green line) (b) Examples of computer generated line-space patterns simulating the most common defects of EUV patterns (LER) and DSA (line wiggling)*

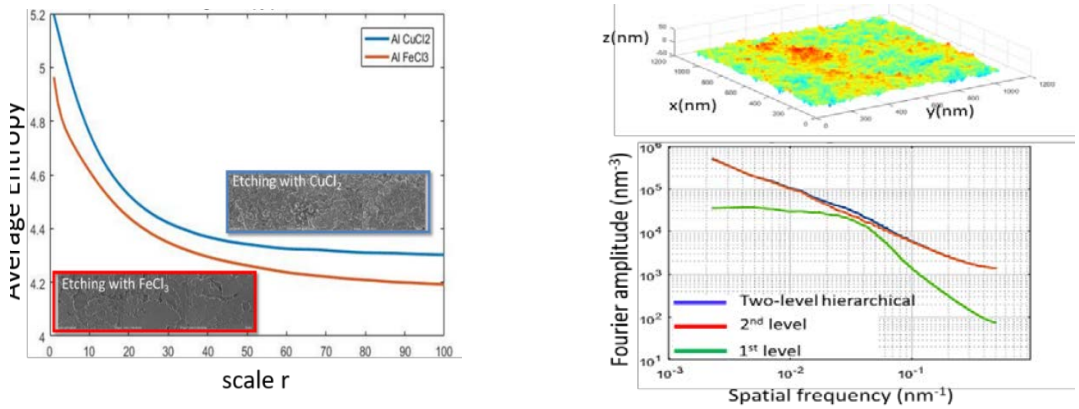
CM2. Nanometrology of open (freeform) surfaces

(A. Arapis, G. Papavieros, V. Constantoudis and external collaborators from NKUA, ETH, Univ. Leeds)

Multiscale nanostructured surfaces play a crucial role in micro and nanotechnology, since they are able to exhibit multifunctionality by exploiting the rich range of scales in their morphology. Despite the plenty use of terms complex and hierarchical to characterize such surfaces, a systematic definition and mathematical analysis of these terms is missing. To fill this gap,

a) we developed a methodology for the characterization of surface complexity focusing on the information content it carries versus inspection scale which can be quantified by the Shannon/information entropy of the mean values of surface heights (around each point at a specific scale of inspection. The method has been validated in synthesized surfaces and applied in real experimental surfaces revealing very interesting links to their properties (see Fig.CM2a).

b) We built a theoretical framework for the definition and classification of hierarchical surfaces and developed modelling algorithms for the generation of simulated surfaces from all types of hierarchy in surfaces. Utilizing the simulated surfaces, we investigated thoroughly and identified the impact that hierarchical types has on the Fourier and correlation analysis of surfaces. Quite surprisingly, we showed that the second level can be hidden and has very subtle impact on these analysis methods (see Fig.CM2b).



(a) **(b)**

Fig.CM2 (a) Entropy versus scale of Al surfaces wet etched with $CuCl_2$ (blue line) and $FeCl_3$ (red line). Notice the clear difference of entropies in all scales in harmony with the increased heat transfer coefficient of $CuCl_2$ etched surfaces. (b) Example of a two-level hierarchical surface (top) comprising two stochastic level morphologies along with the Fourier transform (bottom) of two levels and the hierarchical surface. We can notice that although the hierarchical nature of the shown surface is almost invisible it can be detected by close inspection of and Fourier spectrum which exhibits a slight knee in their shape coming from their different scaling behaviour.

Process Analysis & Simulation (PS)

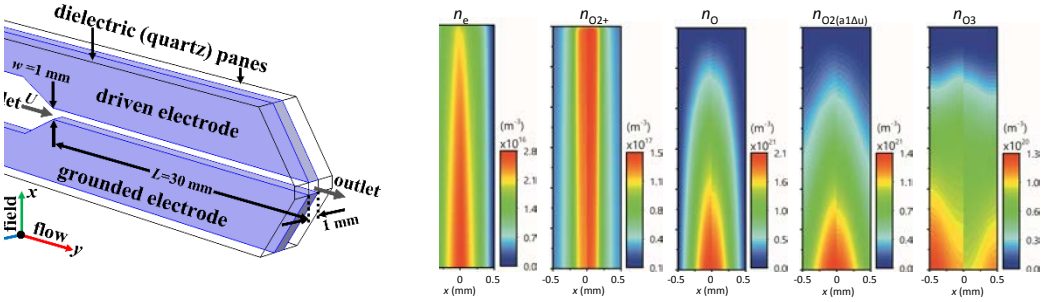
PS1. Modeling & simulation of atmospheric pressure plasma jets

(S. Mouchtouris, D. Passaras, G. Kokkoris & external collaborators)

Atmospheric pressure plasma jets have been the subject of intense scientific research during the last years, investigated for a wide range of different applications (e.g., decontamination, wound healing, surface modification, film deposition, water and food treatment). Our work aims to the design of new processes and/or geometries and reactors, a task requiring both accurate and fast computations.

The first example focuses on the acceleration of computations in atmospheric pressure plasmas. In particular, a novel 2D fluid model for capacitively coupled and cross-field atmospheric pressure plasma jets is developed, coming from the simplification of a detailed 2D plasma fluid model. The simplification was based on a set of reasonable assumptions and is applied systematically through a formalism based on dimensionless numbers (e.g., Peclet and Damkohler), although common in chemical engineering, utilized for the first time in the

context of plasma jets and plasma modeling in general. The simplified 2D fluid model, namely the cross-field plasma model (CFPM), consists of a number of 1D plasma fluid models which are solved serially using a multi-time-scale framework. In the COST reference jet with He/O_2 feed, the CFPM can reproduce detailed 2D calculations ~10 times faster than the detailed 2D model.



(a) **(b)**

Fig.PS1 *(a) Schematic of the COST jet. (b) Comparison of the results of the CFPM (from 0 to 0.5 mm) and the detailed 2D model (0.5 to 1 mm) in the discharge channel of the COST jet. Density of electrons, O_2^+, O, $O_2(a1\Delta u)$ and O_3. Conditions: 0.2 W, 13.56 MHz, 1.5 slm of He/O_2 (0.5%), gas temperature of 300 K.*

The second example focuses on the proper choice of turbulent flow model in atmospheric pressure plasma jets, which is crucial for accurate results. In particular, the 3D Large Eddy Simulation (LES) model, i.e., a detailed model entailing a high computational cost, is compared to simplified and lower cost models, namely the 2D standard *k-ε* and realizable *k-ε* models. For the kINPen plasma jet with Ar feed, the LES model predicts better mixing of air species with the feed gas at the plasma effluent and is more accurate as it directly resolves 98% of the turbulence kinetic energy and avoids the Boussinesq approximation of *k-ε* models.

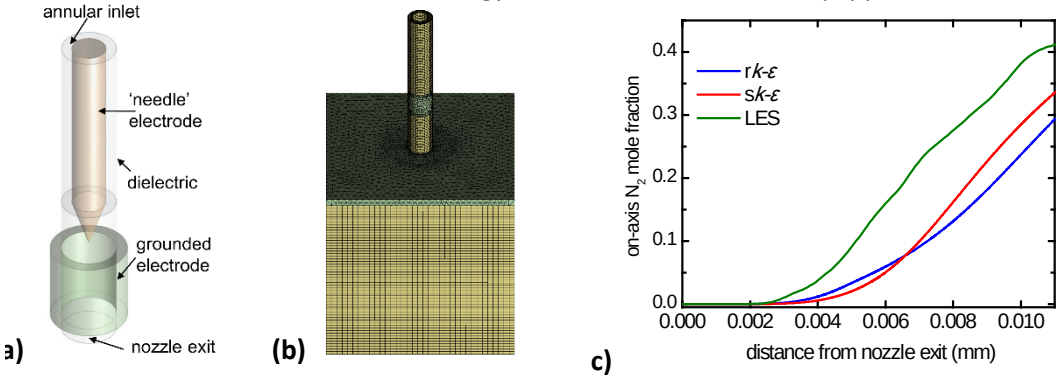


Fig.PS2 *(a) Schematic of the kINPen 09 plasma jet. (b) The 3D computational domain used for the LES model. (c) Comparison of the on-axis mole fractions of N_2 by the standard k–ε (sk–ε), realizable k–ε (rk–ε) and LES models.*

PS2. Modeling & simulation of plasma etching and roughening of surfaces

(G. Memos, G. Kokkoris & external collaborators)

Plasma is widely used for the surface treatment of polymeric substrates, inducing both geometrical (roughening) and chemical modifications (production of polar functional groups) on the surface. The aim of our work was to capture both effects of plasma and for this we developed a hybrid modeling framework, which couples kinetic Monte Carlo and level set models, incorporating a series of novelties in the implementation, such as the consideration of the surface morphology in kMC model and the conservation of the local variables of the evolving surface profile. The focus was on roughness evolution during plasma etching of poly(methyl methacrylate) PMMA with oxygen (O_2) chemistry. The prediction of roughness evolution was consistent with measurements versus time and at different operating conditions. The potential

of the framework to additionally handle the oxidation of the surface (by the surface coverage by O), is demonstrated, enabling the study of the wetting behavior of plasma etched polymeric surfaces.

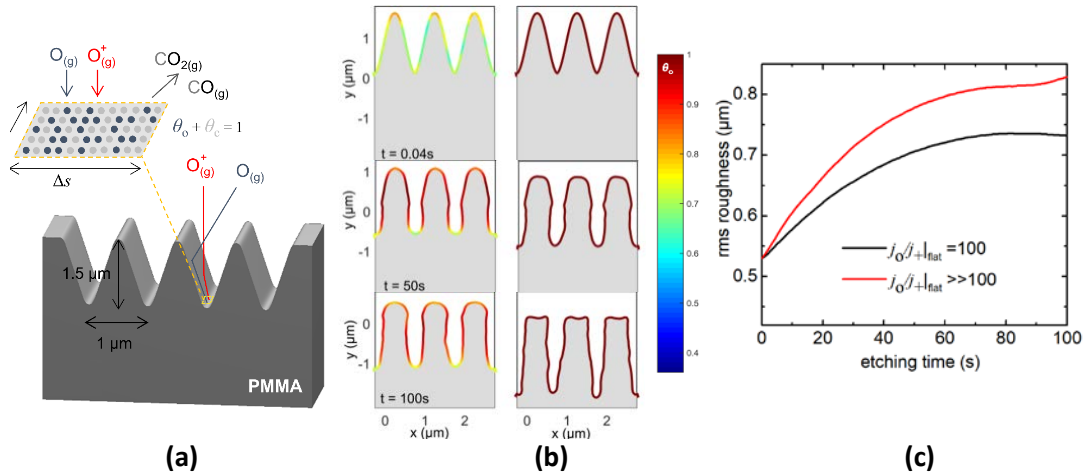


Fig.PS3 *(a) Processes on an elementary PMMA surface etched with O_2 plasma. (b) Snapshots of the surface profile for different etching times. (c) rms roughness versus time when $j_{iO}/j_+ = 100$ and $j_O/j+ >> 100$ (j stands for flux, O for Oxygen atoms and "+" for Oxygen ions).*

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 US provisional patent application from the results of the project.

A1.2 Antibacterial Surfaces

(D. Kefallinou, K. Ellinas, E. Gogolides, A. Tserepi and collaborators from INN and IB)

Bacterial attachment and colonization to hygiene sensitive surfaces, both public and nosocomial, as well as in food industry areas, poses a serious problem to human healthcare. Wehave recently developed smart, universal, metal-sputtered superhydrophobic surfaces, with bifunctional antibacterial behavior, demonstrating both antifouling and bactericidal action. In this work, we aim to present the optimization process that led to the realization of these "hybrid" antibacterial surfaces. To this end, two bactericidal agents, silver and copper, were tested for their efficiency against Gram-negative bacteria, with copper showing a stronger bactericidal action. In addition, between two low surface energy coatings, the fluorinated-alkyl self-assembled chlorosilane layer from perfluorinated octyltrichlorosilane (pFOTS) solution and the fluorocarbon layer from octafluorocyclobutane (C4F8) plasma, both were approved for their anti-adhesive properties after immersion in bacterial solution. However, the latter was found to be more efficient when engrafted with the bactericidal agent in shielding its killing performance. Furthermore, the thickness of the plasma-deposited fluorocarbon layer was optimized, in order to simultaneously retain both the superhydrophobicity of the surface and its long-term bactericidal activity.

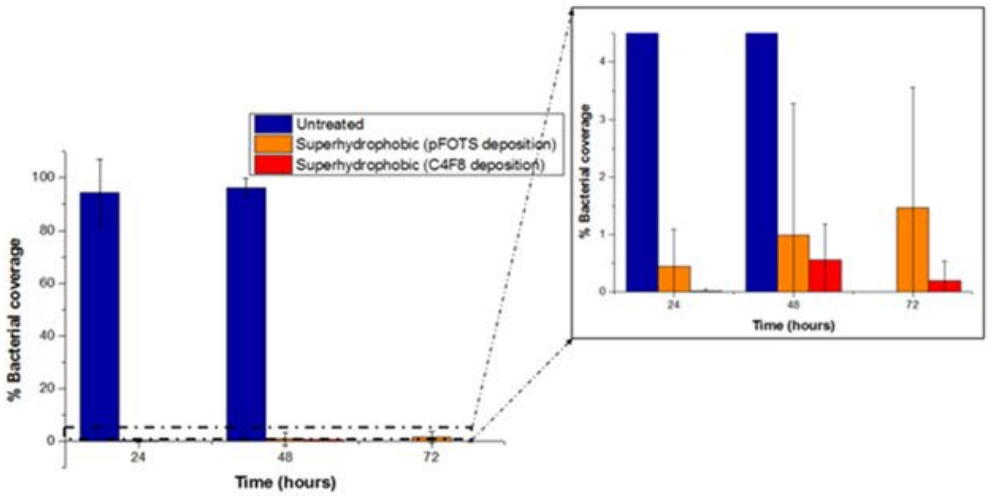


Fig.A1 *Optimization process of the metal-sputtered superhydrophobic antibacterial PMMA surfaces. Anti-adhesive activity of micro-nanotextured superhydrophobic PMMA surfaces, expressed as percentage bacterial. Fluorocarbon layer from C4F8 plasma was selected over the fluorinated chlorosilane from pFOTS solution as hydrophobic coating, for its ability to better resist bacterial colonization.*

A1.3 Cancer Cell selective enrichment and separation on plasma nanotextured surfaces

(A. Kanioura, A. Tserepi, E. Gogolides, and collaborators from INRASTES and UoA)

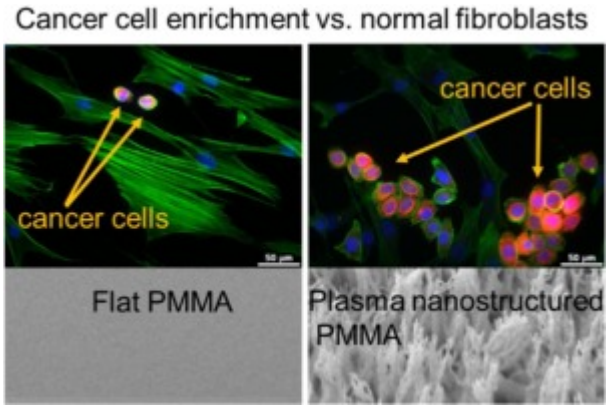


Fig.A2 *Top fluorescence images of normal fibroblasts and cancer cells on flat and nanostructured PMMA cells (Their SEM images are also shown).*

The enrichment of cancer cell population when in mixtures with normal ones is of great importance for cancer diagnosis. Thus, poly (methyl methacrylate) films have been processed applying different oxygen plasma conditions to fabricate surfaces with varying roughness, which were then evaluated with respect to adhesion and proliferation of both normal and cancer human cells. In particular, normal skin and lung fibroblasts, and four different cancer cell lines, A431 (skin cancer), HT1080 (fibrosarcoma), A549 (lung cancer), and PC3 (prostate cancer), have been employed. It was found that adhesion and proliferation of cancer cells was favored when cultured onto the hierarchical micro/nanostructured surfaces as compared to untreated ones. On the other hand, although the adhesion of normal fibroblasts was not influenced by the micro/nanostructured surfaces, their morphology and proliferation were significantly impaired. The reduced proliferation rate of adherent fibroblasts was linked to reduced focal points formation, as it was verified through vinculin staining, and not to apoptosis. The micro/nanostructured surfaces prepared with plasma treatment at −100 V for 3 min (hierarchical topography with mean height of ~800 nm) were selected as substrates for normal and cancer cell co-culture experiments. It was found that 25–80 times enrichment of cancer over the normal cells was achieved on the nanostructured surfaces after 3-day culture, while it was 5–8 times lower on the untreated ones. Thus, the nanostructured surfaces hold a strong promise as culture substrates for separation and enrichment of cancer cells from mixtures with normal ones that should find application in cancer diagnostics.

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. More results will be presented in our upcoming publication and in the 2021 report.

A1.5 Low friction surfaces (K. Ellinas, E. Gogolides, Supported by State Scholarship Foundation)
Superhydrophobic surfaces with a very low coefficient of friction COF that enables liquid mobility without any external stimuli are fabricated and studied.

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. In detail, the group has pioneered the modification of membrane surfaces (roughness and hydrophobization) for the enhancement of membrane water distillation systems. In addition, the modification of polymeric surfaces (superhydrophobic/superhydrophilic) provides a new method of water collection, that of atmospheric water harvesting (Fog collection – Dew harvesting). Last but not least, the modification of metallic and polymeric surfaces (superhydrophobic) results in the enhancement of heat transfer coefficient, which has big impact in industrial applications where condensation takes place (e.g. heat exchangers). More results will be reported during 2021.

Application 3 (A3) Plasmas for food, agriculture, environment and medicine

A3.1. Plasmas for food (P. Dimitrakellis, and external collaborators NTUA and Demeter)
The effect of Cold Atmospheric Plasma (CAP) on Ready-to-Eat (RTE), fresh cut, leafy rocket salad was investigated, aiming at quality retention and shelf life extension. CAP was generated via a Surface Dielectric Barrier Discharge source and its efficiency on rocket leaves was evaluated at different processing times through microbial, texture, pH-value and color analysis. A reduction of up to 1 logCFU/g was observed for the total microbial load of the samples depending on process conditions. Intense process led to microbial load decrease but also in significant degradation of color and texture of the rocket. A CAP processing time of 10 min was considered as optimum, for a sufficient reduction of the microbial load while maintaining color and texture. The shelf life of the optimum CAP processed rocket stored at 2-9^{o}C was estimated through quality analysis. *Pseudomonas spp*. growth was considered to be the dominant deterioration factor. CAP processing led to a two-fold increase of the shelf life of the rocket leaves compared to unprocessed samples.

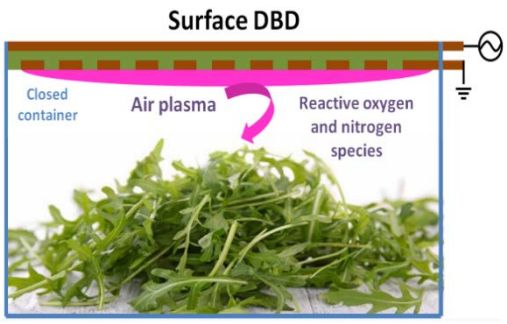


Fig.A3 Atmospheric plasma for fresh salad decontamination and shelf-life extension.

Funding

1. Contract with NCSR Demokritos and Bic Violex for Industrial Postdoctoral Programme “Optimizing Razor Blades using Plasma Processing” 01/07/2017 – 30/06/2020, total budget €82.950,00 , budget for 2020 €13.825,00

2. 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 2020 €27.650,00
3. 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 2020 €11,550,00
4. “HARMoNIC”, H2020-FETOPEN-1-2016-2017, Contract No. 801229, 01/10/2018 – 31/03/2022, total budget €762.900,00 , budget for 2020 €254.300,00
5. “NOVISH”, Contract No. MIS 5019170, 12/04/2019 – 11/04/2022, total budget €165.812,02 , budget for 2020 €41.453,00
6. “LagoMeal”, Contract No. MIS 5067491, 27/11/2020 – 26/05/2023, total budget €68.745,00 , budget for 2020 €2.300,00
7. 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 2020 €10.800,00
8. 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 2020 €9.802,80
9. 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 2020 €13.200,00
10. PLagri – COST Action 19110, Plasma applications for smart and sustainable agriculture, 06/10/2020 – 05/10/2024.

OUTPUT

Publications in International Journals

1. Giannoglou M., Stergiou P., Dimitrakellis P., Gogolides E., Stoforos N.G., Katsaros G., Effect of Cold Atmospheric Plasma processing on quality and shelf-life of ready-to-eat rocket leafy salad. *Innovative Food Science & Emerging Technologies* **66**, art. no. 102502 (2020). DOI: 10.1016/j.ifset.2020.102502
2. Kanioura A., Constantoudis V., Petrou P., Kletsas D., Tserepi A., Gogolides E., Chatzichristidi M., Kakabakos S., Oxygen plasma micro-nanostructured PMMA plates and microfluidics for increased adhesion and proliferation of cancer versus normal cells: The role of surface roughness and disorder. *Micro and Nano Engineering* **8**, art. no. 100060 (2020). DOI: 10.1016/j.mne.2020.100060
3. Kanioura A., Petrou P., Kletsas D., Tserepi A., Chatzichristidi M., Gogolides E., Kakabakos S., Three-dimensional (3D) hierarchical oxygen plasma micro/nanostructured polymeric substrates for selective enrichment of cancer cells from mixtures with normal ones. *Colloids and Surfaces B: Biointerfaces* **187**, art. no. 110675 (2020). DOI: 10.1016/j.colsurfb.2019.110675
4. Kefallinou D., Ellinas K., Speliotis T., Stamatakis K., Gogolides E., Tserepi A., Optimization of antibacterial properties of “hybrid” metal-sputtered superhydrophobic surfaces. *Coatings* **10** (1), art. No. 25 (2020). DOI: 10.3390/coatings10010025
5. Gogolides E., Homer meets nano: Shrinking 2700 year old Greek poetry with state-of-the-art nanotechnology. *Micro and Nano Engineering* **8**, art. no. 100061 (2020). DOI: 10.1016/j.mne.2020.100061
6. Vekinis A.A., Constantoudis V., Neural network evaluation of geometric tip-sample effects in AFM measurements. *Micro and Nano Engineering* **8**, art. no. 100057 (2020). DOI: 10.1016/j.mne.2020.100057

7. Vekinis A.A., Constantoudis V., Quantifying geometric tip-sample effects in AFM measurements using certainty graphs. *Micro and Nano Engineering* **8**, 100067 (2020). DOI: 10.1016/j.mne.2020.100067
8. Prud'homme N., Constantoudis V., Turgambaeva A.E., Krisyuk V.V., Samélor D., Senocq F., Vahlas C., Chemical vapor deposition of Cu films from copper(I) cyclopentadienyl triethylphophine: Precursor characteristics and interplay between growth parameters and films morphology. *Thin Solid Films* **701**, 137967 (2020). DOI: 10.1016/j.tsf.2020.137967
9. Passaras D., Amanatides E., Kokkoris G., Predicting the flow of cold plasma jets in kINPen: a critical evaluation of turbulent models. *Journal of Physics D: Applied Physics* **53** (26), 265202 (2020). DOI: 10.1088/1361-6463/ab7d6d

Papers in Refereed Conference Proceedings

1. Stellas A., Giannakopoulos G., Constantoudis V., Hybridizing AI and domain knowledge in nanotechnology: The example of surface roughness effects on wetting behavior (2020) CEUR Workshop Proceedings, 2844, pp. 48-54.

Books/Chapters in Books

1. Ellinas K., *Advances in Smart Coatings and Thin Films for Future Industrial and Biomedical Engineering Applications*, Edited by Elsevier Inc., Chapter 18 – "Superhydrophobic and superamphiphobic smart surfaces", pp. 487-514 (2020).
https://www.sciencedirect.com/science/article/pii/B978012849870500015X

International Conferences Presentations (invited, oral, poster)

1. Giannoglou M., Chanioti S., Stergiou P., Xanthou M-Z., Dimitrakellis P., Gogolides E., Katsaros G., The effect of semi-direct and indirect cold atmospheric plasma processing on the quality parameters of fish fillets, *IFT Annual Meeting-SHIFT20*, 12-15 July 2020, Chicago, IL (virtual event)
2. Chanioti S., Giannoglou M., Stergiou P., Xanthou M-Z., Efthimiadou A., Katsenios N., Dimitrakellis P., Gogolides E., Katsaros G., Development of corn grains and flour with improved nutritional properties by applying pre-sowing non-thermal technologies, *34th EFFoST (European Federation of Food Science and Technology) International Conference*, 10-12 November 2020, Israel (virtual event)
3. Giannoglou M., Xanthou M-Z., Chanioti S., Stergiou P., Dimitrakellis P., Gogolides E., Efthimiadou A., Christopoulos M., Katsaros G., The Effect of Cold Atmospheric Plasma and Pulsed Electromagnetic Fields on Microbial load and Quality Parameters of whole fresh Strawberries, *34th EFFoST (European Federation of Food Science and Technology) International Conference*, 10-12 November 2020, Israel (virtual event)
4. Giannoglou M., Christopoulos M., Xanthou M-Z., Efthimiadou A., Dimitrakellis P., Gogolides E., Katsaros G., Effect of novel Nonthermal technologies on Whole Fresh Pistachio Kernels quality characteristics and aflatoxin-producing potential, *34th EFFoST (European Federation of Food Science and Technology) International Conference*, 10-12 November 2020, Israel (virtual event)
5. Constantoudis V., Arapis A., Chatzigeorgiou M., Makarona E., Milionis A., Cheuk Wing, Lam E., Poulikakos D., Gogolides E., The challenge of nanocomplexity (invited oral), *17th International Conference on Nanosciences & Nanotechnologies (NN20)*, 7-10 July 2020, Thessaloniki, Greece (hybrid event)
6. Constantoudis V., Williams B., Kehagias N., Papavieros G., Torres C.M.S., Gogolides E., Characterization of defects in line/space patterns (oral), *SPIE Advanced Lithography and Patterning Techniques, Metrology, Inspection, and Process Control for Microlithography XXXIV* **11325**, 23-27 February 2020, San Jose, California, US

7. Mouchtouris S., Kokkoris G., Fast 2D computations in the COST reference jet with an 1D plasma model (virtual poster), *VIRTUAL The 73rd Annual Gaseous Electronics Conference (virtual GEC 2020)*, 5-9 October 2020, Central Daylight Time, USA.
8. Passaras D., Kontosis K., Amanatides E., Kokkoris G., Fast computations in atmospheric pressure plasma jets (virtual poster, 2nd prize award), *VIRTUAL The 73rd Annual Gaseous Electronics Conference (virtual GEC 2020)*, 5-9 October 2020, Central Daylight Time, USA.
9. Smyrnakis A., Lekkas A., Papanastasiou D., Instrumentation developments in omnitrap technology for advanced processing of gas phase ions (poster), *53nd Conference of the German Society for Mass Spectrometry (DGMS)*, 1-4 March 2020, Munster, Germany
10. Papanastasiou D., Kosmopoulou M., Smyrnakis A., Zubarev R., Multiple Stage Tandem Mass Spectrometry of Protein Ions in the Omnitrap Platform Involving Variable Energy Electrons and Hydrogen Atoms (oral), *53nd Conference of the German Society for Mass Spectrometry (DGMS)*, 1-4 March 2020, Munster, Germany
11. Kosmopoulou M., Smyrnakis A., Papanastasiou D., Fort K., Makarov A., Zubarev R., Top-down Analysis of Intact Antibodies under Denatured and Native Conditions on the Omnitrap Platform Coupled to an Orbitrap Mass Spectrometer (poster), *68th ASMS Conference on Mass Spectrometry and Allied Topics* (Rebooted, Online Version), 1-12 June 2020, Houston, USA
12. Wei J., Papanastasiou D., Kosmopoulou M., Smyrnakis A., Tang Y., Zaia J., Hong P., Costello C., Cheng Lin, EED MS2-guided -MS3 on Q Exactive-Omnitrap: a novel approach toward automated, de novo glycan sequencing, *68th ASMS Conference on Mass Spectrometry and Allied Topics* (Rebooted, Online Version), 1-12 June 2020, Houston, USA

Teaching and Training Activities

1. "Microelectronics and Microsystems fabrication processes", (E. Gogolides, D. Davazoglou), Postgraduate Programs on Microsystems and Nanodevices of the National Technical University of Athens and Micro and Nano Electronics of the National and Kapodistrian 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. "Plasma Processing for Micro and Nano Fabrication", (E. Gogolides, G. Kokkoris, V. Constantoudis, A. Tserepi), Postgraduate Program on Microelectronics of the National and Kapodistrian University of Athens
4. "Superhydrophobic surfaces, wetting theory and applications" (K. Ellinas), Postgraduate Program "Preservation of monuments of cultural heritage" University of West Attica.
5. "Mathematical modeling in Nanotechnology" (G. Kokkoris, V. Constantoudis), Postgraduate Program "Mathematical modeling in Modern Technologies and Finance", National Technical University of Athens
6. "Introduction to Complex Systems" (V. Constantoudis, A. Provata, Y. Kominis, T. Bountis), Postgraduate Program "Mathematical modeling in Modern Technologies and Financial Engineering", National Technical University of Athens
7. Lecture on how wetting control can be used for the preservation of monuments of cultural heritage
(K. Ellinas), Master program "preservation of monuments of cultural heritage" University of West Attica

Master Dissertations completed in 2020

1. Georgios Saridis
Stochastic Analysis of rough surfaces implementing Markov models
Research Supervisor at NCSR: V. Constantoudis
National and Kapodistrian University of Athens (Department of Mathematics)

2. Sofia Tsilidou
Bayesian inference on rough surfaces nanometrology problems
Research Supervisor at NCSR: V. Constantoudis
National and Kapodistrian University of Athens (Department of Mathematics)

3. Athanasios Arapis
Complexity measures of nanostructured surfaces
Research Supervisor at NCSR: V. Constantoudis
National Technical University of Athens (School of Applied Mathematics and Physical Sciences)

Conference / Workshop Organisation
Conference Title, Conference dates, location
Special issues
Kosmas Ellinas and Panagiotis Dimitrakellis were Guest Editors for the special issue: "Micro and Nanotechnology: Application in Surface Modification" in Processes (MDPI).

Patents

Methods and systems for forming a blade of a shaving device
Christos Pandis, Konstantinos Mavroeidis, Evangelos Gogolides, Kosmas Ellinas, Dimitrios Davazoglou
United States provisional patent application No 63/074,121, 3 September 2020.

Method to fabricate chemically-stable plasma-etched substrates for direct covalent biomolecule immobilization
Greek patent application 20140100319 – 03/06/2014, Patent grant No. 1009057
European patent application 15386014.3 – 29/05/2015, Patent grant No. EP3284581
Filed in UK, France, Germany 3/2020

Polymeric microfluidic device for Nucleic Acid purification fabricated via plasma micro – nanotexturing
Greek patent application 20150100398 – 09/09/2015, Patent grant No. 1009425
European patent application 16386017.4 – 08/09/2016, Patent grant No. EP3141298
Filed in UK, France, Germany 10/2020

Exploitation of Results
During 2020 the group continued its closed collaboration with the two spin-out companies of the group and of NCSR Demokritos, namely nanoplasmas p.c. (www.nanoplasmas.com) and nanometrisis p.c. (www.nanometrisis.com).

Awards
- 1st place Food-tech startup Trophy-Τροφή challenge 2020 (https://trophychallenge.gr)

POLYMER BASED SENSORS AND SYSTEMS

Project Leader: Ioannis Raptis

Permanent Research Staff: N. Papanikolaou, G. Papageorgiou, P. Argitis, M. Sanopoulou, P. Petrou, S. Kakabakos

Post Docs: Grigorios Zisis

PhD Candidates: Athanasios Botsialas

Objectives

- Development & Characterization of Lithographic materials & processes
- Development & Characterization of Chemocapacitive sensors
- Development & Characterization of Optical biosensors

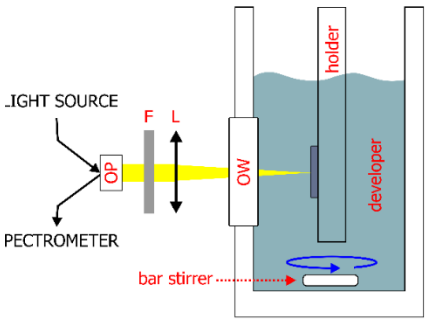
- **Activities and Main Results**

A) Lithographic Materials & Processes

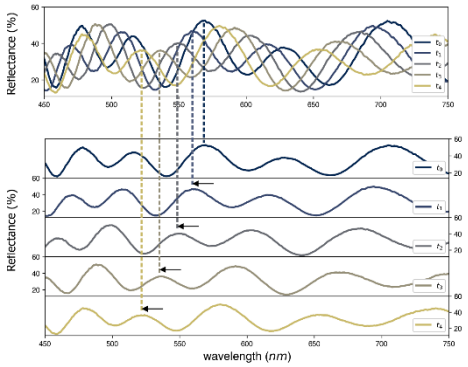
Patterning processes represent a significant percentage of the overall cost of the fabrication of high-end chips in High Volume Manufacturing (HVM) environment. Lithography tool costs grew from <10% of wafer capital equipment in 80's to more than 25% at the middle of the present decade, and currently as EUV lithography finally enters HVM, lithography for high-end chips represents ~50% of the wafer cost. In order to make such high-resolution lithography tools economically attractive, the optimization of the resist material(s) is of paramount importance and one of the top priorities.
In any lithographic process the last step is the development step, where selected resist areas are dissolved in a dedicated for the resist material, developer and in this way the exposed layout is revealed in the resist layer. The optimization of the development conditions is crucial for the overall lithographic performance while the study of the development step provides useful information regarding the properties of the lithographic material. In this work, in-situ monitoring of the resist thickness is conducted through fitting of the spectroscopic reflectance of resist films coated on dielectric layers on Si wafers. The recorded results prove that in-situ dissolution monitoring is a powerful tool for the generation of experimentally based development models for the lithographic materials employed in high resolution lithography. These dissolution rate (DR) values could be correlated with energy deposition profiles in order to improve the accuracy of the simulation and decrease the number of actual test exposures for process optimization.

Principle of Operation

The dissolution studies performed by employing a FR-pRo VIS/NIR (ThetaMetrisis) film thickness tool, equipped with a FR-Liquid kit. At WLRS, the operation principle of FR-pRo tool, light emitted from a light source is coupled to the illumination branch of the reflection probe and incidents vertically onto the sample under investigation. The incident light, partially reflected to each one of the sample's interfaces (liquid/resist, resist/SiO_2, SiO_2/Si), produce interference fringes across the reflectance spectrum. This reflectance signal, collected by the collection branch (a central optical fiber of a 200um core diameter) of the reflection probe, is guided to a spectrometer of a high spectral sensitivity for spectral analysis.

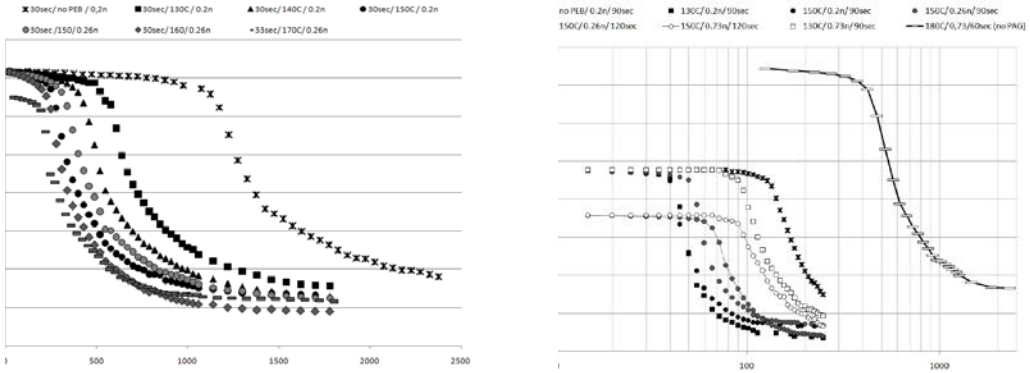


The schematic of the Dissolution Rate Monitor. OP: optical probe, F: 450nm long pass filter, L: lens, OW: optical window



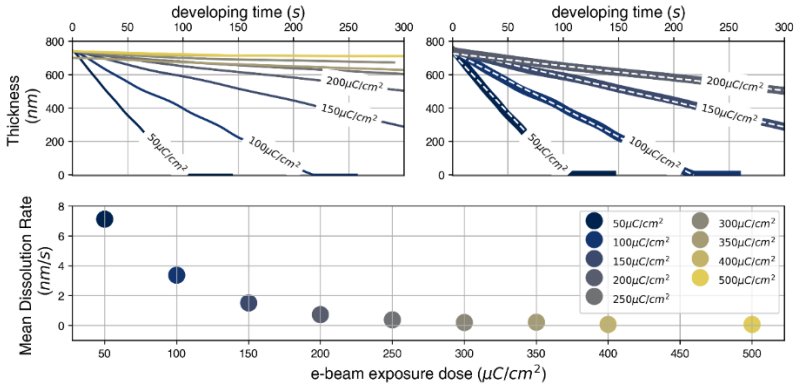
The evolution of the reflectance spectrum during the dissolution of a positive resist

Medusa 82 Ultra-high Resolution Negative Resist



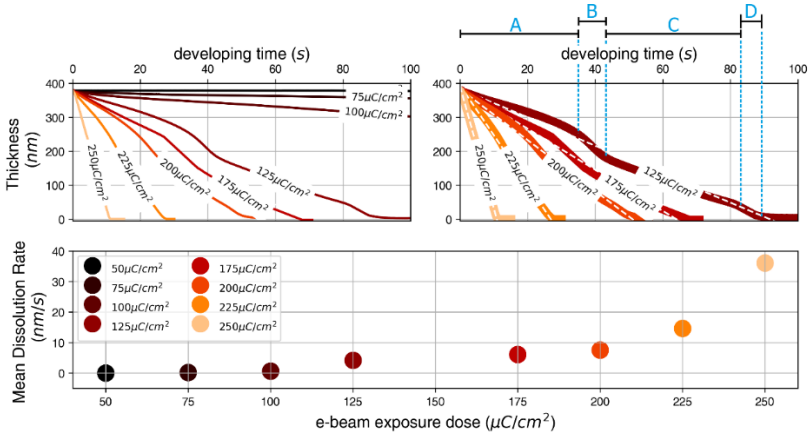
(Left) Average dissolution rates versus exposure dose for ascending T_{PEB} in the case of Medusa 82, for fixed development duration (30sec). (Right) Average dissolution rates for Medusa 82 UV for selected processing conditions. A Medusa 82 dissolution curve has been included for contrast.

AR-N High Resolution Negative Resist



(top-left) Thickness evolution during the development step corresponding to all selected exposure doses, and (top-right) only to high development rates. (bottom) The mean dissolution rates expressed as a function of e-beam exposure dose.

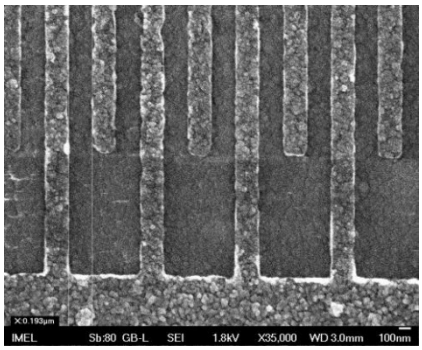
AR-P high Resolution Positive Resist



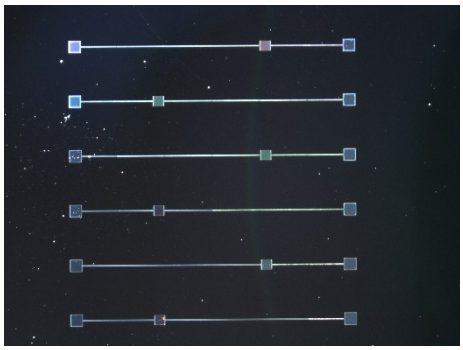
(top-left) Thickness evolution during the development step corresponding to all selected exposure doses, and (top-right) only to high development rates. (bottom) The mean dissolution rates expressed as a function of e-beam exposure dose.

B) Chemocapacitive sensors

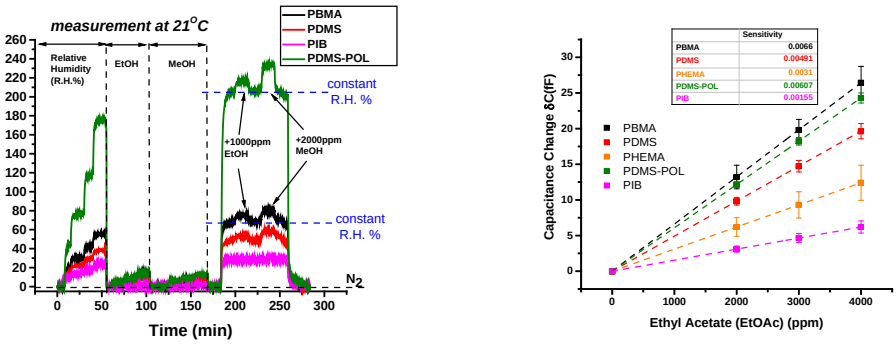
InterDigitated Capacitors (IDCs) is a generic platform for a wide range of diverse applications with their implementation in sensing modules being a major one. We introduced the use of IDCs with deep sub-micron critical dimension; equally spaced electrodes of 200nm width for enhanced sensing performance and also the method of their fabrication. The transducer configuration was studied theoretically with a finite element method simulation by using COMSOL Multiphysics. The miniaturization of the IDCs down to 200nm critical dimension with an adequate sensing area for the deposition of the polymeric materials is considered beneficial in terms of sensitivity gain. The IDCs were designed to deliver capacitance values of few pF in order to be compatible with already developed miniaturized low-power readout electronics. The transducers fabrication is performed with conventional microelectronic/micromachining processing and then coated with several semi-selective polymeric films. Besides the fabrication of multiple sensor arrays (chips) on the same silicon wafer, the miniaturization offers the integration with the readout electronics on the same chip. The evaluation of the sensing performance of the semi-selective polymer coated sensors is performed upon exposure to vapours of pure and binary mixtures of VOCs and humidity in various concentrations. The sensors demonstrate high sensitivity to the examined analytes as a result of the miniaturization, while their semi-selectivity is a key for applications in complex vapour environment discrimination.



Top-down SEM image of the IDE structures.



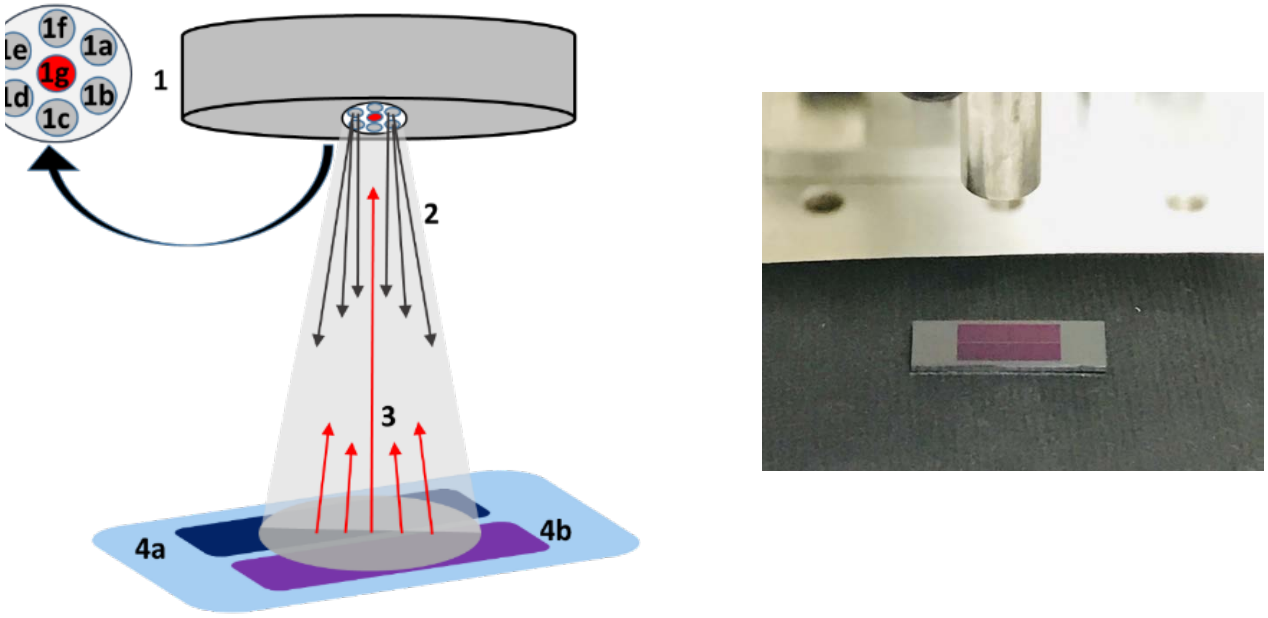
The Si transducer with the six IDE structures, imaged by a stereoscope.



(left) Dynamic measurement of the different polymer coated sensors to various concentrations of pure analytes and selected binary mixtures of them. (right) Equilibrium responses of different polymer coated sensors upon exposure to various concentrations of ethyl acetate vapours.

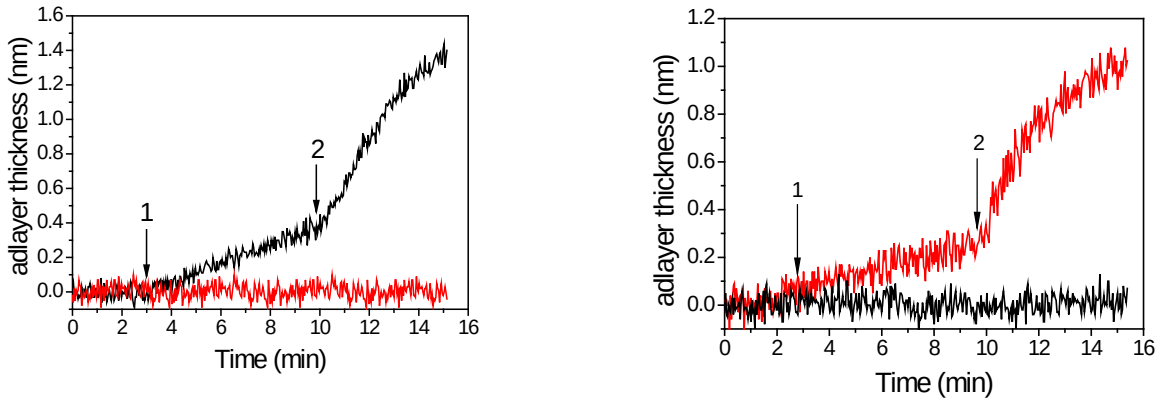
C) Biosensors

Biosensing through White Light Reflectance Spectroscopy (WLRS) is based on monitoring the shift of interference spectrum due to the binding reactions occurring on top of a thin SiO_2 layer deposited on a silicon chip. In this work, a new approach (MARS), which is based on patterning the sensor surface to create areas with different SiO_2 thickness, is developed and evaluated for multi-analyte determinations with the WLRS set-up. The areas of different thickness can be interrogated by a single reflection probe placed on a fixed position over the chip and the reflection spectrum recorded is de-convoluted to the spectra corresponding to each area allowing the simultaneous monitoring of the bioreactions taking place at each one of them. The optimum chips were then used for the simultaneous determination of two mycotoxins, aflatoxin B1 and fumonisin B1. A competitive immunoassay format was followed employing immobilization of mycotoxin-protein conjugates onto the SiO_2 of different thickness. It was found that the dual-analyte assays had identical analytical characteristics with the respective single-analyte ones. The detection limits achieved were 0.1 ng/mL for aflatoxin B1 and 1.25 ng/mL for fumonisin B1, with dynamic ranges extending up to 10 and 100 ng/mL, respectively. The sensor was also evaluated for the determination of the two mycotoxins in whole grain samples (wheat and maize). The extraction protocol was optimized and recoveries ranging from 85 to 113% have been determined. Due to lack of moving parts, the novel multi-analyte format is expected to considerably facilitate the built-up of a portable device for determination of analytes at the Point-of-Need.



(left) Schematic of MARS set-up for reflectance spectrum acquisition from chips with two SiO_2 areas of

different thickness. (right) Image of the MARS chip with the two sensing areas under the reflection probe.



l-time responses obtained from a dual-analyte chip when running over (left) a mixture of zero brator with anti-AFB1 Mab or (right) a mixture of zero calibrator with anti-FB1 Mab. Black lines respond to response from the area functionalized with the AFB1-BSA conjugate and red lines from the a functionalized with the FB1-OVA conjugate.

