6th IC4N

2019

6th International Conference from Nanoparticles & Nanomaterials to Nanodevices & Nanosystems

BOOK OF ABSTRACTS

CORFU, GREECE • JUNE 30 – JULY 3

Edited by: Efstathios I. Meletis

ORGANIZERS:

Efstathios I. Meletis
The University of Texas at Arlington
USA

Wolfram Schommers
Karlsruhe Institute of Technology – Germany
The University of Texas at Arlington
USA

Constantin Politis
University of Patras – Hellas
The University of Texas at Arlington
USA

Yue Zhang
University of Science and Technology Beijing
P.R. China

IC4N SPONSORS

北京科技大学
UNIVERSITY OF SCIENCE AND TECHNOLOGY BEIJING · 1952 ·

KIT
Karlsruher Institut für Technologie

UNIVERSITY OF
TEXAS
ARLINGTON
COLLEGE OF
ENGINEERING

ΠΑΝΕΠΙΣΤΗΜΙΟ ΠΑΤΡΩΝ
UNIVERSITY OF PATRAS

BOOK OF ABSTRACTS

2019

6th International Conference from Nanoparticles & Nanomaterials to Nanodevices & Nanosystems

Edited by: Efstathios I. Meletis

CORFU, GREECE • JUNE 30 – JULY 3

This work is licensed under a Creative Commons Attribution 4.0 International License.
(https://creativecommons.org/licenses/by/4.0/)

It can be accessed in the University of Texas at Arlington's institutional repository, ResearchCommons, at: http://hdl.handle.net/10106/28271

Publication Design and Formatting by Brittany Griffiths
Cover Design by Brittany Griffiths

Published and made openly accessible by:
University of Texas at Arlington Libraries
702 Planetarium Pl.
Arlington, TX 76019

Published in 2019

ISBN 978-0-9898878-6-1

Mavs Open Press
2019 University of Texas at Arlington

Table of Contents

Plenary Lecture

Keynote Lectures

Conference Abstracts

Foreword

Dear Colleagues,

On behalf of the Organizing Committee, it is my great pleasure to welcome you to the 6th International Conference from Nanoparticles and Nanomaterials to Nanodevices and Nanosystems (IC4N). Following the first five conferences, this year's event in the series travels to the exclusive and beautiful island of Corfu (Kerkyra), Greece. The conference theme is designed to bring together scientists from diverse disciplines within the common framework of nanoscience and nanotechnology. This particular conference features scientists from some 35 countries around the world to address current global societal needs in terms of energy, environment and human health. We are delighted to have Sir Fraser Stoddart 2016 Nobel Laureate in Chemistry to open this conference with a Plenary Lecture along with more than 150 Keynote, invited and contributed talks and posters presenting recent scientific findings.

Nanoscience and nanotechnology brought up an unprecedented excitement in the scientific and engineering communities, especially during the last two decades. The recent revolutionary advances in nanoscale phenomena open exciting, new avenues for research and discovery and also introduction of new technologies in the market place to address current global technological needs. This year's event is focused on twelve thrust topics Fundamentals of Nanomaterials and Materials Genome, Advances in Additive Manufacturing and Nanofabrication, 2D Materials Beyond Graphene, Nano Medicine and Biotechnology, Nanoscale Photochemistry, Charge Transfer and Energy Conversion, Functional Electroactive Materials and Nanostructures, Energy Conversion and Storage, Coatings and Materials for Extreme/Special Environments, Nanoscale Materials for Optoelectronics and Photonics, Environmental Applications and Implications, Nanoporous Materials and Membranes and Magnetism at the Nanoscale. Recent progress in other areas of nano sciences and nanotechnology are addressed in the Nano Multidisciplinary and New Directions Symposium.

We have made every effort to provide a stimulating environment for interaction and foster collaboration among participants. We believe and hope that progress in this field can have an unprecedented impact on critical global issues.

We count on your support for making the 6th IC4N a memorable event.
On behalf of the Organizing Committee,

Efstathios "Stathis" I. Meletis, Conference Chair
University of Texas at Arlington

Conference Symposia

- **Fundamentals of Nanomaterials/Materials Genome: Theory, Experiments and Simulations**
  Wolfram Schommers (Univ. of Texas, Arlington, USA/Karlsruhe Inst. of Technol., Germany)

- **Advances in Additive Manufacturing & Nanofabrication**
  Constantin Politis (Univ. of Texas, Arlington, USA/Univ. of Patras, Hellas)

- **2-D Materials Beyond Graphene**
  Traian Dumitrica (Univ. of Minnesota, USA)

- **Functional Electroactive Materials and Nanostructures**
  Serge Nakhmanson (Univ. of Connecticut, USA),
  Pamir Alpay (Univ. of Connecticut, USA),
  Seungbum Hong (Korean Adv. Inst. Sci. Technol., S. Korea),
  Brahim Dkhil (Ecole Central Paris, France)

- **Nano Medicine/Biotechnology**
  Kelly Velonia (Univ. of Crete, Hellas)
  Yaowu Hao (Univ. of Texas, Arlington, USA)
  Teja Guda, & Rena Bizios (Univ. of Texas, San Antonio, USA)

- **Nanoscale Photochemistry, Charge Transfer and Energy Conversion**
  Valentine Vullev (Univ. of California, Riverside, USA)
  Krishnan Rajeshwar (Univ. of Texas Arlington, USA)

- **Energy Conversion & Storage**
  Alberto Vomiero (Lulea Univ. of Technology, Sweden)
  George Demopoulos (McGill Univ., Canada)

- **Coatings/Materials for Extreme/Special Environments**
  Valentin Craciun (Nat. Inst. for Laser, Plasma & Rad. Physics, Romania)
  Petr Zeman & Jaroslav Vlcek (Univ. of West Bohemia, Czech Republic)

- **Nanoscale Materials for Optoelectronics and Photonics**
  Anton Malko (Univ. of Texas, Dallas, USA)
  Omar Mohammed (King Abdullah Univ. of Sci. & Technol., Saudi Arabia)

- **Environmental Applications & Implications**
  Dionysios Dionysiou (Univ. of Cincinnati, USA)
  Sami Rtimi (EPFL, Switzerland)

- **Nanoporous Materials & Membranes**
  Nick Kanellopoulos (NCSR Demokritos, Hellas)

- **Magnetism at the Nanoscasle**
  Panayiotis Poulopoulos (Univ. of Patras, Hellas)
  Andreas Nye (Johannes Kepler Univ. Linz, Austria)

- **Nano Multidisciplinary/New Directions**
  Efstathios I. Meletis (Univ. of Texas, Arlington, USA)

Plenary Lecture

Radical Molecular Nanotechnology

Sir Fraser Stoddart

2016 Nobel Laureate in Chemistry
Board of Trustees Professor of Chemistry
Chemistry Department, Northwestern University, Evanston, IL, USA