Funding INNOVATION-EL

OUTPUT

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1. Mpatzaka Th, Zisis G., Raptis I., Vamvakas V., Kaiser Ch., Mai T., Schirmer M., Gerngroß, M. Papageorgiou G., "Process study and the lithographic performance of commercially available silsesquioxane based electron sensitive resist Medusa 82*" Micro Nano Eng.* **8** 100065 (2020) DOI: 10.1016/j.mne.2020.100065
2. Mpatzaka T., Papageorgiou G., Papanikolaou N., Valamontes E., Ganetsos Th., Goustouridis D., Raptis I., Zisis G. "In-situ characterization of the development step of high-resolution e-beam resists" *Microelectron. Eng.* **9** 100070 (2020) DOI: 10.1016/j.mne.2020.100070
3. Nika A., Oikonomou P., Manouras Th., Argitis P., Vamvakaki M., Sanopoulou M., Raptis I., Chatzichristidi M., "Reversible chemocapacitor system based on PDMAEMA polymers for fast sensing of VOCs mixtures" *Microelectron. Eng.* **227** 111304 (2020) DOI: 10.1016/j.mee.2020.111304
4. Oikonomou P., Botsialas A., Papanikolaou N., Kazas I., Ntetsikas K., Polymeropoulos G., Hadjichristidis N., Sanopoulou M., Raptis I. "Gas sensitivity amplification of interdigitated chemocapacitors through etching" *IEEE Sensors* **20** 463(2020) DOI: 10.1109/JSEN.2019.2939016
5. Wang Z., Syed A., Bhattacharya S., Chen X., Buttner U., Iordache G., Salama K., Ganetsos Th., Valamontes E., Georgas A., Raptis I., Oikonomou P., Botsialas A., Sanopoulou M. "Ultra miniaturized InterDigitated Electrodes platform for sensing applications" *Microelectron. Eng.* **225** 111253(2020) DOI: 10.1016/j.mee.2020.111253
6. Budkowski A., Petrou P., Awsiuk K., Misiakos K., Raptis I., Kakabakos S. "Spatially selective biomolecules immobilization on silicon nitride waveguides through contact printing onto plasma treated photolithographic micropattern: step-by-step analysis with TOF-SIMS chemical imaging" *Appl. Surf. Sci.* **506** 145002(2020) DOI: 10.1016/j.apsusc.2019.145002
7. Anastasiadis V., Koukouvinos G., Petrou P.S., Economou A., Harjanne M., Heimala P., Goustouridis D., Raptis I., Kakabakos S.E. "Multiplexed mycotoxins determination employing white light reflectance spectroscopy and silicon chips with silicon oxide areas of different thickness" *Biosens. Bioelectron.* **153** 112035(2020) DOI: 10.1016/j.bios.2020.112035
8. Stavra El., Petroua P.S., Koukouvinos G., Economou A., Goustouridis D., Misiakos K., Raptis I., Kakabakos S.E.,"Fast, sensitive and selective determination of herbicide glyphosate in water samples with a White Light Reflectance Spectroscopy immunosensor" *Talanta* **214** 1 120854(2020) DOI: 10.1016/j.talanta.2020.120854

THEORETICAL MODELING OF WAVES IN THE MICRO AND NANO SCALE

Project Leader: N. Papanikolaou

Researchers: I. Raptis, N. Stefanou (National Kapodistrian Univ. of Athens) .

Research Associates: E. Almpanis

PhD Candidates: E. Panagiotidis

Objectives

- The goal of this project is to study the interaction of waves in micro and nanostructures that have characteristic dimensions of the order of the wavelength. In particular we focus on:

- Design, modeling, fabrication and optical characterization of periodic metallodielectric metasusrfaces that control the light wavefront as well as integrated photonic devices.

- Development of computational methods for the study of the interaction of electromagnetic, elastic, and spin waves in complex periodic structures.

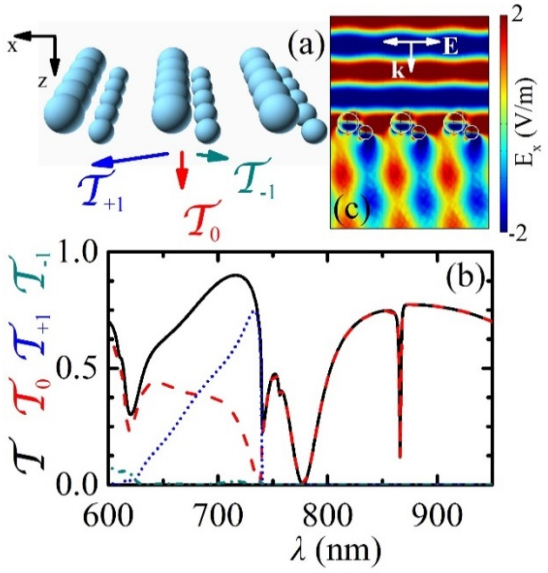
- Study the interaction of light with classical fields, in particular magneto-optic and acousto-optic interaction. We consider structures that can sustain simultaneous wave propagation of different fields with similar wavelengths.

Activities and Main Results

Development of the Layer Multiple Scattering Method for calculation of light transmission through complex multilayer structures

We use a layer multiple scattering method which was extended for the calculation of the optical properties of multilayers with 2D periodic complex unit cells. The method is suitable for layered structures of periodic arrays of particles and solves Maxwell's equations by using a spherical wave expansions of the electromagnetic field around each particle. It is fast and accurate for spheres and particles close to the spherical shape, like spheroids and low aspect ratio cylinders. The extension allows the study of designed, nanopatterned, surfaces (metasurfaces) that can control the wavefront of light.

The method was used to design periodic rectangular arrays of pairs of Si nanospheres that can efficiently diffract light in reflection or transmission mode at large angles as well as split light with minimum back-reflection, by properly adjusting the geometry of the structure. In particular, we highlighted the crucial role of hybrid modes, of predominant quadrupolar character, in all-dielectric diffractive arrays when diffraction channels are open. We demonstrated three non trivial ways to guide light incident normally on the surface towards a desired direction. The underlying design principles, which are based on the interaction between electric and magnetic multipole Mie resonances,can be applied to other similar systems such as cylinders, or even more complex particles, on a substrate.



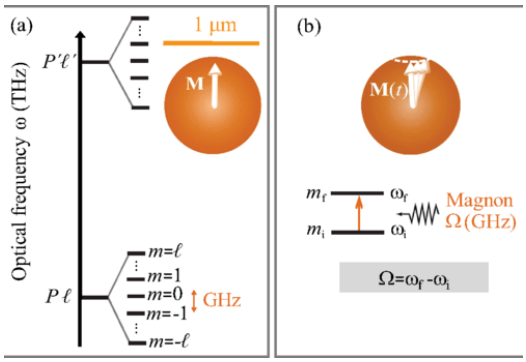
Metasurface design to efficiently bend light at large angles, for a specified wavelength. (a) Periodic array of Si spheres, (b) Transmission spectrum for normally incident light for the different diffraction orders. (c) Electric field along the x-direction indicating the strong bending of normally incident light close to 770 nm.

Accurate thickness and refractive index mapping of 2D materials by reflectance spectroscopy and imaging techniques (SLICE)

The purpose is to develop an accurate thickness and refractive index mapping of multilayer surfaces by reflectance spectroscopy and imaging techniques. This is a joint Industrial Fellowships Program funded by Stavros Niarchos Foundation, between ThetaMetrisis S.A. company and NCSR ”Demokritos”. The main objective of the project is to provide a simple yet powerful surface analytical technique based on reflectance spectroscopy in a broad wavelength range (UV-Vis-NIR) and a variation of optical reflection microscopy.

Magneto-photonics

Tailoring and enhancing the interaction between visible/near-infrared (Vis/NIR) light and spin waves in dual, so-called optomagnonic or photomagnonic, cavities have recently attracted a lot of attention, mainly due to the promising potential in realizing magnon-based microwave-to-optical transducers appropriate for quantum-computing applications. We studied theoretically the transition probability between 2 optical modes due to a magnon excitation. Such triply resonant photon transitions between Zeeman-split Mie modes, are driven by a uniform-precession spin wave, in magnetic garnet microspheres. We derived selection rules based on group theory considerations, and evaluated the corresponding transition amplitudes to first-order Born approximation. By reducing the magnon mode volume to few micrometers, the predicted optomagnonic coupling strengths are almost three orders of magnitude larger than those expected in corresponding transitions between WGMs of respective (sub)millimeter-sized resonators as reported in the relevant literature. These findings were also supported, and further elucidated, by approximate analytical calculations based on closed-form formulas that we derived in the low coupling regime. Our results suggest a viable route towards enhanced magneto-optic interaction in the near-infrared.



(a) Schematic representation of Mie mode degeneracy lifting (Zeeman splitting) in a dielectric magnetic microsphere. In the unmagnetized sphere, polarization P[transverse electric or transverse magnetic] and a given angular momentum number l. For magnetic garnet spheres in the Vis/NIR part of the EM spectrum, Zeeman splitting can attain large values, of the order of 10 GHz. (b) Graphical illustration of the triple-resonance condition in a one-magnon absorption (photon frequency up-conversion) process: Photon transition from a mode at ω_i to a mode at ω_f by absorption of one magnon.

Funding
Post Doctoral Fellowship S. Niarchos Foundation, G. Zisis,
IKY PhD Fellowship E. Panagiotidis

OUTPUT

Publications in International Journals

1. Almpanis E. Amanollahic M. Zamanic M., *Controlling the transverse magneto-optical Kerr effect with near-zero refractive index bi-gyrotropic metamaterials* Opt. Mat. **99**, 109539 (2020). DOI: 10.1016/j.optmat.2019.109539.
2. Mpatzaka, T., Papageorgiou, G., Papanikolaou, N.,Raptis, I., Zisis, G., *In-situ characterization of the development step of high-resolution e-beam resists,* Micro and Nano Engineering, **9** 100070 (2020). DOI: 10.1016/j.mne.2020.100070.
3. Panagiotidis, E., Almpanis, E. Stefanou, N. Papanikolaou, N., *Multipolar interactions in Si sphere metagratings* J. Appl. Phys., **128**(9), 093103 (2020). DOI: 10.1063/5.0012827.
4. Oikonomou, P., Botsialas, A., Papanikolaou, N., Sanopoulou, M.,Raptis, I., *Gas Sensitivity Amplification of Interdigitated Chemocapacitors through Etching* IEEE Sens. J., **20**(1), 463-470, 8822731 (2020) DOI: 10.1109/JSEN.2019.2939016.
5. Almpanis, E., Zouros, G.P. Pantazopoulos, P.A., Tsakmakidis, K.L., Papanikolaou N., and Stefanou N., *Spherical optomagnonic microresonators: Triple-resonant photon transitions between Zeeman-split Mie modes,* Phys. Rev. B, **101**, 054412 (2020). DOI: 10.1103/PhysRevB.101.054412.

Teaching and Training Activities

N. Papanikolaou
Lectures on Micro/Nanotechnology – Development of semiconductor devices/in the course Applied Optoelectronics, April-May 2018, 8h lectures, University of Patras.

N. Papanikolaou
Lectures on Semiconductor and Nanodevice Optoelectronics in the course Applied Optoelectronics, Oct-Dec 2018, 8h lectures, University of Patras.

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)

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.

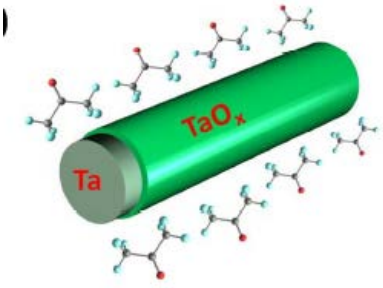
Activities and Main Results

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.

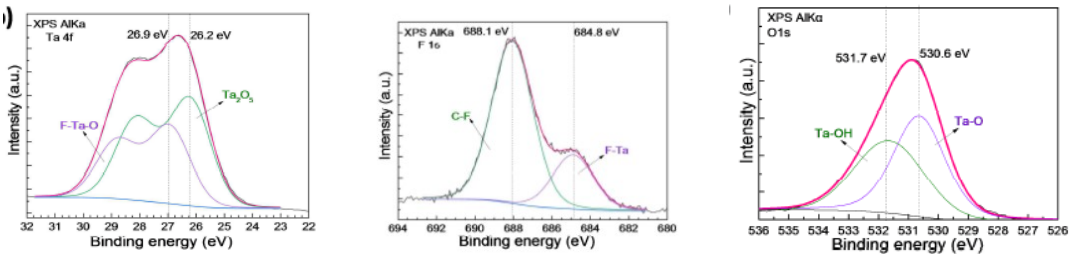
2. Deposition of carbon-doped tantalum dioxyfluoride films

TaO_2FC_x films were deposited in a home-made MOCVD system with a stainless steel reactor by using TaOx and hexafluoroacetone (C_3F_6O) vapors. TaOx vapors were produced by heating a superficially oxidized metallic (Ta) filament at 1000 °C (see figure 1). The C_3F_6O vapor was introduced in the deposition chamber by a N_2 stream bubbling through a saturator maintained at 60 °C. For the deposition, substrates were loaded on a copper susceptor fixed between two Cu current leads and located 5 cm below the filament. The chamber was evacuated to 10^{-2} Torr, and then a flow of 100 sccm of N_2 and the C_3F_6O vapors were introduced in it and the pressure was stabilized to 1 Torr with the aid of an automatic pressure control system consisting of a baratron manometer and an automatically driven butterfly valve. Finally, the temperature of the filament was raised to 1000 ^oC with the application of an AC (50 Hz) current to produce the TaOx vapors. Bias voltage and deposition time were used to control film thickness with time varying between 1 and 60 s. The deposition of pristine TaOx films was obtained in N_2 environment without the presence of C_3F_6O vapors inside the chamber. During deposition, the substrate was maintained near room temperature.



. 1. A Ta filament superficially covered a "native" TaOx layer, heated in C_3F_6O ors for the deposition of TaO_2FC_x films.

The stoichiometry of the TaO2FCx films obtained with this method was studied with x-ray photoelectron spectroscopy (XPS). Typical XPS spectra of the Ta 4f, F1s and O1s peaks are shown in Fig. 2.



2. Ta 4f, (c) F 1s and (d) O 1s XPS peaks of the carbon-doped tantalum dioxyfluoride film osited on ITO substrate.

The obtained carbon-doped tantalum dioxyfluoride films were used as a superior electron transport material for high performance organic optoelectronic devices.

3. 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.

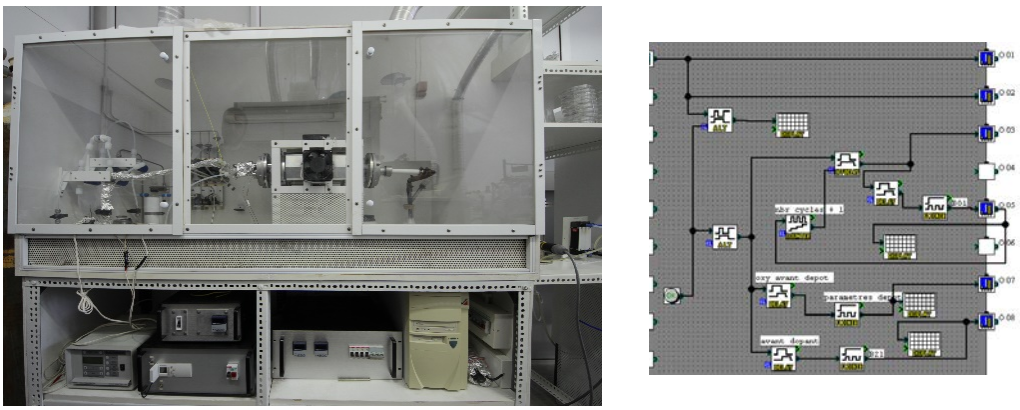


Fig. 3. The APCVD system developed for the deposition of SnO2 films (left) and the graphic representation of the process, as displayed on the screen of the personal computer that controls the process (right).

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).

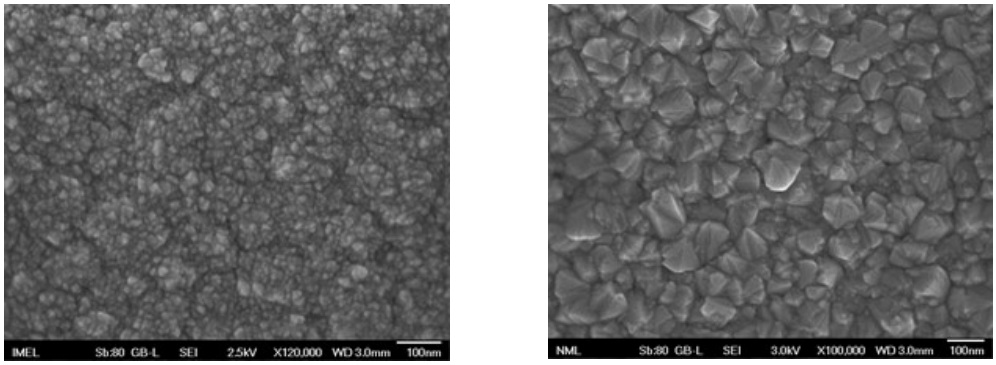


Fig. 4. SEM micrographs taken on two APCVD SnO_2 samples grown at 390 ^oC using water (a) and methanol (b) as oxidizing agents.

OUTPUT

1. Filippatos P.-P, Kelaidis N., Vasilopoulou M., Davazoglou D and Chroneos A. Atomic structure and electronic properties of hydrogenated X (=C, Si, Ge, and Sn) doped TiO2: A theoretical perspective, AIP Adv. Vol. 10, (2020) Article no 115316
2. Palilis L.C., Vasilopoulou M., Verykios A., Soultati A., Polydorou E., Argitis P., Davazoglou D., Mohd Yusoff A.R.B. and Nazeeruddin M.K., Inorganic and Hybrid Interfacial Materials for Organic and Perovskite Solar Cells, Adv. Mater. Vol. 10 (2020) Art. No 2000910
3. Soultati A., Verykios A., Armadorou K.-K., Tountas M., Vidali V.P., Ladomenou K., Palilis L., Davazoglou D., Coutsolelos A.G., Argitis P., Vasilopoulou M. Interfacial engineering for organic and perovskite solar cells using molecular materials. J. Phys. D., Appl. Phys. Vol. 53, (2020) Art. No 263001
4. Vasilopoulou M., Yusoff A.R.B.M., Kuganathan N., Bao X. Verykios A., Polydorou E., Armadorou K.-K., Soultati A., Papadimitropoulos G., Haider M.I., Fakharuddin A., Palilis L.C. , Kennou S., Chroneos A., Argitis P. and Davazoglou D., A carbon-doped tantalum dioxyfluoride as a superior electron transport material for high performance organic optoelectronics, Nano Energy Vol. 70 (2020) Art. No 104508

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)
3. Location/Academic Institute: NSCR “Demokritos”

Funding
ECODROPDENSER, GSRT (120 KEuros), N. V. is funded by the SNF.

THIN FILM 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 in the following areas:

- 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.
- 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

As polycrystalline silicon thin film technology does not lend itself to very low temperature processing, our work has focused on the development of thin molybdenum disulfide (MoS_2) films and devices based on them. MoS_2 is the most important of various transition metal dichalcogenide thin films widely investigated for applications in TFTs and sensors. Other transition metal chalcogenide films are also under consideration. Dielectric films suitable for such devices like AlO_3 and Ta_2O_5 are used.

Task 1: Morphological and chemical characteristics of MoS_2 and oxide films

MoS_2 films intended for FETs are grown via HW-CVD with samples at room temperature. In their unprocessed, as grown form they are a low conductivity, low mobility 46 nm-thick porous medium as deduced from electrical measurements, spectroscopic ellipsometry (SE) and Scanning Electron Microscopy (SEM) (see Figures 1a, 1c and Figure 3, respectively). The long range amorphicity of the films is confirmed via X-ray diffraction (XRD) and Raman spectroscopy (Figures 1e and 1f, respectively), as well as from UV-vis absorbance. The latter indicates absence of the excitonic A and B bands at 670 and 610 nm, which constitute the typical fingerprint of ordered 2H-MoS_2 structures, showing only transitions from the valence to the conduction band around 400 nm that, additionally, appear broad due to extended structural disorder. From SE measurements' analysis the as-grown material bandgap is estimated to be 1.27 eV with no characteristic peaks or features in their spectral refractive indices (Figure 1a), suggesting a bulk-like, amorphous material with indirect gap.

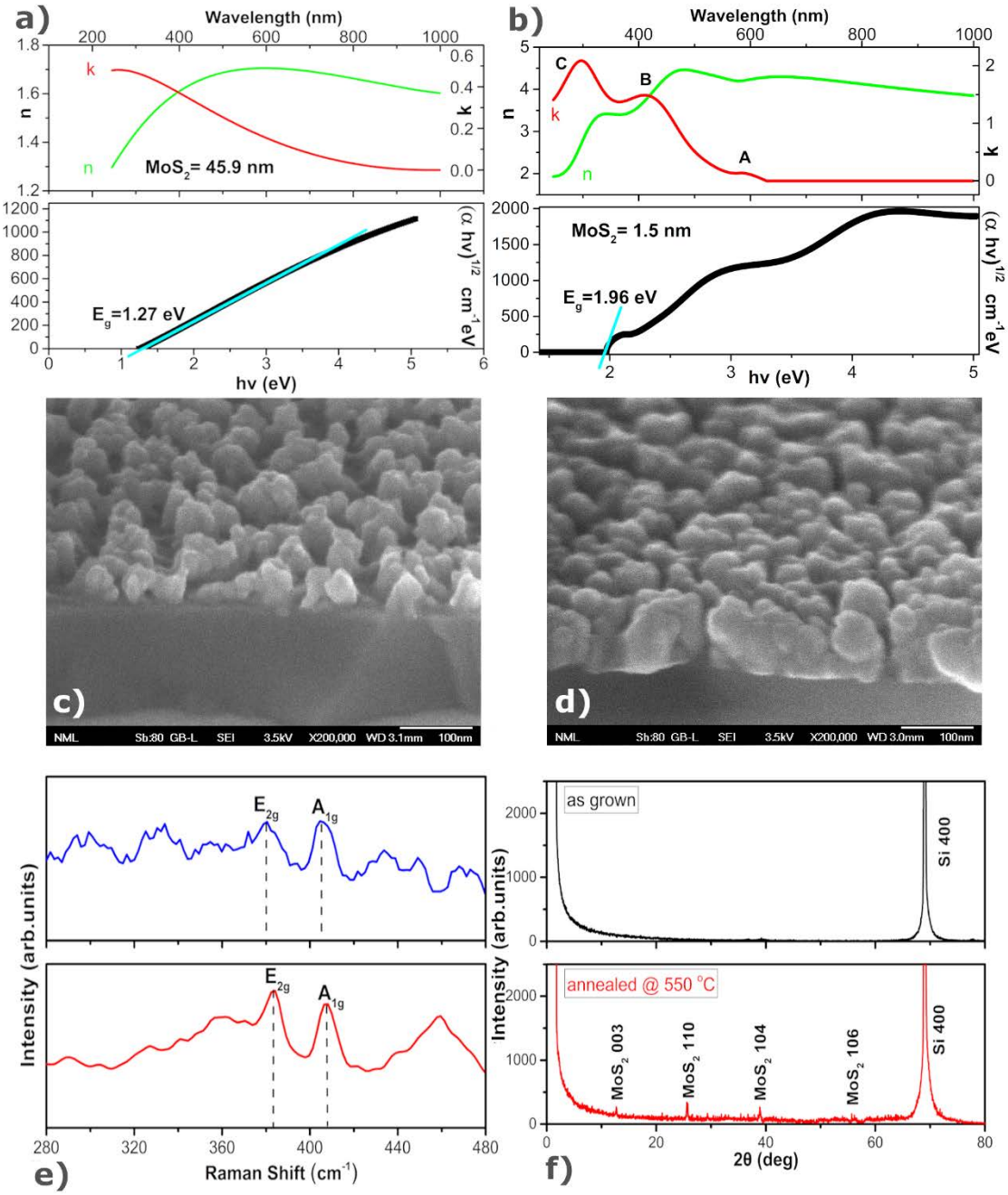


Figure 1. *a) top: Experimentally determined MoS_2 complex refractive index (n, k) as derived from spectroscopic ellipsometry data analysis. bottom: extracted Tauc plot along with the corresponding MoS_2 bandgap (E_g) for the as-grown film and b) same data for films annealed at 550°C. c) FE-SEM image of as-grown and d) FE-SEM image of annealed MoS_2 film, highlighting material migration along the growth axis upon thermal treatment. e) typical Raman spectra of the as grown (blue) and annealed (red) MoS_2 thin films demonstrating the MoS_2-characteristic E_{2g} and A_{1g} peaks at 383,8 cm^{-1} and 408 cm^{-1}. The peaks become more intense and narrower upon annealing, highlighting an overall transition from amorphous to a crystal-like structure. f) XRD spectra of as grown (black) and annealed (red) MoS_2 films highlighting a transition from amorphous to multi crystalline material upon annealing, in accordance to Raman spectra*.

However, after a mild annealing treatment at 550°C the complex refractive index of amorphous MoS_2 (Figure 1a) is transformed to the information-rich case of Figure 1b, the result of which is consistent with published results for crystalline MoS_2. The three peaks in the spectral indices of Figure 1b correspond to the A, B and C

excitons of the dielectric function, with the A and B peaks related to the transition from the spin-orbit split valence bands to the lowest conduction band at the K and K' points and the C peak associated with the transition from the valence band to the conduction band along the Λ → Γ path of the Brillouin zone. The ellipsometrically-determined bandgap is also increased after annealing to 1.96 eV, a value consistent with the direct bandgap dominant in mono- or oligo-layer MoS_2 and MoS_2 nanosheets and concerns the bottom layers of the structure, remaining covered by the amorphous MoS_2 matrix as confirmed via XRD (Figure 1f) and SEM images of Figure 1d. The latter indicate a more coherent structure at the bottom of the film which evolves into a highly porous formation of increasing pore size towards the film top.

The surface chemical composition of the films was analyzed using X-ray photoelectron spectroscopy (XPS). The survey spectra show the expected Mo and S core and Auger lines for MoS_2, along with signals from C and O and smaller signals from S, F and Na. Analysis of the Mo 3*d* (Figure 2a) and S 2*p* (Figure 2b) core level spectra reveal the presence of MoS_2 as well as significant amounts of additional sulfur species (S-H/N). The Mo $3d_{5/2}$ binding energy (BE) is found to be 229.7±0.1 eV and the Mo $3d_{3/2}$ BE is 232.9±0.1 eV, resulting in a spin-orbit-split (SOS) of 3.2 eV, all consistent with values previously reported in the literature for MoS_2. The Mo 3d core level is very close in BE to the S 2*s* line and two chemically shifted components are observed at 225.9±0.1 eV (MoS_2) and 227.9±0.1 eV (S-H/N), with the higher BE component dominating. This is also reflected in the main S 2*p* core line showing a main component at 163.7±0.1 eV from S-H/N environments and a smaller feature at lower BE (162.6±0.2 eV) associated with MoS_2.

In the Au-free spectra of Figure 2a, 2b the contribution of annealing can be isolated. Spectra suggest a shift to lower BE for both Mo 3*d* (Figure 2a) and S 2*p* (Figure 2b) spectral components from MoS_2 upon annealing, indicating a rigid shift of the Fermi level, thereby suggesting the thermally-induced p-type doping of the MoS_2 matrix. Minute amounts of Mo oxides are also observed in both the Mo 3*d* and O 1*s* spectra (Figures 2a and 2c, respectively). The O 1*s* spectra may suggest a slight increase in the level of oxidation for the annealed sample with Au electrodes, in possible accordance with the observation reported by Salazar et al. that Au causes the reduction of precursor MoO_x species used in MoS_2 growth, leading to the appearance of Mo in several different oxidation states and influencing the sulfidation and growth of layered MoS_2 structures.
MoS_2 strongly interacts with Au itself, inducing n-doping to the portion of MoS_2 that is in close contact with the metal while remote portions remain undoped. The phenomenon is more pronounced in the case of annealed samples and appears as a shift of the Au 4*f* doublet to higher BE from the energy window commonly reported for pure gold consequent to contact with MoS_2 and a further 0.3 eV shift to higher BE upon annealing of the Au-MoS_2 system (Figure 2d). Possible formation of Au–S bonding could also contribute to this shift to higher BE with both mechanisms acting to enhance electrical conduction between MoS_2 – bridged Au contacts.

For as grown samples a small Si 2*s* signal from the Si substrate is visible (Figure 2b), that is in agreement with the porous nature of the films observed in SEM micrographs (Figures 1c and 1d). This peak is significantly weakened upon annealing, due to material migration and structural rearrangement of the films. This becomes clearer with the aid of SEM topographies of Figure 1, where annealing is shown to induce material migration along the growth axis leading to the formation of a robust oligo-layer bottom followed by a porous surface away from the SiO_2/MoS_2 interface.

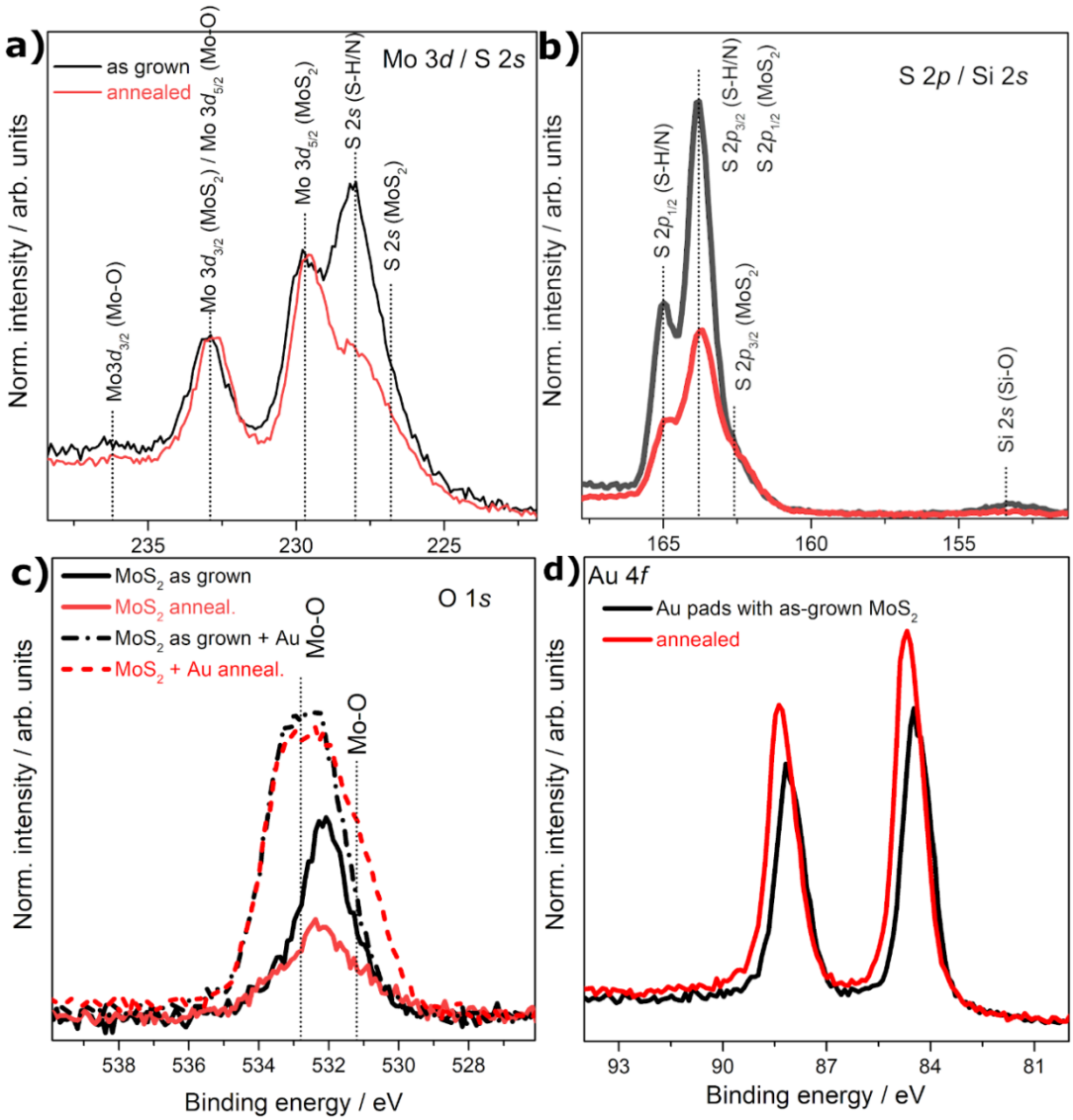


Figure 2. *a) Mo 3d and S 2s, b) S 2p and Si 2s, c) O 1s and d) Au 4f XPS core level spectra collected for as grown MoS_2 and the film after annealing at 550°C as well as for films deposited on Au-equipped chips. S 2s and S 2p contributions to signals are being highlighted to enable better visualization of energy shifts between sample signals.*

Task 2: Fabrication and characterization of MoS_2 thin film transistor structures utilizing a scheme of liquid gates and hybrid liquid-solid state 3D thin film topologies

In this task we follow an unconventional path to fabricate competitive state of the art flexible MoS_2 devices, namely, shaping and using on-site high-performance hybrid (liquid/solid state) MoS_2 channels directly inside amorphous precursors of relative impurity. To achieve this, a processing protocol involving low thermal budget annealing and ionic liquid doping was developed and applied. The active channel is shaped while being engraved in a multifunctional precursor matrix consisting of amorphous MoS_2 including MoO_x and non-bound sulfur species, as well as an ionic liquid filler. The latter serves simultaneously as gate dielectric, mobile carrier supplier and passivation layer for the channel. In this way an air stable self-encapsulating high mobility p-type channel is formed, making this approach effective, facile and scalable.

The annealed MoS_2 matrix 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. For this purpose, a μm-diameter droplet of copper phthalocyanine / butanol (CuPc/bu) ionic liquid is placed onto a MoS_2 FET device of global backgate topology and exposed channel matrix (Figure 3a). The ionic liquid droplet acts as

both a top gate and a top dielectric through the formation of an electric double layer as schematically depicted in Figure 3.

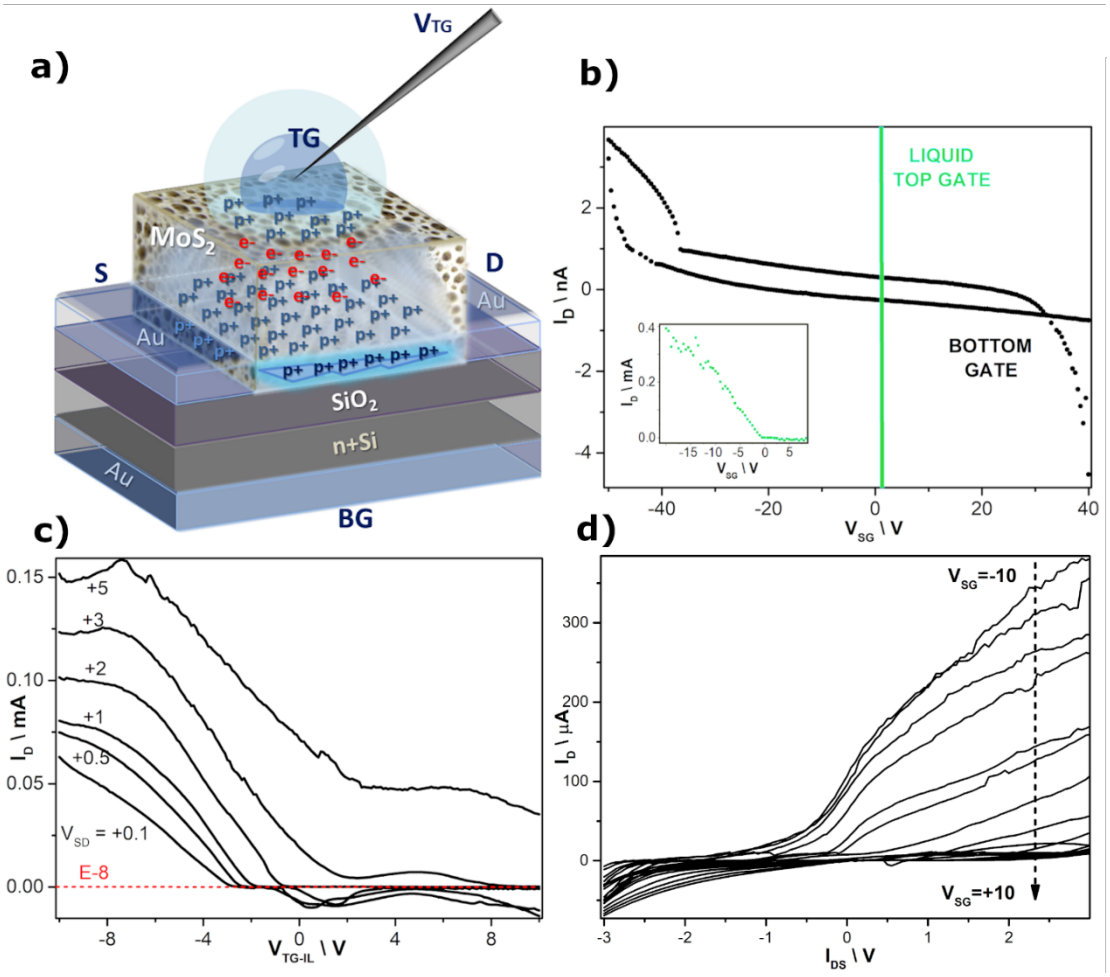


Figure 3. *a) Schematic of the formation of an electric double layer. b) DC characterization of a hysteresis loop for amorphous HW-grown MoS_2 transistors showing clear evidence of electron trapping and de-trapping during a full BG sweep (black curve). Transfer characteristics of the same device in CuPc/bu IL-top gated configuration in P-type operation (cyan curve). c) Transfer characteristics of the liquid-gated amorphous MoS_2 transistor for V_d varying from linear operation regime (V_d= 100 mV) to saturation. d) Respective Output characteristics.*

Electrical, spectroscopic and structural characterization, as well as theoretical modelling using the finite element method, is performed in order to gain further insight into the nature of MoS_2 physical and structural changes upon the utilized low thermal budget annealing, as well as into the ionic liquid/MoS_2 hybrid on-site channel formation and operation mechanisms.

With this technique, we achieve a low-lying contact resistance (R_c) of 2.6 kΩ·µm, which competes with the R_c values obtained on monolayer MoS_2 with engineered contacts. A high ON-current of 1.5×10^4 A for holes is achieved at room temperature in air for a 5 µm channel length liquid-gated FET at 2 V drain-to-source voltage (V_{DS}) and no back-gate overdrive. The low voltage field-effect mobility (μ_{FE}), determined to be 1.93×10^{-7} $cm^2V^{-1}s^{-1}$ in the annealed back-gated MoS_2 devices, is being boosted more than eight orders of magnitude to values as high as 45.8 $cm^2V^{-1}s^{-1}$ for the liquid-gated topology, competing with the mobilities of high quality polysilicon TFTs, that of the most competitive OFETs, dielectrically screened monolayer MoS_2, graphene/MoS_2 heterointerface FETs and graphene nanoribbon FETs, thereby paving a new way for fabricating high performance low cost flexible FETs. The device addresses the unattainability of p-type

conduction in MoS_2, thereby extending its pertinency to PN diodes and complementary integration logic. In addition, photo-enabled switching and memory functionality is demonstrated, while the devices are fabricated utilizing CMOS-compatible low energy expenditure, low thermal budget processes. 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 advanced 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.
Owing to the fact that CuPc is an intensive UV-Vis light absorber, the CuPc-containing IL top gated TFT can naturally realize photoswitching (Figure 4a) as well as non-volatile memory functions (Figure 4b) in a single cell. The response demonstrated in Figure 4b can be considered analogous to experience-based learning in synapses, rendering such devices a promising candidate for future MoS_2 transistor components that could electrically mimic the release and absorption of neurotransmitter ions in biological systems.

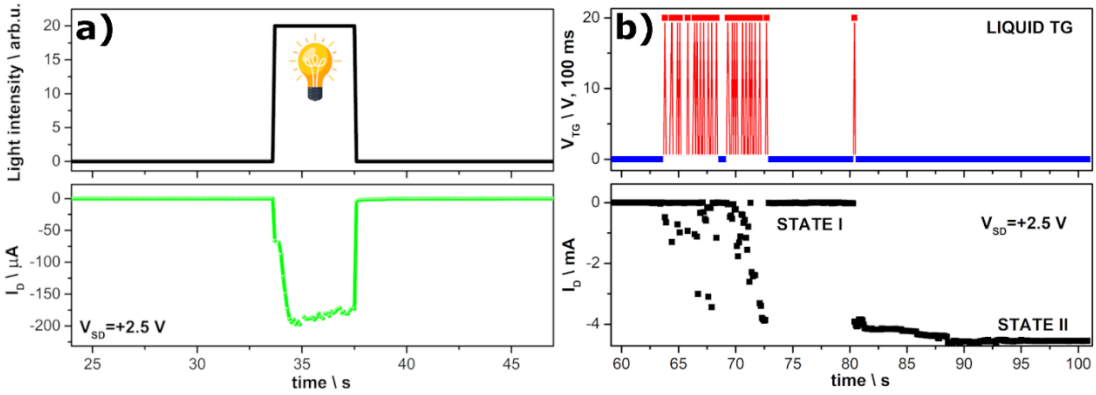


Figure 4. *Transient I_{SD} response of CuPc/bu IL-gated MoS_2 FETs in ambient conditions. The pulsed signals were applied to the liquid top gate and the response of the drain current (I_D) to these pulses was measured at a constant source-drain bias (V_{SD}=+2.5 V). a) I_{SD} upon application of a 4 s white light pulse from a xenon lamp, demonstrating real time photoresponse. b) I_{SD} response of the same cell upon a 20 V / 100 ms pulse train "training", highlighting non-volatile memory functionality, thus, the "learning" ability of the device.*

Task 3: Development of MoS_2 thin film sensors

The aim of this research is to examine hot-wire molybdenum disulphide ($hwMoS_2$) thin films as sensory materials in chemical sensors. The samples remain at room temperature during the growth of films rendering hot-wire deposition suitable for polymeric substrates. The sensing of hydrogen, carbon monoxide, moisture, acetone and other organic compounds is being investigated.
For the tests of the sensing properties, the $hwMoS_2$ films were packed in classic dual in-line packages (DIL) using the wire bonding technique. On the surface of the $hwMoS_2$ films a photoresist film was applied by spinning. Then interdigitated electrodes were opened followed by gold e-beam evaporation using titanium as adhesion layer. The sensing properties of the samples are tested using a home-made setup consisting of a small volume stainless steel chamber and a heater capable of reaching temperatures up to 500^{o}C. The gas concentrations are controlled by means of mass flow controllers. The sensors are stabilized in synthetic air before their exposure to gases (hydrogen, carbon monoxide, moisture, acetone etc). The current changes of the sensors are measured with an electrometer connected to a personal computer via a GPIB interface. This research is ongoing; important results have been obtained in 2021.

Funding

KRIPIS II (GSRT), 25.000 €.
ESPA (MIS 5047822) 2020-21, 50.050 €.

OUTPUT

Publications in International Journals

1. Balliou, A., Papadimitropoulos, G., Regoutz, A., Davazoglou, D. and Kouvatsos, D.N., "Low-cost high gain MoS_2 FETs from amorphous low mobility film precursors", submitted to ACS Applied Electronic Materials.

International Conference Presentations (invited, oral, poster)

2. Papadimitropoulos, G., Balliou, A., and Kouvatsos, D.N., "Growth of molybdenum sulphide ultra-thin films and their characterization", 17th International Conference on Nanosciences & Nanotechnologies (NN20), Thessaloniki, Greece, 7-10 July 2020.
3. Papadimitropoulos, G., Theodorakos, J., Zergioti, I. and Kouvatsos, D.N., "Laser annealing of amorphous molybdenum sulphide ultra-thin films", 17th International Conference on Nanosciences & Nanotechnologies (NN20), Thessaloniki, Greece, 7-10 July 2020.

PHOTONIC CRYSTALS, METAMATERIALS AND NOVEL RF SYSTEMS

Project Leader: Dr. 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 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 RF transceivers. Special emphasis in Internet of Things (IoT) and 5g/6g applications.

- **Activities and Main Results**
  - **A broadband polarized Artificial Magnetic Conductor metasurface**

New generations of mm-wave integrated radio transceivers offer very large bandwidths and data transmission speeds, leading to a multitude of 5g platforms and future 6g systems currently under study at even higher frequencies. Due to the high frequencies involved, antennas and arrays can for the first time be realistically integrated on the package of the transceivers, as the areas involved are commensurate with transceiver package sizes and, further, smart composite materials may also be integrated in these form factors. These possibilities are very promising for 5g and 6g networks but also for Internet of Things (IoT) applications that can be deployed in those bands [1].

Metamaterials are a class of artificially designed materials possessing important physical properties not found in natural homogeneous materials. One important class of metamaterials is Artificial Magnetic Conductors (AMC), possessing unique physical properties [2-4]. In the case of metal conductors, the reflection coefficient of electromagnetic waves $S_{11} \approx -1$ for all but optical frequencies, with the limiting value -1 corresponding to a Perfect Electric Conductor (PEC). Thus a PEC reflects perfectly all incident electromagnetic radiation but with a very special phase. This property has the important physical consequence that the total electric field on the surface of a metallic conductor has no tangential component, and that a good electric conductor creates images of opposite electric charge and current from those located in front of the conductor surface. AMC's, on the other hand, are novel artificial composite materials specifically designed to act as shields that totally reflect electromagnetic radiation, similar to electric conductors, but having the *opposite property* regarding the phase of the reflection coefficient S_{11}, i.e., $S_{11}(f) \approx +1$ for a specific band of frequencies $\{f\}$. AMC's *amplify* the tangential incident electric field by 100%, rather than canceling it as electric conductors do, and they create images of electric currents that have the same sign as the original excitations that illuminate them. Refs. [4-5] show how to embed antennas and AMC metamaterials on mm-wave in-package platforms for a completely integrated solution.

In this work we present a *polarization-sensitive* AMC material which is composed of a single surface of metallic scatterers printed on a dielectric substrate. This artificial monolayer behaves as a metasurface that has a polarization-dependent functionality: For a certain polarization of electromagnetic waves impinging on the metasurface the functionality is that of an AMC total reflector, while for the orthogonal polarization the monolayer behaves as a transparent filter. Thus, the metasurface exhibits birefringence. Polarization-dependent or anisotropic metamaterials are the subject of recent research activity for a variety of optical and microwave applications, such as polarization conversion, microwave lenses and tunable polarizers. To the best of our knowledge, this is the first time a birefringent AMC metasurface is presented. We have selected design parameters scaling the AMC behavior at mm-wave frequencies, but the design is frequency-scalable. A metasurface sample has been fabricated and characterized via Ka-band waveguide measurements which have validated the approach. We demonstrate the usefulness of this metasurface by an application consisting of co-located integrated antennas, exhibiting interesting properties relevant to current and future 5g/6g and IoT technologies.

- **A BIREFRINGENT AMC METASURFACE AT MM-WAVE FREQUENCIES**

The metasurface is composed of long metallic strips printed in the middle of a dielectric slab, with very narrow gaps between them. The dielectric material chosen in Rogers 3203, due to its low loss and fairly standard permittivity value. The relative complex permittivity of the dielectric is $\epsilon = 3.04(1 - j0.0016)$ and the metal strips are made out of Cu. The general layout of the optimized design, scaled to operate at the band [20-40]GHz, appears in Fig. 1a which shows 4 unit cells of the metasurface. The 1-dimensional unit cell of the metasurface consists of a dielectric slab which contains an embedded metal strip in the middle of the slab thickness, so that the material is symmetric with respect to the two external dielectric surfaces. The unit cell width is d=1.75mm, while the metal strip width is w=1.55mm. Hence, the gaps between metal strips are only 200 μm. The unit cell half-thickness (distance of metal strip from the dielectric slab surface) is t=1.525mm and the metal strip thickness is 35μm. We study the performance of the metasurface under plane-wave electromagnetic incidence, as shown in Fig. 1a. A similar performance can be obtained by studying the structure within the shielded environment of a rectangular waveguide. This set-up lends itself for a more accurate characterization of the fabricated samples and validation of the presented design.

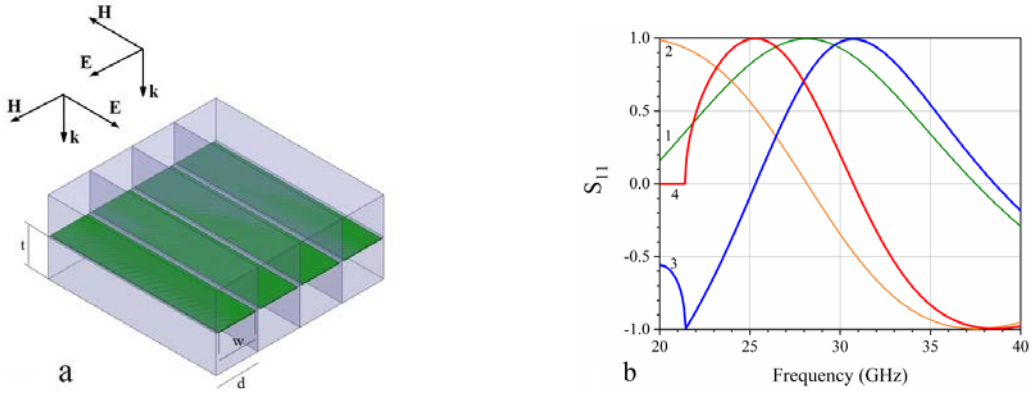


Fig. 1 (a) General layout of the metasurface. Four unit cells are shown with 1-dimensional periodicity d. Normal plane-wave incidence excitations shown, for parallel polarization (electric field vector parallel to the metal strips) and perpendicular polarization (electric field vector perpendicular to the metal strips). The length of the unit cells is infinite for the normal plane-wave incidence simulations. (b) Simulated complex reflection coefficients: $S_{11} = (1) + j(2)$ for normal plane-wave incidence; $S_{11} = (3) + j(4)$ for the TE_{10} waveguide excitation.

Fig. 1b shows theoretically simulated complex reflection coefficients for parallel polarization under plane-wave incidence and waveguide excitation. In both cases the metasurface acts as an AMC, reaching the perfect AMC limit of $S_{11}(f) \approx +1$ at around 30 GHz, which is the intended frequency band of operation in this work.

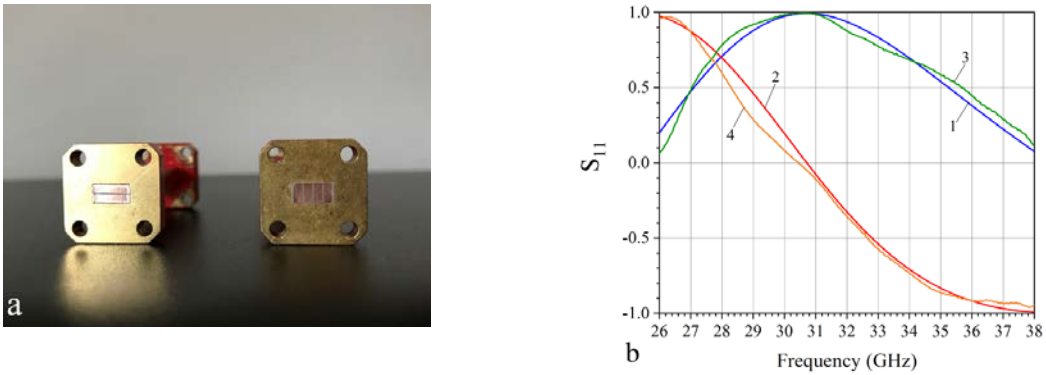


Fig. 2 (a) Photograph of the fabricated prototype samples inserted into the waveguide, for perpendicular (left) and parallel (right) polarizations. Half the monolayer sample, showing the printed metal strips, is shown. (b) Complex reflection coefficients for parallel polarization: Theoretical $S_{11} = (1) + j(2)$ versus measured $S_{11} = (3) + j(4)$ for the TE_{10} waveguide excitation.

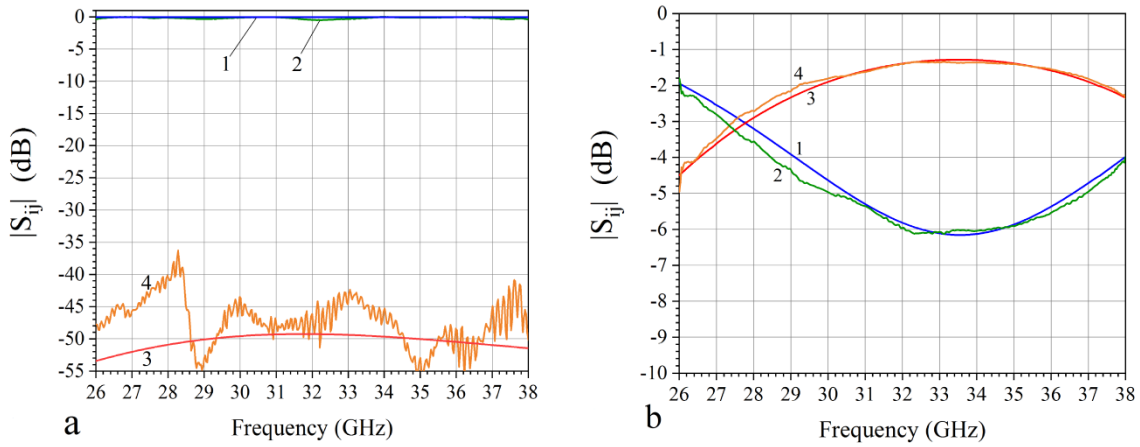


Fig. 3 (a) Parallel polarization amplitude of reflection coefficients $|S_{11}|$ (dB), for theoretical simulations (1) and measurements (2); Amplitude of transmission coefficients $|S_{21}|$ (dB), for theoretical simulations (3) and measurements (4). (b) Perpendicular polarization amplitude of reflection coefficients $|S_{11}|$ (dB), for theoretical simulations (1) and measurements (2); Amplitude of transmission coefficients $|S_{21}|$ (dB), for theoretical simulations (3) and measurements (4).

The results of Figs. 2, 3 validate the design of the metasurface and its functionality. In particular, Figs. 2b, 3a show that for parallel polarization the metasurface acts as a broadband AMC reflector reaching the perfect AMC limit at 31 GHz, while the magnitude of the reflection coefficient $|S_{11}|\approx$0dB, and that of the transmittion coefficient $|S_{21}|\approx$-50dB across the band. In contrast, for perpendicular polarization, Fig. 3b shows that the metasurface functions as a mostly transparent low-loss homogeneous dielectric. We should mention that the AMC functionality of the metasurface remains the same if we omit half of the dielectric layer in Fig. 1a (the back dielectric), and still consider the reflection coefficient at the front dielectric surface. In the measurements, we preferred to use the front-back symmetric sample which shows greater transparency, despite having twice the material thickness, because it is much less reflecting under perpendicular polarization.

APPLICATION ON ANTENNA TECHNOLOGY: Pattern-diversity of co-located dipoles integrated on the birefringent metasurface

We summarize a design of two dipoles perpendicularly collocated and integrated on the metasurface, and demonstrate the system's properties through full-wave numerical simulations. The overall system is shown in Fig. 4a.

The two dipoles are placed on top of 2 unit cells of the metasurface of Fig. 1a and are of different lengths, in order to be tuned at the same frequency, because each dipole orientation interacts differently with the underlying metal strips at the bottom. Notice that we have not included the dielectric behind the metal strips, since it is not needed for the responses of Figs. 2, 3, thus reducing the overall thickness of the metasurface by half. In Fig. 4b we show the return loss of the two antennas.

Both dipoles are tuned at the same frequency, designed to be the frequency of maximum AMC response of the metasurface, in Fig. 2b. In Fig. 4c we present the 3-dimensional radiation pattern of the system, when only the dipole perpendicular to the strips is firing. The figure shows the total radiation gain of the system (in dBi) at 31 GHz, with an orientation identical to that of Fig. 4a. This corresponds to the metasurface response of Fig. 3b, which is that of an essentially uniform and almost transparent dielectric slab. It is therefore not surprising that the radiation pattern is that of a standard dipole printed on a homogeneous low-loss

dielectric slab, radiating omnidirectionally with maximum gain 1.85 dBi, fully linearly polarized along the dipole direction, *despite the existence* of the underlying metallic strips occupying most of the substrate surface, which appear invisible.

Fig. 4d shows the corresponding 3-dimensional radiation gain of the system at 31 GHz, when only the dipole parallel to the strips is firing. This corresponds to the metasurface response of Figs. 2b, 3a, which is the functionality of an almost ideal AMC at that frequency. We see now that the pattern is very different from the omnidirectional pattern of Fig. 4c.

The dipole becomes a directional antenna, since the metasurface acts as a perfect AMC reflector, but without shorting the dipole printed on its surface, as would happen with an ordinary electric conductor. Hence, we obtain a directive beam of 6.2 dBi gain, a gain increase of 170% relative to the perpendicular dipole, and the front-to-back ratio of the antenna gain is about 15dB. Therefore, this becomes a very directive antenna with negligible back radiation, despite the fact that the whole system in Fig. 4a, including the AMC reflector area, has a very compact lateral size of about 1/3 wavelengths.

This system is of interest, because it demonstrates that antennas can be co-located on this metasurface and, due to the metasurface's designed birefringence, they can have complementary radiation properties which are very useful for increased channel capacity applications (such as pattern diversity) of multifunctional radiation links for both transmitters and receivers, while occupying modest areas. Such capabilities are important for novel IoT or RF harvesting systems.

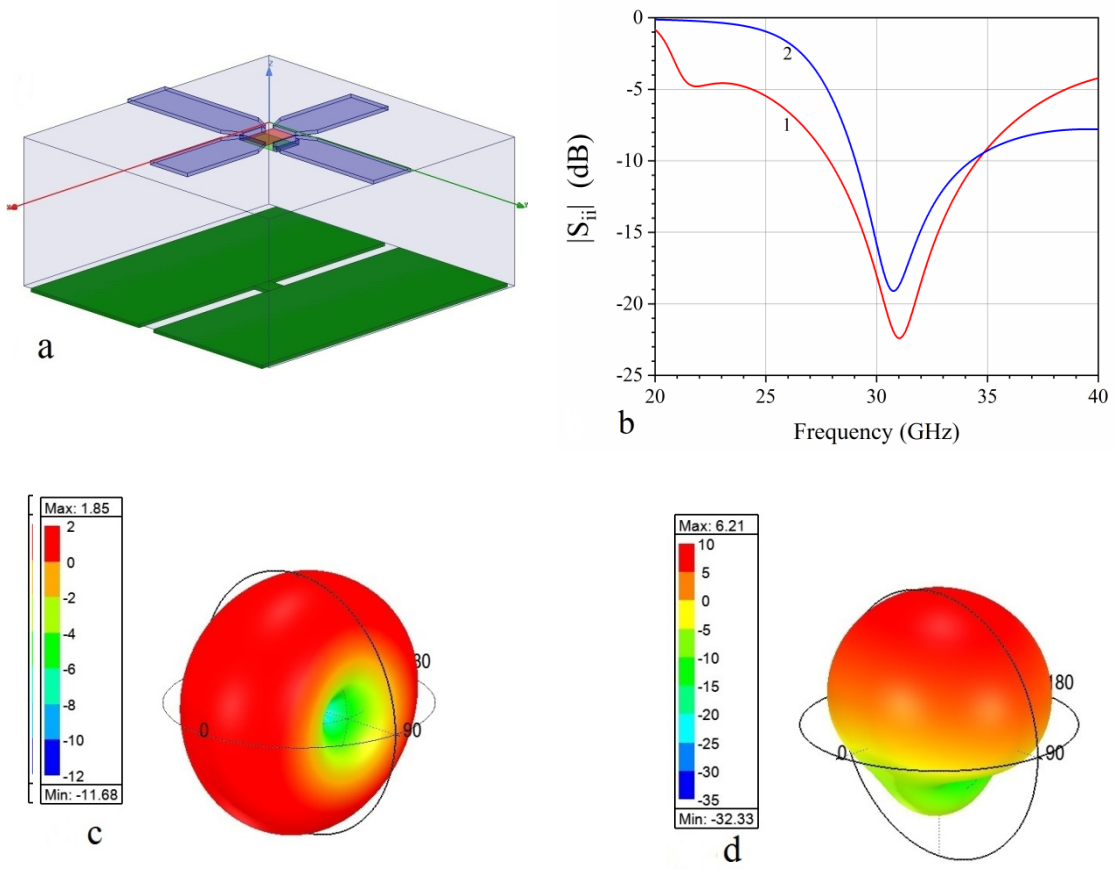


Fig. 4 (a) Two perpendicularly-collocated dipole antennas printed on the metasurface of Fig. 1a, without the back dielectric layer. (b) Perpendicular (1) and parallel (2) polarization amplitudes of reflection coefficients $|S_{ii}|$ (dB), for the two perpendicularly collocated dipoles on the metasurface of Fig. 4a. (c) 3-dimensional radiation gain pattern (in dBi), for the collocated dipoles of Fig. 4a when only the dipole perpendicular to the metasurface strips is firing. (d) 3-

dimensional radiation gain pattern, for the collocated dipoles of Fig. 4a, when only the dipole parallel to the metasurface strips is firing.

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OUTPUT

Publications in International Journals

1. Contopanagos H.F. A broadband polarized artificial conductor metasurface. *Journal of Electromagnetic Waves and Applications* **vol 34**, pp. 1823-1841 (2020). DOI: 10.1080/09205071.2020.1791259

Program 3

Magnetism and Superconductivity
Advanced Materials and Applications

CRYSTALLOGRAPHY AND COORDINATION CHEMISTRY OF MATERIALS

Project Leader: V. Psycharis

Permanent Research Staff: C.P. Raptopoulou

Post Docs: D. Dermitzaki

PhD Candidates: S. Tzani

Master Students: F. Fonti

Research Collaborators (emeritus or visiting): A. Terzis (former project leader)

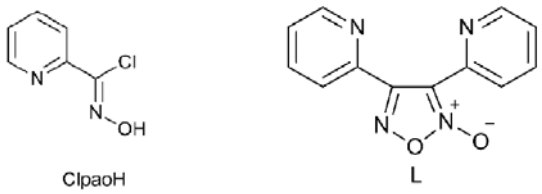
Objectives

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.

Activities and Main Results

In the work by Tsantis et al., *Inorganics* **8**, 47, (2020) it is shown that the reaction of pyridine-2-chloroxime (Scheme 1) and hydrated zinc(II) nitrate in methanol led to complex $[ZnCl_2(L)]$ (**1**) (Figure 1). containing the 3,4-di(2-pyridyl)-1,2,5-oxadiazole-2-oxide or di(2-pyridyl)furoxan ligand (L) (Scheme 1).



Scheme 1. *pyridine-2-chloroxime (ClpaoH) (right) and 3,4-di(2-pyridyl)-1,2,5-oxadiazole-2-oxide or di(2-pyridyl)furoxan ligand (L) (left).*

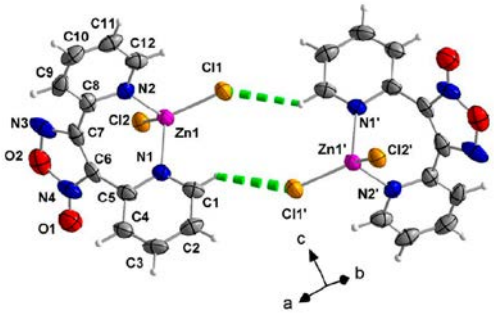


Figure 1. *Partially labeled Ortep plots of dimers in the structure of complex **1**. Dashed light green lines indicate intermolecular C1-H1···Cl1´ hydrogen bonds.*

The chloro ligands arise from ClpaoH. The tetrahedral complex exhibits interesting supramolecular features and was fully characterized by three techniques (IR, Raman and photoluminescence spectroscopies) in the solid state. In Figure 2a the Hirshfeld Surfaces (HSs) for the two molecules forming the dimer is presented, decorated with d_{norm} property in the orientation shown in Figure 1, with one of them presented in transparency mode. Figure 2b presents the fingerprint plot with the contribution for all type of interactions

and those related to hydrogen bonds contribute with 21.6, 16.7 and 12.5 % for Cl···H/H···Cl, O···H/H···O and N···H/H···N correspondingly. The pairs of red areas indicated with labels (A1, A2), [(B1, B2), (C1, C2)] and (D1, D2) in both figures correspond to the hydrogen bonds. The HS analysis reveal the intermolecular interactions of neighboring clusters through Cl···π interactions (Figure 2c) which results in the formation of stacks long a-axis (Figure 2e). The areas on the d_{norm} decorated surface where these types of interactions contribute are indicated with the white ellipse (acceptor area) and the pink one (donor area) (Figure 2a). These parts of HS correspond to Cl···C/C···Cl, Cl···N/N···Cl, Cl···O/O···Cl type of interactions (labeled as F, G, I in Figure 2b), they contribute 8.7, 2.8 and 2.0 % respectively, in the fingerprint plot of interactions of complex **1** and in the area indicated with an ellipse in Figure 2b. All the type of intermolecular interactions mentioned above (hydrogen bond type and Cl···π type) add up to a total of 64.3% contribution in the fingerprint plot. The rest 35.7%, are of H···H (12.2%), C···H (17.1%, labeled as E1, E2 at the characteristic wing shaped areas for these type of interactions, Figure 2b. The complementarity of the parts of neighboring complex contacts indicated with ellipses in Figure 2a, are also supported by the HS mapped with electrostatic potentials values (Figure 2d).

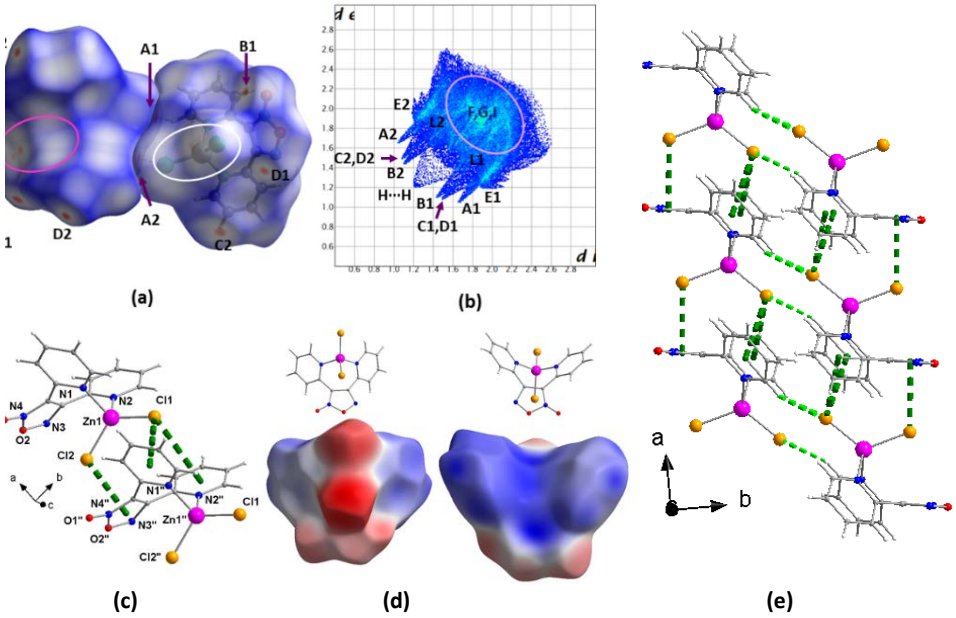
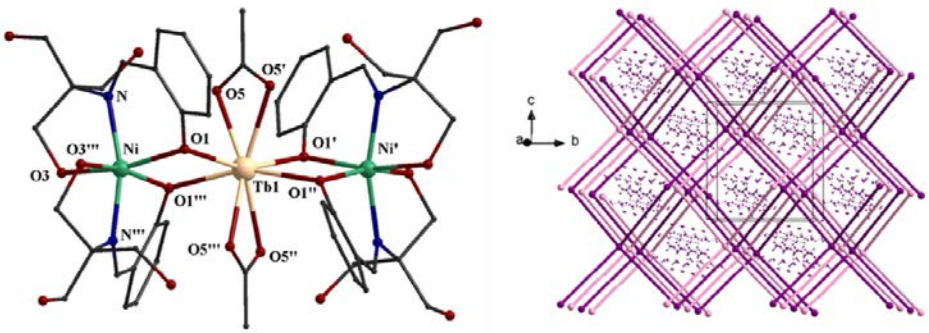


Figure 2. Hirshfeld surface analysis plots for compound **1**. **(a)** HS decorated with d_{norm} property. A1, B1 C1 and D1 points indicate the area of acceptor atoms and A2, B2, C2 and D2 the area of the hydrogen atom of the donors in the C(1)-H1···Cl(1)', C(10)-H(10)···O(1)', C(11)-H(11)···O(1) and C(3)-H(3)···N3' and hydrogen bonds respectively. Fingerprint plot: **(b)** for all type of interactions, with labels indicating the contribution for each type of interactions. **(c)** Cl···π intermolecular interactions indicated with thick green dashed lines. **(d)** Front and back view of the HS decorated with Electrostatic potentials. **(e)** Stack of dimer of complexes along a-axis formed through Cl···π intermolecular interactions indicated with thick green dashed lines.

The most salient feature of this work is the ClpaoH → L transformation during the reaction. Complex **1** is only the third structurally characterized compound containing L as a ligand. The two previously reported compounds $[Cu_2Cl_4(L)_2]$ and $[Cu(NO_3)_2(L)]$ (the latter has just been published) were prepared by completely different methods. The dinuclear complex was prepared by using the pre-synthesized ligand L, whereas the mononuclear compound was synthesized upon metal-assisted oxidation of a dioxime-type ligand. In all three complexes, L behaves as a $N_{pyridyl}$, $N'_{pyridyl}$-bidentate chelating ligand, forming an unusual seven-membered ring. From detailed DFT studies in MeOH (the solvent in which **1** was prepared), it is proposed that the formation of the Zn(II) complex occurs via an unprecedented, uncatalyzed cross-coupling reaction between two coordinated 2-pyridyl nitrile oxide ligands (pao). The presence of a base (Et_3N) is critical, because otherwise **1** cannot be isolated. Since the free ligand L is prepared from metal ion-free media, the in-situ generation of the coordinated L in **1** cannot be strictly considered as Zn^{II}-promoted/mediated. However, it

seems that the Zn^{II} center brings two 2-pyridyl nitrile oxide molecules (produced by dechlorination and deprotonation of ClpaoH) close enough, facilitating the ring formation of the 1,2,5-oxadiazole-2-oxide moiety, i.e., the cross-coupling reaction. Moreover, our study provides strong evidence of the belief that the C-functionalization of oximes proceeds via the generation of intermediate nitrile oxides.
Powder X-ray diffraction (PXRD) measurements were used to characterize magnetite nanoparticiples which were characterized with other techniques as well. The nanoparticles were used in the preparation of magnetic colloids in order to evaluate their heat efficiency through the measurement of their specific absorption rate (SAR) by using different methods (*Physica Medica* 2020, **71,** 39).
The amorphous content in pozzolanic material, used to study the leaching mechanism of hydraulic mortars as part of autogenic self-healing process, was estimated by using the PXRD method (*Journal of Cultural Heritage* 2020, **46**, 1).

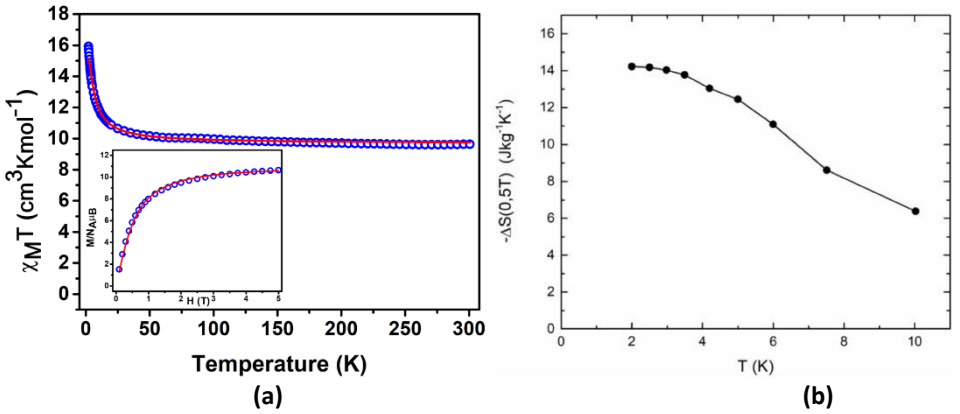
3d/4f heterometallic molecular magnetic materials. As part of our ongoing interest on the coordination chemistry of heterometallic 3d/4f complexes we have reported the trinuclear complexes $[Ni_2Ln(H_3L)_4(O_2CMe)_2](NO_3)$ (Ln = Sm (**2**), Eu (**3**), Gd (**4**), Tb(**5**)) where $(H_3L)^-$ is the monoanion of the Schiff base ligand H_4L, *o*-OH-C_6H_4-CH=N$(CH_2OH)_3$ (*Molecules* 2020, **25**, 2280, 17 pages, *invited feature paper for the Special Issue: Frontiers in Molecule based Magnets*). The complex cations contain the strictly linear Ni^{II}-Ln^{III}-Ni^{II} moiety (Figure 3a). The central Ln^{III} ion is bridged to each of the terminal Ni^{II} ions through two deprotonated phenolato groups from two different $(H_3L)^-$ ligands. Each terminal Ni^{II} ion is bound to two $(H_3L)^-$ ligands through their phenolato oxygen, the imino nitrogen atoms and one of the protonated alkoxo groups, in distorted octahedral N_2O_4 environment. The central lanthanide ion is coordinated to four phenolato oxygen atoms from the four $(H_3L)^-$ ligands, and four carboxylate oxygen atoms from two acetates which are bound in the bidentate chelate mode. The eight-coordination polyhedron around the Ln^{III} ion is square antiprism, SAPR-8.
The lattice structure of **5** is built due to hydrogen bonding interactions. Each trinuclear cluster acts as a 4-connected node and is linked to four neighboring clusters through eight hydrogen bonds which forms a 3D diamond like network. Each trinuclear cluster is translated along *a*-axis resulting in a second 3D diamond like network interacting weakly with the first one through Van der Waals forces, and thus the final architecture of the structure consists of two interpenetrating diamond like lattices (Figure 3b). The topology of each independent lattice is described by the 6^6 Well point symbol or with Schläfli symbol (6,4) and the overall structure as 2-fold based on the Bratten-Robson classification scheme or with topology **dia** belonging to Class **Ia**, with Translational Degree of interpenetration $Z_t = 2$ and translation along [1,0,0] (10.0634 Å) according to Blatov et al.



(a) ***(b)***

Figure 3. (a) *Partially labeled plot of the cationic part of **4**. Color code: Ni^{II} green; Tb^{III} tan; O red; N blue; C grey. Symmetry operations: (') 1.5-x, 0.5-y, z; ('') x, 0.5-y, 1.5-z; (''') 1.5-x, y, 1.5-z.* ***(b)*** *A small part of the 3D supramolecular network of **4** using only the nodes in the representation consisting of two interpenetrating diamond like lattices, indicated with pink and violet colors. In the channels formed along a-axis, the counteranion and the solvent molecules are hosted.*
*The magnetic properties of **2**-**5** were studied. For the {Ni_2Gd} complex **4**, the best fit of the magnetic susceptibility and isothermal M(H) data gave J_{NiGd} = +0.42 cm^{-1}, D = +2.95 cm^{-1} with $g_{Ni} = g_{Gd}$ = 1.98 (Figure 4a). The ferromagnetic nature of the intramolecular Ni···Gd interaction revealed ground state of total spin S = 11/2. The magnetocaloric effect (MCE)*

*parameters for **4** show that the change of the magnetic entropy -ΔS_m) reaches a maximum of 14.2 J kg^{-1} K^{-1} at 2 K (Figure 4b). A brief literature survey of complexes containing the Ni^{II}-Ln^{III}-Ni^{II} moiety is discussed in terms of their structural properties.*



(a) (b)

***Figure 4. (a)** Plot of the $\chi_M T$ vs T at 1000 Oe and M vs H at 2 K (inset) for **3**. Solid lines represent the best fit obtained with the magnetic model described in the text. **(b)** Plot of the maximum entropy change from 0 to 5 T, against temperature for **3**. Solid line is guide to the eye.*

A review summarizing the structural characteristics and magnetic properties of trinuclear complexes containing the Ni^{II}-Ln^{III}-Ni^{II} moiety and also oligonuclear complexes and coordination complexes containing the same trinuclear moiety has been published (*Crystals* 2020, **10**, 1117, 35 pages, *invited feature paper-review for the Special Issue: A 10 Years Journey: Chemical, Physical, and Biological Properties and Applications of Crystals*). The review refers to complexes with Schiff base ligands, reduced Schiff base ligands, oximato, β-diketonato, pyridyl ketone ligands and others. The compounds reported are restricted to those containing one, two and three oxygen atoms as bridges between the metal ions. Examples of carboxylato and oximato bridging complexes are also discussed due to structural similarity. The magnetic properties of the complexes range from ferro- to antiferromagnetic depending on the nature of the lanthanide ion.

- **Funding**
  - 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 2020 (11 months): 12000 €.
  - Characterization of polycrystalline materials with X-ray Powder Diffraction Method, mainly from QC and RND departments of Pharmaceutical Industries. Income: 69.595,00 € for 2020.

OUTPUT

Publications in International Journals

1. Anyfantis, G.C., Ioannou, A., Barkaoui, H., Abid, Y., Psycharis, V., Raptopoulou, C.P., Mousdis, G.A. "Hybrid halobismuthates as prospective light-harvesting materials: Synthesis, crystal, optical properties and electronic structure", *Polyhedron* **175**, 114180 (10 pages) (2020). DOI: 10.1016/j.poly.2019.114180
2. Stamos, N.-A., Ferentinos, E., Chrysina, M., Raptopoulou, C.P., Psycharis, V., Sanakis, Y., Pantazis, A., Kyritsis, P., Mitrikas, G. "Unusual ^{31}P Hyperfine Strain Effects in a Conformationally Flexible Cu(II) Complex Revealed by Two-Dimensional Pulse EPR Spectroscopy", *Inorg. Chem.* **59**, pp. 3666-3676 (2020) DOI: 10.1021/acs.inorgchem.9b03237

3. Georgopoulou, A.N., Pissas, M., Psycharis, V., Sanakis, Y., Raptopoulou, C.P. "Trinuclear Ni^{II}-Ln^{III}-Ni^{II} complexes with Schiff base ligands: Synthesis, structure, and magnetic properties" *Molecules* **25**, art.n. 2280 (16 pages) (2020) DOI: 10.3390/molecules25102280
4. Lioli, E., Psycharis, V., Raptopoulou, C.P., Efthimiadou, E.K., Mitsopoulou, C.A. "Synthesis, characterization, DNA binding and cytotoxicity studies of two novel Cu(II)-2-(2'pyridyl)quinoxaline complexes" *J. Inorg. Biochem.* **208**, 111077 (14 pages) (2020) DOI: 10.1016/j.jinorgbio.2020.111077
5. Tsantis, S.T., Bekiari, V., Tzimopoulos, D.I., Raptopoulou, C.P., Psycharis, V., Tsipis, A., Perlepes, S.P. "Reactivity of coordinated 2-pyridyl oximes: Synthesis, structure, spectroscopic characterization and theoretical studies of dichlorodi{(2-pyridyl)furoxan}zinc(II) obtained from the reaction between zinc(II) nitrate and pyridine-2-chloroxime" *Inorganics* **8**, 47 (20 pages) (2020) DOI: 10.3390/inorganics8090047
6. Raptopoulou, C.P. "Heterometallic complexes containing the Ni^{II}-Ln^{III}-Ni^{II} moiety – Structures and magnetic properties" *Crystals*, Special Issue: A 10 years journey: Chemical, Physical, and Biological Properties and Applications of Crystals, (Feature Paper, Review) **10**, 1117 (35 pages) (2020) DOI: 10.3390/cryst10121117
7. Amenta, M., Karatasios, I., Psycharis, V., Maravelaki, P., Kilikoglou V. "The leaching mechanism of hydraulic mortars as part of autogenic self-healing process" *Journal of Cultural Heritage* **46**, 1 (10 pages) (2020) DOI:10.1016/j.culher.2020.06.012
8. Papadopoulos, C., Efthimiadou, E.K., Pissas, M., Fuentes, D., Boukos, N., Psycharis, V., Kordas, G., Loukopoulos, V.C., Kagadis G.C. "Magnetic fluid hyperthermia simulations in evaluation of SAR calculation methods" *Physica Medica* **71,** 39 (14 pages) (2020) DOI: 10.1016/j.ejmp.2020.02.011

Teaching and Training Activities

Psycharis, V.

Powder X-ray Diffraction, 1 day (23-10-2020)

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.

Master Dissertations completed in 2020

Name: FANI FONTI

Dissertation Title: Synthesis and structural characterization of Ni^{II} coordination polymers with neutral aromatic ligands with N-donor ligands

Research Supervisor at NCSR: C.P. Raptopoulou

University where the Thesis was presented: National and Kapodistrian University of Athens

Patents

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

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

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.

Activities and Main Results

Electronic Structure of Tyrosyl D radical of 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 Evolving Complex (OEC), contains an inorganic Mn_4CaO_5 cluster whose catalytic cycle involves four light-driven 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. 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 (see figure 1 for its cw EPR spectrum). 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. A 2D-HYSCORE investigation in functional PSII of spinach was undertaken in collaboration with Dr G. Mitrikas, INN, in order to determine the electronic structure of Y_D• radical. The hyperfine couplings of the protons that interact with the Y_D• radical were determined and the relevant assignment was provided. 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 were discussed.

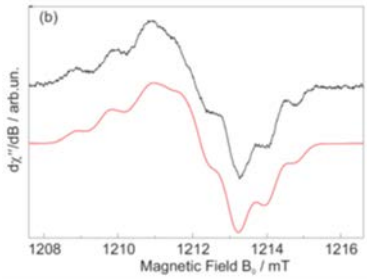


Figure 1. Q-band cw EPR spectrum of YD•at *T* = 160 K. Black trace: experiment. Red trace: simulation. Both spectra were simulated with(*gx*, *gy*, *gz*)=(2.0075, 2.0042, 2.0020).

Spin trapping of ROS produced by visible light illumination of graphitic carbon nitride. Graphitic carbon nitride (g-C_3N_4) has emerged as one of the most promising visible light active photocatalysts. The group of Dr Christos Trapalis at INN created Torus shaped g-C_3N_4 particles for first time via flame spray pyrolysis (FSP) process and tested them for photocatalytic H_2 production under visible light irradiation. It was found that the precursor dispersion concentration is important for the particles final morphology as diverse shapes can be obtained. It was established that the FSP process affects the surface functional groups, while the main g-C_3N_4 network is preserved. The improved H_2 evolution rate was 33.06–41.18 μmol/g/h. The EPR spin trapping results which are illustrated in Figure 2 clearly indicate that under visible light illumination g-C_3N_4 generates superoxide radicals ($O_2^{\bullet -}$) due to the reaction of the CB electrons with dissolved O_2. The exfoliated samples (Exf) demonstrated superior superoxide radical formation in comparison with Bulk and FSP1.5, owing to its higher specific surface area (SSA) and total pore volume V_p that provide abundant active sites.The electron reactivity measurements showed that the exfoliated g-C_3N_4 cause faster chemical reduction of TEMPO to TEMPOH in comparison to the other two materials. Similarly to the EPR spin trapping observations, the rate of TEMPO reduction slightly decreases for sample FSP1.5, indicating that the SSA and V_p of the materials are again the main factors that influence the charge separation efficiency.

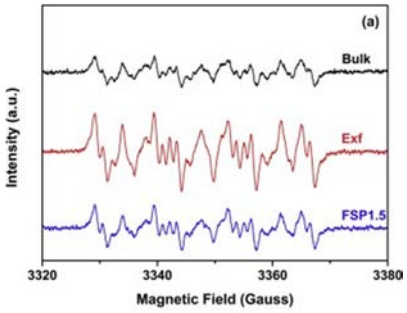


Figure 2. Detection of radical adducts of DMPO upon illumination with visible light.

Spin trapping of radicals during UVA photolysis of chlorinated water. The UV-A/Chlorine process, a promising advanced oxidation process (AOP), was evaluated for the removal of 2-isopropyl-3-methoxy pyrazine (IPMP), a widely reported compound that causes unpleasant taste and odor when present in water at or below the ng L^{-1} level. Experiments performed by the group of Dr Hiskia (INN) concluded that the studied process was efficient for the removal of IPMP in both ultrapure and drinking water. The initial chlorine dosage influenced significantly the degradation efficiency under initial neutral pH values. Degradation efficiency of IPMP was slightly inhibited by using drinking water as matrix. Scavenging experiments highlighted the significant role of various reactive species (e.g. $HO^{\bullet}$, $ClO^{\bullet}$, $Cl^{\bullet}$, $Cl_2^{\bullet -}$) generated during the process that have not been studied comprehensively until now. In addition, the significant role of $HO^{\bullet}$ was further verified by Electron paramagnetic resonance spectroscopy (EPR) experiments (Figure 3).

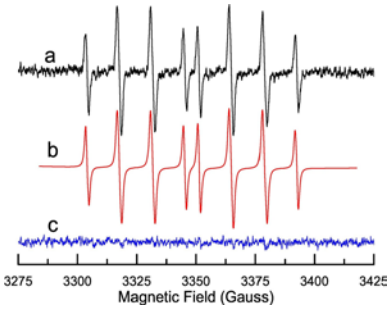


Figure 3. Detection of the hydroxyl adduct of DEPMPO upon illumination of aqueous NaOCl with UV-A light. irradiated, trace (a). Spectral fit of the DEPMPO – hydroxyl adduct species, trace (b). without irradiation, trace (c).

Characterization of nanoparticles prepared by the Flame Spray Pyrolysis (FSP) Method. In collaboration with the group of Prof. Y. Deligiannakis, University of Ioannina, we applied variable temperature Mössbauer Spectroscopy and variable temperature magnetic measurements in order to characterize bismuth iron oxide nanoparticles prepared by the FSP method. In figure 4 we show the room temperature Mössbauer spectra from samples prepared by FSP before and after annealing at 700 °C for 60 min. Prior to annealing the room temperature spectrum comprises a doublet characteristic of Fe^{3+}. Upon annealing the spectrum comprise two quadrupole doublets at 1:1 ratio with parameters $\delta(1)$=0.24 mm/s, $\Delta E_Q(1)$ = 0.98 mm/s and $\delta(2)$ = 0.36 mm/s, $\Delta E_Q(2)$=0.38 mm/s. These doublets constitute the fingerprint for the $Bi_2Fe_4O_9$ phase. In this phase

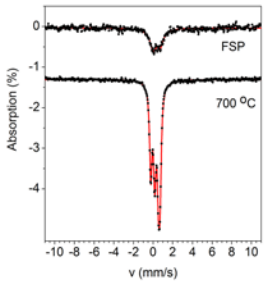


Figure 4. Mossbauer spectra from bismuth iron oxide nanoparticles before and after annealing at 700 °C.

the ferric ions occupy two distinct sites of which one is tetrahedral and one is octahedral. Doublet 1 is attributed to the tetrahedral site whereas doublet 2 is attributed to the octahedral site. Notably, the intensity of the Mössbauer absorption in the case of the as prepared sample is much smaller than the intensity of the spectrum in the annealed sample. These observations suggest that the recoilless fraction in the as prepared sample by the FSP method is remarkably smaller in comparison with the post-treated sample. In figure 5 we show the variable temperature Mössbauer spectra from the annealed samples at zero external magnetic field. Down to 250 K the spectra comprise the two paramagnetic doublets discussed above. Below ~245 K the sample exhibits magnetic hyperfine spectra implying an antiferromagnetic transition. The hyperfine magnetic field increases as the temperature decreases and at 4.2 K the spectrum comprises two sextets at a 1:1 ratio. These sextets are fitted with the following parameters: $\delta(1)$=0.36 mm/s, H(1) = 469 kG and $\delta(1)$=0.49 mm/s, H(2) = 507 kG and are assigned to the tetrahedral and octahedral ferric sites.

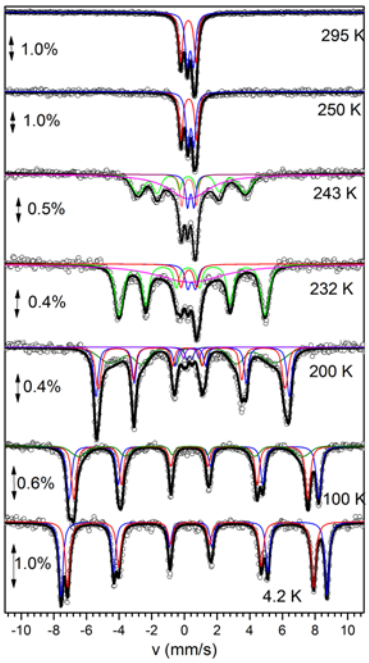


Figure 5. Mössbauer spectra from bismuth iron oxide nanoparticles after annealing at 700 °C at the indicated temperatures.

In figure 6 we show the

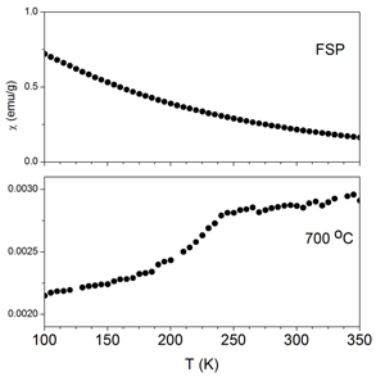


Figure 6. Temperature dependence of χ from Bismuth iron oxide nanoparticles before and after annealing at 700 °C.

temperature dependence of the magnetic susceptibility χ in the 100-350 K range in the presence of a magnetic field of 0.1 kOe from the FSP bismuth iron oxide nanoparticles before and after annealing at 700 °C. The two samples behave differently. Before annealing the sample exhibits a paramagnetic like behavior. After annealing the sample exhibits a cusp at ~245 K which is consistent with the Neel temperature for AF transition for the $Bi_2Fe_4O_9$ phase in agreement with the variable temperature Mössbauer spectra. Similar studies have been carried out with bismuth iron oxide nanoparticles prepared by the FSP method under varying conditions.

Heterometallic 3d-4f clusters. In collaboration with the group of Prof. A. Tasiopoulos, University of Cyprus and Prof. Spyros Perlepes, University of Patras we studied the magnetic and electronic properties of a series of heteronuclear 4f-3d clusters. In figure 7 we show a plot of

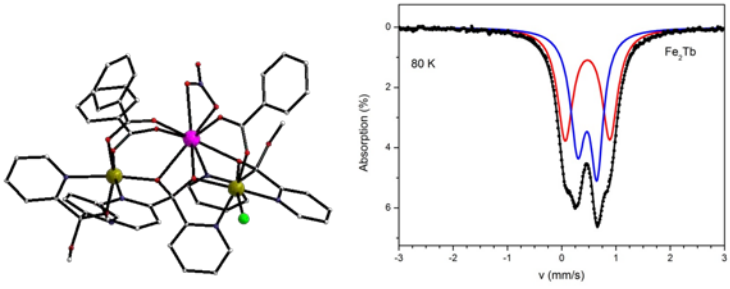


Figure 7. *Left. The crystal structure of a cluster with the general formula $[Fe_2LnCl(PhCO_2)_3((py)_2CO_2)((py)_2C(OMe)O)_2(NO_3)]MeCN$ (Ln= Gd, Dy, Ho, Tb). Right: The Mossbauer spectrum of the Fe_2TbCl cluster at 80K.*

such a cluster with the general formula Fe_2LnCl. In these clusters the iron sites are found in two distinct coordination environments (O_3N_2Cl and O_4N_2). In figure 8 we show the Mössbauer spectrum recorded at 80 K of the Fe_2TbCl cluster. The spectrum comprises two quadrupole doublets at a 1:1 ratio with parameters $\delta(1)$ = 0.47 mm/s and $\Delta E_Q(1)$ = 0.83 mm/s and $\delta(2)$ = 0.47 mm/s and $\Delta E_Q(2)$ = 0.36 mm/s. The isomer shift values for both doublets indicate a high spin ferric ion in an octahedral environment. Doublet 1 with the largest ΔE_Q is attributed to the O_3N_2Cl site and doublet 2 with the smallest ΔE_Q to the O_4N_2 site. Similar spectra are obtained for the other members of this family.

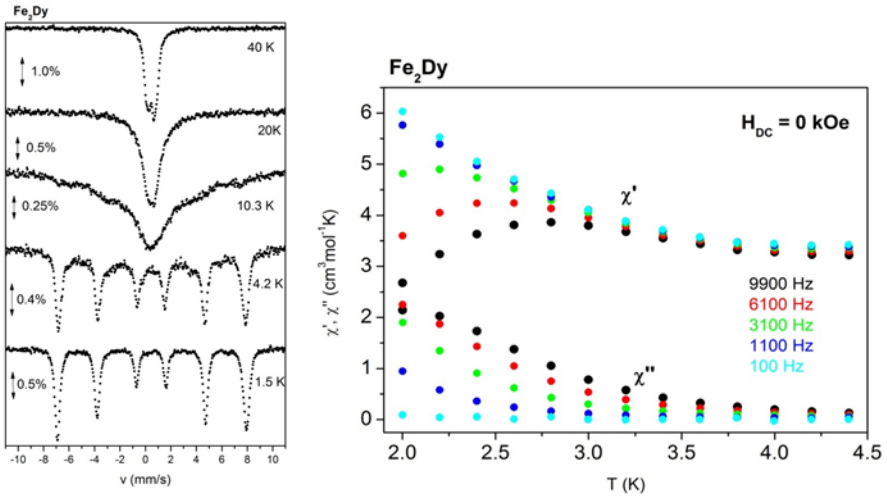


Figure 9. *Left. Temperature dependence of Mössbauer spectra from the Fe_2DyCl cluster in the absence of an external magnetic field. Right. Temperature dependence of the real (χ') and imaginary (χ'') parts of the magnetic susceptibility at the indicated frequencies and at zero external dc magnetic field.*

We studied the dynamic magnetic properties of this class of clusters by variable temperature Mössbauer spectroscopy and ac magnetic susceptibility measurements. As an example, in figure 9 we show the Mössbauer spectra from powder samples of the Fe2DyCl cluster in the 1.5 - 40 K temperature range. Below 40 K the spectra exhibit a line broadening and below 10 K the spectrum comprises a magnetic sextet. This behavior indicates the onset of slow magnetic relaxation with the spin relaxation time becoming longer than the characteristic time of the Mossbauer technique (10^{-7} sec) below 4.2 K. The ac magnetic susceptibility measurements indicate the emergence of frequency dependent non zero χ'' signals below ~3.5 K. A detailed analysis of the frequency and temperature dependence of χ' and χ'' allowed for the determination of the temperature and magnetic field dependence of the spin relaxation time. Similar studies are conducted for the other members of the Fe_2LnCl family of the heterometallic 4f-3d clusters and it is found that their magnetic relaxation properties are dependent upon the lanthanide ion.

Funding

- ELKE-11143, "Helium Liquefaction and Low Temperature Spectroscopy" (services).
- Operational Programme “Human Resources Development, Education and Lifelong
- Learning 2014–2020 (EDBM). “Photosynthetic Water Splitting: The Critical Stages before Oxygen Release” (MIS 5047814).
- Foundation of Research Promotion, Cyprus, EXCELLENCE/1216/0076 Multifunctional Metal Organic Frameworks and the Fine Tuning of their Magnetic, Photoluminescence and Sorption Properties through Single - Crystal Ligand Exchange Reactions.