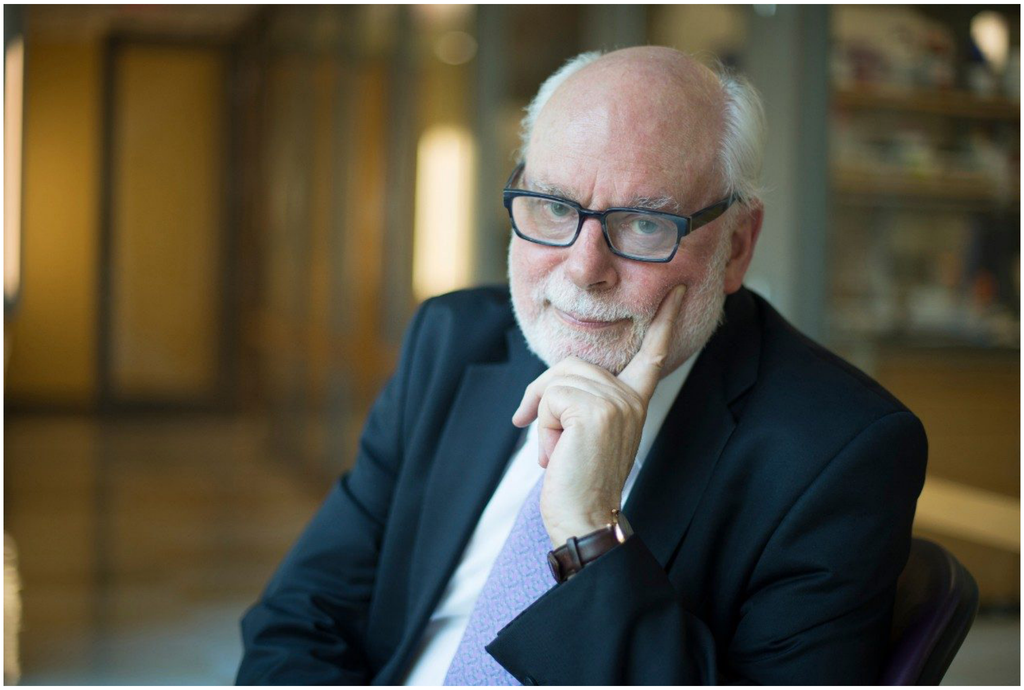


photo by Jim Prisching

Keynote Lectures

Artificial Magnetic Atoms

Björgvin Hjörvarsson*, Vassilios Kapaklis

Department of Physics and Astronomy
Uppsala University

Patterning can be used to engineering additional energy scales into magnetic materials. The obtained properties can be unique and strongly deviating from the parent material, as e.g. exemplified by the formation of permalloy based artificial spin-ice-structures.[1] The shape of the islands can be used to tailor their magnetic meso-spin dimensionality: Elongated islands can be made Ising-like[2] while circular islands can result in a XY-like behaviour.[3] The magnetic interactions in this type of metamaterials are characterised by two energy scales: Atomic interactions within islands and stray field caused interactions between the islands. Consequently, the islands can be viewed as mesospins, interacting via their stray field, in a close analogue to atomic spins. If the inter-island interaction is sufficiently weak, the mesospins exhibit paramagnetic like behaviour.[2] By the same token, if the mesospins are close enough, their mutual interactions can be strong enough to result in ordering.[3] When large arrays of interacting mesospins are formed, an order disorder transition can be obtained, resembling an ordinary phase transition.[5,6] However, the magnetic metamaterials are not restricted to the same rules as their atomic counterparts. For example, it is possible to combine and design the properties of magnetic metamaterials made from magnetic mesospins in almost arbitrary fashion. For example, XY mesospins can be used as an interaction modifier of Ising spins, due to the large difference in activation energies.[6] The results clearly demonstrate the possibility to design energy and length-scales in magnetic metamaterials in a completely new way. A brief outlook is given, emphasising the possibilities of using the interplay between the energy and length scales in artificial magnetic atoms.

References

[1] Artificial 'spin ice' in a geometrically frustrated lattice of nanoscale ferromagnetic islands. R. F. Wang et al., Nature 439, 303–306 (2006).

[2] Thermal transitions in nano-patterned XY-magnets, Unnar B. Arnalds, et al., Appl. Phys. Lett. 105, 042409 (2014); http://dx.doi.org/10.1063/1.4891479

[3] Thermalized ground state of artificial kagome spin ice building blocks, Unnar B. Arnald et al., Applied Physics Letters 101 (11) , art. no. 112404

[4] Melting artificial spin ice, Vassilios Kapaklis et al., New Journal of Physics 14 (2012) 035009 (10pp), IOP Select & highlight selection of 2012

[5] Thermal fluctuations in artificial spin ice, Vassilios Kapaklis et al., Nature Nano DOI: 10.1038/NNANO.2014.104

[6] Interaction modifiers in artificial spin ices, Erik Östman et al., Nature Physics (2018), doi:10.1038/s41567-017-0027-2

Chemistry and Devices from Halide Perovskites Semiconductors

Mercouri G. Kanatzidis

Department of Chemistry
Northwestern University, Evanston, IL, USA

Two-dimensional (2D) metal halide perovskites have made an impressive entry in the field of solar cells and LEDs as highly promising semiconductors. They feature a high degree of structural flexibility and tunable optoelectronic properties. They have a general formula of $(A')_2(A)_{n-1}M_nX_{3n+1}$, where A = Cs^+, $CH_3NH_3^+$ (MA), $HC(NH_2)_2^+$ (FA), M = Ge^{2+}, Sn^{2+}, Pb^{2+} and X = Cl^-, Br^-, I^-, are the perovskite components and A'+ = RNH_3 is an organic spacer. There are four kinds of 2D organic inorganic hybrid perovskites so far: Ruddelsden-Popper, Cation-ordered, Jacobson-Dion and Diammonium Cation. These vary from one another in ways the inorganic slabs stack and the way the spacer cations interact with the inorganic slabs. Generally, 2D perovskites form from solution via the bottom-up self-assembly of individual, semiconducting perovskite sheets having an adjustable slab thickness of up to few nanometers, separated by insulating bulky organic molecules. As a result, they behave as natural multiple quantum wells (QWs) with the semiconducting perovskite layers representing the wells and the insulating organic spacers representing the barriers. The width of the barrier is fixed and depends only on the length of the A' cation, while the width of the well can be adjusted by varying the thickness of perovskite slabs, which is defined by the n variable in $(A')_2(A)_{n-1}M_nX_{3n+1}$. It is critical to understand the thermodynamic and chemical limitations of the maximum layer thickness that can be sandwiched between the organic bilayers while retaining the structural integrity of the 2D perovskite.

Conference Abstracts

Impact of Nanoparticles on Amyloid Peptide and Protein Aggregation

T. John, H.J. Risselada, B. Abel*

Leibniz Institute of Surface Engineering, Leipzig, Germany

Considering that the motions of the quasi particles from nanostructures take place on continuous but non-differentiable curves, in the frame of the Extended Scale Relativity Theory Model (in its Schrödinger – type variant), it is proved that the imaginary part of a scalar potential of velocities can be correlated with the fractal information and, implicitly, with a tensor of "tensions" (a measure of interactions at nanoscale). This tensor becomes fundamental in the defining of any and all constitutive laws of material at nanoscale. In such a procedure, a specific differential geometry based on a Poincaré – type metric of the Lobacevski plane (which is invariant to the homographic group of transformations) and also a specific variational principle (whose field equations represent a harmonic map from the usual space into the Lobacevski plane) occur. Moreover, the fractal information is contained in the nanostructure and thus, in its own space associated to it.

Mechanistics of Spectrum Manipulation, Energy and Electron Transfer Reaction in Hybrid Materials

Maria Abrahamsson*, Elin Sundin, Deise Barbosa de Mattos, Mark Johnstone,
Ambra Dreos, Henrik Sundén

Chalmers University of Technology, Gothenburg, Sweden

*e-mail: abmaria@chalmers.se

Efficient solar energy conversion, to electricity in a photovoltaic (PV) device or to solar fuels in a dye sensitized photoelectrosynthetic cell (DSPEC) relies on efficient utilization of the absorbed photons, either in energy transfer processes or in charge transfer events. The rates for the different energy and electron transfer processes needs to be controlled and tuned, to avoid destructive pathways and to increase the overall efficiencies of the processes.

To some extent, rates can be tuned by molecular design, since molecules typically provide tuning opportunities. However, many applications require solid state materials, or semi-solid state materials, and a material-oriented approach is often favorable to stabilize the highly reduced states generated in the multi-electron transfer processes required for e.g. solar fuels generation. Here, a traditional approach using nano-structured semiconductor electrodes to control primary charge separation and secondary electron transfer will be discussed. The use of patterned dye sensitized mixed-semiconductor thin films results in at least a factor of ca 50 longer-lived charge separated state compared to a single semiconductor thin film. Furthermore, we prove conduction band mediated electron transfer to a catalyst, and preliminary results indicate that we may have a two-electron transfer process if dye:catalyst ratios are favorable. In addition, mechanistic understanding of photophysical and -chemical processes in low molecular weight gelator-materials with relevance to photon upconversion and singlet fission will be discussed.

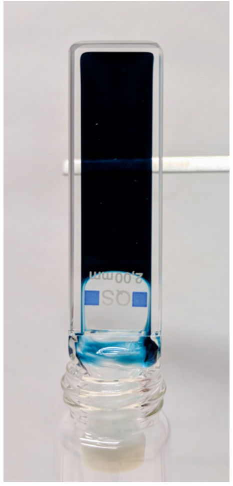


Figure 1. A low molecular weight gel with a chromophore covalently attached to the gelator entities.