OUTPUT

Publications in International Journals

1. Mitrikas, G., Sanakis, Y., Ioannidis, N. Parallel-Mode EPR of Atomic Hydrogen Encapsulated in POSS Cages. *Applied Magnetic Resonance* **51 (11)**, pp. 1451–1466 (2020). DOI:10.1007/s00723-020-01263-5
2. Todorova, N., Papailias, I., Giannakopoulou, T., Ioannidis, N., Boukos, N., Dallas, P., Edelmannová, M., Reli, M., Kočí, K., Trapalis, C. Photocatalytic H_2 evolution, CO_2 reduction, and NOX oxidation by highly exfoliated g-c3n4. *Catalysts* **10 (10)**, pp. 1–27 (2020). DOI:10.3390/catal10101147
3. Antonopoulou, M., Ioannidis, N., Kaloudis, T., Triantis, T.M., Hiskia, A. Kinetic and mechanistic investigation of water taste and odor compound 2-isopropyl-3-methoxy pyrazine degradation using UV-A/Chlorine process. *Science of the Total Environment* **732**, 138404 (2020). DOI: 10.1016/j.scitotenv.2020.138404
4. Matsia, S., Menelaou, M., Hatzidimitriou, A., Tangoulis, V., Lalioti, N., Ioannidis, N., Blömer, L., Kersting, B., Salifoglou, A. Temperature-Sensitive Structural Speciation of Cobalt-Iminodialcohol-(N,N'-Aromatic Chelator) Systems: Lattice Architecture and Spectrochemical Properties. *European Journal of Inorganic Chemistry* **2020 (30)**, pp. 2919–2940 (2020). DOI:10.1002/ejic.202000435
5. Papailias, I., Todorova, N., Giannakopoulou, T., Ioannidis, N., Dallas, P., Dimotikali, D., Trapalis, C. Novel torus shaped g-C_3N_4 photocatalysts. *Applied Catalysis B: Environmental* **268**, 1187332020 (2020). DOI: 10.1016/j.apcatb.2020.118733
6. Ibrahim, I., Kaltzoglou, A., Athanasekou, C., Katsaros, F., Devlin, E., Kontos, A. G., Ioannidis, N., Perraki, M., Tsakiridis, P., Sygellou, L., Antoniadou, M., Falaras, P. Magnetically separable TiO2/CoFe2O4/Ag nanocomposites for the photocatalytic reduction of hexavalent chromium pollutant under UV and artificial solar light. *Chemical Engineering Journal* **381**, 122730 (2020). DOI: 10.1016/j.cej.2019.122730
7. Sanakis, Y., Krzystek, J., Maganas, D., Grigoropoulos, A., Ferentinos, E., Kostakis, M. G., Petroulea, V., Pissas, M., Thirunavukkuarasu, K., Wernsdorfer, W., Neese, F., Kyritsis P. Magnetic Properties and Electronic Structure of the S = 2 Complex $[Mn^{III}\{(OPPh_2)_2N\}_3]$ Showing Field-Induced Slow Magnetization Relaxation *Inorg. Chem.* **59**, 13281-13294 (2020) DOI: 10.1021/acs.inorgchem.0c01636.
8. Georgopoulou, A. N., Pissas, M., Psycharis, V., Sanakis, Y., Raptopoulou C. P. Trinuclear Ni^{II}-Ln^{III}-Ni^{II} Complexes with Schiff Base Ligands: Synthesis, Structure, and Magnetic Properties *Molecules* **25**, 2280. DOI:10.3390/molecules25102280.
9. Stamos, N-A, Ferentinos, E., Chrysina, M., Raptopoulou, C. P., Psycharis, V., Sanakis, Y., Pantazis, D. A., Kyritsis, P., Mitrikas, G. Unusual ^{31}P Hyperfine Strain Effects in a Conformationally Flexible Cu(II) Complex Revealed by Two-Dimensional Pulse EPR Spectroscopy. *Inorg. Chem.* **59,** 3666−3676 (2020) DOI: 10.1021/acs.inorgchem.9b03237
10. Sanakis, Y., Pissas, M., Krzystek, J., Ozarowski, A., Telser, J., Raptis, R. G. Ferromagnetically-coupled, triangular, $[Bu_4N]_2[Cu^{II}_3(\mu_3\text{-}Br)_2(\mu\text{-}4O_2N\text{-}pz)_3Br_3]$ complex revisited: The effect of coordinated halides on spin relaxation properties *Polyhedron*, **177**, 114258 (2020) DOI: 10.1016/j.poly.2019.114258
11. Varouti, E., E. Devlin, E., Sanakis, Y., Pissas, M., Christides, C., Tomara, G.N., Karahaliou, P.K., Georga, S.N., Krontiras C.A. A systematic Mössbauer spectroscopy study of $Y_3Fe_5O_{12}$ samples displaying different magnetic ac-susceptibility and electric permittivity spectra *J. Magn. Magn. Materials***, 495,** 165881 (2020) DOI: 10.1016/j.jmmm.2019.165881
12. Halevas E., Pekou. A., Papi, R., Mavroidi, B., Hatzidimitriou, A. G., Zahariou, G., Litsardakis, G., Sagnou, G., Pelecanou, M. Pantazaki, A. Synthesis, physicochemical characterization and biological properties of two novel Cu(II) complexes based on natural products curcumin and quercetin *J. Inorg. Biochem.* **208**, 111083 (2020) DOI: 10.1016/j.jinorgbio.2020.111083

International Conferences Presentations (invited, oral, poster)

1. Chrysina, M., Zahariou, G. 2D-Hyperfine Sublevel Correlated Investigation of the Tyrosyl Radicals of Photosystem II", Athens Conference on Advances in Chemistry, 10-14 March 2020, Athens, Greece. Oral presentation

Teaching and Training Activities
Yiannis Sanakis
Graduate course "Molecular Magnetism", Spring 2020, 3 hrs
University of Ioannina

NANOFUNCTIONAL AND NANOCOMPOSITE MATERIALS LABORATORY

Project Leader: Christos Trapalis

Permanent Research Staff: Christos Trapalis

Other Staff (scientific): Tatiana Giannakopoulou, Nadia Todorova

Post Docs: Ilias - Ioannis Papailias, Niki Bardi, Dimitra Magadouka

PhD Candidates: Sofia Karapati, Niki Plakantonaki, Michalis Vagenas

Master Students: Georgios Brouzos

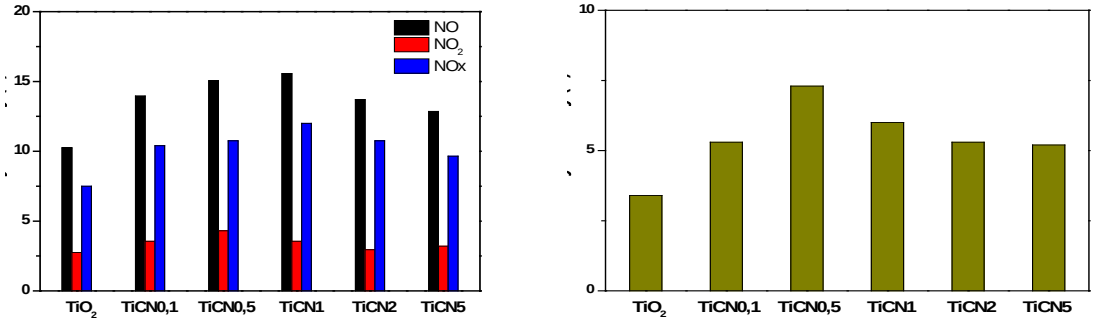
Objectives

- Development of novel photocatalytic coatings for air pollutants oxidation and antibacterial applications.
- CO_2 waste gases conversion to valuable solid-state nanocarbons.
- Novel Electrochemical Processes and nanocarbon electrodes for water desalination.
- Evaluation of desalination performance of different electrode materials
- Synthesis and characterization of Conductive Polymer/Carbon nanocomposite materials
- 2D MXene nanocrystals for antistatic, photocatalytic and antibacterial coatings.
- Synthesis of 2D MXenes and estimation of their EMI shielding effectiveness.
- CNTs and graphene-based composites for one-dimensional (1D) and two-dimensional (2D) 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. Novel photocatalytic coatings for air pollutants oxidation and antibacterial applications

Novel photocatalytic coatings were prepared in collaboration with NanoPhos SA, by adding small amounts of g-C_3N_4 into a known commercial product. The resulting suspensions were deposited on a-block substrates of suitable dimensions using the Z-020-Tornador BLACK sprayer and then studied for air pollutants oxidation and antibacterial activity. As can be seen in Fig. 1, the addition of g-C_3N_4



1. Photocatalytic activity of the coatings for NOx removal (left) and acetaldehyde oxidation (right).

significantly enhances the photocatalytic activity of the coatings. Particularly under visible light irradiation, the TiCN0.5 and TiCN1 coatings show twice the activity of the commercial TiO_2 coating, both for NOx removal and acetaldehyde oxidation. As it stands, addition of just 0.5 wt% of g-C_3N_4 is sufficient for the improvement of the photocatalytic activity. The colonies grown in petri-dishes under dark and visible light irradiation are shown in Fig 2. As can be seen, after irradiation the coated samples show almost three times fewer colonies than the non-coated samples. This activity is attributed to the photogenerated $^{\bullet}O_2^-$ and $^{\bullet}OH$ radicals that are formed on the surface of the photocatalysts. These radicals are responsible for the oxidative "stress" against the microorganisms, thus leading to the reduction of the grown colonies.

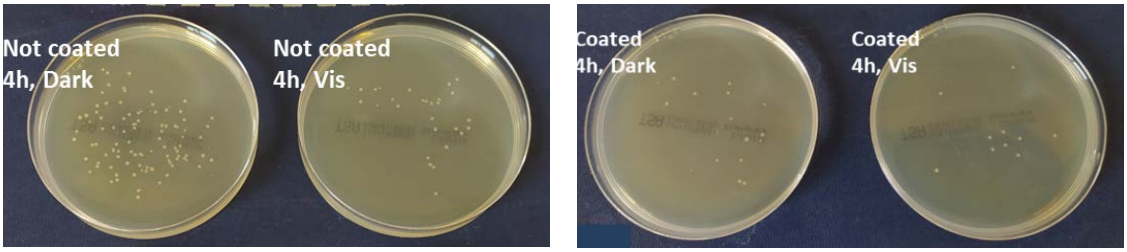
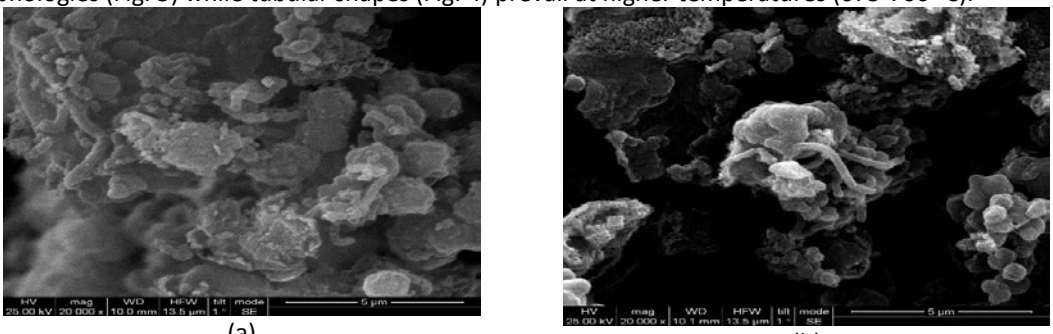


Fig. 2. *Colonies grown under dark and visible light irradiation, for the non-coated (left) and the coated (right) a-block samples.*

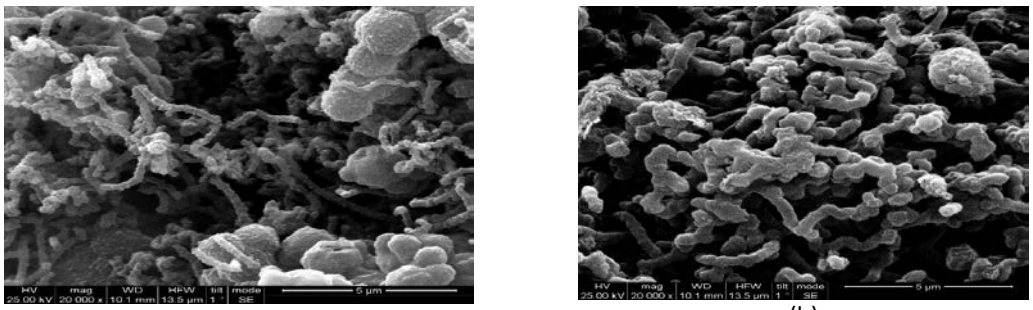
2. CO_2waste gases conversion to valuable solid-state nanocarbons

The reduction of gaseous CO_2 using metallothermic technique with Mg reducing agent was carried out. Different reduction temperatures in a wide range from 600 to 1000 ^{o}C were examined. The work demonstrates the formation of a variety of carbon morphologies that include graphene, tubular and spherical nanocarbons. At temperatures lower than the melting point of Mg (650 ^{o}C), graphenic carbons and spherical morphologies are the predominant morphologies (Fig. 3) while tubular shapes (Fig. 4) prevail at higher temperatures (675-700 ^{o}C).



(a) (b)

3. *SEM micrographs for samples prepared at 600 (a) and 650 ^{o}C and CO_2 flow rate of 20 mL/min.*



(a) (b)

Fig4. *SEM micrographs for samples prepared at 675 (a) and 700 ^{o}C and CO_2 flow rate of 80 mL/min.*

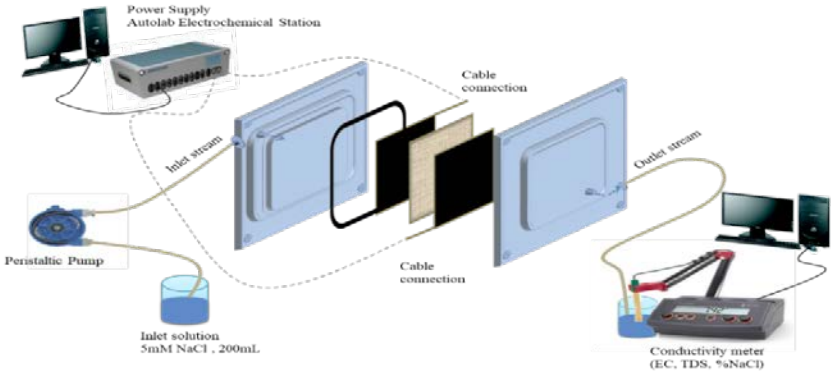
In the range of 800-1000 ^{o}C (Fig. 5), the tubular structures gradually disappear and amorphous "fluffy" structures are observed. Also, the reduction at these temperatures is accompanied with a lower carbon yield. The work will be further focused on the influence of the CO_2 flow and the addition of other gases (e.g. Ar). The search for new reducing agents will be also attempted.

(a) (b)

5. *SEM micrographs for samples at 900 (a) and 1000 ^{o}C and CO_2/Ar flow rates of 40 and 10 mL/min, correspondingly.*

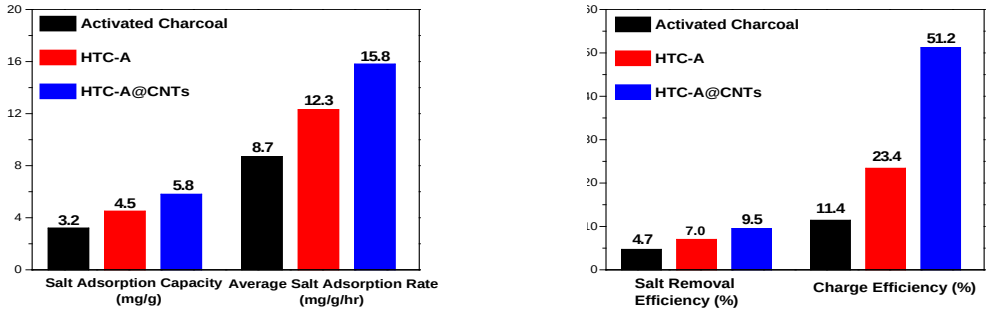
3. Development of novel electrochemical process for water desalination

Single pass CDI experiments with recycling were conducted in order to evaluate the desalination performance of nanocomposite electrode materials. To delineate the effect of porosity and surface area of nanocarbon materials on electrode performance, commercial activated charcoal and a hybrid electrode with a small addition of carbon nanotubes (1wt% of total carbon material) were tested using synthetic NaCl solution. In each CDI experiment, 5mM NaCl salt solution with 200 mL total volume is circulated between the outside reservoir and the deionization cell using a peristaltic pump with flow rate of 35mL/min. The experimental stet-up of process is presented in Fig.6.



6. *CDI experimental set-up.*

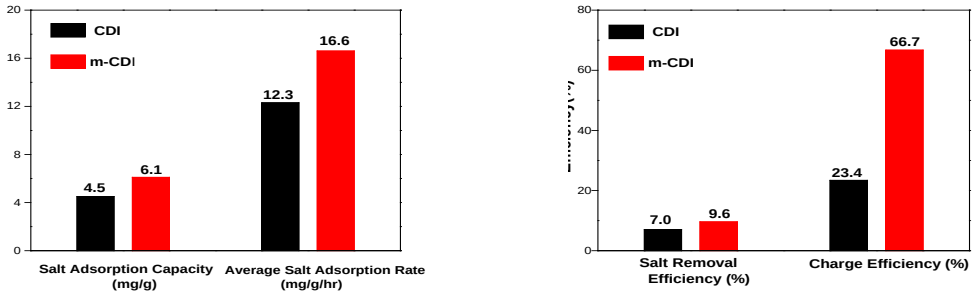
A hybrid electrode with an addition of 1wt% carbon nanotubes (HTC-A@CNTs) and commercial activated charcoal (AC) were tested. The desalination performance of the three porous carbons was evaluated at 1.2 V in terms of diverse CDI performance evaluation metrics and revealed that the synthesized HTC-A exhibited better desalination performance compared with the AC, while the addition of CNTs resulted in significant improvement of desalination efficiency (Fig 7).



7. *Desalination performance of nanocomposite electrode materials.*

The outcome was ascribed to the upgraded electrical conductivity combined with high specific surface area (1495 m^2/g) and specific capacitance (450.4 mF/cm^2) of the synthesized materials making them attractive for application as electrode materials for capacitive deionization.

In order to mitigate the effect of co-ion adsorption, i.e., the adsorption of ions to an electrode carrying the same surface charge, membrane-assisted CDI, MCDI was employed. Therefore, commercial anion-exchange membrane (FAS-50) and cation-exchange membrane (FKS-50) were placed in front of the anode and the cathode of the CDI cell, respectively. Desalination experiments were performed with operating parameters of 1.2 V applied voltage, 300 ppm NaCl concentration, and 35 mL/min flow rate. It was revealed that the addition of ion-exchange membranes (IEMs) leads to high desalination performance of CDI cell in terms of salt removal and charge efficiency (Fig 8).



8. *Comparative plots of CDI and MCDI performance.*

4. Synthesis and characterization of Conductive Polymer/Carbon nanocomposite materials

Nanocomposites of polypyrrole and previously synthesized activated carbon nanocomposites were developed. Interestingly, polypyrrole nanotubes exhibit greater capacitance (143 F/g at 0.1mA), regarding their prominent specific surface area compared to conventional globular polypyrrole particles. Moreover, polypyrrole nanotube calcination in Nitrogen atmosphere led to the formation of Nitrogen-doped carbon nanotubes. Those CNTs are potential carbon materials in carbon nanocomposites in order to study their capacitive/ desalination performance and affinity with conducting polymers.

5. Novel 2D Nanocrystals for Smart Coatings Applications

MXenes with different particle size were synthesized via effective MILD method from MAX phase. The prepared MXene exhibited typical crystalline structure and morphology. MXene-containing composites with CNTs, TiO_2 and rGO were synthesized via hydro- and solvothermal routes. The physicochemical properties of the materials were determined. Regarding the functional properties, progress was made in the evaluation of the electrical conductivity and EMI shielding effectiveness and photocatalytic activity in NOx oxidation.

6. 2D Lightweight Materials and Coatings for EMI Shielding Applications

MXene, Graphene (reduced Graphene oxide) and MXene/GO composites were developed. Then, dispersions of these nanomaterials in different solvents were prepared. The dispersions were incorporated in different resins and deposited as coatings on polymeric flexible surfaces. The microwave properties of the pure nanomaterials were determined and the EMI shielding effectiveness of the coatings was tested. The targeted SE of 30-40 dB for coating material with ~50 wt.% shielding component and thickness 1-2 mm was reached. Moreover, the SE 30-40 dB was achieved by epoxy coating with lower loading of 20% graphene and lower thickness 125 μm.

7. Graphene based nanocomposite electrodes for high energy density supercapacitors

Electrophoretic deposition (EPD) was employed for fabrication of 2D films on copper and stainless steel, using stable aqueous dispersions of graphene, graphene oxide (GO) and carbon nanotubes (CNTs) and their mixtures. The functional groups of GO and the surfactant were the charging agents that drove the EPD. The prepared electrodes exposed to prolonged solar irradiation using a xenon lamp. Characterization of the electrode materials was carried out by SEM, Energy Dispersive X-ray spectroscopy, X-ray diffraction, Raman spectroscopy, ATR-FTIR and X-ray Photoelectron spectroscopy. All-solid-state symmetric supercapacitors were successfully fabricated with the use of a gel electrolyte and the respective electrodeposited films on the electrodes.

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) "Novel Phytomining production of advanced metal-nanoparticles graphene catalytic membranes", 2017-2020, ISN, 90.000 €, 15.000€.

OUTPUT

Publications in International Journals

1. Todorova, N., Papailias, I., Giannakopoulou, T., Ioannidis, N., Boukos, N., Dallas, P., Edelmannova, M., Reli, M., Koci, K., Trapalis, C. Photocatalytic H_2 Evolution, CO_2 Reduction, and NOx Oxidation by highly Exfoliated g-C_3N_4, Catalysts 10 1147 (2020). DOI: https://doi.org/10.3390/catal10101147

2. Papailias, I., Todorova, N., Giannakopoulou, T., Ioannidis, N., Dallas, P., Dimoticali, D., Trapalis, C. Torus Shaped g-C_3N_4 by Flame Spray Pyrolysis, Applied Catalysis B: Environmental 268 118733 (2020). DOI:https://doi.org/10.1016/j.apcatb.2020.118733

3. Chaitoglou. S., Giannakopoulou. T., Papanastasiou. G., Tsoutsou. D., Vavouliotis. A., Trapalis. C., Dimoulas. A. Cu vapor-assisted formation of nanostructured Mo_2C electrocatalysts via direct chemical conversion of Mo surface for efficient hydrogen evolution reaction applications. *Appl. Surf. Sci* . vol 510, pp. 145516 (2020). DOI: https://doi.org/10.1016/j.apsusc.2020.145516

4. Giannakopoulou, T., Todorova, N., Erotokritaki, A., Plakantonaki, N., Tsetsekou, A., Trapalis, C. Electrochemically deposited graphene oxide thin film supercapacitors: Comparing liquid and solid electrolytes, *Appl. Surf. Sci.* vol. 528, pp. 146801 (2020). DOI:https://doi.org/10.1016/j.apsusc.2020.146801

5. Athanasoulia, I.G., Giachalis, K., Korres, D., Todorova, N., Giannakopoulou, T., Tarantili, P., Trapalis, C. Study of thermomechanical, structural and antibacterial properties of poly (lactic acid) reinforced with graphene oxide nanoparticles via melt mixing, *Polym. In.* 69 pp. 995-1007 (2020). DOI: https://doi.org/10.1002/pi.6054

6. Bardi, N., Giannakopoulou, T., Vavouliotis, A., and Trapalis, C., One-step, environmental-friendly electrodeposited films from Graphene and Carbon Nanotubes for supercapacitor application, *ACS Appl. Nano Mater.* 3 (10), pp. 10003–10013, (2020). DOI:https://doi.org/10.1021/acsanm.0c02002.

Teaching and Training Activities

Name: Christos Trapalis
Activity Title, Dates/Duration of lectures/training: Anti-Pollution Processes / 5/10/2020 - 31/12/2020.
Location/Academic Institute: Athens/Hellenic Open University.

Doctoral Dissertations completed in 2020

Name: Ilias-Ioannis Papailias
Dissertation Title: Development of novel photocatalysts with pyrolysis techniques for environmental and energy applications
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€.

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.): 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

- **Objectives**
  - Implementation of advanced 1D and 2D solid state (ss) NMR in the study of topological insulators and semimetals (such as Bi_2Se_3/Bi_2Te_3, WTe_2/$MoTe_2$, etc.).
  - Implementation of NMR crystallography methods (combining advanced ssNMR techniques with Density Functional Theory (DFT) methods) in the study of the electronic properties of various nanocatalysts, such as transition-metal based phosphide nanoparticles, supported 2D dichalcogenides (e.g. MoS_2), nanozeolites, etc.
  - NMR studies of nanofluidic processes in restricted geometries (e.g. water and ionic liquid motion in carbonaceous and silica nanoporous structures).
  - Development of novel ferrofluids suitable for (i) oil reservoir characterization and enhanced oil recovery, (ii) medical applications
  - NMR studies of gelation processes of industrial interest, such as cements, and self-healing coatings for the aerospace technology.

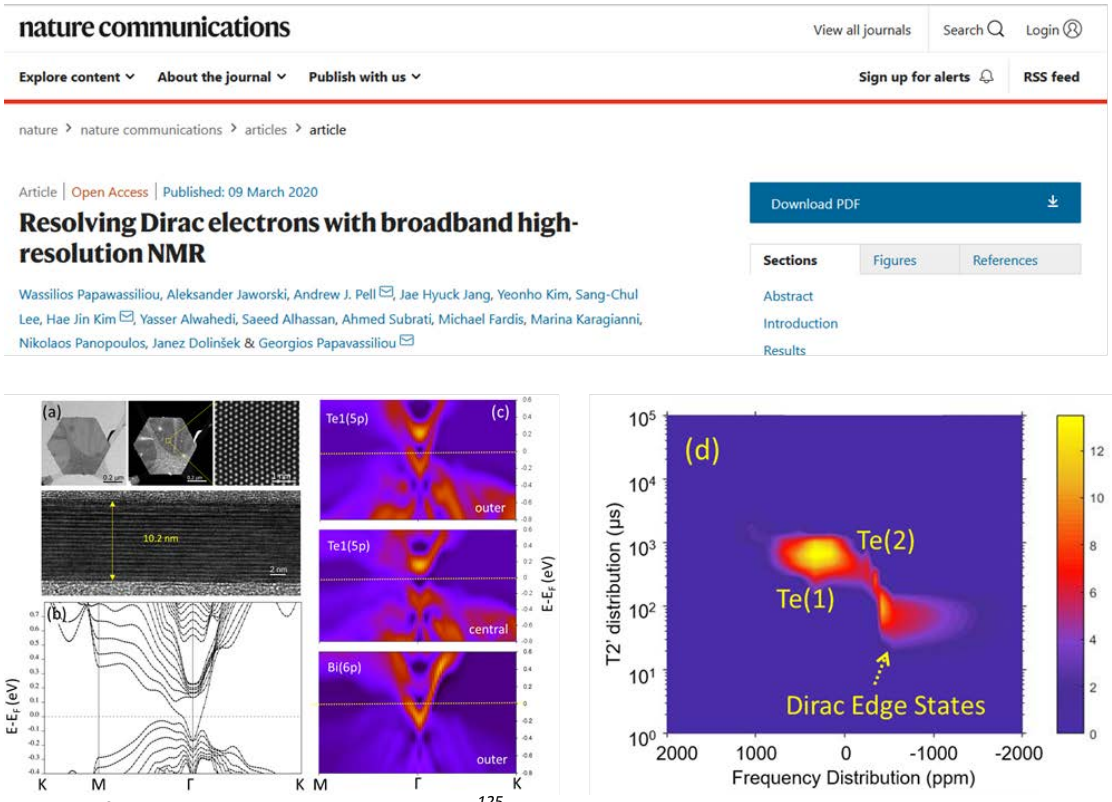
- **Activities and Main Results**
  - **NMR studies of nanosized topological Insulators (ultrathin Bi_2Se_3 and Bi_2Te_3 nanoplateletes).**

Topological Quantum Materials (TQMs) constitute a class of novel materials with unthinkable until today applications that have placed them at the center of scientific interest over the last decade. Their distinct quantum properties emanate from the unique topology of their electron energy band structure with bands crossing linearly (E~k) at specific points of the Brillouin zone the so called Dirac or Weyl nodal points.

In the last year great part of our efforts have been devoted in the study of Topological Materials with state-of-the-art NMR methods, combined with advanced DFT calculations and sub-Angstrom resolved Transmission Electron Microscopy. This work is accomplished 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).

Central role in all efforts to unveil the Dirac and Weyl physics of TQMs is played by the ability to monitor topological electrons and their low energy excitations, i.e. Dirac and Weyl fermions. In a recent publication in Nature Communications, we have succeeded for the first time to detect topological electrons on the surface of a nanostructured topological insulator (Bi_2Te_3) by combining advanced Nuclear Magnetic Resonance (NMR) methods with Density Functional Theory (DFT) calculations and ultra-high resolution Transmission Electron Microscopy (HRTEM). *In this way, the properties of the Dirac electrons were revealed in much more detail than previously, particularly with regard to how the Dirac electrons penetrate below the surface into the bulk interior of TIs, providing a pertinent experimental approach in the study of topological quantum properties.*

(**Nature Communications** | (2020) 11:1285 | https://doi.org/10.1038/s41467-020-14838-4).



Dirac surface electron states detected with ^{125}Te NMR nanocrystallography methods on Bi_2Te_3 nanoplatelets. "Resolving Dirac Electrons with broadband high resolution NMR", Papawassiliou, W., et al., Nature Communications 11, 1285 (2020). https://doi.org/10.1038/s41467-020-14838-4

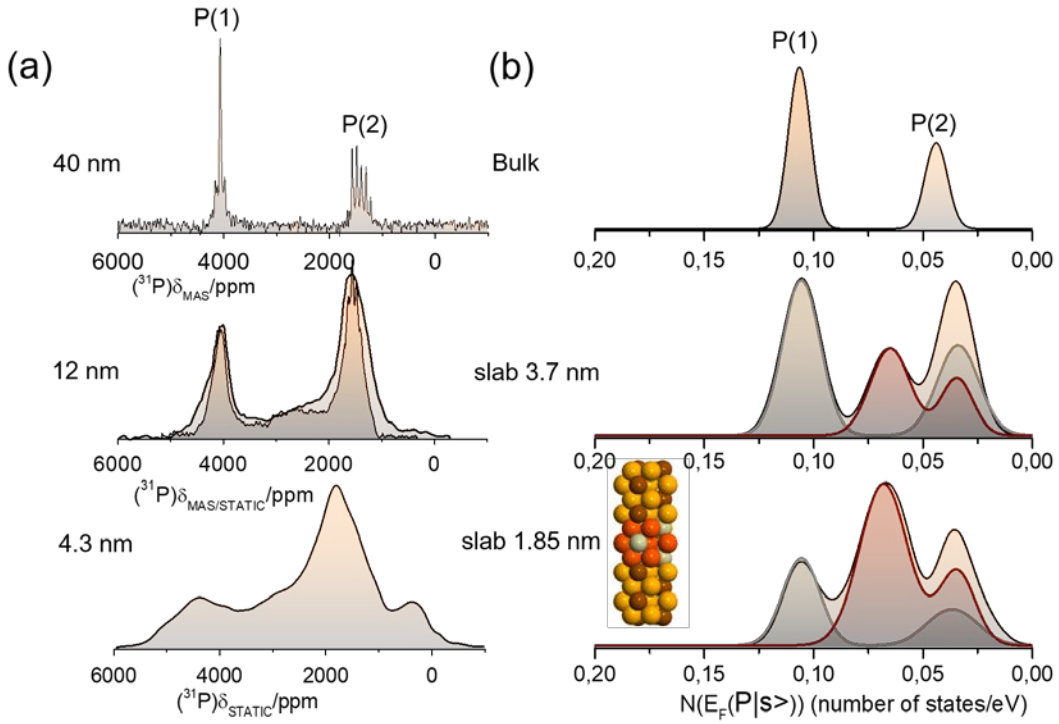
- **Crystal and electronic facet analysis with solid-state NMR nanocrystallography**

Acquiring the crystal and electronic structure of material surfaces and interfaces is at the heart of Modern Surface Science, especially after the dawn of the era of novel 2D materials. It is also of significant importance in the study of materials related with major industrial processes such as heterogeneous catalysis and renewable energy sources. An impressive number of state-of-the-art methods ranging from Angle Resolved Photoemission Spectroscopy to Aberration Corrected HRTEM and STM have been successfully engaged in resolving the complicated issues related with the crystal and electronic structure of surfaces and nanostructured materials. However, by reducing the material size down to nanoscale, atomically resolved information is most of the time obscured, especially in the case of light elements.

In the last years the ssNMR group is strongly involved in the implementation of NMR crystallography methods in the study of metals and semi-metals with complex electronic properties (combining advanced ssNMR methods with Density Functional Theory (DFT) calculations to acquire precise electronic and crystallographic information at the nanoscale).

In this work, we demonstrated how NMR Nanocrystallography, implemented on ultrafine Ni_2P nanoparticles (down to 5nm), succeeds in a unique way to visualize at atomic scale resolution the size-induced structural and electronic changes taking place in this exceptional Hydrogen Evolution Reaction (HER) nanocatalyst.

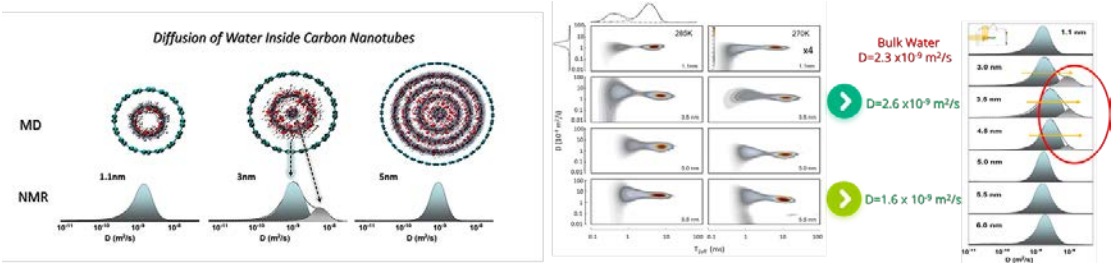
This work was published in chemrxiv.13338905.v1; (https://doi.org/10.26434/chemrxiv.13338905.v1), (*see publ. no 4 under: Publications in International Journals*) and subsequently in year 2021 in *Nature Communications* **12,** 4334 (2021). https://doi.org/10.1038/s41467-021-24589-5



Correlating ^{31}P ssNMR spectra (left column) with DFT calculations (right column). Papawassiliou, W., et al., "Crystal and electronic facet analysis of ultrafine Ni_2P particles by solid-state NMR nanocrystallography". (https://doi.org/10.26434/chemrxiv.13338905.v1)

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

The study of water diffusion inside Carbon Nanotubes (CNTs) has attracted great interdisciplinary interest as a conduit for understanding nanofluidic properties in a variety of nanoporous systems having potential in many applications, such as water treatment technologies, drug delivery, intracellular solute transport control and energy storage systems. When confined at the nanoscale, water behavior diverges significantly from that of bulk water, acquiring ultrafast diffusion and extraordinary fragility. The dependence of this microscopic behavior on the channel size has previously been studied mostly theoretically. In our recent publication in Biomicrofluidics (Biomicrofluidics **14**, 034114 (2020); https://doi.org/10.1063/5.0005398) we report a fast and scalable method to acquire nanofluidic diffusion experimentally at nanoscale resolution by using two-dimensional NMR diffusion − relaxation ($D-T_2$) measurements. Our experiments revealed a stratified water arrangement inside the CNT channels, and identified a favorable CNT diameter range (3:0–4:5 nm), at which maximum water diffusion occurs, thus providing **the first experiment result** which confirms MDS predictions.

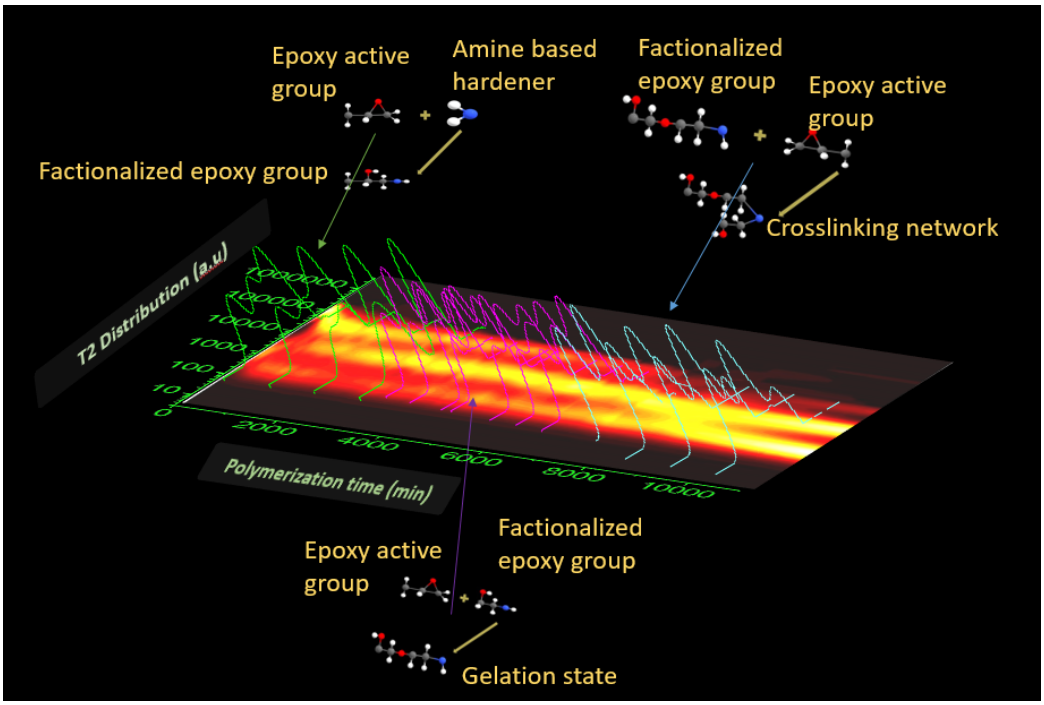


The significance of these findings was emphasized by Scilight of the American Institute of Physics which devoted ***a scilight (https://aip.scitation.org/doi/10.1063/10.0001492) to our publication.***

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

Self-healing materials received a considerable amount of scientific interest in recent years due to their ability to automatically repair small or medium- scaled damage, mimicking the self-healing function of living organisms. In the last years the ssNMR group has systematically applied advanced NMR techniques to study

the healing efficiency of microcapsule-based self-healing materials. Solid state NMR spectroscopy is an established non-destructive evaluation (NDE) method, most suitable for monitoring in real time the evolution of the polymerization process of the self-healing agent. In this work the distribution of the spin-spin relaxation time T_2 has been exploited to map the polymerization process.



Spin-spin relaxation time T_2 -resolved mapping of the polymerization process.

- **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 €.
4. *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).

OUTPUT

Publications in International Journals

1. Papawassiliou, W., Jaworski, A., Pell, A.J., Jang, J-H., Kim, Y., Lee, S-C., Kim, H-J., Alwahedi Y., Alhassan, S., Subrati, A., Fardis, M., Karagianni, M., Panopoulos, N., Dolinsek, J., and **Papavassiliou, G.***. "Resolving Dirac Electrons with broadband high resolution NMR". *Nature Communications* **11,** 1285 (2020); https://doi.org/10.1038/s41467-020-14838-4
2. Gkoura, L., Diamantopoulos, G., Fardis, M., Homouz, D., Alhassan, S., Beazi-Katsioti, M., Karagianni, M., Anastasiou, A., Romanos, G., Hassan, J., and **Papavassiliou, G.***. "The Peculiar Size and Temperature Dependence of Water Diffusion in Carbon Nanotubes studied with 2D NMR Diffusion-Relaxation D-T_{2eff} Spectroscopy". *Biomicrofluidics* **14**, 034114 (2020); https://doi.org/10.1063/5.0005398 – **Editor's peak** (2020). Interviewed by Scilights of API.
3. Subrati, A., Kim, Y., AlWahedi, Y., Tzitzios, V., Alhassan, S.,* Kim, H-J.*, Sanggil Lee, S., Sakellis, E., Boukos, N., Stephen, S., Lee, S-M., Lee, J-B, Fardis, M. and **Papavassiliou, G.*.** "Monitoring the multiphasic evolution of bismuth telluride nanoplatelets". *CrystEngComm* **22**, 7918-7928 (2020); https://doi.org/10.1039/D0CE00719F
4. 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.. "Crystal and electronic facet analysis of ultrafine Ni_2P particles by solid-state NMR nanocrystallography". 10.26434/chemrxiv.13338905.v1; (https://doi.org/10.26434/chemrxiv.13338905.v1), published in year 2021 in *Nature Communications* **12,** 4334 (2021). https://doi.org/10.1038/s41467-021-24589-5

Teaching and Training Activities

Papavassiliou, G.

Solid State NMR Spectroscopy (theory & experimental exercises). Interdepartmental Postgraduate Course in Materials Chemistry and Technology, spring 2020, University of Ioannina

Undergraduate Theses and Internships completed in 2020

Name: Ballas Christos

Traineeship Title: "*Nuclear Magnetic Resonance studies of Ionic Liquids confined in Mesoporous and Nanoporous Materials".*

Research Supervisor at NCSR: Dr. G. Papavassiliou

University where the Thesis was presented: University of Glasgow, UK.

MAGNETIC THIN FILMS, METAMATERIALS AND THERMOELECTRICS

Project leader: Dr. E. Devlin.

Dr. Dr. M. Gjoka, Dr. Th. Speliotis.

V. Alexandrakis,Dr .A. Kaidatzis.

PhD Candidates: George Sempros, Alexandra Pilidi, Nikolaos Koutsokostas, Athanasios Tzanis, Dimitris Anastasakos

Master Students: Zoi Plevri, Athanasios Tzanis.

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 content.

L10 Alloys

On L10 MnAl ferromagnetic thin films the main focus of our work was to determine the optimum conditions for growing ferromagnetic thin films onto commercially available Si substrates, compatible with microelectronics. We first studied the crystal structure of carbon-doped Al-rich MnAl thin films deposited on Si substrates. The effects of carbon content and vacuum heat treatment parameters were studied. It was shown that the carbon content, in combination with heat treatment, allows the tailoring of structural phase transitions in the films. The main phases detected are Al2Mn3, pure Mn, and pure C. As the carbon content increases, the amount of Al2Mn3 phase decreases and the content of pure crystallized Mn phase increases. In addition, it was shown that as the heat treatment temperature increases – up to 500 °C – the Al2Mn3 phase content increases, whereas a pure C phase appears at lower temperatures. The parameter ranges studied did not allow us to obtain ferromagnetic C-doped MnAl films. The focus now is on Mn-rich C-doped MnAl thin films.

1:12 Alloys

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. Mössbauer spectroscopy shows that the quadrupole splitting is correlated with the magnetic anisotropy. These results highlight the possibility to tune the magnetic anisotropy of the NdFeTi-alloy for permanent magnet applications without the use of nitrogenation. These alloys are good candidates for permanent magnets, provided the correct microstructure is developed to optimize the coercivity.

MnBi Alloys: Mn1.05CoxBi1-ySny (Co: x=0.2;0.04, Sn: x, y=0.02-0.04)

In this work we extend the last research on stability of modified MnBi alloys by small partial additions of (Co, Fe, Cu) instead of substitution, and 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^o C. 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.
We have produced Mn1.05CoxBi1-ySny (Co: x=0.2;0.04, Sn: x, y=0.02-0.04) alloys with small addition of Co and small substitutions of Bi for Sn. No traces of metallic Co were detected, proving the successful incorporation within the structure. Increasing Co addition and decreasing Sn substitution does not favor the stability of LTP of MnBi. Annealing of samples at 350 ^{o}C leads to increased Bi decomposition.

1:5 Alloys: $Sm_{1-x}MM_xCo_5$ (x = 0.1 – 1.0, MM = mischmetal)

$SmCo_5$ 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 $SmCo_5$ alloys may reduce the demand for Sm in some applications.
Single phase samples of nominal stoichiometry Sm1-xMMxCo5 (x = 0.1 – 1.0) were successfully synthesized by conventional metallurgy methods. The hexagonal structure of the mother SmCo5 compound is retained. Main intrinsic magnetic properties, Curie temperature and mass magnetization, are weakening, especially for higher Mischmetal replacement for Sm, more than 30%. This effect is minimal for lower Ce-La content; considering the low cost and the availability of the specific minerals we conclude that the possibility of introducing Mischmetal in commercial SmCo5 permanent magnets is feasible.

High Entropy Alloys and Permanent magnets

For centuries the design concepts of alloys has been based on only one or two principle elements, while minor fractions of other elements are added for property enhancement. This classical approach was broken in 2004 by Yeh (Yeh, J. W et al, Adv. Eng. Mater. 6, 299-303) who suggested of a new alloy design concept, which he called high entropy alloys. The original definition was “multiprincipal elements alloys composed of five or more elements in equal or near-atomic percentages”. Most of the current dominant (PMs) are intermetallic compounds containing rare earth elements e.g. NdPr or Sm and Co, both expensive and originating mainly from either China or Congo. These natural elements from the periodic table have fixed atomic radii, fixed valence electron configuration and specific electronegativity, parameters that are crucial for the formation of intermetallic compounds. By creating artificial elements of the type of HEAs based on multicomponent rare-earth elements (RE-HEAs) and HEAs based on multicomponent transition metal elements (TM-HEAs), we have created a library of elements with tunable atomic radii, valence electron configuration and electronegativity. This approach enhances the opportunities for discovering novel permanent magnets. Preliminary Results are summarized in the table below.

Sample	Ms(emu/g)	H_A(T)	Tc (K)	$_{(expected)}$ (T)	$(H)^{theor}_{max}$ (MGOe)
(RE-HEAs)-Co5	75-90	>10	> 800	>1	8-18
Sm-$(TM\text{-}HEAs)_5$	65-80	> 8T	> 800	>1	8-15
(RE-HEAs)-$Fe_{11}TiN_x$	120-135	>6 T	570-600	>0.8	9-18

2. Magnetocaloric Materials

Generally, structural and magnetic properties of NiMn-based metamagnetic Heusler alloys in form of thin films can dramatically differ from those in the bulk, particularly, due to the interaction between the film and the substrate. Martensitic transformation (from the cubic austenite phase to the lower symmetry martensitic structure) in thin films cannot occur without twinning, because the surface area of the film on rigid substrate should remain the same during the transformation.

It was found that constraints from the film/substrate interface block the martensitic transformation in the 20 nm thick film. The increase of the film thickness results in a progressive stress relaxation and, as a result, the martensitic transformation becomes possible starting from 50 nm. Twinning of the films is required to conserve the films surface area. The elastic energy balance between the film/substrate interface and the twin boundaries leads to the formation of a submicron wide, stripe like, periodical structure of twins. The width of the twin variants increases with the film thickness growth, resulting in a significant modification of magnetic properties.

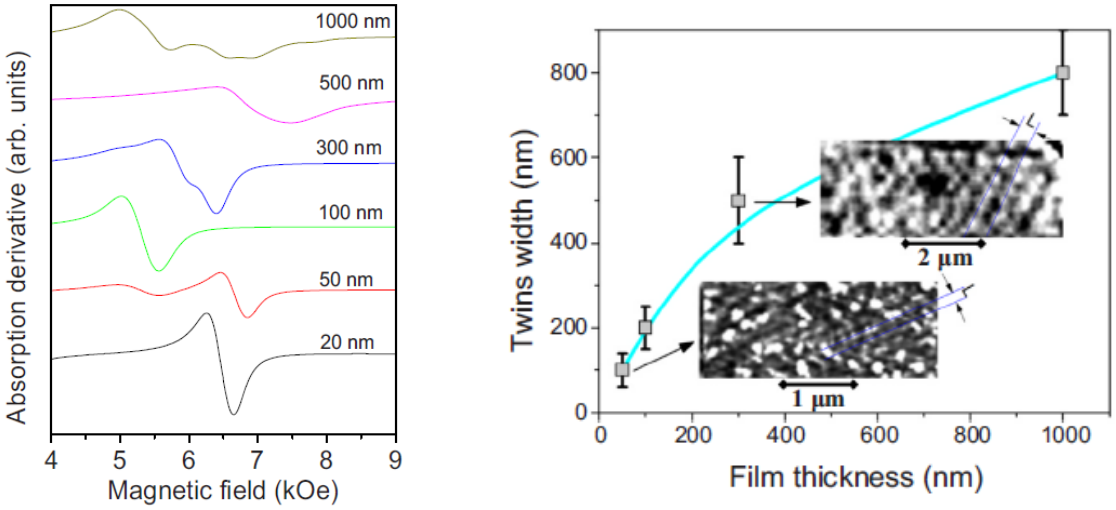


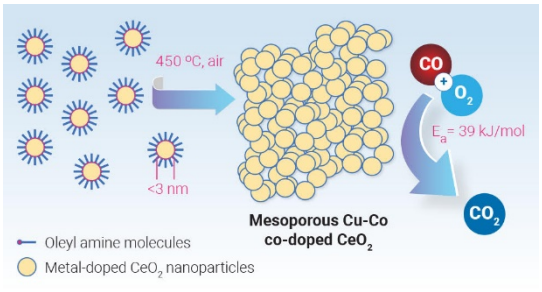
Figure 1. Left panel: The magnetic resonance spectra of the films of different thicknesses recorded at 120 K. The external magnetic field is perpendicular to the film plane. **Right panel:** The dependence of the twin variants width (*L*) on the films thickness. AFM images of martensitic phase areas with the twin structure for the 50 and 300 nm-thick films are also shown. The line is a fit to square root dependence.

3. Chemical synthesis of Multi-Functional Nanomaterials

The project aims towards the discovery and development chemical liquid phase synthetic approaches for the fabrication of colloidal particles in the nanosize regime including (a) magnetic nanoparticles for permanent magnets applications, (b) nano-catalysts for energy and environmental applications (c) hard-soft matter coupling with potential for technological advancements in the display and sensor industry.

Chemically ordered bimetallic nanoparticles. Chemically ordered ($L1_0$), bimetallic CoPt nanoparticles have attracted great scientific and technological interest during the last few decades because of their potential applications in a variety of fields such as permanent magnets, high density magnetic storage media, catalysis, and biomedicine. Our results show that highly ordered CoPt nanoparticles have been synthesized by a novel

liquid phase approach by the addition of bismuth. The low surface energy of bismuth is suggested as the cause of the enhanced surface segregation of the dopant. The CoPt nanoparticles reveal room temperature coercivities up to 14.6 kOe, the highest value reported to date for similar materials. These binary $L1_0$ MPt nanostructures are very promising candidates for a variety of applications from exchange coupled permanent magnets to catalyst for ORR and HER reactions.



Environmental Applications of Nanoparticles. Ultrasmall ceria (CeO2) and metal-doped CeO2 nanoparticles in the sub-3 nm size regime were synthesized via a facile, single-step, liquid-phase thermal decomposition reaction in a monosurfactant medium, which plays the role of a solvent and coordination molecule. The results show that all the materials are highly crystalline in the as-synthesized form and monodispersed with a near-spherical shape. N2 sorption studies and porosity analysis confirm that the prepared materials after thermal treatment at 450 °C possess a very high specific surface area, up to 240 m2 g−1, and additionally a hierarchical mesoporous structure. The CeO2 and doped-CeO2 particles demonstrate superior catalytic activity for the low-temperature CO oxidation. Among the different kinds of doping, the Cu−Co co-doped CeO2 nanoparticles are the most active for the CO oxidation (T_{50} ≈ 54 °C and Ea = 39.5 kJ mol^{-1}) followed by the Cu and Sm-doped CeO2 ones.

Toxic gases such as hydrogen sulfide (H2S) constitute major environmental hazards in the petroleum/petrochemical industry. Removal of H2S can be done via a variety of approaches. Among them the dry adsorption-based processes and the catalytic selective oxidation of H2S hold significant potential for turning the environmental challenges into economic opportunities. Here we develop a novel class of hybrid materials based on mesoporous silica “plated” of metal oxides and particular Cu and Fe oxides for sorption and the selective oxidation of H2S. The sulfur capacity reaches 10.224 mmol/gCuO. This capacity far exceeds all regenerable capacities reported in literature in similar materials, while over Fe oxides the selective H2S oxidation achieve > 90 % conversion maintaining sulfur selectivities above 90 %. Finally, it is worth to mention the utilization of elemental sulfur, an oil industry by product, for the development of high refractive index (up to 1.6), materials, via in-situ inverse vulcanization of sulfur with polystyrene.