From Carbon-Rich Molecules to Carbon-Rich Materials

Igor Alabugin

Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL, USA

e-mail: alabugin@chem.fsu.edu

In the first part, I will discuss the advantages of alkynes as high-energy carbon-rich precursors for extended polyaromatics, the two general patterns of oligoalkyne folding into an aromatic ribbon, and the use of supramolecular effects in the design of traceless directing groups for radical reactions.[1]

In the second part, I will present a mild method for oxidative C(sp3)–H amination from unprotected anilines and C(sp3)–H bonds. In this process, basic, radical, and oxidizing species work together in a coordinated sequence of deprotonation, H-atom transfer and electron transfer that forges a new C–N bond. I will also show how reductant upconversion, a new concept in catalysis, can be used for preventing the premature activation of oxidants.[2]

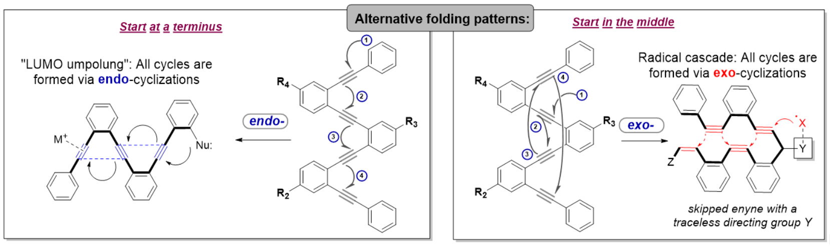


Figure 1. Alternative folding patterns for conversion of oligoalkynes into aromatic ribbons

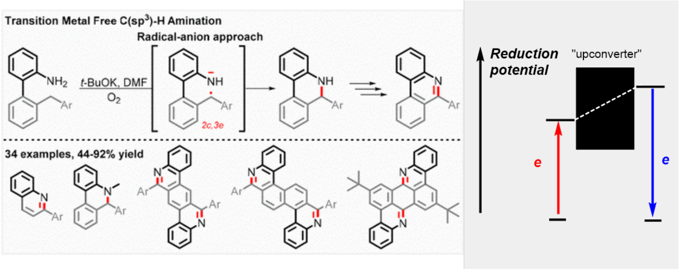


Figure 2. Double C-H amination for the preparation of N-heterocycles and the principle of reductant upconversion.

References

[1] Alkyne Origami: Folding Oligoalkynes into Polyaromatics. I. V. Alabugin, E. Gonzalez-Rodriguez. Acc. Chem. Res., 51, 1206 (2018).

[2] Upconversion of Reductants. M. A. Syroeshkin, F. Kuriakose, E. A. Saverina, V. A. Timofeeva, M. P. Egorov, I. V. Alabugin. Angew. Chem. Int. Ed., 57, in print (2019).

Preparation and Characterization of Nanostructured AgNiO Thin Films

A. Stamatelatos[1], N. Kanistras[1], D. I. Anyfantis[1*], E. Violatzi[1], D. Geralis[1],
S. Grammatikopoulos[2], M. Tsarmpopoulou[1], M.M. Sigalas[1], P. Poulopoulos[1]

[1]*Materials Science Department, University of Patras, Patras, Greece*
[2]*Department of Mechanical Engineering, Technological Educational Institute (T.E.I.) of Western Greece, Patras, Greece*

[*]e-mail: up1057157@upatras.gr

Thin films of noble nanoparticles embedded in a dielectric matrix present enormous scientific interest, mainly due to their attractive properties for applications. Recently we investigated the optical properties of nanostructured thin films of metal alloys by growing Au nanoparticles in NiO matrix via short annealing.[1]

In the present work, we investigate the growth of Ag nanoparticles inside a NiO matrix and the optical properties of it. We have attempted various ways of growth. Namely, (i) we exchanged the series of growth between the Ni and Ag metallic films and (ii) we have selected different annealing temperatures for the oxidation of Ni and the self-organization of Ag nanoparticles.[2] The metallic films have been produced in two chambers by means of direct current and radiofrequency magnetron sputtering. The annealing was performed in a furnace in air at temperatures between 400 – 500℃. The growth of selected samples was performed by Atomic Force Microscopy. Optical measurements have been performed via ultraviolet-visible spectroscopy. We have observed localized surface plasmonic resonances (LSPRs) in a few samples. The position and features of them are correlated to the growth recipe. The results are discussed within the framework of Rigorus Coupled Wave Analysis method.

Acknowledgements

This work was partially co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code:T1EDK-04659).

References

[1] "Growth of Au Nanoparticles in NiO via Short Annealing of Precursor Material Thin Film and Optimization of Plasmonics", S. Grammatikopoulos et al., Phys. Status Solidi A 214, 1700303 (2017).

[2] "Microstructure and plasmonic behavior of self-assembled silver nanoparticles and nanorings", A. G. Chronis et. al., J. Appl. Phys. 125 (2018).

Responsive Self-Assembled Peptide Biomaterials and Applications

Chrysanthi Pinelopi Apostolidou*, Anna Mitraki

Department of Materials Science and Technology, University of Crete, Heraklion, Greece
Institute of Electronic Structure and Laser (IESL), FORTH, Heraklion, Greece University of Crete

*e-mail: chrysana@materials.uoc.gr

Hydrogels represent an important family of biomaterials. They are three dimensional, hydrophilic networks capable of absorbing large amount of water and biological fluids. The high water content and mechanical properties that resemble natural tissues make hydrogels attractive for tissue engineering applications and encapsulation and drug delivery. In this work, we carried out self-assembling studies on an 11 amino acid peptide sequence, which consists of a beta sheet forming core, an RGD sequence at the N-terminus and a histidine residue at the C-terminus. According to theoretical and experimental studies this peptide self-assembles into amyloid fibrils in parallel arrangement where the RGD motif is exposed to the surface of the material.[1] The RGD is the cell recognition motif, found in fibronectin and other adhesive ECM proteins, that mediates cell attachment via interaction with integrins. The histidine amino acid at the C terminus region acts as a molecular switch that controls hydrogelation in response to the pH changes. We studied the ability of the peptide to form hydrogels under different pH, salt concentration and temperature. The goal is to design the optimal responsive hydrogels to external stimuli that will function as an adjustable platform for attachment and distribution of cells and drugs. Our target is to design scaffolds that will be biocompatible, economical, reliable and accessible to the general public.

References

[1] "Computational design of amyloid self-assembling peptides bearing aromatic residues and the cell adhesive motif Arg-Gly-Asp", Jonnalagadda, S.V.R., Ornithopoulou, E., Orr, A.A., Mossou, E., Forsyth, V. T., Mitchell, E. P., Bowler, M. W., Mitraki, A., Tamamis, P., Molecular Systems Design and Engineering 2: 321-335 (2017)

Coexistence of Ferroelectricity and Two-Dimensional Electron Gas at an Oxide Interface

A. Ariando

Department of Physics & NUSNNI, National University of Singapore, Singapore

e-mail: ariando@nus.edu.sg

Integrating multiple properties in a single system is crucial for the continuous developments in electronic devices. However, some physical properties are mutually exclusive in nature. In this talk, we demonstrate the coexistence of two seemingly mutually exclusive properties-ferroelectricity and two-dimensional electron gas-in ferroelectric $Ba_{0.2}Sr_{0.8}TiO_3$ thin films at the $LaAlO_3/Ba_{0.2}Sr_{0.8}TiO_3$ interface. The ferroelectricity of a ~3.2 nm $Ba_{0.2}Sr_{0.8}TiO_3$ thin film is preserved with a two-dimensional mobile carrier density of ~0.05 electron per unit cell. We show that the electronic reconstruction resulting from the competition between the built-in electric field of $LaAlO_3$ and the polarization of $Ba_{0.2}Sr_{0.8}TiO_3$ is responsible for this unusual two-dimensional conducting ferroelectric phase. The general concept of exploiting mutually exclusive properties at oxide interfaces via electronic reconstruction may be applicable to other strongly-correlated oxide interfaces, thus opening windows to new functional nanoscale materials for applications in novel nanoelectronics.

Mechanism of Wear with Functionalized Nanoparticles

Vinay Sharma[1], Kimaya Vyavhare[1], Ali Erdemir[2], Richard Timmons[1],
Pranesh B. Aswath[1*]

[1]*The University of Texas at Arlington, Arlington, TX, USA*
[2]*Argonne National Laboratory, Chicago, IL, USA*

[*]e-mail: aswath@uta.edu

In recent years, nanoparticles are being considered as vehicles to deliver specific functionality to surfaces to improve their tribological properties such as friction, adhesion and wear. In this context, we are using nanoparticles to deliver desired antiwear and antifriction chemistries to rubbing surfaces to improve their properties. Plasma functionalization was used to develop a core-shell structure with multiple layers of additive chemistry with tailored properties. These functionalized nanoparticles were dispersed in a lubricant and their tribological properties were evaluated.

Polytetrafluoroethylene (PTFE) nanoparticles were selected as the carrier and hexamethyldisiloxane (HMDSO) and trimethoxyboroaxine (TMB) and glyceryl methacrylate were monomers used for plasma deposition of thin films on the surface of PTFE nanoparticles. A variety of process parameters including flow rate, pressure, power and duty cycles were changed to optimize the process. In tribological tests Phosphorus level for ZDDP was kept at 350 ppm and four different oil formulations were prepared and the details about each test formulation is shown Table 1.

The test configuration selected was high-frequency reciprocating cylinder on flat surface. The surfaces of the tribological contact region were examined using a variety of surface analytical tools including XANES, XPS, AFM and SEM.

Results clearly reveal that the addition of the plasma functionalized PTFE nanoparticles to the base oil with ZDDP provide a very significant improvement in reducing wear, clearly outperforming samples having only ZDDP, or ZDDP plus un-functionalized particles. The improved wear performance is attributed to stable tribofilm formation with polyphosphates of Si and F doped Zn when ZDDP is used in combination with functionalized PTFE nanoparticles. The mechanism of tribofilm formation is discussed in the context of the improved wear and frictional properties.

Name	Formulation
B.O	Group III Base oil (B.O): B.O
B.O + ZDDP 350	B.O+ZDDP with 350 ppm of Phosphorus treat rate: B.O + ZDDP 350
B.O + ZDDP 350 + 0.33wt% PTFE	B.O+ZDDP with 350 ppm of Phosphorus treat rate + 0.33 wt. % PTFE
B.O + ZDDP 350 + 0.33wt% PHGM	B.O+ZDDP with 350 ppm of Phosphorus treat rate + 0.33 wt.% Functionalized PTFE

Table 1. Oil formulations used in tribological tests

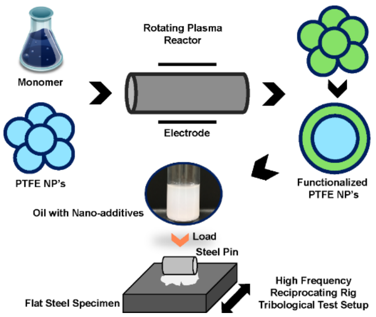


Figure 1. Schematic of tests conducted.

Highly Efficient Solar Sea-Water Splitting at Semiconductor Metal Oxide Electrodes

Jan Augustynski

Centre for New Technologies, University of Warsaw, Poland

e-mail: jan.augustynski@unige.ch

Photo-electrolysis of water employing semiconductor electrodes is a widely investigated approach to the direct chemical storage of solar energy. Besides optoelectronic properties of the photo-materials, i.e. the range of the absorbed solar wavelengths and energetic positions of the band-edge levels, the principal issue is the long-term stability of the employed electrodes.

This presentation will focus on recent improvements in photo-electrochemical properties of tungsten trioxide WO_3 thin films achieved in our laboratory. Use of appropriate mixtures of tungstic acid and organic structure-directing agents that form the WO_3 film precursor, combined with a two-step annealing, allows the formation of highly crystalline (of monoclinic structure) electrodes with controlled porosity. Both are the key features that allow reducing photogenerated charge recombination in the fabricated photo-material and obtaining large photo-oxidation currents that attain the saturation point at potentials around 1 V vs reversible hydrogen electrode.

Photo-electrolysis experiments employing synthetic sea water electrolyte in a two compartment cell demonstrated dominant formation of chlorine at the WO_3 photo-anode with remarkably stable photocurrents exceeding 4.5 mA cm^{-2}. The possibility of using sea-water electrolyte for a larger scale photo-electrochemical hydrogen generation would also release the strain on vital fresh water resources.

New Hemocompatible Mesoporous Bioglass Nanospheres for Sustained Release of Ibuprofen

Diana Elena Baciu[1*], Eleni K. Efthimiadou[1, 2], Theodore Steriotis[1],
Georgia Charalambopoulou[1]

[1]*National Center for Scientific Research "Demokritos", Aghia Paraskevi Attikis, Greece.*
[2]*Inorganic Chemistry Laboratory, Chemistry Department, National and Kapodistrian University of Athens, Panepistimiopolis, Zografou, Greece*

[*]e-mail: dianabaciuro@yahoo.com

In the last decade, the use of mesoporous bioactive glasses for drug delivery and bone tissue regeneration has grown significantly due to their high specific surface area and pore volume, excellent bioactivity, biocompatibility, osteoconductivity and capability to encapsulate and deliver both hydrophilic and hydrophobic drugs. In this work, new mesoporous bioglass nanospheres (MBG) of the system SiO_2-CaO/SrO (denoted as CaBG and SrBG) have been successfully synthesized and optimized by a sol-gel method using PEG as non-ionic co-surfactant and CTAB as cationic surfactant, respectively. The structural properties of the prepared materials were investigated by SEM, XRD and N^2 adsorption at 77K, while the effect of the full substitution of Sr for Ca on their bioactivity was studied by immersing them in simulated body fluid (SBF) at 37℃ and pH 7.4 for 14 days. Ibuprofen, a widely used anti-inflammatory drug was encapsulated into the MBG nanospheres in order to evaluate their loading capacity and release behavior. Finally, hemolysis tests were performed to assess the effect of bioglass nanospheres on red blood cells (RBCs).

SEM results of both CaBG and SrBG bioglasses showed that calcination at 600℃ leads to the formation of porous nanospheres with diameter between 70-130 nm. Both materials exhibit an ordered mesoporous structure with certain uniformity in pore size and morphology (CaBG was found to have a BET area of 853 m^2/g and a mean pore size of ca. 2.5-2.8 nm, while the respective values for SrBG were 1024 m^2/g and 2.5 nm, respectively). XRD patterns of the materials after their immersion in SBF exhibited peaks that can be assigned to hydroxyapatite and strontium apatite, indicating biomineralization. Both bioglasses showed high drug-loading capacity and encapsulation efficiency (as high as 90%), but also a sustained ibuprofen release profile. The hemolysis test showed that both bioglasses did not affect the integrity of RBCs, therefore meeting the standard requirements for biological materials. Concluding, the advantageous textural and structural characteristics, the highly bioactive and hemocompatible behavior, in combination with the drug uptake/release ability, may suggest the use of the developed MBG nanospheres for drug delivery and bone tissue regeneration.

Nanoscale Ferromagnetism in Alloy Thin Film Via Lattice Disordering

R. Bali[1*], A. Schmeink[1], B. Eggert[2], J. Ehrler[1,3], V. Liersch[1], A. Semisalova[1],
G. Hlawacek[1], K. Potzger[1], J. Fassbender[1,3], T. Thomson[4], H. Wende[2], J. Lindner[1]

[1]*Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, Dresden, Germany*
[2]*Universität Duisburg-Essen, Fakultät für Physik, Duisburg, Germany*
[3]*Technische Universität Dresden, Fakultät Physik, Dresden, Germany*
[4]*University of Manchester, School of Computer, Oxford Road, Manchester, UK*

[*]e-mail: r.bali@hzdr.de

Structural disorder in certain alloys leads to the onset of strong ferromagnetism. Disorder can be induced in desired locations, at the nanoscale, making such materials useful for magnetic nanopatterning. Examples of these alloys include $Fe_{60}Al_{40}$,[1] $Fe_{50}Rh_{50}$,[2] and $Fe_{60}V_{40}$.

Disorder can be generated locally using focussed ion- as well as laser- beams,[1-3] inducing nanoscale ferromagnetism. Furthermore, the effect can be reversed via thermal re-ordering of the alloy, achieving re-writeable magnetic structures.

Insights into the mechanisms of the ferromagnetic onset in prototype systems, helps achieve a broader understanding of magneto-structural correlations in general. For instance, in paramagnetic B2-ordered $Fe_{60}Al_{40}$ as well as $D8_b$-type $Fe_{60}V_{40}$, the ferromagnetic onset is caused by antisite defects, *i.e.*, site swapping of the Fe and Al (V) atoms, resulting in a transition to the bcc (A2) structure. An increase of antisite defects can cause the M_s of $Fe_{60}Al_{40}$ as well as $Fe_{60}V_{40}$ to increase from nearly-zero in the ordered structures to 780 and 660 kAm^{-1}, in their respective disordered structures. In contrast, in B2 $Fe_{50}Rh_{50}$ the well-ordered film is antiferromagnetic, and static disordering may be sufficient to fully transform the alloy to the ferromagnetic phase, possessing an M_s of ~ 1250 kAm^{-1} at 300 K. Thus, whereas the M_s in the above alloys increases drastically with lattice disorder, the microscopic nature of the disordering varies.