Hard-soft matter composites. Dispersions of micro- and nano-particles in liquid crystals (LCs) can have dramatic effects upon the nematic order parameter. They can affect macroscopic structural properties as in the case of glass colloidal nematics as well as the dielectric anisotropy and the conductivity bearing considerable impact for the LC display technology. Of particular scientific interest, the self-assembly of colloidal structures and nanoparticles in the anisotropic environment of liquid crystals, has for a long time attracted considerable attention.

4. Magnetic – Dielectric Nanocomposites

Topological Matter

The research for the relationship between the magnetic properties of topological insulators and their electronic band structure offer new insights into recent debates regarding the evolution of the band structure with temperature in these materials, which exhibit uncommon quantum phenomena and are proposed to be critical in next-generation electronics and quantum computers. This unique characteristic allows these materials to host of a plethora of exotic quantum phenomena that would be useful for quantum computers and advanced optoelectronic systems. The main results obtained include: Equilibrium bismuth crystals grown by sputtering (world first), magnet moment doping in topological insulators structures, intrinsic magnetic topological insulators, single crystal growth of topological materials, weak antilocalization phenomena, quantum oscillations in single crystals.

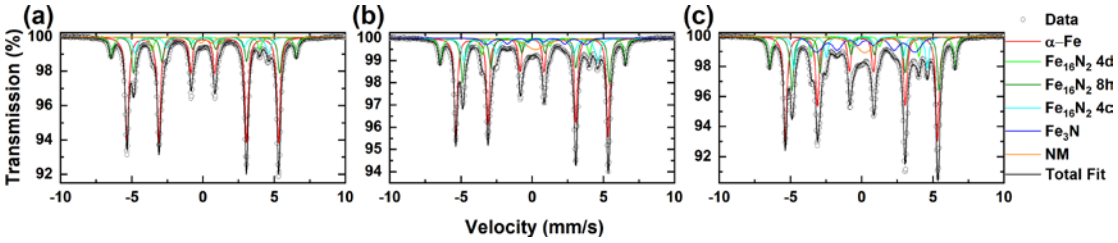
Magnetism for human beings

The objectives of the current research are the first steps towards introducing flexible hard magnets with high coercivity into the family of flexible magnetoelectronics by the growth of hard magnetic materials on flexible Kapton substrates by means of magnetron sputtering. With the successful demonstration of high coercivity films on flexible substrates, novel flexible electronic platforms can be equipped with more magnetic

functionalities for wearable devices in human-health monitoring, biomedical applications, MEMS, sensorics, space technologies and much more.

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 use of MS in the characterization of $Fe_{16}N_2$ magnetic nanoparticles Having identified a high concentration of the hard ferromagnetic $Fe_{16}N_2$ phase in the synthesized flakes, the feasibility of permanent magnet production using these powders for extrusion based 3D printing was assessed.



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": 50 k€.

Mössbauer Spectroscopy Services 2020 20,000 €

OUTPUT

Publications in International Journals

1. Kaidatzis, A., del Real, R.P., Alvaro, R., Niarchos, D, Vázquez, M, García-Martín, J.M. "Nanopatterned hard/soft bilayer magnetic antidot arrays with long-range periodicity". J. Magn. Magn. Mat. **498**, 166142 (2020) 10.1016/j.jmmm.2019.166142.
2. Basina, G., Elmutasim, O., Ali Gaber, D., Ali Gaber, S., Lu, X., Tzitzios, V., Vaithilingam, B.B., Baikousi, M., Asimakopoulos, G., Karakassides, M., Panagiotopoulos, I., Spyrou, K., Thomou, E., Sakellis, E., Boukos, N., Xu, D,, Tsapatsis, M., Al Amoodi, N., Al Wahedi, Y., On the selective oxidation of H2S by heavy loaded Nanoparticles Embedded in Mesoporous Matrix (NEMM), *Applied Catalysis B: Environmental,* **278**, 5, 119338 (2020). DOI: 10.1016/j.apcatb.2020.119338.
3. Basina, G., Polychronopoulou. K., Zedan, A.F., Dimos, K., Katsiotis, M.S., Fotopoulos, A.P., Ismail, I., and Tzitzios, V., Ultrasmall Metal-Doped CeO2 Nanoparticles for Low-Temperature CO Oxidation, *ACS Applied Nano Materials,* **3**, 11, 10805–10813 (2020). DOI: 10.1021/acsanm.0c02090.
4. Wadi, V.S., Jena, K.K., Halique, K., Rožič, B., Cmok, L., Tzitzios, V., Alhassan, S.M., Scalable High Refractive Index polystyrene-sulfur nanocomposites via in situ inverse vulcanization, *Scientific Reports,* **10**, 14924 (2020). DOI: 10.1038/s41598-020-71227-z.

5. Cordoyiannis, G., Lavrič, M., Trček, M., Tzizios, V., Lelidis, I., Nounesis, G., Daniel, M., Kutnjak, Z., Quantum dot-driven stabilization of liquid-crystalline blue phases, *Frontiers in Physics, **8**,* 315 (2020). DOI: 10.3389/fphy.2020.00315.
6. Basina, G., Gaber, D.A., Al Yafei, S., Tzizios, V., Gaber, S.A., Ismail, I, Vaithilingam, B.V., Polychronopoulou, K., Hashimi, S.S., Al Wahedi, Y., Mesoporous silica "plated" copper hydroxides/oxides heterostructures as superior regenerable sorbents for low temperature H2S removal, *Chemical Engineering Journal,* **398**, 125585 (2020). DOI: 10.1016/j.cej.2020.125585.
7. Lavrič, M., Cordoyiannis, G., Tzizios, V., Kralj, S., Nounesis, G., Lelidis, I., Amenitsch, H., Kutnjak, Z., The effect of CoPt-coated reduced-graphene oxide nanosheets upon the Smectic-A to Smectic-C* phase transition of a chiral liquid crystal, *Liquid Crystals,* **46**, 6, 831-837 (2020). DOI: 10.1080/02678292.2019.1680757.
8. Lavrič, M., Cordoyiannis, G., Tzizios, V., Lelidis, I., Kralj, S., Nounesis, G., Žumer, S., Daniel, M., Kutnjak Z., Blue phase stabilization by CoPt-decorated reduced-graphene oxide nanosheets dispersed in a chiral liquid crystal, *Journal of Applied Physics, **129**, 095101 (2020). DOI: 10.1063/1.5141930.*
9. Yildiz, S., Cetinkaya, M.C., Ozbek, H., Tzitzios, V., Nounesis, G., High-resolution birefringence investigation on the effect of surface-functionalized CdSe nanoparticles on the phase transitions of a smectic — A liquid crystal, *Journal of Molecular Liquids,* **298**, 112029, (2020). DOI: 10.1016/j.molliq.2019.112029.
10. Subrati, A., Kim, Y., Al Wahedi, Y., Tzizios, V., Alhassan, S., Kim, H.J., Lee, S., Sakellis, E., Boukos, N., Stephen, S., Lee, S.M., Lee, J.B., Fardis, M., Papavassiliou, G., Monitoring the multiphasic evolution of bismut telluride nanoplatelets, *Cryst. Eng. Comm,* **22**, 7918-7928 (2020). DOI: 10.1039/D0CE00719F.
11. Kaidatzis, A.K., del Real, R.P., Alvaro, R., Niarchos, D., Vázquez, M., García-Martín, J.M., "Nanopatterned hard/soft bilayer magnetic antidot arrays with long-range periodicity". *J. Magn. Magn. Mat*. **498**, 166142 (2020) 10.1016/j.jmmm.2019.166142.
12. Zirhli, O., Gunduz Akdogan, N., Odeh, Y.N., Misirlioglu, I.B., Devlin, E., Akdogan, O., Fabrication and Characterization of Fe16N2 Micro-Flake Powders and Their Extrusion-Based 3D Printing into Permanent Magnet Form Advanced *Engineering Materials*, **22** (11), (2020)art. no. 2000311
13. Khurshid, A., H., Abdu, Y.A., Devlin, E., Issa, B.A., Hadjipanayis, G.C., Chemically synthesized nanoparticles of iron and iron-carbides", *RSC Advances*, **10** (48), pp. 28958-28964 (2020)
14. Ibrahim, I., Kaltzoglou, A., Athanasekou, C., Katsaros, F., Devlin, E., Kontos, A.G., Ioannidis, N., Perraki, M., Tsakiridis, P., Sygellou, L., Antoniadou, M., Falaras, P., Magnetically separable TiO2/CoFe2O4/Ag nanocomposites for the photocatalytic reduction of hexavalent chromium pollutant under UV and artificial solar light, *Chemical Engineering Journal*, **381**, art. no. 122730, . (2020) 10 (48), pp. 28958-28964.
15. Varouti, E., Devlin, E., Sanakis, Y., Pissas, M., Christides, C., Tomara, G.N., Karahaliou, P.K., Georga, S.N., Krontiras, C.A., A systematic Mössbauer spectroscopy study of Y3Fe5O12 samples displaying different magnetic ac-susceptibility and electric permittivity spectra, (2020) *Journal of Magnetism and Magnetic Materials*, **495**, art. no. 1658.
16. Hadjipanayis, G.C., Gabay, A.M., Schönhöbel, A.M., Martín-Cid, A., Barandiaran, J.M., Niarchos, D., ThMn12-Type Alloys for Permanent Magnets, *Engineering*, **6** (2), pp. 141-147. (2020)
17. Chen S.,Horn Von Hoegen M., Thiel P.A. ,Kaminski A., Schrunk B., Speliotis Th.,Conrad E.H., and Tringides M.C., High Layer Uniformity of Two-Dimensional Materials Demonstrated Surprisingly from Broad Features in Surface Electron Diffraction, *Journal of Physical Chemistry Letters*, **11**(21) 8937 – 89435 (2020). DOI: 10.1021/acs.jpclett.0c02113.
18. Pilidi A., Tzanis A., Helm T., Arfanis M., Falaras P. and Speliotis Th., Nanometer-thick bismuth nanocrystal films for sensoric applications, *ACS Applied Nano Materials* **3**(10) 9669 - 967823 (2020).
19. Pilidi, A., Speliotis, Th., Litsardakis, G., Structural and magnetotransport characterization of magnetron sputtered Co-doped Bi2Te3 thin films, *Journal of Magnetism and Magnetic Materials*, **511**, art. no. 166971. (2020).
20. Sanida, A., Stavropoulos, S.G., Speliotis, T., Psarras, G.C. Probing the magnetoelectric response and energy efficiency in Fe3O4/epoxy nanocomposites, *Polymer Testing*, **88**, art. no. 106560, (2020).

21. Sanida, A., Stavropoulos, S.G., Speliotis, T., Psarras, G.C., Development and characterization of multifunctional yttrium iron garnet/epoxy nanodielectrics, *Journal of Thermal Analysis and Calorimetry* **142**(5) December 2020, Pages 1701-1708.
22. Tarkhanyan, R.H., and Niarchos, D., Thermoelectric figure of merit in transverse magnetic field under adiabatic and isothermal conditions, *J of Magnetism and Magnetic Materials*, **493**, 165669 (2020).
23. Alexandrakis V., Barandiaran J.M., Pérez-Checa A., Lázpita P., Decker P., Salomon S., Feuchtwanger J., Ludwig A., Chernenko V., "Combinatorial synthesis of Ni–Mn–Ga-(Fe,Co,Cu) high temperature ferromagnetic shape memory alloys thin films, *Scripta Materialia, Volume* **178**, Pages 104 – 10715, (2020).

Preprints

1. Tzizios, V., Pillai, V., Gioti, C., Katsiotis, M., Karagiannis, T., Gournis, D., Karakassides, M.A., Alhassan, S., Ultra-fine Ni2P nanoparticles decorated r-GO: Novel Phosphidation approach and Dibenzothiophene Hydrodesulfurization, *ChemRxiv*, (2020). DOI: 10.26434/chemrxiv.12706235.v1
2. Papavassiliou, V., Carvalho, J.P., Panopoulos, N., Alwahedi, Y., Wadi, V.K.S, Lu, X. , Polychronopoulou, K., Lee, J.B., Lee, S., Kim, C.Y., Kim, H.J., Katsiotis, M., Tzizios, V., Marina Karagianni, Fardis, M., Papavassiliou, G. and Pell, A.J., Crystal and electronic facet analysis of ultrafine Ni2P particles by solid-state NMR nanocrystallography, *ChemRxiv* (2020).

Papers in Refereed Conference Proceedings

1. Gjoka, M., Sarafidis, C., Khaila, W., Niarchos, D., Structural stability and magnetic properties of $Mn_{1.05}R_xBi_{1-y}Sn_y$ (R=Co, Fe, Ni ; x, y=0.02-0.04) compounds, *Proceedings of International Workshop on* ***Rare Earth Permanent Magnets and Advanced Magnetic Materials and Their Applications (REPM 2020*****)** Note: The REPM-2020 was postponed to 2021.
2. 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), *Proceedings of International Workshop on* ***Rare Earth Permanent Magnets and Advanced Magnetic Materials and Their Applications (REPM 2020).*** Note: The REPM-2020 was postponed to 2021

Books/Chapters in Books

1. Kaidatzis, A., Sidorenko, S., Vladymyrskyi, I., Niarchos, D. (Editors), *Modern Magnetic and Spintronic Materials: Properties and Applications",* NATO Science for Peace and Security Series - B (2020).

International Conferences Presentations (invited, oral, poster)

1. Kaidatzis, A., and Garcia-Martin, J.M., "Magnetic Antidots". IEEE International Conference on "Nanomaterials: Applications & Properties" (NAP-2020) Sumy, Ukraine, 9-13 Nov. 2020 (Invited oral).
2. Kaidatzis, A., Hafarov, A.E., Vladymyrskyi, I.A., and Niarchos, D., "Effect of carbon doping on structural phase transitions in Al-rich MnAl thin films". The Joint European Magnetic Symposia (virtual), 7-11 December 2020, Lisboa, Portugal (poster).
3. Deepchand, V., Tzizios, V., Hadjipanayis G., Structural and Magnetic Properties of Iodide-Mediated Synthesized L12 FePt3 Nanoparticles, Bulletin of the American Physical Society, APS March Meeting 2020, March 2–6, 2020; Denver, Colorado. (poster).
4. Pourmiri, S., Tzizios, V., Hadjipanayis G., Effect of Surfactants on the Shape of Iron Oxide Nanoparticles Synthesized by Thermal Decomposition, Bulletin of the American Physical Society, APS March Meeting 2020, March 2–6, 2020; Denver, Colorado. (poster).
5. Gjoka, M., Sarafidis, C., Khaila, W., Niarchos, D., Structural stability and magnetic properties of Mn1.05RxBi1-ySny (R=Co, Fe, Ni ; x, y=0.02-0.04) compounds, *REPM-2020* (Virtual event, Maryland USA)
6. Sempros, G., S. Giaremis, Gjoka, M., Sarafidis, C., Kioseoglou, J., Ab-initio theoretical calculations and experimental synthesis of Sm1-xMMxCo5 (x = 0.1 – 1.0, MM = mischmetal), 17th *International Conference on Nanosciences& Nanotechnologies (NN20)*, 7-10 July 2020, Thessaloniki, Greece (Virtual event)

7. 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)
   Proceedings of International Workshop on Rare Earth Permanent Magnets and Advanced Magnetic Materials and Their Applications (REPM 2020)
8. Niarchos, D., Psycharis, V., Devlin, E. and Gjokas, M., Artificially synthesized multielements, based on the concept of the high entropy alloys, as building blocks for novel magnetic phases*
   Proceedings of International Workshop on Rare Earth Permanent Magnets and Advanced Magnetic Materials and Their Applications (REPM 2020)

Teaching and Training Activities

M. Gjoka,

Advanced materials for permanent magnets, Dimitris Katsoridas, 1/07/2020-30/09/2020

Laboratory of Magnetism and superconductivity INN/Materials Science at the University of Patras

M. Gjoka,

Advanced materials for permanent magnets, Marialena Christopoulou, 1/06/2020-30/09/2020

Laboratory of Magnetism and superconductivity INN/ Department of Chemistry, at the University of Patras.

Thanassis Speliotis

Laboratory course, “Thin Films”, for the postgraduate program “Physics and Technological Applications” organized by the NTUA and NCSR Demokritos, Greece.

Master Dissertations completed in 2020

Name: Athanasios Tzanis

Dissertation Title: “Development and Characterization of Fine Magnetic Films Deposited on Flexible Substrates (Flexomagnetism) by Means of Magnetron Sputtering Technique”

Research Supervisor at NCSR: Thanassis Speliotis

University where the Thesis was presented: NTUA, School of Chemical Engineering

Patents

Yasser Al Wahedi, Shaima Al Yafei, Georgia Basina, Vasileios Tzitzios, YOLK-SHELL NANOPARTICLES FOR THE REMOVAL OF H2S FROM GAS STREAMS, PCT/IB2019/058169

Awards:

Thanassis Speliotis: Fulbright Scholar for the Academic Year 2019-2020, The Fulbright Foundation.

SUPERCONDUCTIVITY AND MAGNETIC OXIDES

Project Leader: Michael Pissas

PhD Candidates: Varouti, V. Panagopoulos

Master Students: M.Bazini, K. Baskourelos, T. Poulis

Research Collaborators (emeritus or visiting): Ass. Prof. C. Christidis, Univ. of Patras; Ass.Prof. D. Stamopoulos.

Objectives

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

Activities and Main Results

Ordered $LiFe_5O_8$ ferrite, first discovered by Braun in 1952 [1] (and studied over the years by several techniques [2-4]), is one of the few ferrimagnetic insulators with low microwave losses and high saturation magnetization and Curie temperature. These properties may be useful in the construction of ultra-wideband photonic devices for 5G

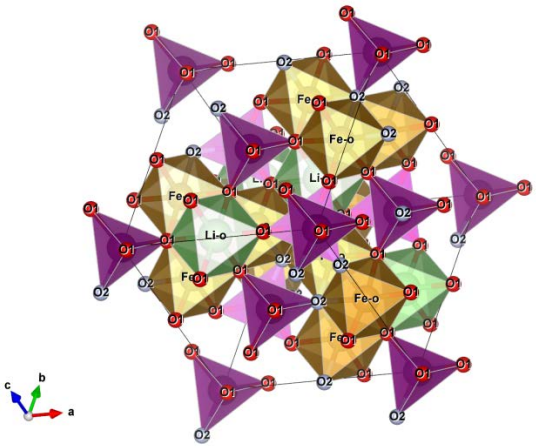


Fig 1. Unit cell of the ordered form of $LiFe_5O_8$. Li and Fe occupy the octahedral 4b and 12d sites respectively. The tetrahedral sites 8c occupied by Fe. In the disordered form iron and lithium atoms randomly occupy the two octahedral sites

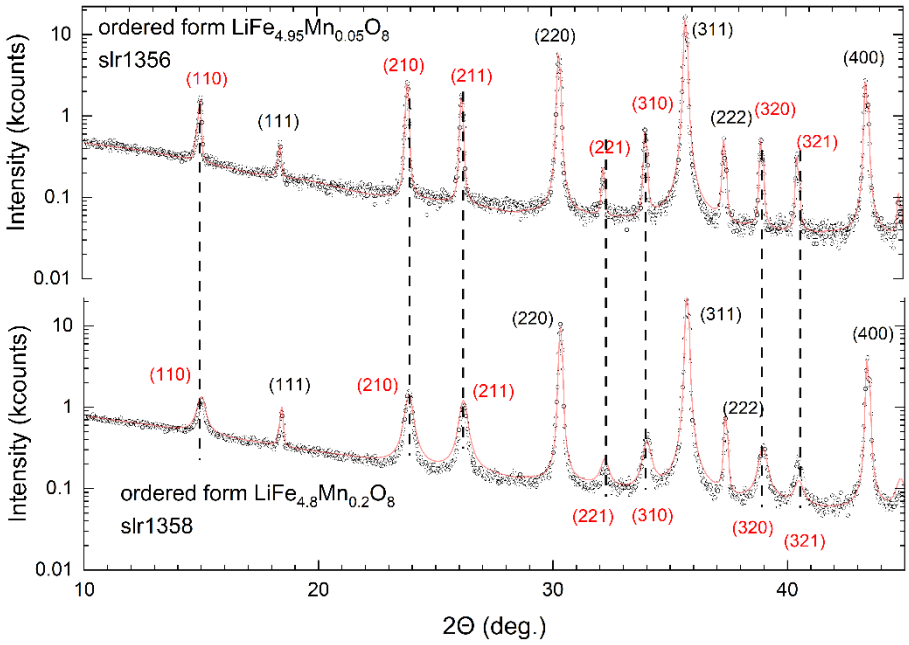


Fig. 2 Rietveld plot of the ordered $LaFe_{5-x}Mn_xO_8$, (x=0.05, 0.2) samples. The peaks with red Miller indices arising from Li ordering

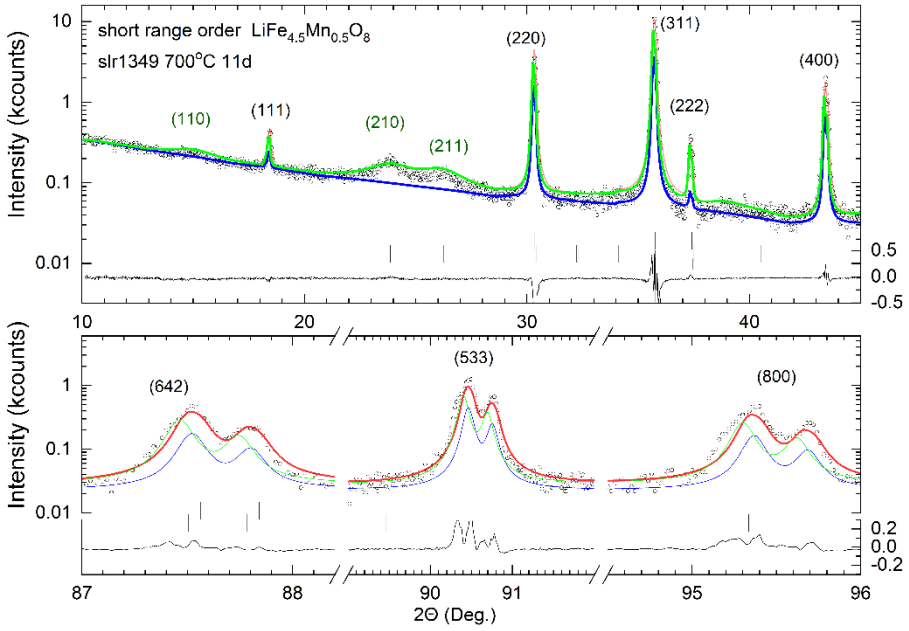
communication systems. The Li deficient version of $LiFe_5O_8$ ferrites may be used for the development of all-solid-state battery technologies. Apart from the high interest in pure lithium ferrite, mixed $LiFe_{5-x}M_xO_8$ compounds, where M is a transitional metal cation other than Fe, may display interesting physical properties for important emerging technologies. Here we highlight some preliminary results concerning the preparation of $LiFe_{5-x}M_xO_8$ compounds, and the crystal structure and microstructure characterization, using powder x-ray diffraction data. Samples quenched from T>900^{o}C to water at ambient conditions crystalize into the so-called disordered inverse spinel structure (space group Fd-3m) with Li occupying randomly with Fe the octahedral sites [(16d) (1/2,1/2,1/2)], with ratio 0.25:1.75. The remaining Fe cations exclusively occupy the tetrahedral [(8a), (1/8,1/8,1/8)] sites. Oxygen anions occupy the [(32e), (x,x,x)] sites. Below T_{OD}=740^{o}C, $LiFe_5O_8$ compound undergoes an ordered-disordered transition which involves only the octahedral Fe and Li cations. The ordered form can be described by non-centrosymmetric $P4_332$ space group. Fig. 1 shows the unit cell of the ordered form of $LiFe_5O_8$. The tetrahedral [(8c), (x,x,x), x=-0.0017] and the octahedral [(12d) (1/8,y, -y+1/4), y=0.0366] sites, are exclusively occupied by iron. The Li ions occupy the octahedral [(4b), (5/8,5/8,5/8)] sites. The O(1) ions occupy the general position [(24e), (x,y,z)], and O(2) the [(8c) (x,x,x), x=0.385]. The ferrite was prepared with a solid-state reaction of stoichiometric amounts of high purity Li_2CO_3 (99.99%), Fe_2O_3 (99.99%) and MnO_2 (99.99%). The pastilles were heated at 1100^o C for 24h (repeated three times). The disordered form of $LiFe_5O_8$ is produced by quenching the pastilles to water (room temperature). The ordered form was obtained, by lowering the furnace temperature to 700^{o}C and keeping it, for a week. The powder x-ray diffraction patterns for all the quenched samples were Rietveld refined with one phase model adopting the reverse spinel structure. Within the experimental error we found that Li occupies exclusively the octahedral sites together with iron. From x-ray diffraction data we cannot determine the location of Mn. Based on Mossbauer spectra and crystal chemistry arguments, we suggest that Mn ions occupy the octahedral sites. Microstructural analysis of the x-ray diffraction patterns, based on the Bragg peak broadening indicates that coherence diffraction domains for these samples are above 500 nm.

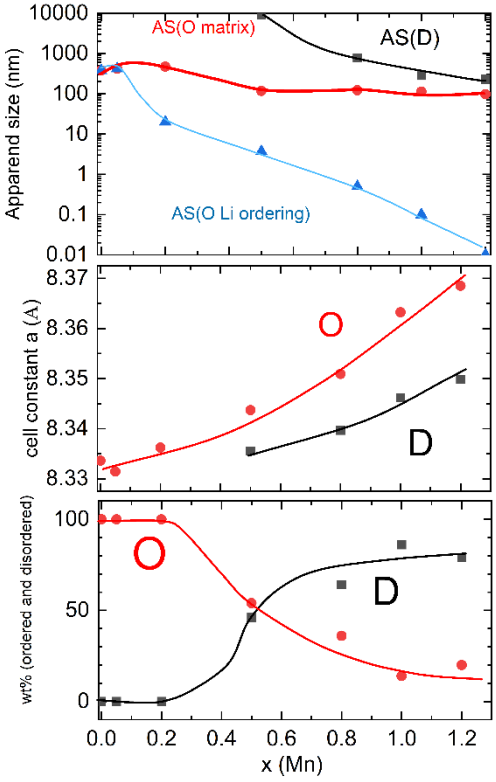
Fig. 2 shows the Rietveld plots of the samples annealed at 700oC for a week, with x=0.05 and x=0.2. The XRD pattern of the x=0.05 sample, was refined with a single-phase model. The apparent size of the Li ordered domains (LOD) is resolution limited. For the x=0.2 sample a selective broadening of the additional peaks (arising from Li ordering) was observed. The apparent size broadening for the LOD was estimated at about 19 nm. For higher Mn content (x>0.2) the samples are phase separated. They consist of a mixture of ordered and disordered phases. The apparent size of the LOD decreases with x (e.g. for x=0.5, the apparent size is 3.7 nm).
As the Mn content increases (e.g. x>0.3) the x-ray diffraction patterns (see Fig. 3) uncover a novel phase separation. The XRD data can be Rietveld refined with a two-phase model, consisting of the disordered and ordered form of $LiFe_5O_8$ ferite. Interestingly, the diffraction peaks arising from the Li ordering in the ordered form of $LiFe_5O_8$ are wider than

those of classical spinel structure. Thus, a phase separation and nanosize ordered domains within the ordered form of $LiFe_5O_8$ has been observed. For Mn content x=0.8, as the Rietveld plot of Fig. 3 shows, the size of the Li ordered domains are below 1 nm. Their diffraction signature is hidden by the background ($20<2\Theta<30^o$).

Fig. 4 shows the variation of the cell constants (middle panel) and the percentages (lower panel) of the ordered and disordered phases, as a function of Mn concentration. The upper panel depicts the apparent size of the diffraction domains (estimated by Fullprof suite of programs) of the Li ordering in the ordered matrix, and the apart sizes of the disordering and ordering phases, estimated from spinel structure diffraction peaks. We believe that the observed behavior is inherent of the first order character of structure transition occurring at 750^oC and in the presence of Mn ions. Our results demonstrate an interesting method to produce nanomaterials inside a crystal matrix.

Fig. 3 Rietveld plots of the ordered $LaFe_{5-x}Mn_xO_8$ (x=0.5, 0.8) samples





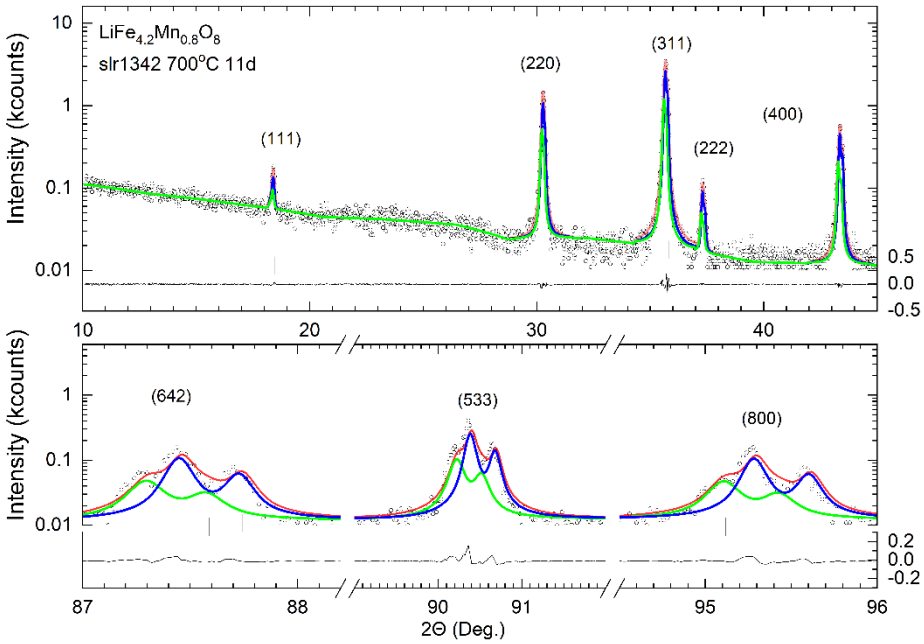


Fig. 4 variation of the cell constants (middle panel) and the percentages (lower panel) of the ordered and disordered phases, as a function of Mn concentration. The upper panel displays the apparent size of the diffraction domains (estimated by Fullprof suite of programs) of Li ordering in the ordered matrix, and the apart sizes of the disordering and ordering phases estimated from spinel structure diffraction peaks.

[1] P. B. Braun, Nature, A superstructure in spinels, vol. 27, 1243, 1952, [2] R. G. West and A. C. Blankenship J. Am. Ceram, Magnetic properties of dense Lithium Ferrites, vol. 50, 343-349, 1967., [3] K. K. Kumawat et. al. J. All. Comp. Structural and magnetic properties of ordered inverse spinel $Li_xFe_5O_8$, vol., 865, 158849 2021., [4] R. Koferstein, J. Sol. St. Chem., Thermoanalytical, optical, and magnetic investigations on nanocrystalline $Li_{0.5}Fe_{2.5}O_4$ and resulting ceramics prepared by a starch-based soft-chemistry synthesis, vol. 287, 121380, 2020.

OUTPUT

Publications in International Journals

1. Varouti E. Devlin E., Sanakis Y., Pissas M., Christides C., Tomara GN., Karahaliou PK., Georga SN., Krontiras CA., A systematic Mossbauer spectroscopy study of Y3Fe5O12 samples displaying different magnetic ac-susceptibility and electric permittivity spectra, JMMM, 495, pp. 165881 (2020). https://doi.org/10.1016/j.jmmm.2019.165881
2. Georgopoulou A., Pissas M., Psycharis V., Sanakis Y., and Raptopoulou C., Trinuclear NiII-LnIII-NiII Complexes with Schiff Base Ligands: Synthesis, Structure, and Magnetic Properties, *Molecules* 25, pp. 2280 (2020). https://doi.org/10.3390/molecules25102280
3. Papadopoulos C., Efthimiadou E., Pissas M., Fuentes D., Boukos N., Psycharis V., Kordas G., Loukopoulos V., Kagadis G.. Magnetic fluid hyperthermia simulations in evaluation of SAR calculation methods, *Physica Medica* 71, pp. 39-52 (2020). https://doi.org/10.1016/j.ejmp.2020.02.011.
4. Sanakis Y., Krzystek J., Maganas Dimitrios, Grigoropoulos Alexios, Ferentinos Eleftherios, Kostakis Marios G., Petroulea Vasiliki, Pissas Michael, Thirunavukkuarasu Komalavalli, Wernsdorfer Wolfgang, Neese Frank, and Kyritsis Panayotis, Magnetic Properties and Electronic Structure of the S = 2 Complex [MnIII{(OPPh2)2N}3] Showing Field-Induced Slow Magnetization Relaxation, *Inorg. Chem*. 59 pp. 13281–13294 (2020) https://doi.org/10.1021/acs.inorgchem.0c01636
5. Sanakis Y., Pissas M., Krzystek J., Ozarowsk A., Telser J., Raptis R. Ferromagnetically-coupled, triangular, [Bu4N]2[CuII3(μ3-Br)2(μ-4-O2N-pz)3Br3] complex revisited: The effect of coordinated halides on spin relaxation properties, *Polyhedron* 177, pp. 114258, (2020). https://doi.org/10.1016/j.poly.2019.114258

Books/Chapters in Books

Varouti E., Manios E., Tsiachristos I., Alexandridis A., Pissas M. Modern Magnetic and Spintronic Materials. NATO Science for Peace and Security Series B: Physics and Biophysics, Springer Dordrecht , Edited by Kaidatzis A., Sidorenko S., Vladymyrskyi I., Niarchos D. ch. 2 pp. 27-47**, (**2020). https://doi.org/10.1007/978-94-024-2034-0_2

Teaching and Training Activities

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

M. Pissas
Graduate course “Experimental methods” of the graduate program “Physics and technological applications”, 1/3/2020-31-06/2020, co-organized by the School of Applied Mathematical and Physical Sciences of National Technical University of Athens and NCSR Demokritos.

M. Pissas
Undergraduate course “Methods of material characterization”, 2020, co-organized by School of Applied Mathematical and Physical Sciences of National Technical University of Athens and INN Demokritos.

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 2019-20.

Master Dissertations completed in 2020

Name: Maria Bazini
Dissertation Title: Correlation of the mechanical stress concentration with the remanence magnetic field at the surface of magnetic steels
Research Supervisor at NCSR: Michael Pissas

Presented at The School of Applied Mathematical and Physics Science, NTUA

Name: Kostas Baskourelos
Dissertation Title: Solution of the wave propagation in waveguides with finite element method
Research Supervisor at NCSR: Michael Pissas
Presented at The School of Applied Mathematical and Physics Science, NTUA

SYNCHROTRON AND NEUTRON SCATTERING STUDIES OF BULK AND NANOSTRUCTURED MATERIALS

Project Leader: Evangelia Moschopoulou

Permanent Research Staff: Evangelia Moschopoulou

Research Collaborators (emeritus or visiting): Olivier Isnard

- **Objectives**

● Synthesis of the quantum materials $RE_mT_nIn_{3m+2n}$ (RE = rare earth, T= Co, Rh, Ir; $m = n = 1$, $m = 2$, $n = 1$)
● Structural and morphological characterization of these materials by advanced synchrotron and neutron-based scattering, spectroscopy and imaging probes as well as by electron diffraction and microscopy
● Determination of their physical properties down to low temperatures, medium pressures and up to high magnetic fields
● Establishment of the structure-properties relationship
● Understanding the role dimensionality and strong electron correlations of these complex materials
● Understanding the role of structure and composition on the cooperative phenomena of magnetism and superconductivity in quantum materials
● Understanding the role of structure and composition on the cooperative phenomena of magnetism and superconductivity in quantum materials
● Understanding the role of disorder on the cooperative phenomena of magnetism and superconductivity in quantum materials

- **Activities and Main Results**

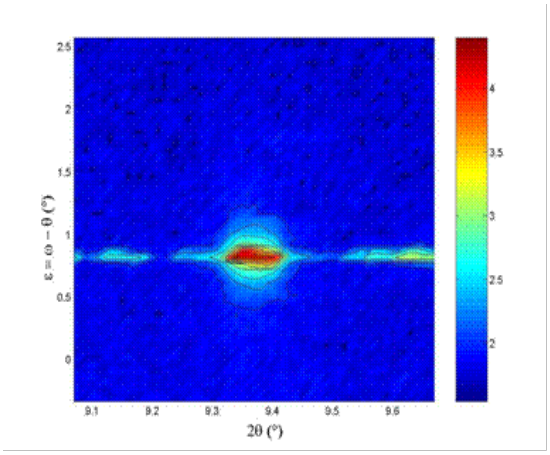
In the class of quantum materials, called heavy fermion materials (HF) materials, the strong coupling between the conduction electrons and the local *f*-electron moment fluctuations enhances considerably the effective mass of the conduction electrons and produces unexpected low-temperature properties. Even in the absence of disorder, HF materials are unconventional solids: their properties are not anticipated within the conceptual framework containing the band theory, the phonon-mediated theory of conventional superconductivity and the spin wave theory of solids. The presence of even weak (by metallurgical standards) disorder has dramatic effects on their properties.

The homologous series of HF compounds $RE_mT_nIn_{3m+2n}$ (RE = rare earth, T= Co, Rh, Ir; $m = n = 1$, $m = 2$, $n = 1$) opened unique possibilities to address the long-standing question of the role of spatial dimensionality on the low-temperature behavior of quantum materials and on the cooperative phenomena of magnetism and superconductivity.

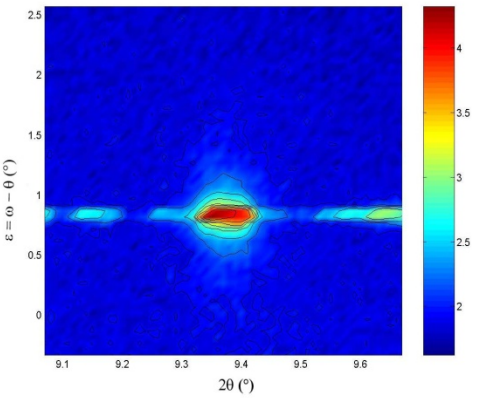
We were focused mostly on the Ce-analogues of this homologous series. A comprehensive structural investigation of the first members of the series $Ce_mT_nIn_{3m+2n}$ (T= Co, Rh, Ir; $m = n = 1$, $m = 2$, $n = 1$) has been carried out by single crystal X-ray diffraction, powder neutron diffraction, reciprocal space mapping by synchrotron X-rays and electron diffraction and microscopy. Our studies established the ordered, quasi 2-Dim nature of the crystal structure and the presence of planar disorder at some members of the series. Our investigations also demonstrated that a crystal or lattice engineering has been achieved for first time in the lattice of the well-known heavy fermion system $CeIn_3$. Furthermore, our structural investigations contributed to understanding the structure-property relationship in this unique family of dimensionally tunable quantum materials.

A representative example of disorder as revealed by synchrotron X-ray reciprocal space mapping is given at figure 1. It presents synchrotron X-ray reciprocal space maps (i), and the corresponding peak profiles (ii) of

the (002) reflection at RT and 8 K of single crystals of one member of the series the two-layer quantum material Ce_2RhIn_8. Disorder is revealed as structured diffuse intensity between Bragg peaks.



(ii)

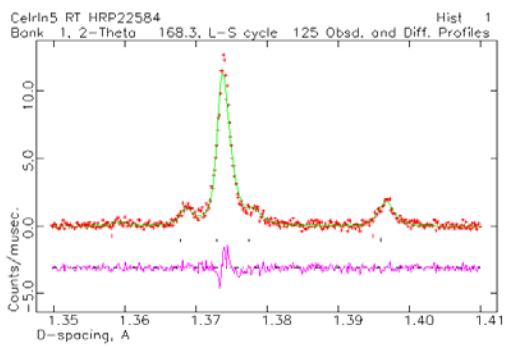


(ii)

Fig. 1. Reciprocal space maps (i) and the corresponding peak profiles (ii) of the (002) reflection at: RT and 8 K. The horizontal axis is the direction of the ω-2θ scan (direction of the diffraction vector), and the vertical axis is the offset in the ω-scan direction.

Our synchrotron X-ray reciprocal space mapping experiments revealed that structure of Ce_2RhIn_8 is disordered exhibiting a complex interplay of random planar defects, coexistence and segregation of polytypic phases (induced by periodic planar "defects"), mosaicity (i.e. domain misalignment) and non-uniform strain. These effects evolve as a function of T but they remain down to low T's. The RT diffraction data are best represented by a complex mixture of two polytypic phases, which are affected by random planar defects, differ slightly in their tetragonal structures, and exhibit different mosaicities and strain values. Ce_2RhIn_8 approaches the paracrystalline state, rather than the classic crystalline state and thus several of the concepts of conventional single-crystal crystallography are inapplicable. These structural results are important for understanding the role of disorder in the HF state and the interplay between superconductivity and magnetism. Ce_2RhIn_8 exhibits fascinating low-temperature physics. It is a HF antiferromagnet below T_N = 2.8 K it is superconductor at pressure of ~18 kbar below T_c = 2 K and it exhibits Sommerfeld coefficient $\gamma \approx 200$ mJ/(moleK^2).

Powder neutron diffraction carried out at the one layer quantum material $CeIrIn_5$ revealed similar type of disorder as the one in Ce_2RhIn_8. Fig. 2 presents expanded regions of the diffraction profile of $CeIrIn_5$ for single phase (i) and two-phase (ii) models.



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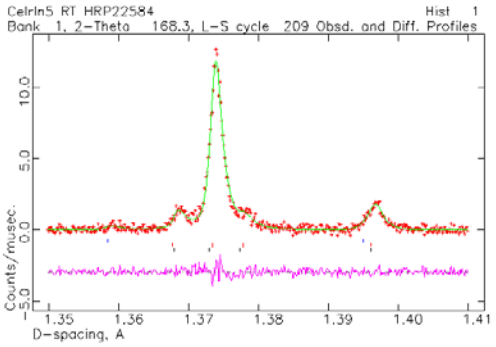


(ii)

Fig. 2. Expanded regions of the powder neutron diffraction profile of $CeIrIn_5$ for single phase (i) and two-phase (ii) models.

The RT structure of $CeIrIn_5$ is consistent with a bimodal distribution of lattice parameters and microstrain. These structural results are critical for correlating structural signatures at the HF state and at the interplay between superconductivity and magnetism. $CeIrIn_5$: exhibits intriguing low-temperature properties. It is a HF superconductor with Sommerfeld coefficient $\gamma \approx 750$ mJ/(moleK^2), resistivity $\rho = 0$ below $T_0 = 1.2$ K and bulk superconducting transition at $T_c = 0.4$ K.

Detecting the type, strength and spatial extent of disorder of HF materials in particular and quantum materials in general, as just outlined, is essential for determining the underlying physics. The reason of the sensitivity of the HF materials to disorder involves their very basic physics and energy scales. The local spins in HF's are coupled via the exchange parameter J to the conduction electrons and they are compensated below a small energy scale, the Kondo temperature, T_K, which depends exponentially on $|J|$. There is an obvious competition between the low-temperature compensated state and the magnetically ordered state of the uncompensated moments. The energy scale of the latter is the Ruderman-Kittel-Kasuya-Yosida (RKKY) temperature, T_{RKKY}, which characterizes the moment-moment interaction in metals and changes as $|J|^2$. The competition between the single-site Kondo screening, and inter-site RKKY spin coupling depends, besides $|J|$, on the density of the conduction electrons, on disorder and on the spatial dimensionality. Even modest disorder leads to modest variations of J which, because it is amplified exponentially, can lead to wide distributions of T_K and thus to dramatic changes of the low-temperature properties. Theoretical predictions are most commonly compared with experimental results from materials exhibiting chemical disorder caused by doping, since doping is a rather standard way to bring these systems to the QCP and to induce non-Fermi liquid behavior. While this synergy between experiment and theory provided us with significant results, identifying HF's, as the ones we study and present here, that exhibit intrinsic disorder should advance our present understanding of the interplay between interactions-disorder-correlations.
By investigating these issues in HF materials, we set the stepping stone for gaining insight in the physics and properties of the broader class of quantum materials.

- **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., "Synchrotron X-ray RMS of Ce_2RhIn_8 single crystals" COST online-Meeting 16 April, 2020.

Oral

1. Moshopoulou E.G., "Temperature dependence of the crystal structure of $Ce_mM_nIn_{3m+2n}$ versus m, M and T (M = Rh, Ir, Co)" COST online-Meeting 6 November, 2020.

Program 4

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 (PCInano, started 1/2018), Eleni-Marina Kasimati, MSc (partially funded by Kripis-II, started 2/2018).

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

Activities and Main Results

A. Designed positively charged cyclodextrin derivatives (PCCDs) for applications in nanobiotechnology: Amino-terminated PCCDs for antibiotic delivery in biofilms has been pursued in collaboration with microbiology groups (Prof. Ericson and Farewell, U. Gothenburg, Sweden). A major reason for the difficulty in treating antibiotic-resistant biofilms linked with chronic infections is the very limited penetration of antibiotics inside the bacterial colonies. The positively charged derivative octakis[6-(2-aminoethylthio)-6-deoxy]-γ-CD (γCys) was tested to improve the delivery of the antibiotics oxacillin and rifampicin to *Staphylococcus epidermidis* biofilm cultures grown *in vitro*. Multiphoton laser scanning microscopy and super-resolution fluorescence microscopy experiments revealed that fluorescein-labeled γCys is distributed uniformly inside live biofilm cultures. NMR spectroscopic data in aqueous solution confirmed that γCys forms inclusion complexes with antibiotics oxacillin and rifampicin. The efficacy of γCys/antibiotic treatments was evaluated by measuring the viability of the biofilms. The results showed that the γCys/rifampicin combination reduced the biofilm viability to background levels demonstrating a remarkable improvement over rifampicin alone. The results also revealed a strong synergistic effect, suggesting interference of γCys with mechanisms that affect the integrity of the biofilm and its susceptibility to rifampicin. The work was published in the International Journal of Pharmaceutics (Thomsen, H. *et al., Int. J. Pharm.*, **2020** *587*, 119646). The research activity regarding designed PCCDs with aromatic substituents with non-toxic profile for use as bacterial toxin pore blockers is in progress. (manuscript in preparation*)*.

B. Cyclodextrin-photosensitizer covalent conjugates for applications in phototherapy: The well known tendency of photoactive porphyrinoid compounds to form water-insoluble aggregates hampers their biomedical applications. The contribution of cyclodextrins to restore and even augment the photophysical properties of porphyrinoids, increase their solubility in aqueous solutions, modulate their uptake in cancer cells and finally exert strong and controlled photoxic outcome in tumors *via* various photodynamic therapy

approaches has been reviewed and published in the Journal of Medicinal Chemistry (Mavridis, I.M., Yannakopoulou, K. *J. Med. Chem.* **2020** *63, 7*, 3391-3424). The related lab research deals with design and synthesis of suitable porphyrins as possible guest compounds for inclusion into selected cyclodextrins or of covalent porphyrin-cyclodextrin conjugates. The resulting supramolecular complexes and assemblies are used to alleviate aggregation and reconstitute the photophysical characteristics (absorption, emission intensity and lifetime) of the compounds in aqueous solution while simultaneously endowing the compounds with drug-carrier properties. The work is in progress (manuscripts in preparation).

C. Inhibitor of human insulin-regulated aminopeptidase (IRAP). IRAP is a transmembrane zinc metalloprotease with diverse biological functions, including in immune response and cognitive function. It is therefore of high medical relevance and a promising pharmacological target. In the framework of a long-standing collaboration with the Protein Chemistry Laboratory (Dr. E. Stratikos, INSRASTES, DEMOKRITOS), we solved the X-ray crystallographic structure of IRAP in complex with a macrocyclic peptide inhibitor (HA08) that combines structural elements of IRAP's natural substrates oxytocin and vasopressin in the brain and its natural inhibitor angiotensin IV (Mpakali *et al., ACS Med. Chem. Lett. 11,* 1429-1434, 2020). The structure provides insight into the enzyme's and inhibitor's selectivity and mechanisms of action.

D. Disulfide bond protein D (DsbD). The structure of a modified N-terminus of DsbD with an excised protective cap-loop that isolates the cysteines of the active site was solved, in collaboration with the Biochemistry Department, Oxford University. That protein is crucial to correct protein folding in Gram-negative bacteria. This study, combined with other studies of that protein within the framework of the same collaboration allow the detailed understanding of the enzymatic mechanism of that protein, but also more general insights on the structural changes of an enzyme upon substrate recognition (Stelzl, L.S. *et al., eLife* **2020**, *9*:e54661).

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. **Kripis-II**: participation of the group in the Institute-wide funded program, "Development of Materials and Devices for Industrial, Health, Environmental and Cultural Applications" (MIS 5002567) which is 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).

3. **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.