Here we deploy ion-irradiation to sensitively induce lattice disorder in the above binary alloy systems, while tracing the manifested ferromagnetic onsets, thereby obtaining insights into the correlation between magnetic behaviour and the structure. Properties of magnetic arrays and magneto-transport devices produced using lattice disorder will be discussed.

References

[1] "Printing Nearly-Discrete Magnetic Patterns Using Chemical Disorder Induced Ferromagnetism", R. Bali et al., Nano Letters 14, 435 (2014).
[2] "Tuning the antiferromagnetic to ferromagnetic phase transition in FeRh thin films by means of low-energy/low fluence ion irradiation", A. Heidarian et al., Nucl. Instrum. Methods Phys. Res. B 358, 251 (2015).
[3] "Laser-Rewriteable Ferromagnetism at Thin-Film Surfaces", J. Ehrler et al., ACS Appl. Mater. Interfaces 10, 15232 (2018).

Gas-Phase Investigations of Nanoclusters $[Mo_3S_{13}]^{2-}$ and $[Mo_2S_{12}]^{2-}$ as Model Catalysts for the Hydrogen Evolution Reaction

Aristeidis Baloglou[1*], Milan Ončák[1], Marie-Luise Grutza[2], Stefan Jageregger[1],
Manuel Plattner[1], Christian van der Linde[1], Philipp Kurz[2], Martin K. Beyer[1]

[1]Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Innsbruck, Austria
[2]Institute for Inorganic and Analytical Chemistry, Albert-Ludwigs-Universität Freiburg, Freiburg, Germany

[*]e-mail: aristeidis.baloglou@uibk.ac.at

As hydrogen is a chemical fuel of high energy density, Power-to-Hydrogen is an attractive approach for achieving the goals of the 2030 climate & energy framework of the EU. Molybdenum sulfide based nanomaterials are potent photo- and electrochemical hydrogen evolution reaction (HER) catalysts.[1] A better understanding of the molecular mechanisms involved, may facilitate the targeted design of precious metal free HER-catalysts. However, the detailed mechanism of H_2 formation is still under debate and mechanistic investigations on amorphous MoSx are particularly difficult.[2] Herein we use the bottom-up approach and study precisely defined nanoclusters, like $[^{92}Mo_3S_{13}]^{2-}$ and $[^{92}Mo_2S_{12}]^{2-}$ in gas-phase, as key building blocks of said materials. Coupling Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) with laser spectroscopy techniques, allows us to conduct various types of experiments. Collision Induced Dissociation (CID) experiments provide insight into the structural flexibility of the clusters, indicating that roaming H/SH moieties may be a key feature of HER catalysis.[3] With photodissociation spectroscopy in the UV-Vis region (0.5 – 5.5 eV) we can probe the electronic structure of the examined clusters. Here, $[HMo_3S_{13}]$- for example, shows a broad absorption band starting at 1.7 eV, with distinct features in the UV at 3.7 eV and 4.5 eV. Furthermore, infrared multiphoton dissociation spectra of, for instance, protonated $[HMo_3S_{13}]$- and $[HMo_2S_{12}]$-, show distinct H-S stretching vibrations at 2450 cm^{-1} and 2530 cm^{-1} respectively. Combining these results with theoretical calculations allows us to identify terminal disulfide units as H adsorption site, hence implying a sulfur-centered HER mechanism.

References

[1] “Catalyzing the Hydrogen Evolution Reaction (HER) with Molybdenum Sulfide Nanomaterials”, J. D. Benck, T. R. Hellstern, J. Kibsgaard, P. Chakthranont, T. F.Jaramillo, ACS Catal, 4, 3957-3971 (2014)

[4] “Hydrogen evolution catalysis by molybdenum sulfides (MoSx): are thiomolybdate clusters like $[Mo_3S_{13}]^{2-}$ suitable active site models?”, M.-L. Grutza, A. Rajagopal, C. Sterb, P. Kurz Sust. Energy Fuels, 2, 1893-1904 (2018).

[3] “Structural Properties of Gas Phase Molybdenum Sulfide Clusters $[Mo_3S_{13}]^{2-}$, $[HMo_3S_{13}]^{-}$, and $[H_3Mo_3S_{13}]^{+}$ as Model Systems of a Promising Hydrogen Evolution Catalyst”, A. Baloglou, M. Ončák, M.-L. Grutza, C. van der Linde, P. Kurz, M. K. Beyer, J. Phys. Chem. C, in print DOI:10.1021/acs.jpcc.8b08324.

Excited States in Strongly Coupled Bimetallic Ruthenium Polypyridines

Luis M. Baraldo*, Bruno M. Aramburu-Trošelj, Paola S. Oviedo, Alejandro Cadranel, Germán Pieslinger

Departamento de Química Analítica, Inorgánica y Química Física, INQUIMAE,
Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina

*e-mail: baraldo@qi.fcen.uba.ar

We have examined the excited state dynamics of a family of cyanide-bridged bimetallic Ru(II),Ru(II) polypyridines using ultrafast vis-NIR transient absorption spectroscopy. All these complexes show the presence of an excited state which exhibit intense photoinduced absorptions in the NIR. We assign these transitions as a photoinduced intervalence charge transfer (PIIVCT) transitions like the one observed in the ground state of the mixed-valence form of these complexes. The energy and shape of the transitions observed for this state indicates that the vacant orbital runs parallel to the bridge and is substantially delocalized between both metallic ions. We label this state as ^{3}MLCTz.

Notable is that the lifetime of this state varies widely depending of the coordination sphere on the ruthenium ions. This is due to the presence of two other excited states that lack any photoinduced absorption in the NIR. For both states we assign a localized configuration with the hole perpendicular to the cyanide-bridge precluding an intense PIIVCT. These states differ in the localization of the hole. In one is in the same ion as the radical anion (^{3}MLCTxy) and in the other it lays in the remote Ru ion (^{3}MLCTr).

The lifetimes of the delocalized state depend strongly on the energy order between the states. In some systems, the delocalized state has a lifetime of only a few picoseconds, while for the [Ru^{II}(tpy)(bpy)(μCN)Ru^{II}(py)$_4$Cl]$^{2+}$ complex (tpy = (2,2';6',2"-terpyridine, bpy = 2,2'-bipyridine, py = pyridine), the ^{3}MLCTz state is the emissive state and have a longer lifetime than the related monometallic complexes.

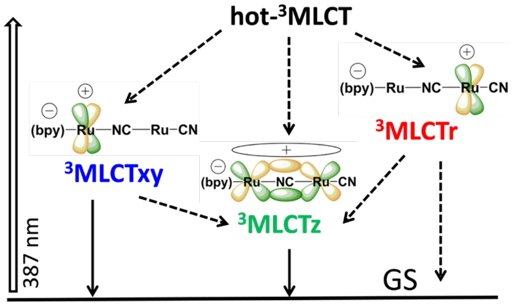


Figure 1. Proposed mechanism to fit the picosecond pump-probe data recorded for [Ru^{II}(tpy)(bpy)(μCN)Ru^{II}(py)$_4$Cl]$^{2+}$ upon 387 nm excitation.

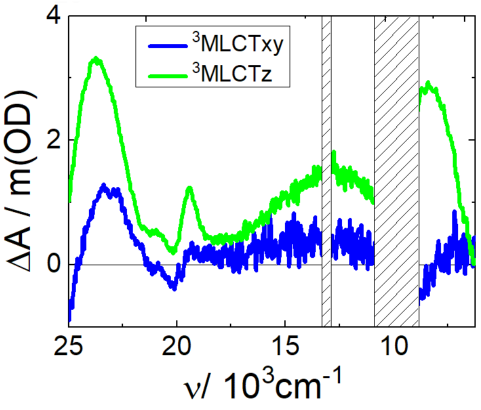


Figure 2. Species-associated differential spectra; ^{3}MLCTz in green and 3MLCTxy in blue.

Synthesis, Properties and Enviromental Applications of Nanostructured Ag-ZnO

A. Barnasas[1*], N. Kanistras[1], A. Stamatelatos[1], N. Dimopoulou[1], E. Mystiridou[1],
N. Bouropoulos[1], M.V. Karavasilis[2], C. Aggelopoulos[2], C.D. Tsakiroglou[2], C. Politis[3],
P. Poulopoulos[1]

[1]*Materials Science Department, University of Patras, Patras, Greece*
[2]*Foundation for Research and Technology Hellas-Institute of Chemical Engineering Sciences (FORTH/ICE-HT), Patras, Greece*
[3]*Department of Materials Science and Engineering, University of Texas at Arlington, Arlington, TX, USA*

[*]e-mail: mparnalex@gmail.com

During the last years, much attention has been paid on the decontamination of water matrices (e.g. groundwater, effluents of wastewater treatment plants). Photodegradation of these contaminants via photocatalysis has become a very active research topic in the past several decades.[1]

In this work, well-aligned zinc oxide (ZnO) and silver-covered ZnO (Ag-ZnO) foils via the direct current magnetron sputtering method were naturally oxidized via a simple, low-cost, low-temperature, scalable thermal process. Ag-ZnO nanorods were grown on Zn foils by treating their surface with various agents (e.g. acids), and annealing in an oven at temperatures 385-400℃. The ZnO and Ag-ZnO films were characterized by X-ray diffraction, scanning electron microscopy (SEM) and photoluminescence spectroscopy. A simple photolytic reactor was fabricated and later used to find the optimum experimental conditions for photocatalytic performance. Ag-ZnO demonstrated superior photocatalytic activity under UV-vis. irradiation. The optimized doping of Ag in Ag-ZnO enhanced photocatalytic activity in a simple reactor design and indicated potential applicability of Ag-ZnO for large-scale purification of water under UV-vis. light irradiation.[2]

Acknowledgements

We thank Dr. V. Karoutsos for the SEM images. This work was implemented under the Action "Supporting Enterprises for Research Projects in the Microelectronics and Advanced Materials" and is co-financed by the European Union and National Resources through the Operational Program "Western Greece 2014-2020" (project title: "Development of materials for energy autonomous water purification units for its safe reuse – YLENDOR"; project code: MIS 5029472).

References

[1] "Photocatalytic paper using zinc oxide nanorods", Sunandan Baruah, Mayuree Jaisai, Reza Imani, Mousa M Nazhad & Joydeep Dutta, Science and Technology of Advanced Materials 11, 055002 (2010).
[2] "One dimensional-ZnO nanostructures: Synthesis, properties and environmental applications", Innocent Udoma, Manoj K. Rama, Elias K. Stefanakos, Aloysius F. Hepp, D. Yogi Goswami, Materials Science in Semiconductor Processing 16, 2070 (2013).

Magnetic Materials with Predefined Exchange Coupling Strength Profiles at the Nano-Scale

Lorenzo Fallarino[1], Patricia Riego[1,2], Brian Kirby[3], Casey Miller[4], Andreas Berger[1*]

[1]*CIC nanoGUNE, E-20018 Donostia - San Sebastian, Spain*
[2]*Departamento de Física de la Materia Condensada, Bilbao, Spain*
[3]*Center for Neutron Research, NIST, Gaithersburg, MD, USA*
[4]*School of Chemistry and Materials Science, RIT, Rochester, NY, USA*

[*]e-mail: a.berger@nanogune.eu

We have recently investigated magnetization structures and magnetization reversal properties in materials that exhibit predefined exchange coupling strength profiles along their depth.[1-3] The exchange coupling strength is hereby modified by means of compositional changes at the nano-scale in suitable alloys, such as NiCu,[1] CoCr,[2] and CoRu,[3] while even achieving epitaxial growth.[2, 3] We observe that our ferromagnetic model systems behave as if they consisted of nearly independent segments characterized by "local" Curie temperatures, despite the fact that ferromagnetism is a collective phenomenon and the materials systems we are investigating represent itinerant ferromagnets.

A possible utility of these types of structures is indicated in Fig. 1, which displays data of three different magnetic films that exhibit a minimum exchange coupling strength in their central layer. Due to the "local" TC behavior, one can now induce temperature dependent magnetic correlation (yellow or blue states) or decorrelation (green state) in between the various parts of one sample by designing the material adequately.

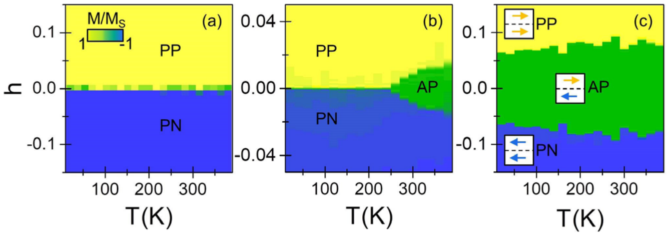


Figure 1. Field-dependent magnetization data as a function of temperature and external magnetic field strength for samples with a predefined exchange coupling strength profile (exhibiting a minimum "local" TC in the film center). The "local" TC of the central layer is 400 K in (a), 260 K in (b), and 5 K in (c). The data are plotted as color-coded maps (normalized to MS), so that M/MS equal to 1 represents positive magnetic saturation (PP/yellow color), -1 indicates negative saturation (PN/blue color), while 0 illustrates a net antiparallel case (AP/green color) of the magnetization state.

References

[1] B. J. Kirby et al., Phys. Rev. Lett. 116, 057202 (2016)
[2] L. Fallarino et al., Phys. Rev. B 95, 134445 (2017)
[3] B. J. Kirby et al., Phys. Rev. B 98, 064404 (2018)

Intrinsic Properties of Molybdenum Sulfide Clusters, The Key Constituents of a Potent HER Catalyst

Aristeidis Baloglou[1], Milan Ončák[1], Marie-Luise Grutza[2], Stefan Jageregger[1], Manuel Plattner[1], Christian van der Linde[1], Philipp Kurz[2], Martin K. Beyer[1*]

[1]Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Innsbruck, Austria
[2]Institute for Inorganic and Analytical Chemistry, Albert-Ludwigs-Universität Freiburg, Freiburg, Germany

[*]e-mail: martin.beyer@uibk.ac.at

Molybdenum sulfide nanoclusters, such as $[Mo_3S_{13}]^{2-}$ and $[Mo_2S_{12}]^{2-}$ are highly active hydrogen evolution reaction (HER) catalysts, which can be supported on various electrode surfaces.[1] Additionally, the $[Mo_3S_{13}]^{2-}$ nanocluster was reported to be a potent photochemical catalyst for HER.[2] In order to facilitate the targeted optimization of the catalysts, comprehension of the molecular mechanisms involved is of major significance. In the present project, we use the bottom up approach and investigate individual reaction steps quantitatively with the help of atomically precisely defined gas-phase nanoclusters. We couple Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) with photodissociation spectroscopy to identify and characterize reactants, products and reactive intermediates. Of particular interest are the protonated forms of $[HxMo_3S_{13}]^{-/+}$ (x = 1, 3) and $[HMo_2S_{12}]$- as they serve as models of adsorbed H atoms on the clusters. Herein, we investigated the structural flexibility of the clusters by collision induced dissociation (CID) experiments.[3] Further, H-S stretching vibrations at 2450 cm^{-1} and 2530 cm^{-1} where observed by Infrared Multiphoton Dissociation (IRMPD) experiments on $[HMo_3S_{13}]$- and $[HMo_2S_{12}]^{-}$. Combing the experimental observations with quantum chemical calculations, suggests a sulfur-centered HER mechanism, with roaming H/SH moieties as a key feature.

Elementary steps of molybdenum sulfide formation are studied with $^{92}Mo_n^+$ (n = 1 - 7). The clusters are exposed to dimethyl disulfide at a collision frequency around 1 s^{-1}. $MoxSy^+$ species are formed in the first reaction step, together with products containing carbon and hydrogen. The reactions illustrate the tendency of molybdenum to form sulfides.[4]

References

[1] "Catalyzing the Hydrogen Evolution Reaction (HER) with Molybdenum Sulfide Nanomaterials", J. D. Benck, T. R. Hellstern, J. Kibsgaard, P. Chakthranont, T. F.Jaramillo, ACS Catal, 4, 3957-3971 (2014).