4. **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. Thomsen, H., Agnes, M., Uwangue, O., Persson, L., Mattsson, M., Graf, F. E. Kasimati, E.-M. Yannakopoulou, K., Ericson, M. B. and Farewell, A. Increased antibiotic efficacy and noninvasive monitoring of Staphylococcus epidermidis biofilms using per-cysteamine-substituted γ-cyclodextrin–a delivery effect validated by fluorescence microscopy. *Int. J. Pharm.* 587, 119646 (2020). https://doi.org/10.1016/j.ijpharm.2020.119646

2. Soultati, A., Verykios, A., Panagiotakis, S., Armadorou, K.-K., Haider, M.I., Kaltzoglou, A., Drivas, Ch., Fakharuddin, A., Bao, X., Yang, C., bin Mohd Yusoff, A. R., Evangelou, E. K., Petsalakis, I., Kennou, S., Falaras, P.,

Yannakopoulou, K., Pistolis, G., Argitis, P., Vasilopoulou, M. Suppressing the Photocatalytic Activity of Zinc Oxide Electron-2 Transport Layer in Nonfullerene Organic Solar Cells with a Pyrene-3 Bodipy Interlayer. *ACS Appl. Mater. Interfaces*, *12(19)*, 21961-21973 (2020). https://doi.org/10.1021/acsami.0c03147

3. Mavridis, I.M., Yannakopoulou, K. Porphyrinoid–Cyclodextrin Assemblies in Biomedical Research: An Update. *J. Med. Chem. 63, 7*, 3391-3424 (2020). https://doi.org/10.1021/acs.jmedchem.9b01069

4. Mpakali, A., Saridakis, E., Giastas, P., Maben, Z., Stern, L.J., Larhed, M., Hallberg, M., Stratikos, E. Structural Basis of Inhibition of Insulin-Regulated Aminopeptidase by a Macrocyclic Peptidic Inhibitor. *ACS Med. Chem. Lett. 11(7),* 1429-1434 (2020). https://doi.org/10.1021/acsmedchemlett.0c00172

5. Stelzl, L.S., Mavridou, D.A.I., Saridakis, E., Gonzalez, D., Baldwin, A.J., Ferguson, S.J., Sansom, M.S.P., Redfield, C. Local frustration determines loop opening during the catalytic cycle of an oxidoreductase. *eLife 9*:e54661 (2020). https://doi.org/10.7554/eLife.54661

Book Chapter

1. Saridakis, E., Coste, F. Thermal Shift Assay for Characterizing the Stability of RNA Helicases and Their Interaction with Ligands. In: Boudvillain M. (ed) *RNA Remodeling Proteins. Methods in Molecular Biology*, vol 2209. Humana, New York, NY. https://doi.org/10.1007/978-1-0716-0935-4_5

Teaching and Training Activities

- E. Saridakis

Lecture at the DEMOKRITOS Summer School 2020, “Crystallography as an aid to Biology and Medicine (Η Κρυσταλλογραφία ως αρωγός της Βιολογίας και της Ιατρικής)”, NCSR DEMOKRITOS.

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

Group Leader: George Mitrikas

Post Docs: Georgia Zahariou, Maria Chrysina

PhD Candidates: Maria Tsoukala

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

Activities and Main Results

EPR investigation of copper(II) artificial metallo-nucleases. The development of metal-based drugs that recognize, bind and react with DNA is an intensive area of research. Several agents have found applications in DNA footprinting, sensing, protein engineering and anticancer therapy. Metal-based drugs are attractive since a variety of binding modes and reactivities can be tuned based on the co-ordination number, shape and charge of the inorganic scaffold. In particular, unique biological reactivity not accessible to organic molecules renders metallodrugs interesting chemotherapeutics with unique cytotoxic mechanisms. Several metal complexes capable of Fenton or Haber-Weiss chemistry have been developed as potential anticancer drugs and, recent research has focused on the design of new copper complexes that possess DNA damaging properties.

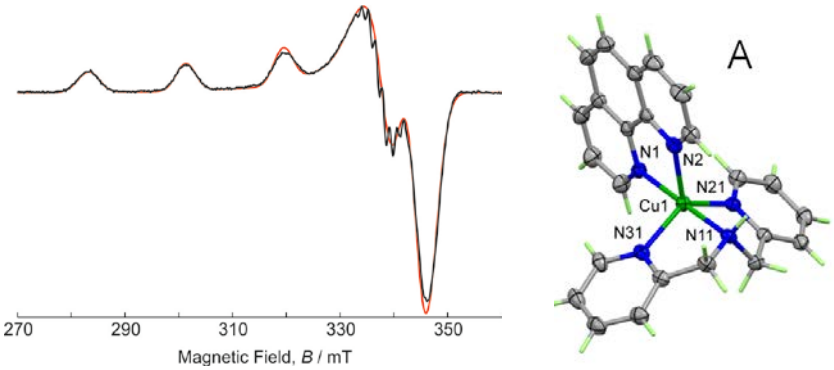


Figure 1. X-band cw EPR spectrum and its simulation (left). Structure of the copper complex (right).

To help prevent dissociation and transmetallation of the copper centre in biological systems, a tetradentate polypyridyl ligand, tris-(2-pyridylmethyl)amine (TPMA) was recently exploited. This design yielded a new type of artificial metallo-nucleases (AMN) with DNA oxidation chemistry departing substantially from Cu-Phen or simple Fenton reagents. The presence of TPMA enhanced complex stability and facilitated rearrangement of the coordination sphere during redox cycles. However, DNA binding and oxidative cleavage were nonetheless hampered by the steric bulk of TPMA which contains three pyridine groups. In this study, we set out to identify if a less hindered polypyridyl ligand di-(2-pycolylamine) (DPA) could provide a balance between complex stabilization and high-affinity DNA binding. Additionally, the penta-coordination of Cu-DPA Phenanthrene might be expected to expose a labile site for oxidation reactions at the DNA interface. Here we report the EPR characterization of complexes with general formula Cu-DPA-N,N' (where N,N' = Phen (Fig. 1), DPQ or DPPZ). The DPA ligand was anticipated to serve as a stabilizing ligand and the phenanthrene unit as a DNA intercalator.

The continuous wave (cw) EPR spectrum of Cu-DPA-PHEN is shown in Fig. 1. The spectrum exhibits axial symmetry with $g_{||} > g_{\perp}$ which implies a $d_{x^2-y^2}$ ground state being consistent with a square pyramidal geometry in the first coordination sphere. This is also supported by the g_z = 2.233±0.005 and Cu $|A_z|$=555±10 MHz principal values which are in line with a $d_{x^2-y^2}$ ground state and a {CuN5} chromophore where the axially coordinated N atom tends to increase g_z=2.2 and decrease $|A_z|$=600 MHz values that are expected for a square planar {CuN5} chromophore. To shed light into structural details of the complexes in solution, we employ pulsed EPR methods like electron nuclear double resonance (ENDOR) and hyperfine sublevel correlation (HYSCORE) spectroscopies.

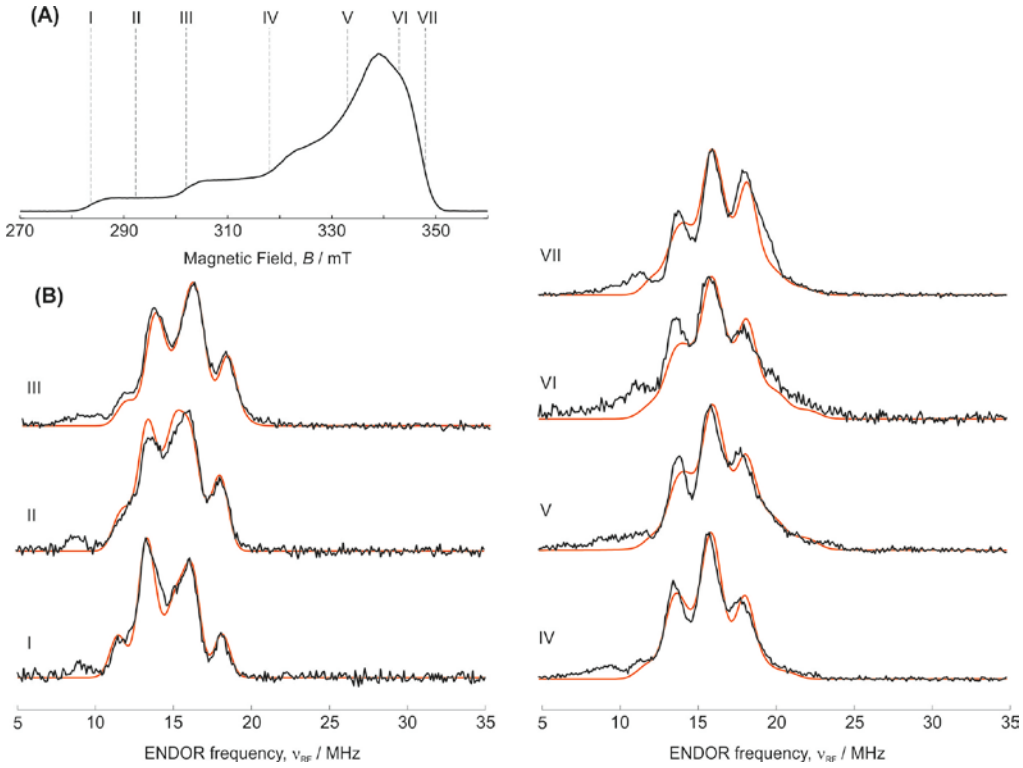


Figure 2: (A) Field-swept FID-detected EPR spectrum of Cu-DPA-PHEN in DMF/toluene (1:1) frozen solution indicating the different observer positions of ENDOR measurements. (B) Davies ENDOR spectra obtained at different field positions. Black lines: experiment; red lines: simulations. Simulations were performed assuming four equatorial nitrogen atoms.

*Fig. 2(B) (lower trace I) shows the ENDOR spectrum measured close to $g_{||}$ for which only molecules having their g-tensor z-axis parallel to magnetic field **B** contribute to the signal. This spectrum is typical for strongly coupled nitrogens with a hyperfine coupling of 30 MHz. Moreover, the shift of spectra to higher frequencies (i.e. larger hyperfine couplings) as the observer position is moving towards $g_{\perp}$, implies equatorial coordination for these nitrogen atoms. A more detailed inspection of the spectrum measured along $g_{||}$ (Fig. 2(B) I) shows that the four peaks have different intensities and splittings as well. The ENDOR features cannot be reproduced assuming only one set of magnetic parameters and, since this spectrum corresponds to a single-crystal like position, this provides strong evidence that the interacting nitrogen atoms are non-equivalent. The very good agreement between experiment and simulations provides strong evidence on the concept of four strongly coupled pyridine nitrogens occupying equatorial positions in a more or less square planar arrangement*.

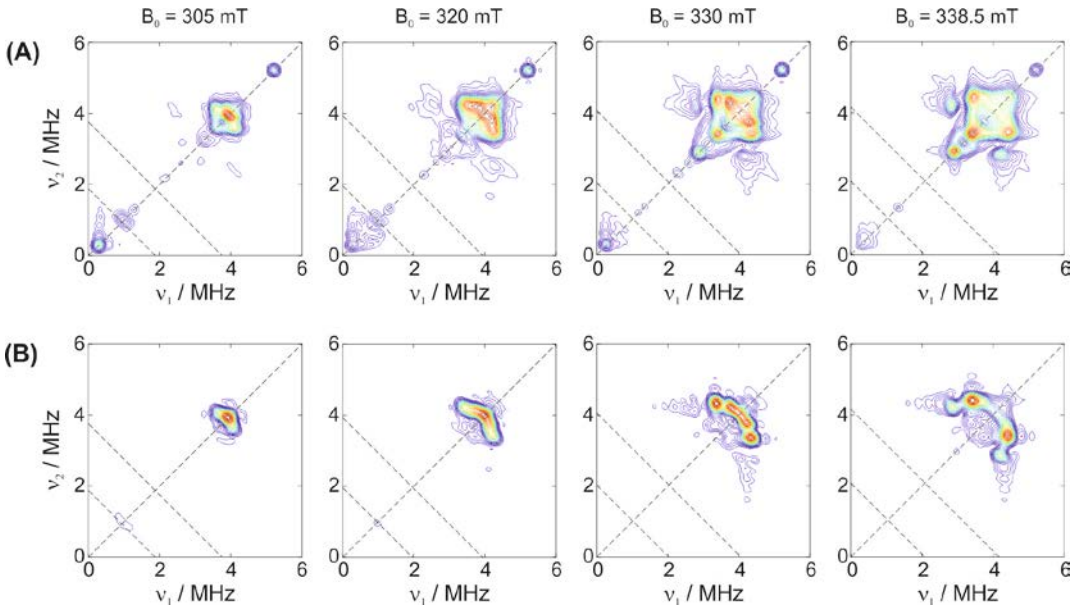


Figure 3: (A) Experimental ^{14}N-HYSCORE spectra of Cu-DPA-PHEN in DMF/toluene (1:1) frozen solution measured at four different observer positions B_0. Anti-diagonal lines denote harmonics of the ^{14}N Larmor frequency at ν_N and $2\nu_N$. (B) Corresponding simulated spectra.

HYSCORE spectroscopy revealed also the existence of a weakly-coupled nitrogen atom, as can be seen in Fig. 3. The detailed simulations of HYSCORE spectra measured at four different field positions (Fig. 3(B)) show that the principal values of the hyperfine coupling tensor fulfil the condition |A1|=|A2|>|A3|, which occurs when the isotropic and the anisotropic parts of the hyperfine interaction have opposite signs. Moreover, assuming that the electron spin is 100% localized on the metal ion, the through space dipole-dipole interaction gives r = 2.3 ± 0.1 Å. This distance together with the obtained orientation of the corresponding tensor (β = 15°), is compatible with a nitrogen atom occupying an axial position, namely atom N2.

In summary, EPR spectroscopy revealed that, upon dissolution, the complex relaxes into a square pyramidal conformation. Four nitrogen atoms occupy equatorial positions in a more or less square planar arrangement, whereas, a fifth nitrogen, possibly the N2 nitrogen of PHEN, occupies an out-of-plane position only slightly deviating from axial orientation.

Parallel-mode EPR of atomic hydrogen. Parallel-mode EPR, where the oscillating microwave magnetic field B_1 is parallel to the static field B_0, is mostly used in biologically relevant studies as they often involve high spin systems. Although such approach may seem meaningless for S = 1⁄2 systems, measurement in the parallel-mode can also give non-zero EPR spectra for hyperfine-coupled S = 1⁄2 systems provided that there is strong mixing of electron (M_S) and nuclear (M_I) spin states, so that M_S is not a good quantum number. A sufficient mixing of states requires that the electron Zeeman and hyperfine interaction terms have comparable strengths, a condition that is met for low-field EPR spectroscopy and/or systems with exceptionally strong hyperfine coupling constants. The hydrogen atom (^{1}H) is the most typical example of an electronic spin S = 1⁄2 , hyperfine-coupled to a proton nuclear spin, I = 1⁄2 , with a large isotropic coupling constant of A_0/h = 1420.40575 MHz. Weil was the first to predict that the forbidden flip–flop ($\Delta M_S = \pm 1$, $\Delta M_I = \mp 1$) EPR transition of (^{1}H) would appear in the parallel-mode EPR spectrum at L-band (1.5 GHz) and might also be detectable even at X-band (9.5 GHz). Interestingly enough, to the best of our knowledge, the experimental demonstration of parallel-mode EPR on S = 1⁄2 systems is still lacking.

Herein, we report the first dual-mode X-band EPR experiments of hydrogen atom (both isotopes ^{1}Hand ^{2}H) encapsulated in polyhedral oligomeric silsesquioxane (POSS) cages of the type $R_8Si_8O_{12}$ with R=OSi(CH$_3$)$_3$, also termed Q_8M_8 (Fig. 4).

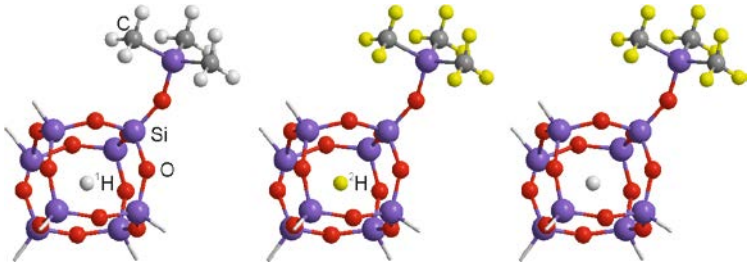


Figure 4: Structures of the POSS molecules $R_8Si_8O_{12}$ with encapsulated atoms. Only one of the eight groups R is shown for each molecule. Left: $^1H@h_{72}Q_8M_8$, middle: $^2H@d_{72}Q_8M_8$, right: $^1H@d_{72}Q_8M_8$ species occurs as a byproduct of due to incomplete isotope substitution or existence of proton-containing organic solvents during γ-irradiation.

Firstly, we extend the theory to the system of an electron spin S = 1⁄2 coupled to a nuclear spin I = 1, and we derive analytical expressions for the resonance fields and the transition probabilities both for perpendicular and parallel modes. We then examine some interesting features of the forbidden transitions like their first-order dependence on the nuclear g-factor, g_n , and the existence of a *clock transition* with f = 307 MHz. Finally, the dual-mode experimental spectra of $^1H@h_{72}Q_8M_8$ and $^2H@d_{72}Q_8M_8$ are given in Fig.5(a) and Fig.5(b)

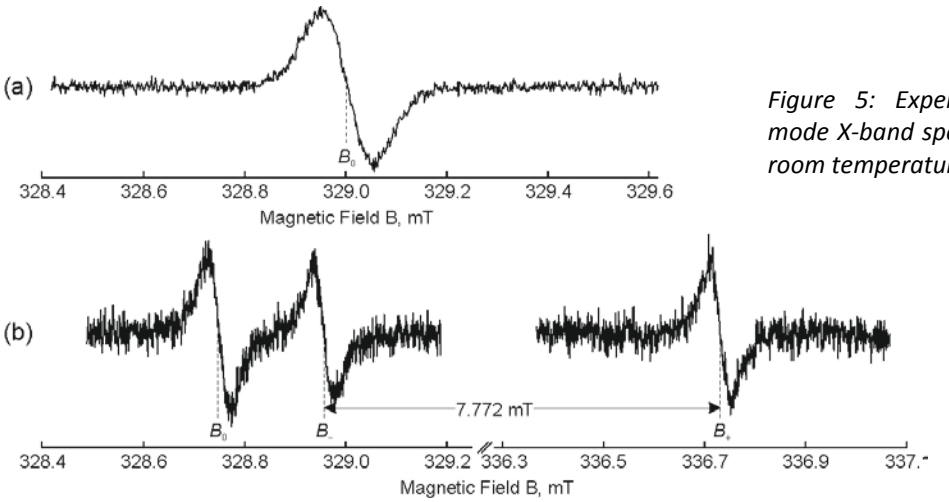


Figure 5: Experimental parallel-mode X-band spectra measured at room temperature

Funding

"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.

"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.

"KRIPIS II": participation of the group in the Institute-wide funded program, "Development of Materials and Devices for Industrial, Health, Environmental and Cultural Applications" (MIS 5002567) which is 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).

OUTPUT

Publications in International Journals

1. Mitrikas, G., Sanakis, Y., Ioannidis, N. Parallel‐Mode EPR of Atomic Hydrogen Encapsulated in POSS Cages, *Applied Magnetic Resonance* **51**, 1451–1466 (2020) DOI: 10.1007/s00723-020-01263-5
2. Mitrikas, G., Menenakou, S. Electron spin relaxation properties of atomic hydrogen encapsulated in octavinyl POSS cages, *Phys. Chem. Chem. Phys.* **22**, 15751-15758 (2020) DOI: 10.1039/d0cp02479a
3. Fantoni, N. Z., Molphy, Z., O'Carroll, S., Menounou, G., Mitrikas, G., Krokidis, M., Chatgilialoglu, C., Colleran, J., Banasiak, A., Clynes, M., Roche, S., Kelly, S., McKee, V., Kellett, A. Polypyridyl-Based Copper Phenanthrene Complexes: Combining Stability with Enhanced DNA Recognition, *Chem. Eur. J.* **27**, 971-983 (2020) DOI: 10.1002/chem.202001996
4. Stamos, N. A., Ferentinos, E., Chrysina, M., Raptopoulou, C. P., Psycharis, V., Sanakis, Y., Pantazis, D. A., Kyritsis, P., Mitrikas, G. Unusual 31P Hyperfine Strain Effects in a Conformationally Flexible Cu(II) Complex Revealed by Two-Dimensional Pulse EPR Spectroscopy, *Inorg. Chem.* **59**, 3666−3676 (2020) DOI: 10.1021/acs.inorgchem.9b03237
5. Michailidi, E. D., Bomis, G., Varoutoglou, A., Kyzas, G. Z., Mitrikas, G., Mitropoulos, A. C., Efthimiadou, E. K., Favvas, E. P. Bulk nanobubbles: Production and investigation of their formation/stability mechanism, *Journal of Colloid and Interface Science* **564**, 371–380 (2020) DOI: 10.1016/j.jcis.2019.12.093

FREE RADICALS IN BIO- AND NANOTECHNOLOGY

Project Leader: Dr. Kyriakos Papadopoulos

Post Docs: Dr. Marios Krokidis

Other Staff: Irene Dousi (technical scientific personel)

Research Collaborators: Dr. Chryssostomos Chatgilialoglu (main scientific collaborator, National Research Council, Bologna, Italy); Andrew Kellett (School of Chemical Sciences and National Institute for Cellular Biotechnology, Dublin City University, Ireland); Eleni Efthimiadou (Department of Chemistry, National and Kapodistrian University of Athens, Greece)

- **Objectives**

The main objectives of the Laboratory in the last year were focused on free radical-based processes related to bio-nanotechnological applications with emphasis on DNA damage biomarkers identifications, phospholipids transformations and membrane lipid reorganizations induced by chemotherapeutic agents and nanocarriers, highlighting side effects of their pharmacological activity. Lastly, our group was also involved in collaborative works regarding DNA damaging properties of novel artificial metallo-nucleases and mechanistic studies related to specific DNA lesions formation.

- **Activities and Main Results**

Biochemical Analysis of DNA damage in cellular disease models and clinical samples

Cockayne Syndrome (CS) is an autosomal recessive neurodegenerative premature aging disorder associated with defects in nucleotide excision repair (NER). Cells from CS patients, with mutations in CSA or CSB genes, present elevated levels of reactive oxygen species (ROS) and are defective in the repair of a variety of oxidatively generated DNA lesions. Using liquid chromatography tandem mass spectrometry, we have determined purine DNA lesions such as the four 5',8-cyclopurines (cPu) lesions and the two 8-oxo-purine (8-oxo-Pu) lesions, in wild type (wt) CSA, defective CSA, wtCSB and defective CSB-transformed fibroblasts under different oxygen tensions (hyperoxic 21%, physioxic 5% and hypoxic 1%). (Krokidis et al., *Cells*, 2020: 9, 1671; Figure 1A).

Chronic inflammation is estimated to be a causative factor in a variety of diseases. We have analyzed the presence of cPu in genomic DNA isolated from adipose tissue biopsies collected from inflammatory bowel diseases (IBD)-affected patients and severely obese subjects, respectively, versus control specimens. In colon biopsies, characterized by a higher gene expression level of inducible nitric oxide synthase (iNOS), a significant increase of 8-oxo-dA and 8-oxo-dG lesions and an accumulation of both diastereomeric cPu have been detected. In contrast, the 8-oxo-dA and 8-oxo-dG levels were extremely lower compared to the colon tissues values and no accumulation of cPu, in the inflamed visceral adipose tissue biopsies isolated from bariatric patients versus the lean counterpart was reported. In addition, in adipose tissue undetectable levels of iNOS have been found (Masi et al., *Redox Biology*, 2020: 34, 101562; Figure 1B).

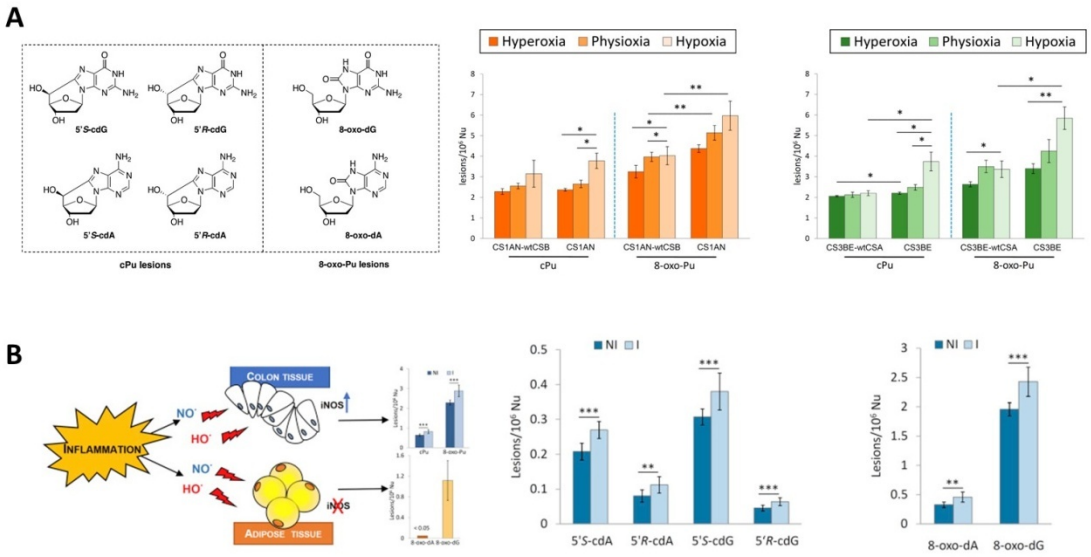


Figure 1: *(A) LC-MS/MS analysis for DNA lesion quantification (cPu and 8-oxo-Pu) in DNA samples isolated from wild type (wt) CSA, defective CSA, (wt) CSB and defective CSB-transformed fibroblasts under different oxygen tensions (hyperoxic 21%, physioxic 5% and hypoxic 1%). (B) LC-MS/MS analysis for DNA lesions measurement in genomic DNA isolated from colon tissues samples from IBD patients.*

Fatty-acid based lipidomic analysis in cellular models upon chemotherapeutics and nanoparticles exposure

Human embryonic kidney (HEK-293) cells were exposed for 24 h to bleomycin and polymeric iron oxide nanoparticles (Fe-NPs), alone or in combination. The fatty acid–based membrane lipidomic analysis evidenced the fatty acid remodeling in response to the treatments. Bleomycin alone caused the increase of saturated fatty acid (SFA) moieties in cell membrane glycerophospholipids with concomitant diminution of monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acid levels. Under Fe-NPs treatment, omega-6 PUFA decreased and trans fatty acid isomers increased. Under coadministration bleomycin and Fe-NPs, all membrane remodeling changes disappeared compared to those of the controls, with only an increase of omega-6 PUFA that elevates peroxidation index remaining (Krokidis et al., *Chemical Research in Toxicology*, 2020, 33, 2565-2572; Figure 2).

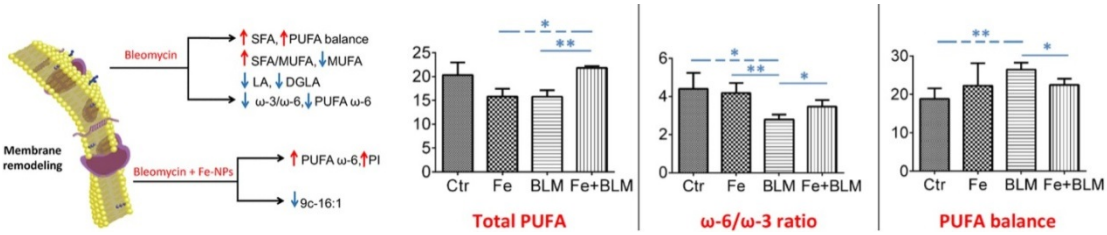


Figure 2 *Membrane homeostasis indexes (total PUFA, ω-6/ω-3 ratio and PUFA balance) in the HEK-293 cells recorded after 24 h treatment with Fe-NPs, BLM or Fe-NPs + BLM (co-treatment).*

Mechanistic models related to oxidatively-induced DNA damage and pharmacological targeting of DNA damage agents

The reaction of $HO^{\bullet}$ radical with DNA was intensively studied both mechanistically and analytically for lesions formation with a 21-mer double-stranded oligodeoxynucleotide (ds-ODNs) in γ-irradiated aqueous solutions under various oxygen concentrations and accurately quantified the six purine lesions by LC-MS/MS analysis using isotopomeric internal standards. By increasing oxygen concentration, the 8-oxo-Pu and the cPu gradually increased and decreased, respectively, reaching a gap of ~130 times at 2.01×10^{-4} M of O_2. Kinetic treatment of the data allows to estimate the C5' radical competition between cyclization and oxygen

trapping in ds-ODNs, and lastly the rate constants of the four cyclization steps. Tailored computational studies by means of dispersion-corrected DFT calculations were performed on the CGC and TAT in their double-strand models for each cPu diastereoisomer (Chatgilialoglu et al., *Journal of the American Chemical Society*, 2020: 142, 5825–5833; Figure 3A).

A series of copper(II) artificial metallo-nucleases (AMNs) was reported and their DNA damaging properties and *in-vitro* cytotoxicity were demonstrated against human-derived pancreatic cancer cells. Characterization was achieved by X-ray crystallography and continuous-wave EPR (cw-EPR), hyperfine sublevel correlation (HYSCORE) and Davies electron-nuclear double resonance (ENDOR) spectroscopies. Oxidative DNA damage occurs in the minor groove and can be inhibited by superoxide and hydroxyl radical trapping agents. The complexes, particularly Cu-DPA-DPPZ, showed promising anticancer activity against human pancreatic tumor cells with *in-vitro* results surpassing the clinical platinum(II) drug oxaliplatin (Fantoni et al.,*Chemistry European Journal*, 2020, 27:971-983, Figure 3B).

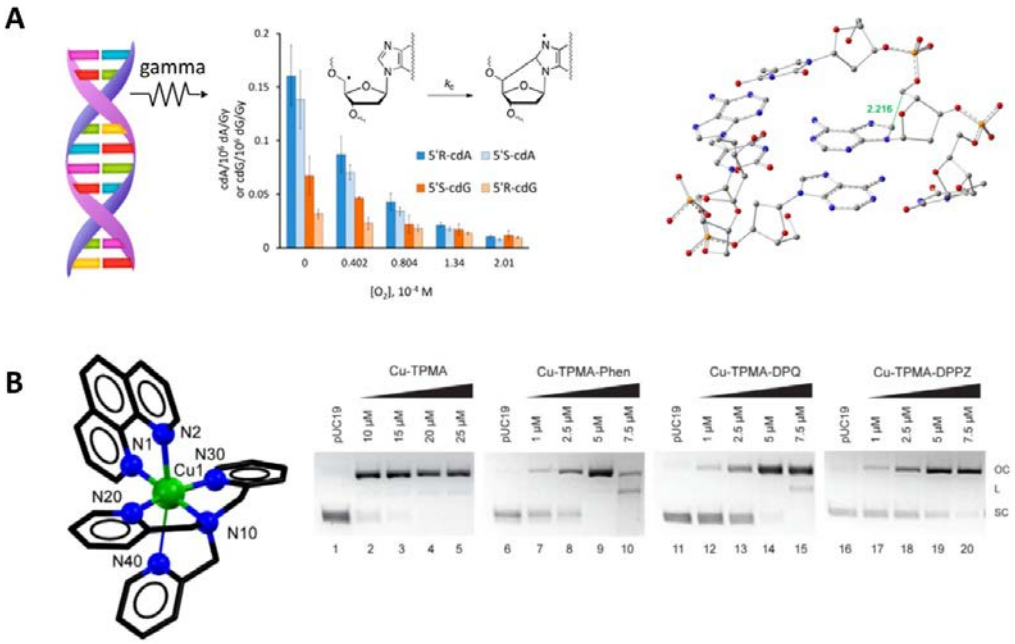


Figure 3 *(A) Radiation induced formation of cPu and two 8-oxo-Pulesions in ds-ODNs at increasing concentrations of oxygen (left); Optimized structures of the different A radicals along the cyclization pathways (right). (B) Perspective view of X-ray crystal structure of Cu-TPMA-Phen cation (left); Release of topological tension from supercoiled plasmid DNA using the topoisomerase I-mediated relaxation assay in the presence of increasing concentrations of Cu-TPMA , Cu-TPMA-Phen, Cu-TPMA-DPQ and Cu-TPMA-DPPZ (right).*

- **Participation in European Networking Research Frameworks (COST Actions) in 2020**

Name: Dr. Marios Krokidis
Title of the Action: EU COST Action CA17140 "Nano2Clinic: Cancer Nanomedicine - from the bench to the bedside", Role: MC Substituted Member- Early Career Investigator, Duration: 2018-2022, Chair of the Action: Professor Barbara Klajnert-Maculewicz, Department of General Biophysics, University of Lodz, Poland

Name: Dr. Marios Krokidis
Title of the Action: EU COST Action CA18113 "EuroMicropH: Understanding and exploiting the impacts of low pH on micro-organisms", Role: MC Substituted Member- Early Career Investigator, Duration: 2019-2023, Chair of the Action: Dr. Peter Lund, School of Biosciences, University of Birmingham, United Kingdom

OUTPUT

Publications in International Journals

1. Marios G. Krokidis, Mariarosaria D'Errico, Barbara Pascucci, Eleonora Parlanti, Annalisa Masi, Carla Ferreri, Chryssostomos Chatgilialoglu. Oxygen-Dependent Accumulation of Purine DNA Lesions in Cockayne Syndrome. *Cells*, 9, 1671 (2020)
2. **Annalisa Masi, Paola Fortini, Marios G. Krokidis, Erminia Francesca Romeo, Cinzia Bascietto, Paola De Angelis, Valeria Guglielmi, Chryssostomos Chatgilialoglu. Increased levels of 5',8-Cyclopurine DNA lesions in inflammatory bowel diseases**. *Redox Biology*, 34, 101562 (2020)
3. Nicoló Zuin Fantoni, Zara Molphy, Sinead O'Carroll, Georgia Menounou, George Mitrikas,Marios G. Krokidis, Chryssostomos Chatgilialoglu, Martin Clynes, Sandra Roche, John Colleran, Anna Banasiak, Vickie McKee, Andrew Kellett. Polypyridyl-Based Copper Phenanthrene Complexes: Combining Stability with Enhanced DNA Recognition. *Chemistry European Journal*, 27:971-983 (2020)
4. Marios G. Krokidis, Maria Louka, Eleni K. Efthimiadou, Carla Ferreri, Chryssostomos Chatgilialoglu, Fatty acid-based lipidomics and membrane remodeling induced by bleomycin and iron nanoparticles in human embryonic kidney cells. *Chemical Research in Toxicology*, 33, 2565-2572, (2020)
5. Chryssostomos Chatgilialoglu, Leif A. Eriksson, Marios G. Krokidis, Annalisa Masi, Shudong Wang, Rubo Zhang. Oxygen Dependent Purine lesions in double-stranded oligodeoxynucleotides: Kinetic and computational studies highlight the mechanism for 5',8-cyclopurine formation. *Journal of the American Chemical Society*, 142: 5825–5833, (2020)

Books/Chapters in Books

1. Marios G. Krokidis, Transcriptomics and metabolomics in amyotrophic lateral sclerosis *Advances in Experimental Medicine and Biology, Springer*, pp 205-2012 (2020)
2. Chryssostomos Chatgilialoglu, Marios G. Krokidis, Annalisa Masi, Oxidation of the C5' Position in DNA and the Role of Purine 5',8-Cyclo-2'-deoxynucleoside Lesions. *DNA Damage, DNA Repair and Disease*, *Royal Society of Chemistry*, Vol. 1, Ch. 5, pp 117-139 (2020)

ELECTRONIC SPECTROSCOPY LABORATORY: MOLECULAR ENGINEERING OF PHOTO-FUNCTIONAL SUPRAMOLECULAR NANOSYSTEMS

Project Leader: George Pistolis

Visiting Researchers: Angelos Malliaris

PhD Candidates: Adelajda Shahu, Vyron S. Petrakis

External Collaborators: Eric Vauthey, Department of Physical Chemistry, University of Geneva, 30 quai Ernest-Ansermet, CH-1211 Geneva, 4, Switzerland. Florian Pitterl, Institute of Legal Medicine and Core Facility Metabolomics, Innsbruck Medical University, Müllerstraße 44, 6020 Innsbruck, Austria. Dr. Ioannis Petsalakis, National Hellenic Research Foundation, Athens

Objectives:

- 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.

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.

Activities and Main Results

A. Cooperative Self -Assembly of Functional Chromophores into Patterned Supramolecular Assemblies

In the first part of this project we provide spectroscopic, structural and mechanistic insights on metal-ion mediated self-assembly of a charged, amphiphilic perylene-bisimide (PBI) dimer **S** into 2D arrays consisting of parallel columnar PBI stacks with precise spatial arrangement and pattern behavior, using a readily accessible design strategy. The building block (**S**), a centrosymmetric PBI homodimer bearing a disulfonated *trans* – stilbene core (Figure 1), was designed to concurrently feature high complexation directionality with strong binding affinity through multiple supramolecular interactions. In solvents that efficiently solvate PBI e.g., chloroform, the zinc ion interacts strongly through electrostatic interactions with the negatively charged core of **S**, and with the π cloud of the stilbene moiety (cation – π interactions) forming simple 1:1 adducts. In methanol, the findings manifest the efficient formation of well – defined 2D aggregates (Figure 2) with H-type excitonic coupling.

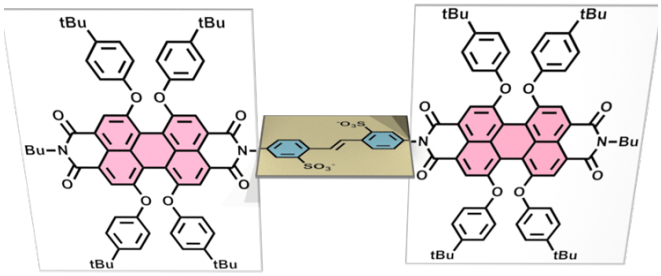


Figure 1. Chemical structure of the PBI dimer

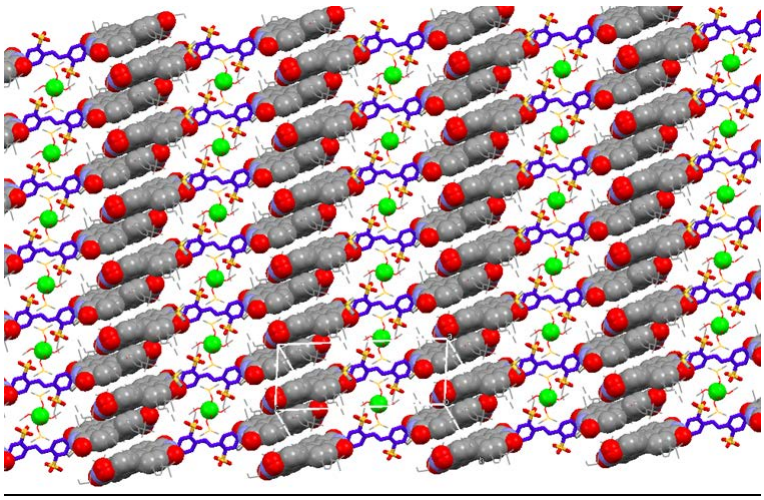


Figure 2. A 2D array parallel to ac plane formed by interdigitation of PBI rings between the columns

B. H and J-type Aggregation in Bodipy Dyes and Aggregation-Induced Emission in the NIR Region

Aggregation Induced Emission (AIE) by simple molecules and especially the NIR emission is of high novelty, with a wide range of applications in photodynamic therapy and bio-imaging. In this part of work we focus on the photophysical investigations of some BODIPY molecules in aqueous solutions by using steady-state and time-resolved spectroscopy. We observe interesting NIR emission bands due to the molecular packing of H- and J-aggregation. We are currently working to correlate the efficient NIR emission of Bodipys accompanied with a large-Stokes' shift with the type of aggregation (Figure 3).

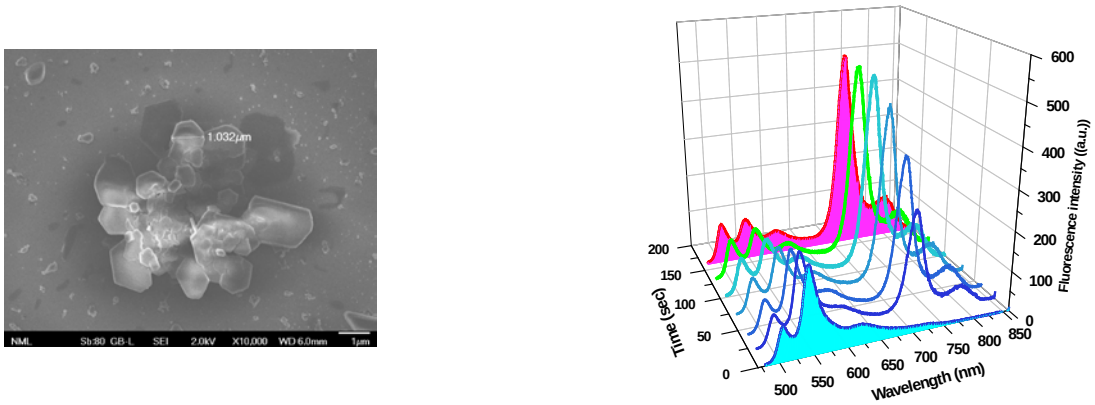


Figure 3: SEM image of BODIPY microcrystals formed in aqueous solution. Fluorescence spectra of an aqueous solution of BODIPY as a function of irradiation time (10-60 sec) with white OLED 1 mW.

Funding

- PROJECT KRHPIS (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)
- Project ΕΡΕΥΝΩ-ΚΑΙΝΟΤΟΜΩ 2020-2023: "OLED_Lumin_FoodPack" WORK CODE T2EDK-04175D- "Development of innovative smart packaging on-site-not destructive food quality assessment with application of organic photonics in the packaging material"
- Project MIS 5002772, implemented under the Action "Reinforcement of the 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).

Publications in International Journals

A. Soultati, A. Verykios, S. Panagiotakis, K.K. Armadorou, M.I. Haider, A. Kaltzoglou, C. Drivas, A. Fakharuddin, XC Bao, C. Yang, AB Yusoff, EK Evangelou, I. Petsalakis, S. Kennou, P. Falaras, K. Yannakopoulou, G. Pistolis, P. Argitis, M. Vasilopoulou **"***Suppressing the Photocatalytic Activity of Zinc Oxide Electron-Transport Layer in Nonfullerene Organic Solar Cells with a Pyrene-Bodipy Interlayer***"** *ACS Applied Materials & Interfaces***, 2020**, 12, 21961-21973

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

PhD Candidates: Alexander Canko

Master Students: Evangelos Georgas, Apostolia Makri, Alexandra Papaioannou, Georgia Nigianni

Undergraduate Students: Christos Zaggelidis

- **Objectives**

Natural products (secondary metabolites; naturally occurring small organic molecules) continue to play a pivotal role in modern drug discovery since they are superior new drug leads compared with purely synthetic compounds (hit rates of ~0.3% vs. <0.001%, respectively). Interestingly however, in most cases the active ingredient of the end-product (drug) is not a natural product but rather a semisynthetic modification or a totally synthetic compound with a natural product-inspired pharmacophore. This highlights the importance of modern synthetic organic chemistry in the exploitation of natural products. In return, natural products, with their diverse and often complex structures and important biological activity, historically define the state of the art of organic chemistry. Today, they continue to drive basic research in synthetic organic chemistry (for the discovery and validation of new methods and strategies) and are valuable tools for Chemical Biology (i.e. the exploration of biological systems using chemistry techniques).

In this context and aiming to facilitate further exploitation of bioactive natural products, objectives of this project are:

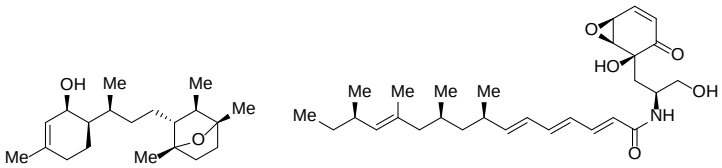
- The total synthesis of natural products with important biological activities.
- The establishment of Structure / Activity relationships.
- The design, synthesis and study of designed analogues thereof.
- The training of young researchers in the "Art and Science" of Natural Products Synthesis.

In parallel, the expertise of the team in the design and synthesis of complex organic molecules is exploited for:

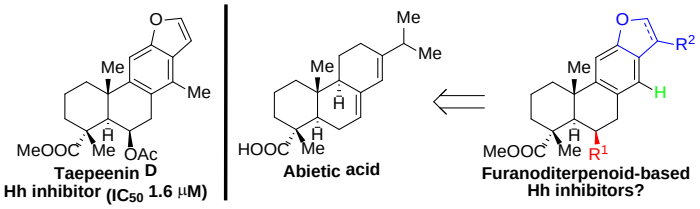
- The synthesis of heterocyclic compounds with possible use as anticancer agents
- The preparation of dyes for their use as diagnostic tools
- The synthesis of organic compounds with biocidal activity against insects
- The preparation of organic molecules with possible technological applications (e.g. photoresist etch enhancement additives, linkers for the preparation of polymers) or molecules with interesting supramolecular behavior.

- **Activities and Main 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.

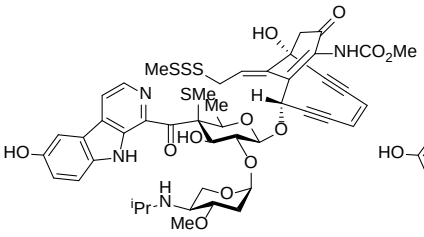


The Hedgehog (Hh) signalling pathway is one of the pathways that control embryonic patterning and cellular proliferation and differentiation. However, its abnormal activation has been linked with the occurrence of basal cell carcinoma and meduloblastoma while several other tumours (such as cancers of 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.

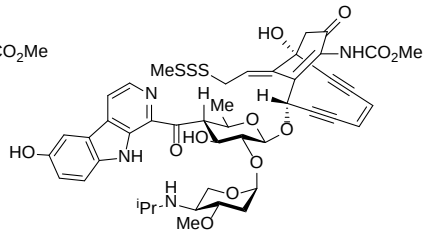


Taepeenin D is a cassane-type diterpenoid originally isolated from *Caesalpinia crista* that has been identified as a constituent of *Acacia pennata* with significant Hh/Gli-mediated transcription inhibitory activity (IC_{50} 1.6 μM) and selective cytotoxicity against cancer cells with increased Hh signalling 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). Based on a novel hexafluoroisopropanol mediated Diels-Alder reaction the enantioselective total synthesis of several cassane-type diterpenoids has been accomplished. Efforts to complete the first total synthesis of Taepeenin D and related cassane-type diterpenoids are ongoing.

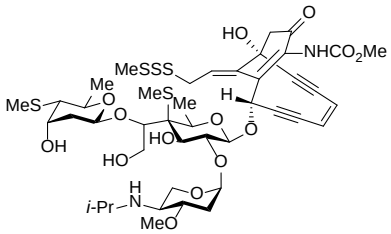
Enediyne antitumor antibiotics: Shishijimicins, Namenamicin and Uncialamycin are among the latest additions to the enediyne family of antitumor antibiotics and they exhibit exceptional potencies against tumour cell lines (e.g., IC_{50} = 0.48 pM against P388 leukemia cells for Shishijimicin A; IC_{50} = 3.3 pM against P388 cells for Namenamicin). Thus, apart from the challenge their complicated structures represent to synthetic organic chemists, these natural products are considered promising payloads for the development of novel Antibody-Drug Conjugates (ADCs).



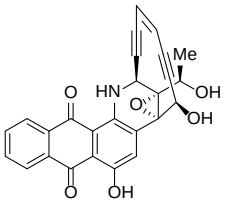
Shishijimicin A



Shishijimicin B



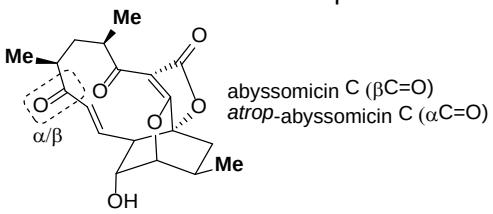
Namenamicin



Uncialamycin

During his sabbatical leave (4/2016–3/2017) to the group of Prof. K. C. Nicolaou at Rice University (Houston, U.S.A.), Dr. E. N. Pitsinos has participated in the synthetic efforts towards these natural products. This collaboration was continued over the next years and has led to: i) a streamlined total synthesis of Uncialamycin and its application to the synthesis of designed analogues for biological investigations; ii) the total synthesis of Shishijimicin A and Namenamicin, as well as, the preparation of derivatives suitable for conjugation with antibodies targeting malignant cells. Furthermore, the availability of synthetic Shishijimicin A has enabled studies aiming to clarify the DNA binding and cleavage modes of this natural product. Further studies aiming to facilitate the medicinal exploitation of these fascinating molecules are under way.

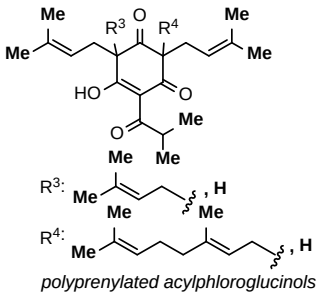
Synthesis of spirotetronate polyketide antibiotics. Spirotetronate polyketides constitute a group of natural products with fascinating structures and important biological activities. Among them, abyssomicin C and its α-atropisomer were the first members that caught-the-eye of the scientific community.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



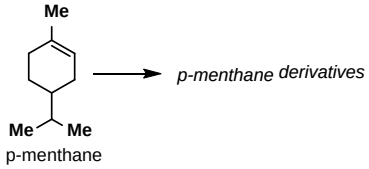
abyssomicin C (βC=O)
atrop-abyssomicin C (αC=O)

Aleksander Canko and Evangelos Georgas worked on the formal synthesis of abyssomicin C and its α-atropisomer in the racemic and asymmetric form via a scalable and high-yielding route surpassing the efficiency of previous methods. Moreover, the developed methodology was applied in the synthetic studies of other members of this family of products. This work will be part of Mr. Canko's PhD thesis and Mr Georgas' master thesis, under the supervision of Dr. V. P. Vidali.

Synthesis of natural products and analogues with insecticidal and larvicidal activity. Natural products and analogues have been widely used in pest control. Among them, several terpenes have been active against *Culex pipiens* and *Sitophilus oryzae.* As part of our ongoing research in the area of pest control, polyprenylated acylphloroglucinols and p-menthane based compounds were synthesized. A part of the synthesized compounds was evaluated for their larvicidal or insecticidal activity, and some conclusions for the relationship between structure and activity were drawn.



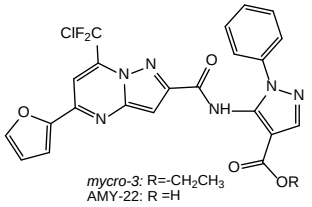
polyprenylated acylphloroglucinols



The project is the subject of two master theses, under the supervision of Dr. V. P. Vidali. This work is implemented in our laboratory by Ms Apostolia Makri and Ms Alexandra Papaioannou in collaboration with the Agricultural University of Athens, the Benaki Phytopathological Institute and the Department of Agricultural Development of the Democritus University of Thrace. This research is was completed in 2020, indicating larvicidal candidates surpassing the potency of known acyl phloroglucinols like deoxycohumulone and hyperforin against Cx. pipiens.

Synthesis of curcumine analogues 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 analogues of curcumin were designed. Their synthesis will be implemented in our laboratory by Ms Georgia Nigianni, and Georgia Athanassopoulou as part of their master thesis, under the supervision of Dr. V. P. Vidali. Synthesis and biological evaluation of these compounds highlighted potent candidates, enriching our knowledge around the structure-activity relationship and set the base for the design of compounds with improved properties. This research is ongoing.

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 a number of severe cancers, such as pancreatic, melanoma, breast cancer and others. Several small molecules, called anti-MYC compounds, have been shown to exhibit 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.



mycro-3: R=-CH_2CH_3
AMY-22: R =H

Based on the above, Dr V. P. Vidali, in collaboration with the Biomedical Research Foundation Academy of Athens (BRFAA), participates in a research project for the development of novel anti-MYC small molecules. This research is ongoing.

Funding

1. Participation in the institute's research project: "Development of Materials and Devices for Industrial, Health, Environmental and Cultural Applications" (MIS 5002567) which is 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).
2. PhD thesis scholarship for the research project:"Synthesis of Bioactive Natural Products" co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project

"Strengthening Human Resources Research Potential via Doctorate Research" (MIS-5000432), implemented by the State Scholarships Foundation (IKY).

3. Participation in the research project: "Development of novel anticancer drugs with therapeutic target the oncoprotein MYC" (MIS-5031813) which is funded by the Operational Program Competitiveness, Entrepreneurship and Innovation (NSRF 2014-2020) co-financed by Greece and the European Union.

OUTPUT

Publications in International Journals

1. Soultati, A., Verykios, A., Armadoroy, A.-K., Tountas, M., Vidali, V. P., Ladomenou, K., Palili, L., Davazoglou, D., Coutsolelos, A. G., Argitis, P., Vasilopoulou, M. Interfecial engineering for organic and perovkite solar cell using molecular materials. *J. Phys. D: Appl. Phys.* **53,** pp. 263001 (2020). DOI: 10.1088/1361-6463/ab7f73
2. Mitsios, A., Chrysanthopoulou, A., Arampatzioglou, A., Angelidou, I., Vidali, V., Ritis, K., Skendros, P., Stakos, D. Ticagrelor Exerts Immune-Modulatory effect by Attenuating Neutrophil Extracellular Traps. *Int. J. Mol. Sci.* **21**, pp. 3625–3642 (2020). DOI: 10.3390/ijms21103625
3. Vidali, V., P., Canko, A., Peroulias, A., D., Georgas, E., T., Bouzas, E., Herniman, J., M., Couladouros, E., A. An Improved Biomimetic Formal Synthesis of Abyssomicin C and atrop-Abyssomicin C. *Eur. J. Org. Chem.* **2020**, pp. 4547–4557 (2020). DOI: 10.1002/ejoc.202000671
4. Pitsinos, E., Mavridis, I., Tzouma, E., Vidali, V., P. Enantioselective Synthesis of Cassane-Type Furanoditerpenoids: Total Synthesis of Sucutiniranes C and D. *Eur. J. Org. Chem.* pp. 4730–4742 (2020). DOI: 10.1002/ejoc.202000724
5. Nicolaou, K. C., Das, D., Lu, Y., Rout, S., Pitsinos, E. N., Lyssikatos, J., Schammel, A., Sandoval, J., Hammond, M., Aujay, M., Gavrilyuk, J. Total Synthesis and Biological Evaluation of Tiancimycins A and B, Yangpumicin A, and Related Anthraquinone-Fused Enediyne Antitumor Antibiotics. *J. Am. Chem. Soc.* **142**, pp. 2549–2561 (2020). DOI: 10.1021/jacs.9b12522
6. Nicolaou, K. C., Li, R., Chen, Q., Lu, Z., Pitsinos, E. N., Schammel, A., Lin, B., Gu, C., Sarvaiya, H., Tchelepi, R., Valdiosera, A., Clubb, J., Barbour, N., Sisodiya, V., Sandoval, J., Lee, C., Aujay, M., Gavrilyuk, J. Synthesis and Biological Evaluation of Shishijimicin A-Type Linker-Drugs and Antibody–Drug Conjugates. *J. Am. Chem. Soc.* **142**, pp. 12890−12899 (2020). DOI: 10.1021/jacs.0c06554

International Conferences Presentations (invited, oral, poster)

1. Vidali, V. P. "Improvements in the Biomimetic Synthesis of Abyssomicin C and Atrop-Abyssomicin C", Results and Perspectives in Virtual Congress on Materials Science and Engineering, 9-10 November 2020 (oral presentation).
2. Pitsinos, E. N. "Natural product-driven chemistry at the interface with biology", 18th Hellenic Symposium on Medicinal Chemistry (18th HSMC), 25–27 February 2020, online symposium (invited plenary lecture).

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

1. Kapella A., Gkeka p., Stellas, D., Vidali, V. P., Papfotika A., Christoforidis S., Cournia, Z., Couladouros, E. A. Design and synthesis of targeted inhibitors of PI3Kα as candidate anti-cancer drugs. *Review of Clinical Pharmacology and Pharmacokinetics* **34**, 77-78 (2020)
2. Vidali, V. P. Synthesis of Natural Products and Designed organic molecules in anticancer drug development. *Review of Clinical Pharmacology and Pharmacokinetics* **34**, 64-65 (2020)

Master Dissertations completed in 2020

Name: Apostolia Makri
Dissertation Title:Synthhesis of acylphloroglucinol derivatives and assessment of their toxicity against larvae of the species *Culex pipiens L. (Diptera: Culicidae)*
Research Supervisor at NCSR: Dr Veroniki P. Vidali
University where the Thesis was presented: Agricultural University of Athens

Name: Alexandra Papaioannou
Dissertation Title: Synthesis of terpenoids and evaluation of their insecticidal activity
Research Supervisor at NCSR: Dr Veroniki P. Vidali
University where the Thesis was presented: Agricultural University of Athens

Name: Georgia Nigianni
Dissertation Title: Synthesis of monocarbonyl derivatives of curcumin and study of their biological activity as inhibitors of the aggregation of Ab- amyloid peptide of Alzheimer's disease.
Research Supervisor at NCSR: Dr Veroniki P. Vidali
University where the Thesis was presented: Department of Chemistry, Univeristy of Patras

MOLECULAR COMPUTATIONAL CHEMISTRY

Project Leader: Dr. Yannis G. Lazarou

- **Objectives**

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

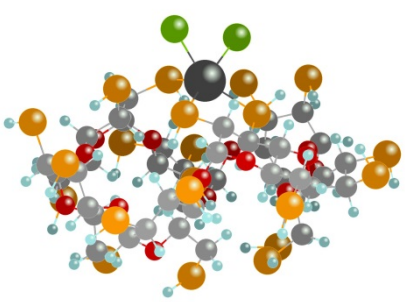
- **Activities and Main Results**

Semi-empirical PM7 theoretical investigation of the interactions between cyclodextrins and mercury species in aqueous solutions

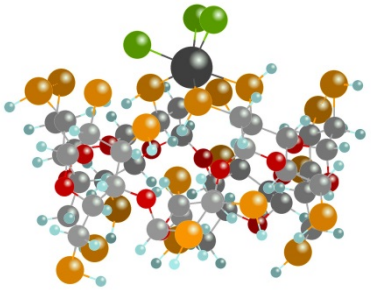
The presence of mercury (Hg) in aqueous systems as a result of natural processes or anthropogenic activities constitutes an environmental threat due to the extreme toxicity of Hg(II) compounds to life forms. In particular, seawater intrusion events into coastal aquifers contained within mercury-rich bedrock may lead to elevated concentrations of total mercury in groundwater used for drinking or irrigation, occasionally exceeding the permissible level of 1 μg/L set by the World Health Organization. In the island of Skiathos, the detection of mercury reaching groundwater concentrations of 6 μg/L prompted a detailed investigation of its natural causes as well as of possible means aiming at alleviating this severe problem.

A promising alleviation approach would involve materials capable of strongly binding with Hg(II) species allowing their removal from water. Therefore, the chemical structure and thermodynamic stability of association complexes of natural and derivatized cyclodextrins (CDs) with Hg(II) species were investigated by the MOPAC program at the semiempirical PM7 level of theory; the treatment of solvent effects in aqueous medium was performed by the Conductor-like Screening Model (COSMO). Environmentally important inorganic Hg(II) species containing hydroxyl (OH) and chlorine (Cl) groups as well as their organomercurial analogs containing methyl (CH_3) groups were considered. Their complexes with natural CDs possessing 6, 7 and 8 glucopyranose units (α-, β- and γ- CD, respectively) were calculated to be unstable, suggesting that neither molecular inclusion nor electrostatic interactions with oxygen-bearing functional groups on the CDs may contribute to the stability of Hg-CD complexes. However, the particularly high affinity of mercury to sulfur suggested the thiolated derivatives of β-CD as potential Hg-removal agents obtained by replacing -OH groups on the rim of CD apertures with sulfhydryl (-SH) groups. Thus, the aforementioned replacement either on the primary or on both CD sides resulted in two types of mercapto-β-CD derivatives. The PM7(COSMO) enthalpies Δ_rH^o of the most stable complex formation reactions for each Hg(II) species with mercapto-β-CDs range from mildly endothermic for organomercurials to highly exothermic (Δ_rH^o < -100 kJ/mol) for inorganic Hg(II). Schematic depictions of the molecular structures of $HgCl_2$, $HgCl_3^-$, HgClOH and CH_3HgCl complexes with per-2,3,6-mercapto-β-CD are presented in Figure 1. The results suggest that the fully S-substituted β-CD tends to form the strongest complexes via multiple binding of Hg(II) with S atoms on the wider secondary side. This is a manifestation of the higher flexibility of per-2,3,6-mercapto-β-CD allowing two or more vicinal S atoms to approach and coordinate around the Hg atom of a Hg(II) species with sufficient strength.

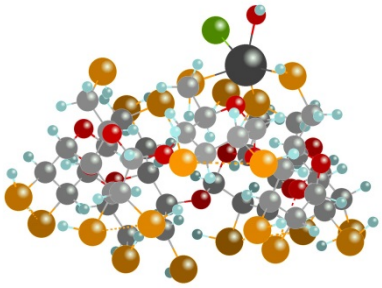
The results suggest that mercapto-β-CDs may effectively bind inorganic Hg(II) species present in contaminated water. However, since binding strength increases by coordination of up to 4 thiol groups regardless of the organic backbone structure, any inexpensive synthetic per-thiolated flexible organic compound anchored on a permeable solid matrix would be comparably effective in a mercury removal approach.



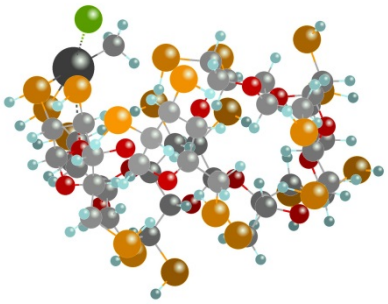
per-2,3,6-mercapto-β-CD ... $HgCl_2$



per-2,3,6-mercapto-β-CD ... $HgCl_3^-$



per-2,3,6-mercapto-β-CD ... HgClOH



per-2,3,6-mercapto-β-CD ... CH_3HgCl

ure 1. *Schematic depiction of PM7(COSMO) optimized geometries for $HgCl_2$, $HgCl_3^-$, HgClOH and CH_3HgCl complexes with per-2,3,6-mercapto-β-CD. (Colors: C:grey, H:pale blue, O:red, range, Hg: dark grey, Cl: green)*

OUTPUT

Publications in International Journals

1. Mekic M., Zeng J., Jiang B.,Li X., Lazarou Y.G., Brigante M. , Herrmann H., Gligorovski S. Formation of Toxic Unsaturated Multifunctional and Organosulfur Compounds from the Photosensitized Processing of Fluorene and DMSO at the Air-Water Interface. *J. Geophys. Res.: Atmospheres* **125**, e2019JD031839 (2020). DOI: 10.1029/2019JD031839

Papers in Refereed Conference Proceedings

1. Spyropoulou A., Laspidou C., Kormas K., Lazarou Y.G. The Impact of Possible Mercury Source-Point Contamination in the Coastal Area of Skiathos Island. *Environ. Sci. Proc.* **2**, 50 (2020). DOI: 10.3390/environsciproc2020002050

International Conferences Presentations (invited, oral, poster)

1. Lazarou Y.G. Applications of theoretical chemistry in the search for a better environment, *Sixth International Symposium on Green Chemistry, Sustainable Development and Circular Economy,* 20-23 September 2020, Thessaloniki, Greece (invited, online).

2. Lazarou Y.G., Spyropoulou A., Kormas K.A., Laspidou C.S. Theoretical investigation of cyclodextrins as scavengers of mercury in aqueous solutions, *Sixth International Symposium on Green Chemistry, Sustainable Development and Circular Economy,* 20-23 September 2020, Thessaloniki, Greece (oral, online).

STATISTICAL MECHANICS AND DYNAMICAL SYSTEMS

Project Leader: Astero Provata

PhD Candidates: Nefeli-Dimitra Tsigkri, Theodoros Kasimatis

Master Students: Alexandros Rontogiannis (up to May 2020).

Undergraduate Students:

Nikolaos Kartsonis (BSc thesis: 1/1-31/12)

Kosmou Anastasia (trainee: 1/9-30/10, collaborator: 1/11-31/12)

Nikos Loukas (trainee 1/9-30/10, co-tutoring with Eleni Charou & Chris Antonopoulos)

Research Collaborators (emeritus or visiting):

Visiting: Prof. Chris Antonopoulos, University of Essex, UK, February 2020

- **Objectives**

The research objectives of the Laboratory of Statistical Mechanics and Dynamical Systems focus on the fields of Statistical Mechanics, Non-linear Dynamics, Complex Systems and Networks. Our aim is the development of methods and models for understanding the emergence and evolution of spatial and dynamical pattern formation (such as Turing patterns and chimera states) and the development of spatial and temporal correlations due to local interactions between particles at the microscopic level. Such structures include spatiotemporal patterns, aggregates, spiral and stripe formations, helices, fractals, Turing patterns, chimera states, etc. which can be experimentally observed in material science, physics, chemistry and biology. Our studies in particular include research on fractal pattern formation and correlations near the critical point in phase transitions but also research in open systems in constant exchange with the environment. Away from the critical point and in closed, isolated systems, short range correlations and spatiotemporal patterns with well-defined length and time scales are studied (eg. spiral and stripe formations, Turing patterns etc.). The study of these structures at the micro-, meso- and macro scales and the interaction between these three levels of description has major technological impact in materials science and physical, chemical and biological processes.

For the study of complex systems in the lab we develop a) statistical methods/tools describing complex morphologies and b) modelling of the dynamics of pattern formation. Statistical methods include thermodynamic approaches, entropic (extensive and non-extensive) approaches, theory of long and short range distributions, and Levi distributions and the 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, numerical integration, exact enumeration methods, real space renormalisation theory, theory of stochastic processes and numerical integration Monte Carlo Methods.

Applications include, among others:

- synchronization phenomena in neuron networks and the brain
- study of the complex fractal architecture of the neuron axons spanning the human brain,
- bioinformatics,
- studies of surface phenomena and aggregates with fractal morphology,
- non-linear studies of reactive dynamics in open and closed conditions as well as the influence of diffusion in dynamical systems.

- **Activities and Main Results**

1. We use extensive computer simulations to study synchronization phenomena in networks of biological neurons. Each individual neuron is modelled using the Leaky Integrated-and-Fire (LIF) scheme, while many neurons are coupled nonlocally in a network. In this system chimera states develop, which are complex states consisting of coexisting synchronous and asynchronous network areas. We study the influence of the network size on the properties and the form of chimera states. We show that for constant coupling strength the number of the synchronous/asynchronous domains depends quantitatively on the coupling ratio. This dependence allows to extract synchronization prop-
erties in large ensembles of neurons after extrapolating from simulations of small networks. Since computer simulations of even small neuron networks are highly demanding in memory and CPU time this property is particularly important in view of the large number of neurons involved in any cognitive function. In total, the number of neurons in the human brain is of the order of 1010 and each of them is connected with an average of 103 other neurons.

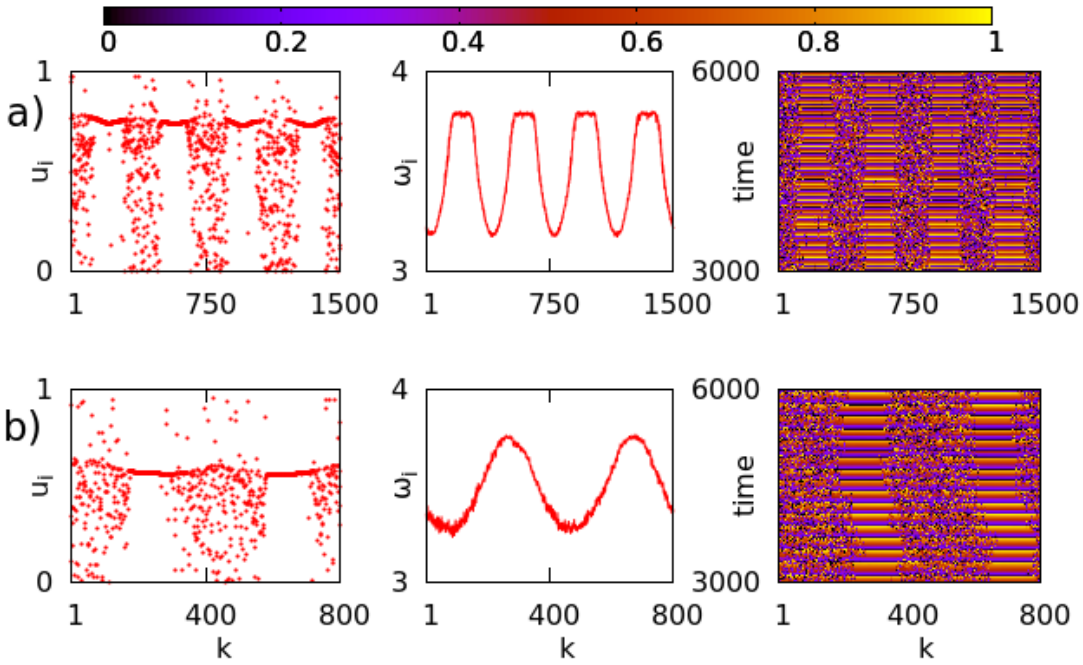


Figure 1: LIF system with nonlocal connectivity and for similar number of connections but diff erent system sizes: a) N = 1500, 2R = 600 and b) N = 800, 2R = 560 links. Typical snapshots (left column), mean-phase velocity (middle column) and space-time plots (right column). All All realizations start from the same initial conditions, randomly chosen and have common all other parameter values.

2. We investigate the robustness of chimera states under the influence of a nonlinear coupling in the form of a power law with exponent α . Taking as working example the Leaky Integrate-and-Fire model coupled in a 1D ring geometry, we show that the chimera states prevail for large values of the exponent α and small values of the coupling strength, while full synchronization is observed in the opposite ends. Our numerical results indicate that the coupling range R does not influence the frequency of oscillations in the coherent or in the incoherent domains. To the contrary, the R value affects the form of the chimera state:
the size of the incoherent domains increase monotonically with R in expense of the size of the coherent ones. As an added value, our numerical results demonstrate that the frequency of oscillations decreases monotonically with the power exponent α. This feature can be useful in controlling the frequency of a

network of oscillators by simply varying the nonlinearity exponent in the coupling, without modifying any of the other network attributes or parameters.

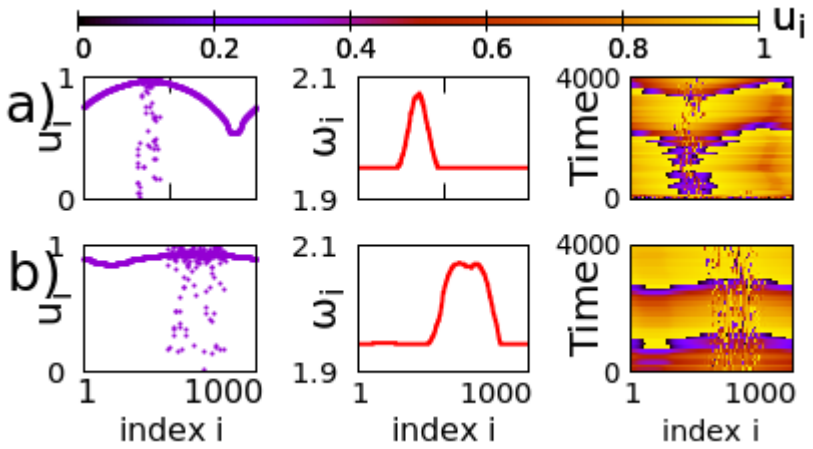


Figure 2: LIF model with nonlinear coupling: Potential profiles ui (left panels), mean phase velocities ωi (middle panels) and spacetime plots (right panels) for coupling ranges a) R = 80, b) R = 200. All simulations start from random initial conditions with nonlinear coupling exponent α=1/2.

3. Dynamical effects on healthy brains and brains affected by tumor are investigated via numerical simulations. The brains are modeled as multilayer networks consisting of neuronal oscillators whose connectivities are extracted from Magnetic Resonance Imaging (MRI) data. The numerical results demonstrate that the healthy brain presents chimera-like states where regions with high white matter concentrations in the direction connecting the two hemispheres act as the coherent domain, while the rest of the brain presents incoherent oscillations. To the contrary, in brains with destructed structures, traveling waves are produced initiated at the region where the tumor is located. These areas act as the pacemaker of the waves sweeping across the brain. The numerical simulations are performed using two neuronal models: (a) the FitzHugh–Nagumo model and (b) the leaky integrate-and-fire model. Both models give consistent results regarding the chimera-like oscillations in healthy brains and the pacemaker effect in the tumorous brains. These results are consd a starting point for further investigation.

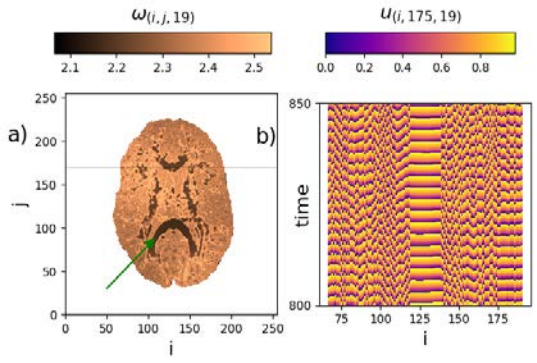


Figure 3: *Representative simulations of the healthy brain: (a) Mean phase velocity profile of slice 19 of healthy subject H(1) using LIF dynamics. (b) Spacetime plot corresponding to the cut for j = 175 indicated in (a) with the gray line. The average in (a) was taken over 2000 time units.*

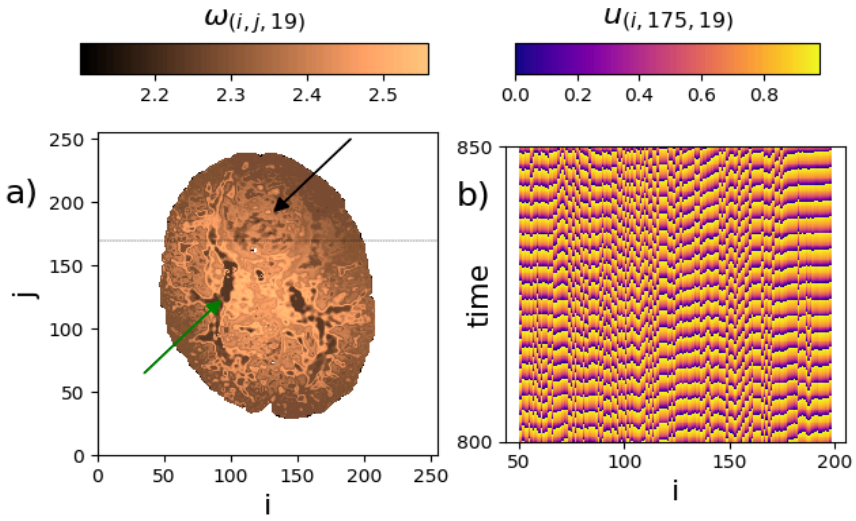


Figure 4: *Representative simulations of brain suffering from tumor: (a) Mean phase velocity profile of slice 19 of healthy subject H(1) using LIF dynamics. (b) Spacetime plot corresponding to the cut for j = 175 indicated in (a) with the gray line. The average in (a) was taken over 2000 time units.*

Funding

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)

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 of 500 000 CPU hours on ARIS-HPC under project CoBrain3 (pr007011) and additional 500 000 CPU hours on ARIS-HPC under project CoBrain3 (pr009012).

OUTPUT

Publications in International Journals

1. Koulierakis, I., Verganelakis, D.A., Omelchenko, I., ...Schöll, E., Provata, A. Structural anomalies in brain networks induce dynamical pacemaker effects. Chaos, **30**(11), 113137 (2020). DOI: https://doi.org/10.1063/5.0006207
2. Provata, A. Chimera states formed via a two-level synchronization mechanism. Journal of Physics: Complexity, **1**(2), 025006 (2020). DOI: https://doi.org/10.1088/2632-072X/ab79bd
3. Muni, S.S., Provata, A. Chimera states in ring–star network of Chua circuits. Nonlinear Dynamics, **101**(4), pp. 2509–2521 (2020). DOI: https://doi.org/10.1007/s11071-020-05910-1

4. Provata, A., Venetis, I.E., Chimera states in Leaky Integrate-and-Fire dynamics with power law coupling. European Physical Journal B, **93**(8), 160 (2020).
DOI: https://doi.org/10.1140/epjb/e2020-10252-9

Books/Chapters in Books

1. Tsigkri-DeSmedt, N.-D., Vlamos, P., Provata, A., Finite Size Effects in Networks of Coupled Neurons, in Advances in Experimental Medicine and Biology, vol. 1194, pp. 397–407 (2020).

International Conferences Presentations (invited, oral, poster)

1. Provata A., The influence of connectivity and dimensionality in the morphology of chimera states, International conference-online 6th Dynamics Days Central Asia, 2-5 June 2020, Nazarbayev University, Nur-Sultan, Kazakhstan (invited talk).

2. Provata A., Synchronization phenomena in networks of inteacting neurons, 4th World Congress-online on Neurodegenerative Diseases Research **"GeNeDis 2020"**, 8-11 October 2020, Ionia University and FORTH, Heraklion, Greece (invited talk).

3. Tsigkri N., Synchronization phenomena in coupled neuronal oscillator networks, Department of Physics, University of Athens, 16 September 2020, Athens, Greece (zoom meeting ID: 987 9453 3859)

4. Tsigkri N., PhD defense 'Synchronization phenomena in coupled neuronal oscillator networks', Department of Physics, University of Athens, 5 November 2020, Athens, Greece

Teaching and Training Activities

A. Provata
Methods of Computational Nonlinear Dynamics/ March 2020-June 2020/ 3 hours/week
MSc Program in "Applied Mechanics" at the National Technical University of Athens.

A. Provata
Special Topics in Complex Systems/ September 2019-February 2020/ 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 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
Network: Fundamental Principles and Applications/ September 2019-February 2020/ 3 hours/week
MSc Program in "Mathematical Modelling in Modern Technology and Economics" at the National Technical University of Athens.

Doctoral Dissertations completed in 2020

Name: Nefeli-Dimitra Tsigkri
Dissertation Title: Synchronization phenomena in coupled neuronal oscillator networks
Research Supervisor at NCSR: Astero Provata

University where the Thesis was presented: Department of Physics, National and Kapodistrian University of Athens

Undergraduate Theses and Internships completed in 2020

Internship-Trainee Studies completed in 2020
Name: Nikos Loukas
Study Title: Synchronization phenomena in 2D Hindmarsh-Rose model with chemical and electrical coupling.
Research Supervisor at NCSR: Astero Provata (INN), Eleni Charou (IIT) and Chris Antonopoulos (University of Essex)
University where the Study was presented: School of Electrical and Computer Engineering, National Technical University of Athens

Name: Anastasia Kosmou
Study Title: Non-linear analyses of whole-body MRI images of patients suffering from metastatic melanoma
Research Supervisor at NCSR: Astero Provata
University where Study was presented: School of Electrical and Computer Engineering, National Technical University of Athens

Awards
N. Tsigkri-DeSmedt: 2018-2020 Scholarship from the State Scholarship Foundation IKY. Strengthening Human Resources Research Potential via Doctorate Research-2nd Cycle.

COMPUTATIONAL MODELLING OF NANOSTRUCTURED MATERIALS

Project Leader: Dr. K. Trohidou

Permanent Research Staff: Dr K. Trohidou

Research associates: Dr. M. Vasilakaki

PhD Candidates: F. Gemenetzi

Research Collaborators (emeritus or 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 and Dr. N. Ntallis, Uppsala University, Sweden (5) Dr. J. Nogués, Catalan Institute of Nanoscience and Nanotechnology, Barcelona (ICN2), Spain (6) Dr. A. Lappas, Forth, Crete, Greece(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) Profs V. Peyre, R. Perzynski, E. Dubois, Sorbonne Université, CNRS, France (11) Prof. J. Depeyrot, University of Brasilia.

- **Objectives**
  Numerical study, of the electronic and magnetic properties of nanostructured materials. The research is mainly problem-driven rather than technique-driven and as such is using various approaches and numerical techniques (mean field approach, effective theories, ab-initio calculations, Monte Carlo simulations).

- **Activities and Main Results**
  Currently we use a multiscale modelling approach that includes calculations in various length scales (from atomic to mesoscopic level) for the study of nanoparticle systems for energy, environmental and biomedical applications.

(α) Co Ferrite nanoparticles coated with OA . It has been experimentally verified that surfactants around nanoparticles can determine their colloidal stability and they influence the strength of interparticle interactions. However the degree of coverage can modify the magnetic behavior of the nanoparticles and the charge distribution.
We elucidated the intriguing role of the increase of the number of oleic acid molecules, on the magnetic properties of the Co ferrite nanoparticles when bonded on their surface using a multiscale modeling approach (see Annex 6.1). We provide a detailed study of the underling mechanism that takes place at the organic/inorganic interface offering the opportunity for better control of the magnetic properties of the Co ferrite nanoparticles covered with oleate groups. We calculate the magnetic moments, the magnetocrystalline anisotropy energy (MAE) and the exchange coupling constants for the Co ferrite nanoparticle covered with 2-22 OA molecules corresponding to 2.5% -, 27% percentage of surface coverage respectively.

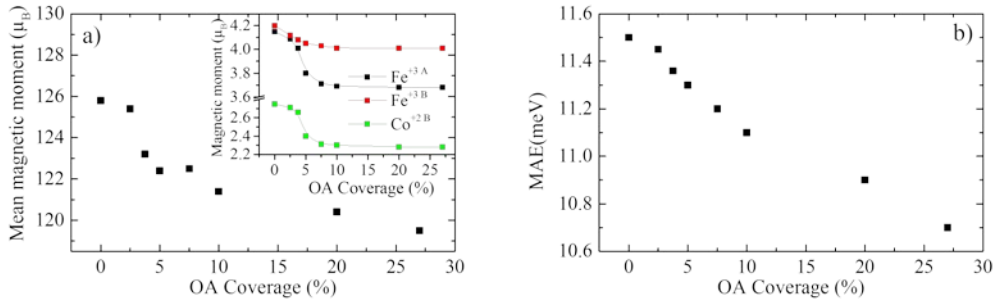


Figure 1. DFT calculations results of the total mean magnetic moment (a) and the magnetic anisotropy energy (MAE) (b) for the $CoFe_2O_4$ spherical nanoparticle as a function of the number of organic molecules attached on its surface. The inset in the Figure (a) shows the variation of the mean magnetic moment for each magnetic ion with the increase of OA molecules coating.

In Figure 1 we have plotted the mean magnetic moment (Figure 1a) and the magnetic anisotropy energy (Figure 1b) as a function of the OA coating. In the inset of the Figure 1a we show the modification of the magnetic mean moment of the magnetic ions with the increase of OA molecules. We observe that the mean magnetic moment and the magnetic anisotropy decrease as the OA coverage increases, this decrease is fast as the coverage increases and then after 20% the decrease is much slower and reaches a plateau for coverage above 27%. In the uncoated nanoparticle, the symmetry breaking at the surface of the $CoFe_2O_4$ nanoparticles due to the missing of some oxygen atoms results to large orbital magnetic moment and magnetocrystalline anisotropy for Co^{2+} in distorted octahedral symmetry. The oleic acid can be viewed as effectively taking the position of the missing atoms. When metal cations at the surface of nanoparticles are coordinated with oleic acid, the spin−orbit coupling and the magnetic moment becomes smaller in good agreement with our DFT calculations. The reduced spin-orbit coupling leads also to the decrease of the surface anisotropy illustrated in Figure 1b.

In order to shed light on the effect of OA coating on the lattice structure of the nanoparticle, we take into account some crystal structure considerations. In Figure 2 we have plotted the Co-O and Fe-O bonding and the corresponding interatomic distances for 4 surface atoms with (Figure 2a and c) and without (Figure 2b and d) OA molecule bonding. By comparing these two groups of figs we see that the bonding angle and distance of the bonds in the case of the OA bonding tend to increase the TM-O interatomic distance and is getting close to the corresponding bulk $CoFe_2O_4$ values (Co-O=1.98 Å Fe^{tet}-O = 2.0Å and Fe^{oct}-O=2.04Å). Therefore, with the increase of the coordination of the OA bonded Co and Fe surface ions, the surface distortion of the uncoated surface Co and Fe ions at the nanoparticle surface gradually reduces. As a result, the anisotropy and the magnetisation decrease as the OA coverage of the particle surface increases. This is also reflected in the change of the exchange coupling bond strength.

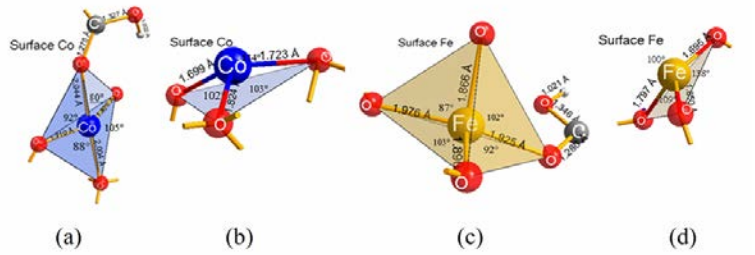


Figure 2. Magnification of the nearest neighboring atoms of selected surface Co (a) and Fe (c) ions bonded with OA and uncoated surface Co (b) and Fe (d) atoms in the relaxed structure of the $CoFe_2O_4$ including also

Next we performed Monte Carlo simulations at the mesoscopic scale to study the effect of the OA surface coverage in an assembly of nanoparticles, where interparticle interactions are present. The results for the hysteresis loop for an assembly of nanoparticles for various percentages of OA surface coverage up to the full coverage (100% coating) are shown in Figure 3. In this Figure we observe an increase of the coercive field with the increase in the OA coverage. This behavior is attributed to the decrease of the exchange coupling as the OA coverage at the surface of the nanoparticles increases. Since the dipolar coupling is weak, the exchange interparticle interactions together with the intra-particle exchange interactions give almost coherent rotation of the spins in the particle. As the OA coverage increases, this effect gradually decreases and finally vanishes at the complete coverage. On the other hand, as the coverage increases the surface anisotropy for each nanoparticle in the assembly decreases. Therefore, the role of the dipolar interparticle interactions becomes the dominant one as the coating on the MNP's surface increases. This behavior is in agreement with the experimental findings.

Interestingly, our mesoscopic scale modeling shows that as the OA surface coverage increases the reduction of the exchange interparticle energy together with the reduction of the effective surface anisotropy of the MNPs gives dominant role to the dipolar interactions and it causes the increase in the coercive field. Our results are in good agreement with the available experimental data paving the way for an optimization of the

hysteresis behavior of organic coated magnetic nanoparticles for their use in energy, industrial and biomedical applications.

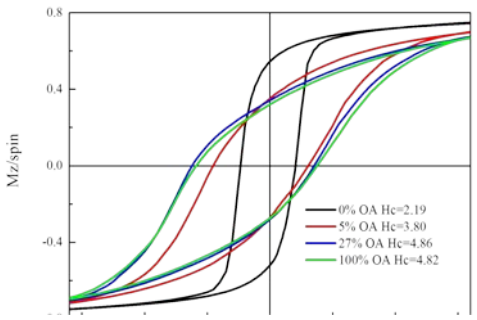


Figure 3. Monte Carlo calculations of the magnetisation hysteresis loop of an assembly of $CoFe_2O_4$ nanoparticles at very low temperature with increasing number of

(b)Study of the thermomagnetic behaviour of magnetic nanoparticles systems: Seebeck coefficient – Concentration dependence.

The role of the interparticle interactions in the formation of an enhanced thermoelectric signal in diluted magnetic nanoparticle assemblies has been studied for the first time by calculating the Seebeck coefficient.

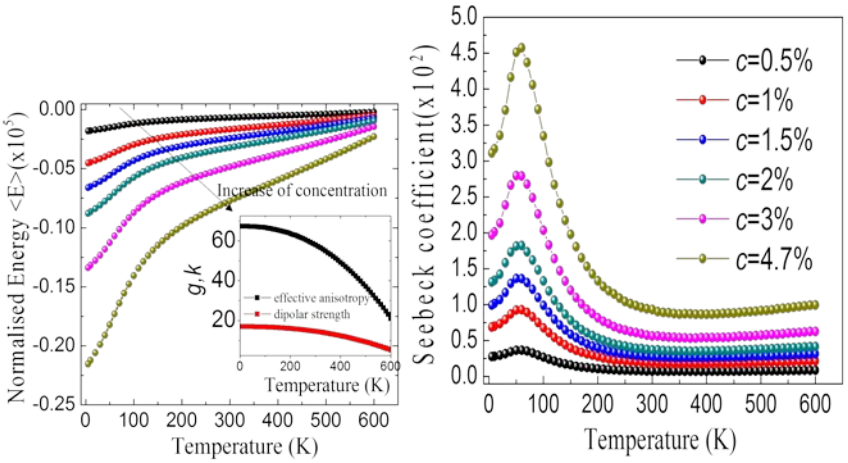


Figure 4. Left: The thermal average energy <$E(T)$> for different maghemite particle concentrations with magnetic anisotropy k=67.4 at T=5K. Inset, the temperature dependence of the dipolar strength $g(T)$ and anisotropy $k(T)$; Right:) The Seebeck coefficient (S_{np}) temperature dependence for six different particle concentrations.

An analytic expression for the Seebeck coefficient of the assembly of MNPs has been derived, taking into account the single particle anisotropy and their magnetostatic interparticle interactions. Here we present our MC simulations results for the Seebeck coefficient and its dependence on the particle concentration for γ-Fe_2O_3 dilute nanoparticles assemblies, which are materials commonly used in ferrofluids. In Figure 4 our Monte Carlo simulations show that in the presence of the magnetic anisotropy energy term the Seebeck coefficient increases with particle concentration and in all cases has a maximum value at around the same temperature, then as the temperature increases it reduces. In agreement with the experimental findings.

(c) Applications based on aggregates of magnetic nanoparticles are becoming increasingly widespread. However, although some applications require a collective behavior, other need a more individual-like response. In our effort to investigate this type of materials with enhanced magnetothermal response, we have performed **Monte Carlo simulations of the magnetic behaviour of core/shell nanoparticles obtained both in hard/soft (Co ferrite /Ni ferrite-CFO/NFO) and inverse soft/hard (Ni ferrite/Co ferrite NFO/CFO) nanoparticles systems.** These magnetic configurations are compared with the experimental findings of our CNR collegues. For both core/shell systems (fig. 5), the hysteresis loops at 5 K indicate the presence of a good

magnetic coupling between the core and the shell. The growth of a soft nickel ferrite magnetic shell affects the hard properties of the cobalt ferrite seeds with a decrease of $\mu_0 H_C$. On the contrary, the more magnetically hard material of a shell increases the coercivity of the soft seeds. The resulting anisotropy of the core/shell systems revealed a strong dependence on the nanoparticle architecture: a magnetically hard core induced hardening of a soft shell and vice versa. Our results are demonstrating the important role of proximity effects between the two phases allowing the control of the magnetic properties of the components in the studied core/shell nanoparticles systems, in good agreement with the experimental findings. Moreover, the implementation of this model allowed us to estimate the effect of intraparticle interaction on the core/shell systems.

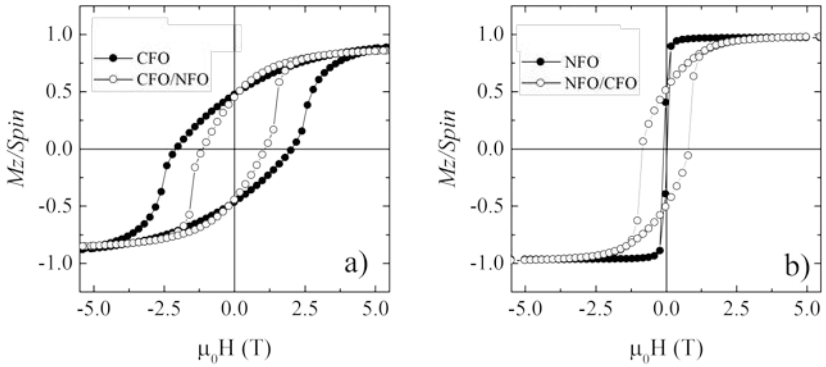


Figure 4 Monte Carlo simulation results for the hysteresis loops at t=0.01 of dipolarly interacting assemblies of (a) CFO and CFO/NFO and (b) NFO and NFO/CFO nanoparticles

Funding

European Union's Horizon 2020 Research and Innovation Programme (FETPROACT-2016): under grant agreement No. 731976 –MAGENTA: Magnetic nanoparticle based liquid Energy materials for Thermoelectric device Applications (1/1/2017-30/06/2021)

OUTPUT

Publications in International Journals

1. Vasilakaki, M., Chikina, I., Shikin, V.B., Ntallis, N., Peddis, D., Varlamov, A.A., Trohidou, K.N. Towards high-performance electrochemical thermal energy harvester based on ferrofluids. *Applied Materials Today* **19**, art. no. 100587(2020). DOI: 10.1016/j.apmt.2020.100587
2. Daffé, N., Zecevic, J., Trohidou, K.N., Sikora, M., Rovezzi, M., Carvallo, C., Vasilakaki, M., Neveu, S., Meeldijk, J.D., Bouldi, N., Gavrilov, V., Guyodo, Y., Choueikani, F., Dupuis, V., Taverna, D., Sainctavit, P., Juhin, A. Bad neighbour, good neighbour: How magnetic dipole interactions between soft and hard ferrimagnetic nanoparticles affect macroscopic magnetic properties in ferrofluids. *Nanoscale*, **12** (20), pp. 11222-11231(2020). DOI: 10.1039/d0nr02023k
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4. Vasilakaki, M., Ntallis, N., Bellusci, M., Varsano, F., Mathieu, R., Fiorani, D., Peddis, D., Trohidou, K.N. Effect of albumin mediated clustering on the magnetic behavior of $MnFe_2O_4$ nanoparticles: Experimental and theoretical modeling study. *Nanotechnology*, **31** (2), art. no. 025707 (2020). DOI: 10.1088/1361-6528/ab4764

Papers in Refereed Conference Proceedings

Vasilakaki, M., Ntallis, N., Trohidou, K.N. Application of Multiscale Computational Techniques to the Study of Magnetic Nanoparticle Systems, *Lecture Notes in Computer Science* (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics), 12044 LNCS, in International Conference on Parallel Processing and Applied Mathematics PPAM 2019: Parallel Processing and Applied Mathematics, pp. 301-311(2020). DOI: 10.1007/978-3-030-43222-5_26

Books/Chapters in Books

Vasilakaki, M., Margaris, G., Ntallis, N., Trohidou, K. Multiscale modeling of magnetic nanoparticle systems in *Computational Modelling of Nanomaterials*, Edited by P. Grammatikopoulos, Frontiers of Nanoscience, Elsevier, Netherlands, Vol. 17, Ch.3, pp. 27-39 (2020). DOI: 10.1016/B978-0-12-821495-4.00003-8

International Conferences Presentations (invited, oral, poster)

1. M. Vasilakaki, J. Chikina, V. B. Shikin, N. Ntallis, D. Peddis, A. Varlamov and K. N. Trohidou, Optimizing the Thermoelectric Behavior of Ferrofluid based Nanomaterials : A Theoretical Study, 65th Annual Conference on Magnetism and Magnetic Materials , 2-6 November 2020, Virtual Conference (oral)

2. K. Trohidou, N. Ntallis and M. Vasilakaki, Tuning the Magnetic Properties of Oleic Acid Coated Co Ferrite Nanoparticles by Varying the Surfactant Coverage: A Multiscale Numerical Approach, 65th Annual Conference on Magnetism and Magnetic Materials , 2-6 November 2020, Virtual Conference (oral)

3. K. Trohidou, C. Binns, A. Lappas, M. Vasilakaki, Tuning structure and Magnetic Properties of Nanoparticles for Enhanced Heating Performance, 1st Training Workshop on Magnetic Nanohybrids for Cancer Therapy, within the framework of the MaNaCa Twinning Horizon 2020 project, April 02-04,2020, Thessaloniki-Greece (Invited)

SOL-GEL NANOTECHNOLOGY AND SURFACE SCIENCE

Project Leader: G. Mitrikas

Research Associate: Eleni K. Efthimiadou

PhD Candidates: M. Theodosiou, T. Koutsikou, D. Prokopiou, Anastasia Stavropoulou, Athina Papadopoulou, Sara Seriah.

- **Objectives**

1. To develop multi sensitive polymeric/liposomal nanostructures for targeted drug delivery
2. Synthesis of iron nanoparticles for hyperthermia measurements
3. Hybrid nanomaterials for real time monitoring
4. Cell cytotoxicity studies/MTT assay/ Cell viability
5. In vivo studies/hyperthermia studies
6. Synthesis of metalic theranostic targeted nanoparticles (magnetic NPs, QDs, hybrid nanoparticles)

- **Activities and Main Results**

Nanostructured delivery and diagnostic systems that induce specific targeting properties by exploiting the local physicochemical tumor characteristics were evaluated in the present work. It is well known that cancer cells have specific physicochemical characteristics, which can be taken into consideration for the design of a broad spectrum of drug delivery systems (DDS). Some of those characteristics including the different temperature environment their susceptibility when temperature ranges between 40-43℃ where cell apoptosis is induced, the intra- and extra- cellular pH which varies from 6.0 to 6.8, for cancer cells, and 6.5 to 7.4 for normal cells respectively, (lysosomes acidic pH ranges 4-5). Additional significant factors are the overexpressed receptors on the tumor surface. Loading and release studies were carried out by using the anthracycline drug Doxorubicin and their cytotoxicity was evaluated by using the MTT assay in healthy and diseased cell lines. The highlight of our work is the in vitro and in vivo study which was performed in order to evaluate different nanostructures as for their biodistribution, pharmacokinetic and toxicity per se.

According to our concept different types of NPs were prepared:

1. Core-shell composite nano-carrier with an inner cavity was formed by soap-free radical emulsion polymerization, based on a variety of monomers with specific sensitivities. The synthetic route contains two steps. In the first step, a non-toxic spherical core is synthesized and in the second step, the shell is formed by a combination of monomers. Each monomer exhibits a unique sensitivity such as pH, thermo and redox sensitivity. Taking advantage of this behavior, we synthesized a nano-container (NC) able to respond to external stimulus causing drug release in a controlled manner. A loading and release study of 3,4-diaminobenzoic acid derivative was also carried out and the cytotoxicity of the synthesized DDS was investigated using MTT assay. The hemolytic activity of the NCs was performed in erythrocytes and in whole blood cells evaluating its biocompatibility. The ability to maintain highest therapeutic efficacy remains an important goal for the development of DDSs.
2. Polymer nanospheres were doped with semiconductor quantum dots (QDs). This hybrid nanomaterial is expected to find use in a variety of in vitro and in vivo biological applications.
3. Magnetic nanoparticles modified with different reducing and coating agents in one step synthesis were synthesized and coated with PEG-co-PLA copolymer. The modified mNPs were evaluated using the MTT assay in different cell lines, healthy and diseased.