[2] "Thiomolybdate $[Mo_3S_{13}]^{2-}$ nanocluster: a molecular mimic of MoS_2 active sites for highly efficient photocatalytic hydrogen evolution", Y. Lei, M. Yang, J. Hou, F. Wang, E. Cui, C. Kong, S. Min, Chem. Commun., 54, 603-606 (2018)

[3] "Structural Properties of Gas Phase Molybdenum Sulfide Clusters $[Mo_3S_{13}]$2–, $[HMo_3S_{13}]^{-}$, and $[H_3Mo_3S_{13}]^{+}$ as Model Systems of a Promising Hydrogen Evolution Catalyst", A. Baloglou, M. Ončák, M.-L. Grutza, C. van der Linde, P. Kurz, M. K. Beyer, J. Phys. Chem. C, in print DOI:10.1021/acs.jpcc.8b08324

[4] "Gas-Phase Reactivity Studies of Small Molybdenum Cluster Ions with Dimethyl Disulfide" A. Baloglou, M. Ončák, C. van der Linde, and M. Beyer, Top. Catal., 61, 20-27 (2017).

The Emergence of Anisotropy and The Role of Intermediates in Nanocrystal Formation

D. Wurmbrand[1], N. Kirkwood[2], M. Seybold[1], K. Boldt[1*]

[1]University of Konstanz, Department of Chemistry, Konstanz, Germany
[2]The University of Melbourne, School of Chemistry, Melbourne, Australia

[*]e-mail: klaus.boldt@uni-konstanz.de

Nanocrystals with anisotropic shape attract tremendous interest, because they provide the prerequisite for directional processes, e.g. self-assembly, charge transport, or direction-dependent magnetic or optical properties like the emission of polarized light. Their formation requires breaking the symmetry. Often selective passivation of specific crystal facets using surfactants and use of intrinsic asymmetry of the underlying crystal structure is assumed,[1] but examples exist where this is not required.[2]

Herein we address the question of how the anisotropy emerges in colloidal Cd chalco-genide nanorods. We present the isolation and characterization of reaction intermediates which take the form of either extended polymers or discrete clusters. The nature of these intermediates can be controlled using polar additives, which has fundamental consequences for the reaction trajectory and the resulting particle shape and size.[3] The polymeric intermediates are the closest relative to the elusive semiconductor monomer and are of special interest, because they constitute a thermodynamically metastable species at high temperatures. They form a mesophase that is able to template its own transformation into nanorods[4]: while pyrolysis at low concentration forms isotropic nanocrystals, nanorods with surprisingly low size dispersity are formed when the intermediate is heated at high concentration (see Fig. 1). These intermediates can be isolated and present a unique opportunity to manipulate the reactive species of nanocrystal formation directly, as well as shape the energy landscape that determines that reaction pathway.

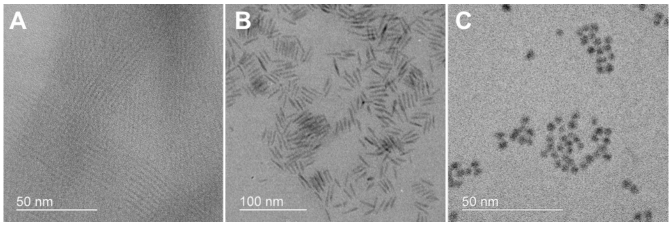


Figure 1. TEM micrographs of (A) polymeric CdSe intermediate and its reaction products after pyrolysis at (B) high and (C) low concentration of the intermediate.

References

[1] L. Carbone, C. Nobile, M. de Giorgi, F. Della Sala, et al., Nano Lett. 7, 2942 (2007).
[2] A. Riedinger, F. D. Ott, A. Mule, S. Mazzotti, et al., Nat. Mater. 16, 743 (2017).
[3] N. Kirkwood, K. Boldt, Nanoscale 10, 18238 (2018).
[4] D. Wurmbrand, J. W. A. Fischer, R. Rosenberg, K. Boldt, Chem. Comm. 54, 7358 (2018).

Terahertz Spin Dynamics in Metallic Thin Films

Stefano Bonetti

Department of Physics, Stockholm University, Stockholm, Sweden
Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, Italy

e-mail: stefano.bonetti@fysik.su.se

The interaction between magnetism and light is receiving considerable interest in recent years, after the ground-breaking experiments that showed that ultrashort (∼100 fs) infrared light pulses can be used to demagnetize or even switch the magnetization of thin nanometer film ferromagnets.[1] However, to date no clear and commonly accepted understanding of the fundamental physical processes governing the ultrafast magnetization has been reached, partly because accurate modelling of the infrared fs laser-induced highly non-equilibrium state remains a key obstacle. It has recently been shown that not only infrared, but also terahertz light pulses can be used to observe ultrafast demagnetization in thin film ferromagnets.[2] In addition, terahertz radiation can be used as a probe of the fundamentals of spin transport.[3] In this talk, I will go through some basic and more advanced concepts in the exciting emerging field of terahertz (THz) magnetism, where electromagnetic radiation in the 0.1-10 THz range, the so-called THz gap, is used to probe or to control spin dynamics in thin ferromagnetic metallic films at these time scales. I will also show some recent implementation of metamaterials aimed at selectively enhancing the terahertz magnetic field in the near-fielz,[4] with the goal of realizing the first table-top precessional or "ballistic" magnetization switching, the fastest possible spin reversal mechanism.

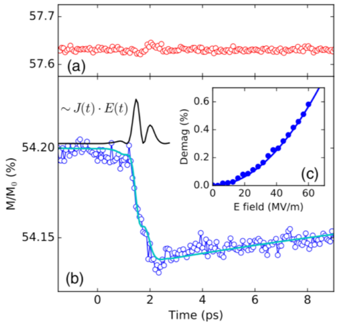


Figure 1. Time-resolved magneto-optical Kerr effect (MOKE) following an intense THz pulse measured in (top) crystalline iron and (bottom) amorphous CoFeB thin films with Only the amorphous film shows measurable demagnetization, which scales as the square of the impinging electric field.[2]

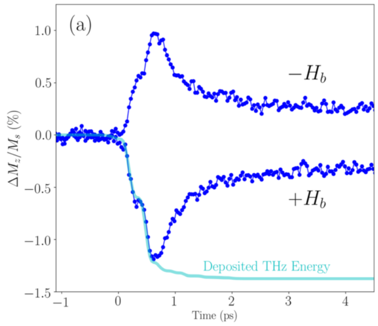


Figure 2. Same as in Fig. 1 but in a CoPt thin film with perpendicular magnetic anisotropy. The demagnetization is ten times enhanced than in the case discussed in Fig. 1. The plot also shows the magnetic nature of the effect, and the two-step demagnetization step which mirrors the energy deposited by the THz field.[4]

References

[1] A. Kirilyuk, A. V. Kimel, and T. Rasing, Rev. Mod. Phys. 82, 2731 (2010)
[2] S. Bonetti et al., Phys. Rev. Lett. 117, 087205 (2016)
[3] Z. Jin et al, Nat. Phys. 11, 761 (2015)
[4] D. Polley et al, J. Phys. D: Cond. Matt. 51, 084001 (2018)

How to Combine Nanoparticles to Useful Nanocomposites: Aggregation and Electrophoresis

M. Bredol*, L. Sarpong, J. Goossen

FH Münster University of Applied Sciences, Steinfurt, Germany

*e-mail: bredol@fh-muenster.de

Nanomaterials are never applied in their pristine form: they are either densified to a compact material or they are incorporated into a matrix; such a matrix in most cases will be a solid, or sometimes a liquid. This process of dispersion, solidification or binding is critical for the functionality of nanomaterials and nanocomposites: the large surface of the individual nanoparticle may (among other factors) be responsible for the properties of the final material or just be useful for embedding and binding. In any case precise and reproducible control of the interface chemistry between nanoparticle and matrix will be mandatory in order to fabricate useful nanocomposites. When it comes to the preparation of thick layers of such nanocomposites, one very versatile method is electrophoretic deposition: it can work with aqueous and non-aqueous dispersions, can be fast, can lead to thick or thin layers, can work with mixtures of nanoparticles and takes place at ambient conditions. The most important prerequisite is a well-tuned particle charge; electrostatic interactions therefore will be important and need to be controlled precisely. In this contribution, two variants of nanocomposite formation in this context will be discussed: homogeneous heteroaggregation vs. electrophoretically driven aggregation and deposition. As an example, fig.1 (left) shows a dense, but terraced layer deposited by electrophoretic deposition of ceramic nanoparticles in contrast with a looser aggregate of ZnS quantum dots on a carbon nanotube (fig.1, right) – both results are controlled by carefully tuned electrostatic interactions.