Funding

Kripis-II: participation of the group in the Institute-wide funded program, “Development of Materials and Devices for Industrial, Health, Environmental and Cultural Applications” (MIS 5002567) which is 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).

OUTPUT

Publications in International Journals

1. Krokidis, M.G., Louka, M., Efthimiadou, E.K., Ferreri, C., Chatgilialoglu, C., Fatty Acid Remodeling of Membrane Glycerophospholipids Induced by Bleomycin and Iron Oxide Nanoparticles in Human Embryonic Kidney Cells, *Chemical Research in Toxicology* **33**, *pp.*2565–2572 (2020), DOI: org/10.1021/acs.chemrestox.0c00162.
2. Nikolopoulou S., G., Boukos, N., Sakellis, E., Efthimiadou, E.K., Synthesis of biocompatible silver nanoparticles by a modified polyol method for theranostic applications: Studies on red blood cells, internalization ability and antibacterial activity, *Journal of Inorganic Biochemistry* **211**, *pp.*111177 (2020), DOI: org/10.1016/j.jinorgbio.2020.111177.
3. Lioli, E., Psycharis, V., Raptopoulou, C.P., Efthimiadou, E.K., Mitsopoulou, C.A., Synthesis, characterization, DNA binding and cytotoxicity studies of two novel Cu(II)-2-(2’-pyridyl) quinoxaline complexes, *Journal of Inorganic Biochemistry* **208**, *pp.*111077 (2020), DOI: org/10.1016/j.jinorgbio.2020.111077.
4. Papadopoulos, C., Efthimiadou, E.K., Pissas, M., Fuentes, D., Boukos, N., Psycharis, V., Kordas, G., Loukopoulos, V.C., Kagadis, G.C., Magnetic fluid hyperthermia simulations in evaluation of SAR calculation methods, *Physica Medica* **71**, 39-52 (2020), DOI: org/10.1016/j.ejmp.2020.02.011.
5. Michailidi, E.D., Bomis, G., Varoutoglou, Efthimiadou E. K., A., Mitropoulos, A.C., Favvas, E.P.,Fundamentals and applications of nanobubbles, *Interface Science and Technology* **30**, pp.69-99 (2020), DOI: org/10.1016/j.jcis.2019.12.093.

International Conferences Presentations (invited, oral, poster)

1. Sara Seriah, Maria Braoudaki, Eleni K. Efthimiadou, Development of Smart Polymeric Nanoparticles as Targeted Drug Delivery System for The Treatment of Paediatric Brain Malignancies, The 52nd Congress of The International Society of Paediatric Oncology (SIOP), 14-17 October, 2020 (Virtual).

Program 5

Cultural Heritage

CERAMICS AND COMPOSITE MATERIALS

Project Leader: Vassilis Kilikoglou

Permanent Research Staff: Anno Hein, Ioannis Karatasios

Post Docs: M. Amenta, D. Koumpouri

PhD Candidates:

S. Papaioannou, University of Ioannina (2018-)
Adamantia Panagopoulou, University of Leiden (2016 -)
Kyriaki Christodoulou, University of Athens (2020 -)
Katerina Maria Pollatou, University of Patras (2020 -)
Catherine Klesner, University of Arizona (2019-2020 *visiting*)

Research Collaborators (emeritus or visiting): Peter Day

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

Activities and Main Results

Provenance and Technology of archaeological ceramics

A long-term research project concerns the manufacturing technology and the dissemination of pottery and utilitarian ceramics in the Eastern Mediterranean Region from the Neolithic Period until the Byzantine Era. For this, an open access online database has been created (*ceradat.net*), which contains currently more than 10.000 individual compositional data records of archaeological ceramics and potential raw materials from the region. Recent case studies were focused on Late Helladic pottery from the Peloponnese (Argolid and Laconia), Geometric ceramics from Central Crete (Prinias), Roman ceramics from Phocis and East Locris and Byzantine glazed ceramics. Furthermore, the group is collaborating in a project on ceramic technology in Central Asia (Bactria) with special focus on potential technology transfer during the Greek colonization. In view of raw material selection several case studies of clay surveys in the Eastern Aegean region and in Greek Mainland have been continued and extended, resulting amongst others in a review article published in 2020. Eventually, the research on the manufacturing technology and use of casting ceramics has been continued with sampling campaigns and investigation in Attica and Euboea.

Multi-scale structural modeling of the performance of composite materials

Multi-scale structural modeling of composite materials and objects manufactured from them allows for investigating their thermo-mechanical performance through simulations using the finite element method (FEM). The models are developed on different scale levels starting from 3D models of the materials' microstructures, the immediate contact areas of indenters during material testing up to the interaction of entire objects or structures, such as deformation and failure of ceramic vessel under mechanical loads or impact forces (Figure 1).

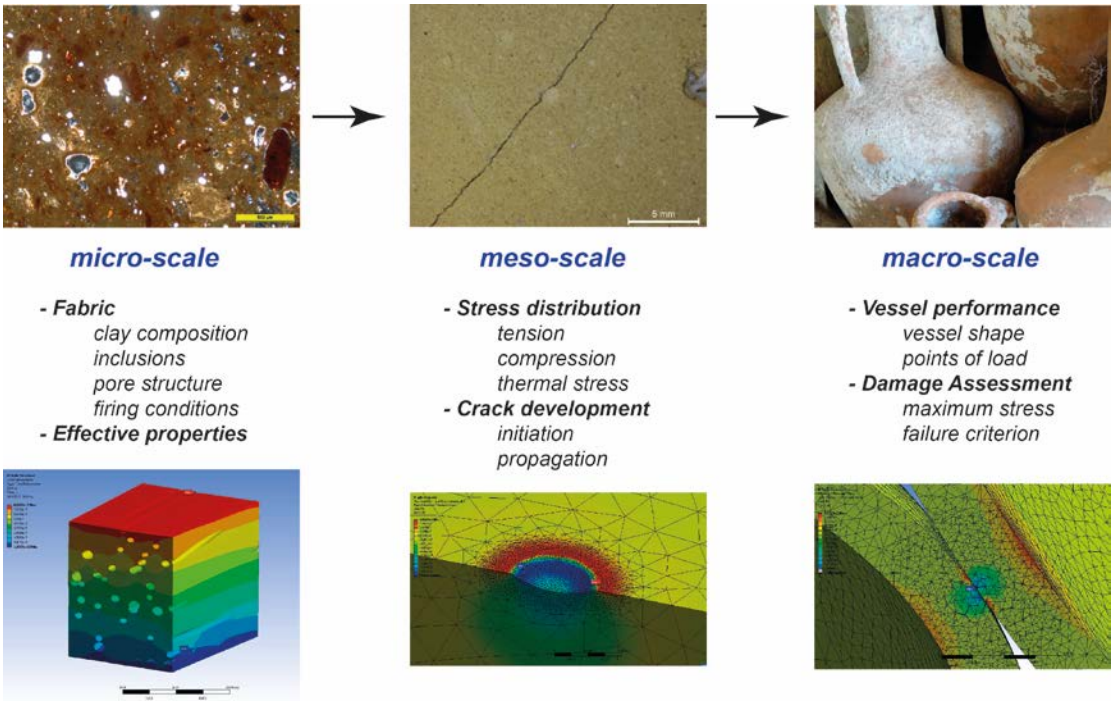


Figure 1 – Multi-scale examination and simulation of composite materials, such as ceramics

In this way material tests can be simulated and interpreted, providing an estimation of effective material properties of composite materials. Furthermore, the performance and even the potential damage risk of objects or structures under thermo-mechanical loads can be predicted. The current research concerns the investigation of apparent elasto-plastic deformation of ceramics under compression due to sub-surface micro-damages, the consideration of which provides appropriate simulations of experimentally determined load displacement curves recorded in material tests. For the generation of realistic 3D models of ceramics' microstructures a collaboration with two external laboratories has been initialized, concerning the examination of ceramic fragments with micro computer tomography (μCT). In view of macro-scale simulations a case study of the development of amphora design during the Hellenistic Period has been finalized taking into account their simulated packaging during transport in cargo ships and the assumed mechanical loads they were exposed to during transport

Portable energy dispersive XRF in the characterization of archaeological materials

The feasibility of handheld portable X-Ray fluorescence spectroscopy (pXRF) for the categorization of archaeological materials has been further examined in case studies analyzing different categories of materials. Apart from ceramic studies, which were focused more on methodological development and data evaluation, further studies concerned pigments and metallurgical residues. In collaboration with the Rhodes Centennial Project (University of Copenhagen) pigments and colorants in wall paintings and on terracotta from Rhodes have been investigated. In collaborations with the University of Gent, conducting the Thorikos Excavation, the study of residues of lead ore processing in millstones in South Attica has been continued.

Nanomaterials for cultural heritage conservation/consolidation

The research was focused on the development of novel nanolime dispersions, focusing on the study of the effect of i) functionalization of the surface of the nanoparticle though the use of different non-ionic surfactants (Fig.3) and ii) the use of different polar dispersion media. The novel nanolime dispersions were characterized in terms of the microstructural characterization of the nanoparticles, the rheological characterization of the dispersions and their penetration ability when applied on different inorganic porous

media. The treated specimens were studied in order to determine the efficiency of the newly formed nanolime dispersions as consolidants.

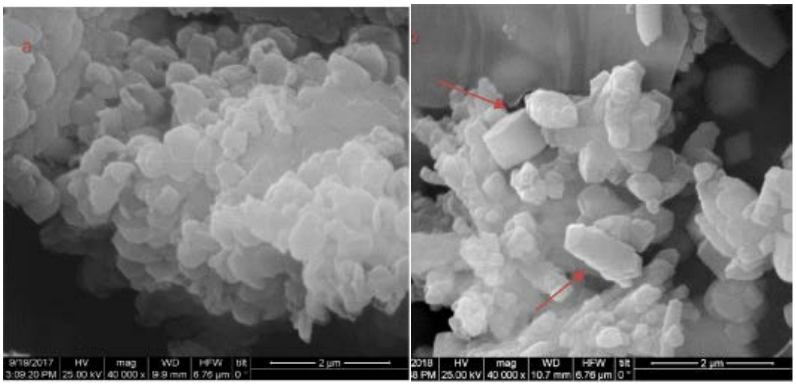
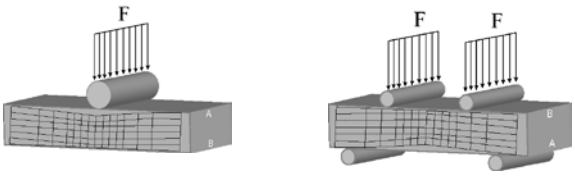


Figure 3. SEM microphotographs of nanoparticle clusters: (a) plate-like Ca(OH)2 nanoparticles and (b) plate-like Ca(OH)2 nanoparticles of hexagonal habit (addition of the non-ionic surfactant Triton X-100)

Self-healing efficiency quantification-Measurement of mechanical strength recovery

The methodology regarding the measurement of mechanical strength recovery has been tested in trial specimens. Mortar specimens were damaged in a controlled way, by different fracture modes (application of three-point bending, compression test and hertzian stress) to ensure the reproducibility of the damage degree and the optimization of the procedure. The main objective of this process is the quantification of damage degree and the measurement of the residual strength after the incorporation of the damage together with the mechanical regains after healing, so that healing efficiency can be accurately assessed.

$D\% = [(f_R^0 - f_d)/f_R^0)]100\%$ $H\% = [(f_h/f_R^1)]100\%$



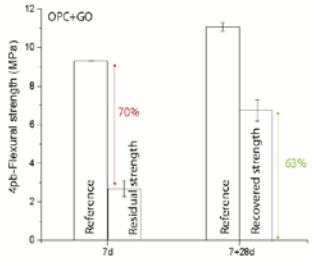


Figure 4 Hertzian contact stress followed by 4-point bending test

Development of encapsulated healing additives

Cement-based spherical capsules were developed according to the pan-coating technique. Capsules properties, such as crushing load and shell microstructure, can be adjusted to the final application. Representative stereomicroscope and SEM images of cement-based capsules, indicating the size and morphology of capsules, as well as the microstructure of the shell are presented in Figure 5.

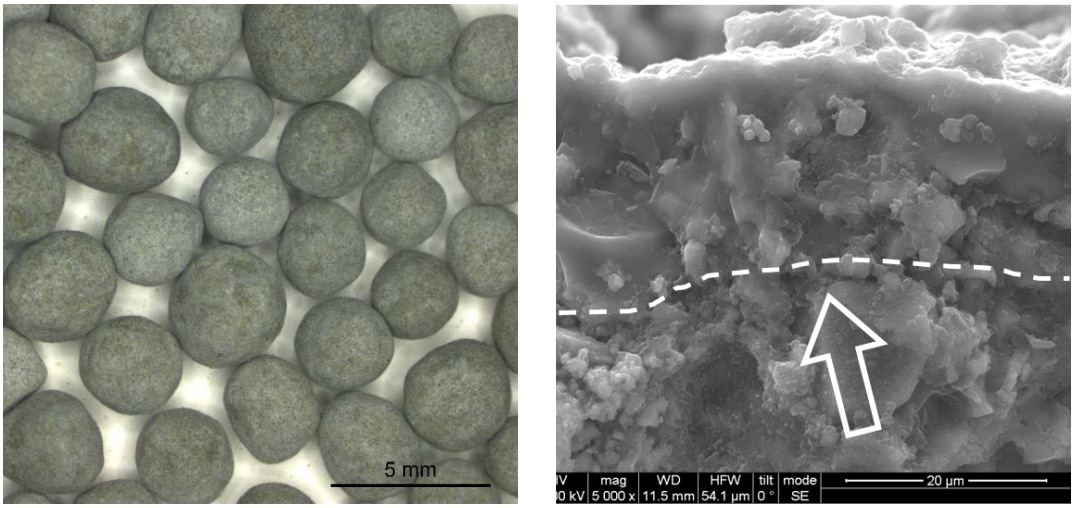
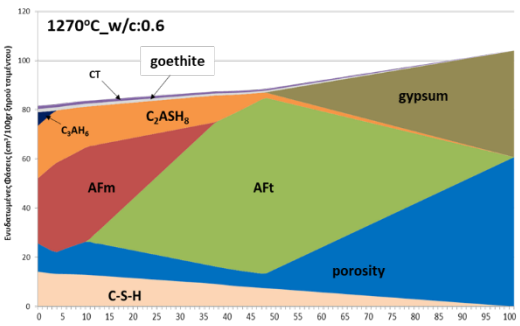
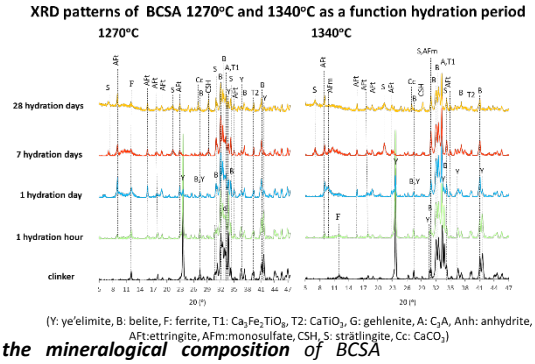


Figure 5. Cement-based capsules observed in stereomicroscope (left) and shell microstructure observed in SEM, indicating the formation of a dense protective layer by the arrow.

Study of low energy Belite Calcium-Sulpho-Aluminate (BCSA) clinker/cement: Hydration mechanism of cements and Physico-mechanical properties of mortars

The current project investigates the study of novel, eco-friendly Belite Calcium-Sulfo-Aluminate (BCSA) type of cements as an alternative for the conventional Portland (OPC). The study of the hydration process of three types of BCSA laboratory cements carried out by simulation modelling by using GEMS thermodynamic software package as well as experimentally by the identification of the hydration products and mechanisms (XRD, DSC/TG and SEM-EDS). The parameters which were examined were the: mineralogical composition of the cement, quantity and quality of additional sulphur source (gypsum and anhydrite), water/cement ratio. Finally, the physico-mechanical properties were determined after 1, 3, 7, 28, 90 days according to the standard EN 196.The results showed that the development of the compressive strength is affected by the mineralogical composition (both in terms of quality and quantity) of the clinker as long as the gypsum addition and the quality improver additives.





(Y: ye'elimite, B: belite, F: ferrite, T1: $Ca_3Fe_2TiO_8$, T2: $CaTiO_3$, G: gehlenite, A: C_3A, Anh: anhydrite, AFt:ettringite, AFm:monosulfate, CSH, S: strätlingite, Cc: $CaCO_3$)

lts of GEMS modelling software package. ***patterns and the mineralogical composition*** *of BCSA for more efficient design of hydration systems were cement ers fired at different temperature are presented, for ralogy, water/cement andsulfur source & amount are tion periods of 1hour, 1day and 7 and 28days. ecting with hydration products and volume stability.*

RADIOCARBON DATING, PROVENANCE OF MARBLE AND COLOUR TECHNOLOGIES

Project Leader: **Dr. V. Kilikoglou**

Permanent Research Staff: **Dr. G.S. Polymeris**

Other Staff (scientific, administrative, technical, auxiliary, etc): **M.E. Kyriazi**

Research Collaborators (Emeritus): **Dr. Y. Maniatis**

Aristotle University of Thessaloniki: **Prof. K. Kotsakis, Prof. Ch. Paliadeli, Prof. G. Kitis, Prof. D. Kondopoulou, Assoc. Prof. E. Aidona.**

Museum of Cycladic Art: **P. Sotirakopoulou, N. Stambolidis**

Laboratorio di Analisi dei Materiali Antichi, Università IUAV di Venezia: **Prof. L. Lazzarini**

Anthropological Team, Vergina University Excavations: **L. Wynn-Antikas**

Globe Institute, University of Copenhagen: **Dr. H. Schroeder**

McDaniel University, USA: **Prof. V. Pagonis**

National Technical University of Athens: **Assist. Prof. C.D. Athanassas**

University of the Aegean: **Dr. Asimina Vafiadou**

Objectives

- Extending the applications of radiocarbon dating for monitoring and comparing human cultural phases of the past in an absolute time framework.
- Developing of methodologies and databases for precise determination of the origin of marble from artifacts, sculptures and monuments.
- Characterization of pigments and wall painting techniques and the use of materials.
- Basic research in age assessment using luminescence techniques – Age limit extension in luminescence dating – improving the accuracy of ages beyond 200 ka
- New technologies in age assessment

Activities and Main Results

1. Radiocarbon Dating - Cultural Phase Monitoring

a. Compilation of a Radiocarbon Dating Archive for the Aegean

This dataset is the outcome of an INSTAP-funded project "An Aegean Prehistory Written in Radiocarbon Dates". It includes 3159 radiocarbon dates from 353 sites in Greece and reflects an attempt to exhaustively collect and cross-check all published radiocarbon dates from existing databases, original publications and preliminary reports using both international and Greek sources (376 sources in total). Although originally targeting prehistoric dates, all dates coming from archaeological or environmental sampling were integrated in the final dataset regardless of chronological period. Sites have been identified and positioned as accurately as possible, while additional information on sampling procedures, sample material and stratigraphic context have been recorded (Katsianis et al 2020).

b. The Earliest Farmers in Europe. Dating of the earliest Neolithic settlements in the Aegean

This longstanding project started in 2013 and was supported by the Institute for Aegean Prehistory (INSTAP) is reaching its end. As described in previous years it aims at creating an absolute time framework for the beginning of Neolithisation in Greece, essential for

addressing key issues regarding the emergence and spreading of farming and stockbreeding in Greece, the Aegean and consequently Europe. In 2020 we dealt with treating and publishing dating results collected in earlier years. One of the most important sites is that of Revenia-Korinos in North Pieria which proved to be one of the earliest settlements of farmers/stock-breeders in Greece where the earliest dwelling was in pits (Fig. 1A).

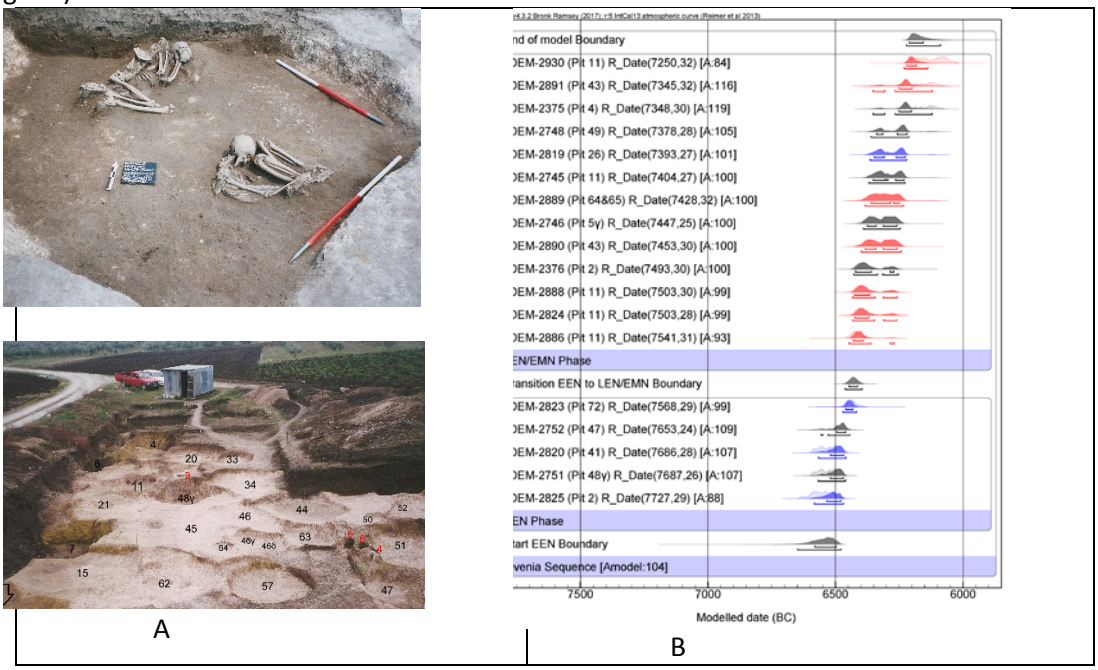


Fig. 1. *The site of Revenia-Korinos. A: Dwellings in pits, B: Modelling of the radiocarbon dates in two Phases Early-Early Neolithic (EEN) and Late Early Neolithic (LEN). Accessed from:* REVENIA-KORINOS: ONE OF THE EARLIEST NEOLITHIC SETTLEMENTS IN NORTH GREECE AS EVIDENCED BY RADIOCARBON DATING | Radiocarbon | Cambridge Core

The radiocarbon dates were modeled according to the two early occupation phases and show that the start of the occupation was at around 6550 BC (Fig. 1B). The geographic spread of these early settlements in relation to time will reveal the pattern of neolithization of Greece and together with DNA genomic analysis will answer the question whether the farming and stock-breeding were developments with the involvement of the pre-Neolithic communities or brought in by experienced farmers that migrated from the East.

c. *The Vergina Royal Burials*

The investigation of the Vergina Royal Burials in the Great Tumulus and the Agora of Vergina continued in 2020. This project aims to obtain data for the identity of the individuals buried there by analyzing the bones with a combination of several scientific techniques, such as Radiocarbon dating, isotopic analysis, anthropological examination and ancient DNA analysis. The analysis and treatment of the results takes time as there are many techniques and combinations involved. This year we prepared the publication for the Tomb I (Tomb of Persephone) in the Great Tumulus of Vergina. We are expecting some additional results from DNA sequencing from the University of Copenhagen, Globe Institute, Faculty of Health and Medical Sciences (Dr. H. Schroeder), one of the collaborators of this project funded partially by CSUS Hellenic Studies Program, in conjunction with the Tsakopoulos Hellenic Foundation.

2. Methodologies and Applications for marble provenance determination

a. Sculpture and society in Roman Greece: political, economic and religious context

A large number of marble sculpture (over 100) from the Archaeological Museum of Thessaloniki from the 4th c. BC to the 3rd c. AD were examined and analysed with a range of scientific techniques, such as in-situ optical

examination, stable isotope analysis, EPR spectroscopy and Grain size measurements in order to determine the provenance of their marble and trace the marble movement across the Aegean in those times (Stefanidou et al 2019). The project involved also field work and sampling of various marble sources in North Greece for extending the databases and ensuring a more accurate determination of the provenance of marble of the ancient sculptures. The treatment of the results has finished the publication is under preparation.

b. Several projects on marble provenance and movement in Antiquity

In 2020 we carried out several projects on important ancient sculptures and monuments in Greece. One of the most important projects is on the provenance of a series of marble statuettes of Roman period from the Athenian Agora in collaboration with the archaeologist Brian Martens. The first results indicate that a large number of them were made in marble from Dokimeion (Afyon) in Asia Minor, and as some were found semi-worked it is assumed that they were made in Athens.

3. Age assessment using luminescence techniques

a. *Basic Research*

Major effort was devoted to understanding the physical mechanism of luminescence in potassium feldspars. These latter minerals, being the most abundant in the earth's crust, could be effectively used as luminescence chronometers; not only in luminescence dating but in thermochronometry as well. Nevertheless, the presence of malign phenomena such as the athermal fading stands as the major drawback in their effective application. Moreover, the applicability of calcium sulfate as a luminescence dosimeter, in all forms, has been studied. At the same time, optimization has been reported for the main experimental parameters during the application of the Single Aliquot Regenerative (SAR) protocol in calcium sulfate samples.

b. *Age limit extension in luminescence dating – improving the accuracy of ages beyond 200 ka*

The landlocked anoxic Black Sea basin was exposed to several transgressions throughout Quaternary by the Mediterranean Sea through the Straits of Istanbul (Bosphorus) and by the Caspian Sea through the Manych-Kerch spillway. Various repeated interconnections among the Black Sea, Caspian Sea and Mediterranean Sea, along with the resulting climatic changes were studied. Sedimentological records and chronological data from deep-sea sedimentary sequences of these connections were enriched based on facies analysis and the optical (OSL) ages of coastal carbonate aeolianites. The imprints of multiple Mediterranean transgressions during Middle Pleistocene in the Black Sea were discussed, bearing in mind that in many cases the ages go beyond 400 ka.

4. New technologies in age assessment

Application of the Lambert W function for the analysis of the luminescence signals. New user-friendly interfaces for luminescence analysis and simulation using the Python programming environment

OUTPUT

Publications in International Journals

1. Theodorakopoulou, K., Kyriakopoulos, K., Athanassas, C. D., Galanopoulos, E., Economou G., Maniatis, Y., Godelitsas, A., Dotsika, E., Mavridis, F., Darlas, A. First Speleothem Evidence of the Hiera Eruption (197 BC), Santorini, Greece. *Environmental Archaeology* **26 (3),** pp 336-348 (2020). DOI: 10.1080/14614103.2020.1755196.
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7. Kaya Keleş, Ş., Polymeris, G.S., Perçinler, B., Meriç, N. Dealing with Non-conventional LM-OSL Curve Shapes In Quartz Following Bleaching; a Deconvolution Approach. *Journal of Luminescence* **220,** pp. 117026 (2020). DOI: 10.1016/j.jlumin.2020.117026
8. Polymeris, G.S., Başdoğan, Çakal, G., M., Aşlar, E., Meriç, N. Gamma dose rate effects in luminescence signals of various artificial, well established dosimetric phosphors. *Radiation Measurements* **133,** pp. 106282 (2020). DOI: 10.1016/j.radmeas.2020.106282
9. Polymeris, G.S., Pagonis, V., Kitis. G. Investigation of thermoluminescence mechanisms during linear and isothermal heating of dosimetric materials. *Journal of Luminescence* **222,** pp. 117142 (2020). DOI: 10.1016/j.jlumin.2020.117142
10. Şahiner, E., Polymeris, G.S., Atlihan, M.A., Aktürk. S., Meriç, N. Indirect dating of an olive tree implantation event using luminescence of the sediments lying beneath the roots of the tree; a pilot study in the South-West part of Anatolia, Turkey. *Journal of Quaternary Science* **35(5)***,* pp. 706–715 (2020). DOI: 10.1002/jqs.3212
11. Pagonis, V., Kitis. G., Polymeris, G.S. Quantum tunneling processes in feldspars: using thermoluminescence signals in thermochronometry. *Radiation Measurements* **134,** pp. 106325 (2020). DOI: 10.1016/j.radmeas.2020.106325
12. Angeli, V., Kitis. G., Pagonis, V., Polymeris, G.S. Sequential two-step optical stimulation in K-feldspars: Correlation among the luminescence signals and implications for modeling parameters. *Journal of Luminescence* **226,** pp. 117425 (2020). DOI: 10.1016/j.jlumin.2020.117425
13. Polymeris, G.S. Optimization of OSL/IRSL experimental measurement parameters on various types of naturally occurring CaSO4 samples; sensitization pattern versus temperature, bleaching properties and slurry effect. *Nuclear Instruments and Methods in Physics Research B* **480**, pp. 38 – 44 (2020). DOI: 10.1016/j.nimb.2020.08.004
14. Aşlar, E., Meriç, N., Şahiner, E., Polymeris, G.S. Determination of entrance surface dose (ESD) and mean glandular dose (MGD) using OSL from BeO dosimeters in mammography. *Radiation Physics and Chemistry* **177***,* pp. 109151 (2020). DOI: 10.1016/j.radphyschem.2020.109151
15. Konstantinidis, P.G., Tsoutsoumanos, E., Polymeris, G.S., Kitis, G. Thermoluminescence response of various TL dosimeters as a function of irradiation temperature. *Radiation Physics and Chemistry* **177**, pp. 109156 (2020). DOI: 10.1016/j.radphyschem.2020.109156

Papers in Refereed Conference Proceedings

1. Panagiotaki, M., Maniatis, Y., Tite, M. Aegean vitreous materials of the Bronze Age: technological transfer and local innovation", In: M. Panagiotaki, I. Tomazos and F. Papadimitrakopoulos (eds), *Cutting Edge Technologies in Ancient Greece*, Proceedings of two conferences held in Rhodes (12-14 Jan. 2018 & 11-13 Jan. 2019), Oxbow books, pp. 89-96, (2020).

Books/Chapters in Books

Maniatis, Y. The Acropolis in Late Antiquity (Appendix in T. Tanoulas), In: *I. Tanaseanu-Döbler and L. von Alvensleben (eds), Athens II: Athens in Late Antiquity,* Mohr Siebeck Tübingen, Germany, pp 83-121 (Appendix: 119-121), (2020).

International Conferences Presentations (invited, oral, poster)

1. Polymeris, G.S., Malletzidou, L., Zorba, T.T., Kouloumpi, E., Paraskevopoulos, K.M., Kitis G., Investigating the possibility of age assessment using pigments and dyes; Preliminary luminescence and UV-VIS measurements. *7th Balkan Symposium on Archaeometry (BSA7),* September 22 – 25 2020, Athens, Greece (poster presentation).
2. Vafiadou, A., Polymeris, G.S., Sfampa, I.K., Giannoulatou, V., Kitis, G., Liritzis, I., A comparative luminescence study on several limestone samples of various origins. *7th Balkan Symposium on Archaeometry (BSA7),* September 22 – 25 2020, Athens, Greece (poster presentation).
3. Kioumourtzoglou, S., Konstantinidis, P., Polymeris, Kitis, G., Extension of age limits by fitting TL/OSL dose response curves using analytical expressions from physical models. *7th Balkan Symposium on Archaeometry (BSA7),* September 22 – 25 2020, Athens, Greece (poster presentation).
4. Malletzidou, L., Sfampa, I.K., Zorba, T.T., Stoulos, E., Paraskevopoulos, K.M., Kitis, G., Polymeris, G.S., Exploring the potential of calcium sulfates as luminescence dating dosimeters. *7th Balkan Symposium on Archaeometry (BSA7),* September 22 – 25 2020, Athens, Greece (oral presentation).
5. Schmidt, C., Chruscinska, A., Polymeris, G.S., Fasoli, M., Martini, M., Sanderson, D., Kreutzer, S., Multi-spectroscopic characterization of luminescence-relevant defects in a reference quartz sample. *German Luminescence and ESR Meeting*, 27 – 2 November 2020, Giessen, Germany (poster presentation).

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

1. Polymeris, G.S., TA – OSL, a tool for extending the luminescence age limits beyond 1 million years; preliminary results from a number of sites. *6th Symposium on Archaeological Research and New Technologies,* 8 - 10 October 2020, Kalamata, Greece.
2. Vafiadou, A., Polymeris, G.S., Kitis, G., Liritzis, I., Thermoluminescence dating of limestone walls from Ithaca (School of Homer). *6th Symposium on Archaeological Research and New Technologies,* 8 - 10 October 2020, Kalamata, Greece.

Doctoral Dissertations completed in 2020

Name: ***Şule Kaya Keleş***
Dissertation Title: *Luminescence and ESR methods used in characterization of various quartz samples*
Research Supervisor at NCSR: Dr. Georgios S. Polymeris
University where the Thesis was presented: Ankara University, Ankara, Turkey.
Name: ***Engin Aşlar***
Dissertation Title: *Combined luminescence and ESR study in characterization of solid state BeO dosimeters*
Research Supervisor at NCSR: Dr. Georgios S. Polymeris
University where the Thesis was presented: Ankara University, Ankara, Turkey.

Master Dissertations completed in 2020

Name: ***Selime Çoskun***
Dissertation Title: *Optimization of OSL measurement parameters using BeO dosimeters*
Research Supervisor at NCSR: Dr. Georgios S. Polymeris
University where the Thesis was presented: Ankara University, Ankara, Turkey.

Teaching and Training Activities

Y. Maniatis,
Radiocarbon dating, December 2020, 4 hours
M.Sc. Course on Cultural technologies, University of Peloponnese, Kalamata.

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) Luminescence dating of past seismic events

Determining the absolute age of the past faulting activity is crucial for assessing seismic hazards and for an assessment of the future tectonic/seismic evolution in a particular area. Historical records can be used for such purposes; however they only provide a relatively recent picture of fault activity, which is generally inadequate for drawing concrete conclusions on the seismicity of an area. As such, geochronology approaches try to address this problem by determining the repeatability of past seismic reactivations, using appropriate dating techniques on earthquake-disturbed materials prior to the time of recorded information.

The employment of the luminescence dating techniques is now widely applied to variety of materials and sedimentary environments (e.g., quartz and feldspar inclusions from heated archaeological material, sand-dunes and fluvial sediments), their application however on fault-deformed materials still limited, since full resetting (due to mechanical crushing/sliding or frictional heat) of their luminescence signal, during a rupture

event, cannot be easily established, but also due to the limited access to appropriate material (e.g., fault gouges; crushed and ground-up rock produced by friction between the two sides when a fault moves). No systematic effort had been made up to now on the use of luminescence in directly dating material from the brittle zone of a fault which is related to faulting or the earthquake event.
To this end, in 2020 our research explored the use of Isothermal Thermoluminescence (ITL) and Optically Stimulated Luminescence (OSL) as well as Electron Spin Resonance (ESR) to date past seismic deformed features which are directly linked to past seismic events. Having established the suitability of these techniques in dating palaeoseismic events, detailed protocols were developed, allowing the assessment of the long-term temporal behavior of a number of seismically active faults in Greece, Italy and Japan.

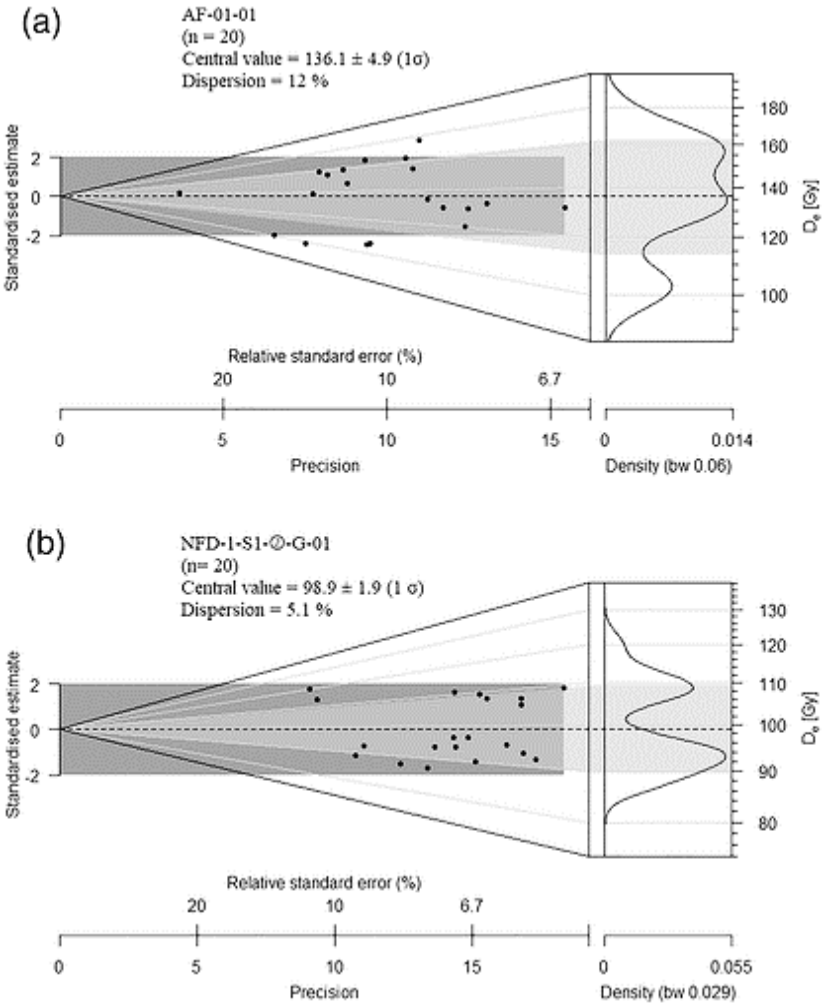

Figure 1. Abanico plots of the DE values from aliquots of samples (a) AF-01-01 and (b) NFD-1-S1-②-G-01 (representative for all Nojima and Asano fault gouge samples).

The present work has indicated that ITL, OSL are potentially promising techniques for dating gouge material developed in the basement rocks, while ages of palaeoseismic events using ESR appeared to be overestimated. This study was a fundamental advancement in the field

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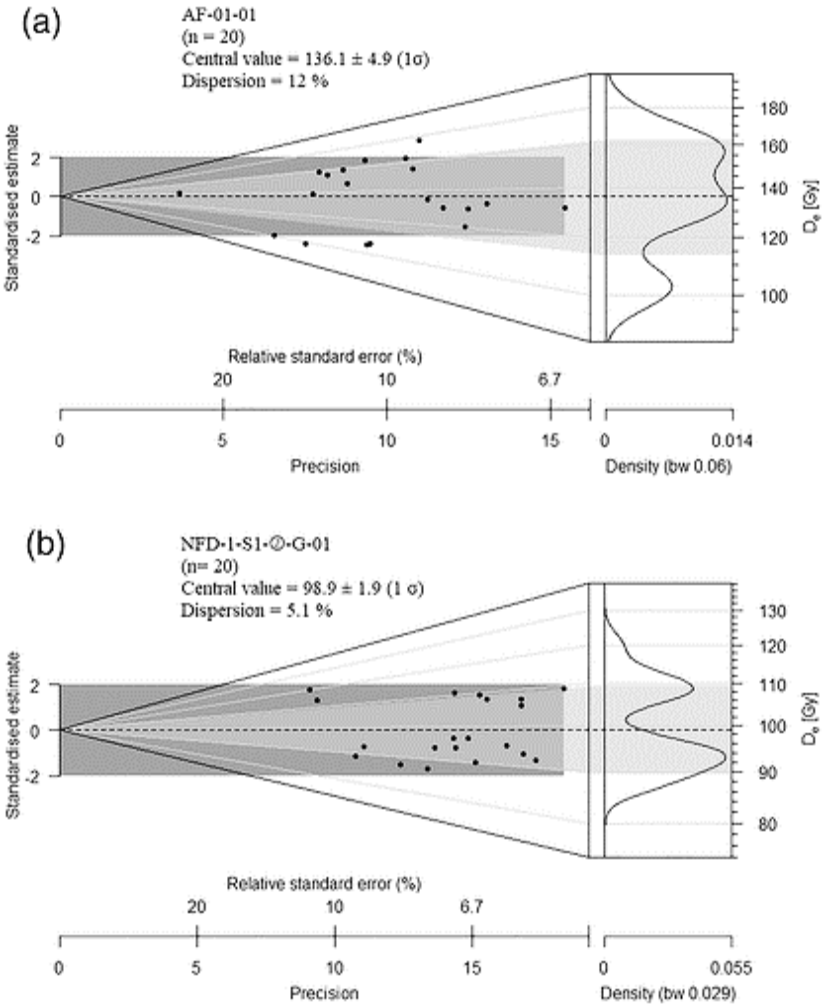

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2) Near-past environmental reconstruction and prediction of sea level transgression

The coastal areas of the Mediterranean have been extensively affected by the transgressive event that followed the Last Glacial Maximum, with many studies conducted regarding the Holocene stratigraphic

configuration of several deltaic successions. Rivers deltas are among the most complex and dynamically changing environments of the coastal zones as many natural factors involved in their evolution. Global sea level rise has significant impact on the evolution of coastal zones, mostly in lowland areas, such as rivers deltas and coastal low-lying areas. Luminescence dating along with geochemical and mineralogical analysis offer excellent potential for establishing the chronological framework for the depositional sequences of such areas as well as a complete representation of the diachronic sedimentary processes that have taken place.
In this regard, during 2020 our research led to the development of morphodynamic prediction models for assessing the future evolution of the coastline and estimated the potentially inundated low-lying coastal areas in a number of places in Greece.

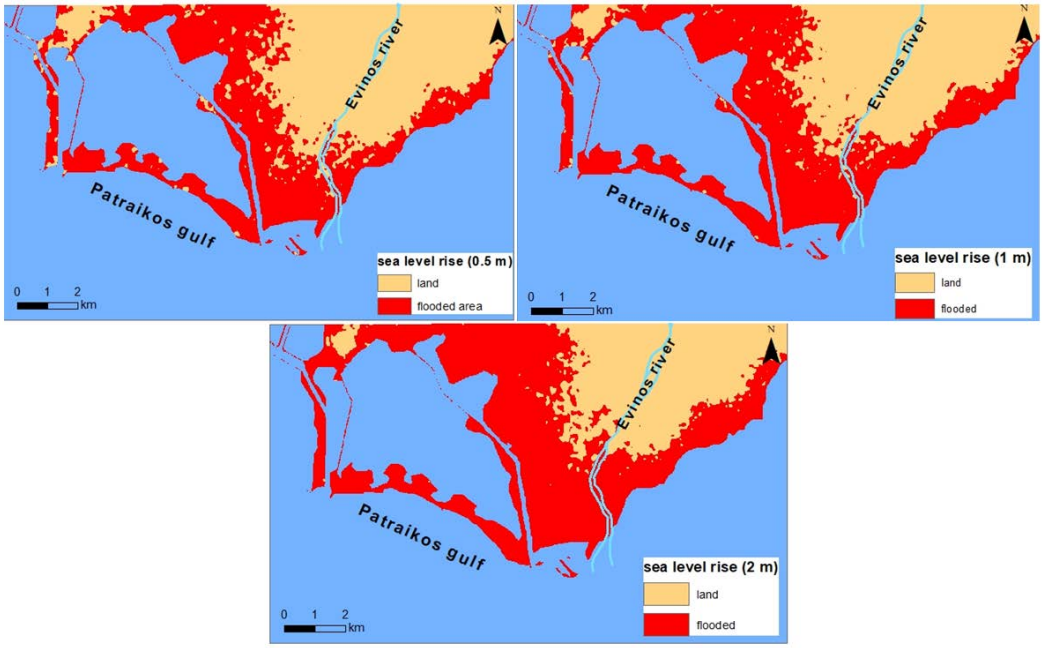

Figure 2. Different coastline change (flooding) scenarios of Messologi laggon.

Furthermore, the impact of sea level rise on coastal areas is assessed by calculating the Coastal Vulnerability Index (CVI). Vulnerability was depicted in the form of a set of colour-coded maps, permitting the most sensitive areas to be easily identified, thus contributing to decision-making in the sustainable and responsible use of coastal resources, the planning and development infrastructure, and integrated coastal management of particular areas.

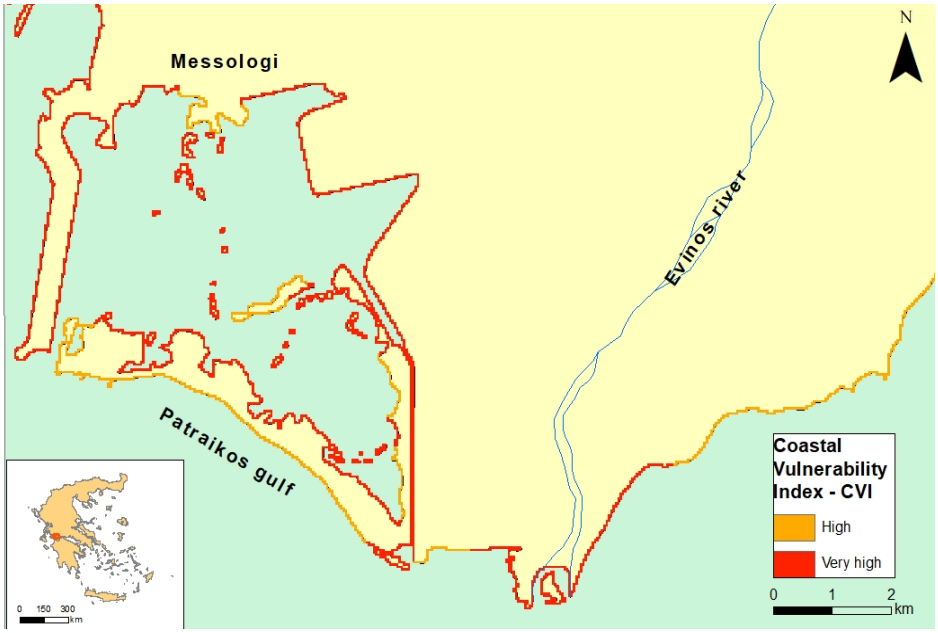

Figure 3. Coastal Vulnerability Index (CVI) of Messologi lagoon.

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

"Seismic Moment and Recurrence (SMR) using Luminescence Dating Techniques – SMR", HORIZON 2020/MSCA, 01/06/2017 – 31/05/2020, budget: 254,871 €.

"Assessing and modeling climate change impacts on the Kalamas river", NSRF, Epirus Operational Programme, MIS 5006050, 01/05/2017 - 31/07/2020, budget: 90,000 €.

"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 €€.

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 Greeece and Cyprus, 20,000 €.

Publications in International Journals

1. Tsakalos, E., Lin, A., Kazantzaki, M., Bassiakos, Y., Nishiwaki, T., Filippaki, E., 2020. Absolute dating of past seismic events using the OSL technique on fault gouge material-A case study of the Nojima Fault Zone, SW Japan. Journal of Geophysical Research: Solid Earth 125 (8), e2019JB019257. https://doi.org/10.1029/2019JB019257
2. Mastrotheodoros GP, Theodosis M, Filippaki E, Beltsios KG, 2020. By the Hand of Angelos? Analytical Investigation of a Remarkable 15th Century Cretan Icon. Heritage 3 (4), 1360-1372 https://doi.org/10.3390/heritage3040075
3. Mastrotheodoros GP, Beltsios KG, Bassiakos Y, 2020. On the blue and green pigments of post-Byzantine Greek icons. Archaeometry 62 (4), 774-795. https://doi.org/10.1111/arcm.12537
4. Mastrotheodoros G., Beltsios K.G., Bassiakos Y. On the red and yellow pigments of post-Byzantine Greek Icons, Archaeometry **63/4**, pp753-758 (2020). DOI https://doi.org/10.1111/arcm.12642

Papers in Refereed Conference Proceedings

1. Georgakopoulou M., Douni K., Ginalas M., Kakavogiani O., Bassiakos Y. Recent Finds from Final Neolithic and Early Bronze Age Silver Production in Southeastern Attica. in Athens and Attica in Prehistory: Proceedings of the International Conferenc , pp185-192 (2020). DOI: 10.2307/j.ctv15vwjjg.24

Undergraduate Theses and Internships completed in 2020

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

MATERIAL AND ENVIRONMENTAL ISOTOPE GEOCHEMISTRY

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
- Dr. Gougoura S., (Forensic Department of Hellenic Police-Biological and Biochemical Analysis Department).

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) 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: Operational Program Competitiveness, Entrepreneurship and Innovation (Call: Research-Create-Innovate), 2020-today
2) Application of modern analytical and chemometric techniques for the quality control-fraud of olive products (Holea)
   Funding source: Operational Program Competitiveness, Entrepreneurship and Innovation (Call: Research-Create-Innovate) 2018-today
3) Restoration of Filippoi Archeological Site Ephorate of Antiquities of Kavala – Thasos. 2019-2020
4) Food Authenticity and Food Traceabilitiy, Funding source: Private commercial funding, 2019-2020

Publications in International Journals

1. Dotsika, E., Correlation Between δ^{18}Ow and δ^{18}Oen For Estimating Human Mobility And Paleomobility Patterns*, Scientific Reports (2020)* ***10****, 15439*
2. Karalis, P., Poutouki, A.E., Nikou, T., Halabalaki, M., Proestos, C., Tsakalidou, E., Gougoura, S., Diamantopoulos, G., Tassi, M., Dotsika, E*,* Isotopic Traceability (^{13}C And ^{18}O) Of Greek Olive Oil, *Molecules (2020)* **25***, 5816*
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