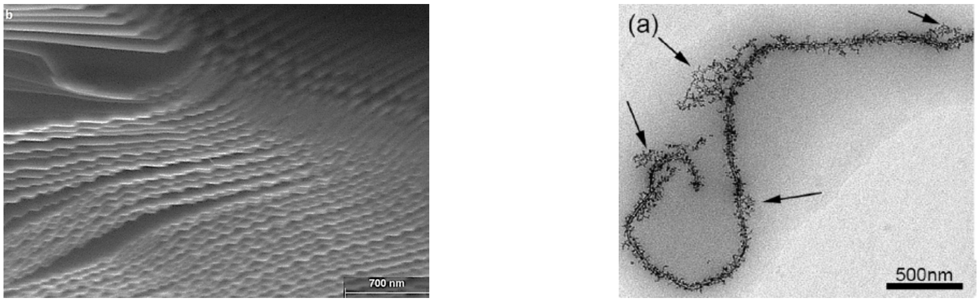


Figure 1. Left: SEM micrograph of a cross section through an electrophoretic deposit of yttrium aluminium garnet nanoparticles (scale bar 700 nm),[1] Right: TEM micrograph of ZnS nanoparticles on a multiwalled carbon nanotube.[2]

References

[1] "Electrophoretic deposition of alumina, yttria, yttrium aluminium garnet and lutetium aluminium garnet", M. Bredol, J. Micior, S. Klemme, J. Mater. Scie 49, 6975 (2014).

[2] "Heteroaggregation of multiwalled carbon nanotubes and zinc sulfide nanoparticles", L.K. Sarpong, M. Bredol, M. Schönhoff, Carbon 125, 480 (2017)

Microfabricated Gold Electrodes Modified By Advanced Nanomaterials for Highly Sensitive Electrochemical Sensing of Glucose

Vuslat Buk*, Martyn E. Pemble

University College Cork, School of Chemistry, Cork, Ireland
Tyndall National Institute, Lee Maltings Complex, Dyke Parade, Cork, Ireland

*e-mail: vuslat.buk@tyndall.ie

We report the lithographic fabrication of several band and disk array electrodes with different size and dimensions to be used as biosensor components for three different approaches to detect glucose. In the first study, we used carbon quantum dots and gold nanoparticles nano-hybrid system for glucose oxidase immobilization onto planar and micro disk array electrode for improved sensitivities.[1,2] The second approach selected was aimed at demonstrating the enzyme free detection of glucose in the presence of copper nanocrystals. Electrodes were prepared by electrodeposition of copper onto gold surface at over negative potentials in acidic environment to form a highly porous 3D foam structures (Fig. 1). The resulting sensors showed a very strong electrocatalytic activity towards glucose and exhibited outstanding sensitivities with wide linear ranges up to 20.55mM. The final approach for glucose detection is the bi-enzymatic system. In this study nanostructured gold and chitosan-carbon nanotubes layer were electrodeposited onto band array electrode, respectively (Fig. 2). Finally glucose oxidase and horseradish peroxidase were immobilized over the surface. The developed bi-enzymatic biosensor exhibited very high sensitivity and excellent analytical performance towards glucose. To summarize, we demonstrate the unique use of several emerging nanomaterials combined with microfabricated gold electrodes as miniaturized, highly sensitive glucose sensing platforms.

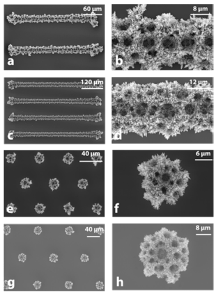


Figure 1. SEM images of copper foam

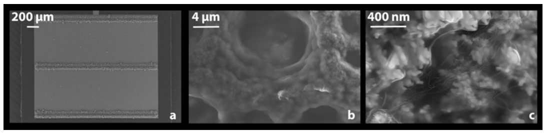


Figure 2. SEM images of gold foam/chitosan- carbon nanotube deposits

---

References

[1] "A highly sensitive glucose biosensor based on a micro disk array electrode design modified with carbon quantum dots and gold nanoparticles", V. Buk, M.E. Pemble, Electrochimica Acta 298, 97-105, 2019.

[2] "Fabrication and evaluation of a carbon quantum dot/gold nanoparticle nanohybrid material integrated onto planar micro gold electrodes for potential bioelectrochemical sensing applications", V. Buk, M.E. Pemble, K. Twomey Electrochimica Acta 293, 307-317, 2019.

Directed Assembly-Based Printing of Nanoelectronics and Sensors

Ahmed Busnaina

Distinguished University Professor, W. L. Smith Professor and Director
NSF Nanoscale Science and Engineering center for High-rate Nanomanufacturing (CHN)
Advanced Nanomanufacturing Cluster for Smart Sensors and Materials CSSM

e-mail: busnaina@coe.neu.edu

A new disruptive technology will be presented that will enable the fabrication of nanoelectronics at a cost of 10-100 times less than conventional fabrication while allowing device designers the use of any organic or inorganic semiconducting, conductive or insulating material on flexible or rigid substrates. This will also include leveraging nanomaterials such as two-dimensional (2D) materials, quantum dots, nanotubes, etc. Printed electronics can significantly lower electronics and sensor costs by 10-100 times. However, most currently printed systems are at 20 micron line width and larger and utilizing mostly organic semiconductors. The new technology is enabled by directed assembly-based nanoscale printing at ambient temperature and pressure that prints 1000 faster and 1000 smaller (down to 20nm) structures than ink-jet based printing. The technology enables a nanoscale printing platform, enabling heterogeneous integration of interconnected circuit layers (like CMOS) of printed electronics and sensors at ambient temperature and pressure. The directed assembly-based printing processes were specifically created to be scalable, sustainable and designed to enable precise and repeatable control of assembly of various nanoelements at high-rate. CHN has created processes to print circuits and structures using nanoparticles, conducting polymers, polymer blends, 2D materials and SWNTs into various structures including 3D architectures at multiple length scales. Printed devices include transistors, inverters, diodes, chemical and biosensors, and interconnects using a variety of nanomaterials including 2D materials. Some of the printed applications include Nano LEDs, Print QDs for display, wearable electronics, micro wearable biosensors for detecting lactate and glucose in Sweat, chemical sensors, etc. We unveiled the world's first Nanoscale fully-automated offset printing system (NanoOPS) prototype with built-in alignment and registration in 2014. This system is designed to print devices and products down to 20 nm minimum feature size or smaller.

HiPIMS Deposition of Ta-O-N Films for Water Splitting Application

UJiří Čapek[1*], Šárka Batková[1], Jiří Houška[1], Stanislav Haviar[1], Tomáš Duchoň[2], Miloš Krbal[3]

[1]Department of Physics and NTIS - European Centre of Excellence, University of West Bohemia, Plzeň, Czech Republic
[2]Department of Surface and Plasma Science, Charles University, Praha, Czech Republic
[3]CEMNAT - Center of Materials and Nanotechnologies, University of Pardubice, Pardubice, Czech Republic

[*]e-mail: jcapek@kfy.zcu.cz

Ta-O-N materials can provide appropriate properties (i.e., band gap width and alignment) for splitting of water into H_2 and O_2 under visible light irradiation (without any external voltage). This could bring a great possibility to convert the solar light into a useful chemical energy. However, it is still a big challenge to prepare electrodes from these materials exhibiting efficient water splitting performance.

In this work we first demonstrate that high-power impulse magnetron sputtering is a suitable technique for deposition of amorphous Ta-O-N films with a finely tunable oxygen to nitrogen (O/N) oncentration ratio and thus their properties. Post-annealing of the films in a vacuum furnace at 900℃ (5 min dwell time) leads to their crystallization without any changes in their elemental composition. XRD patterns of the films prepared at the optimum O/N concentration indicate highly crystalline TaON material with monoclinic lattice structure. This material provides optical band gap width of 2.45 eV (corresponding to visible light absorption up to 505 nm) at suitable alignment of the band gap with respect to the redox potentials. Moreover, when a proper seeding layer is provided, a highly textured film can be obtained. We present photoelectrochemical measurements of the films and report on films modified by nanoclusters, designed to suppress the recombination rate of the photo-generated electron-hole pairs.

Reactivity of Common ALD Precursors with OH and H_2O-Containing Metal Organic Framework Materials

K. Tan[1], S. Jensen[2], L. Feng[4], H. Wang[3], J. P. Klesko[1], R. Rahman[1], Je. Cure[1], K. Wei[1],
H. Zhou[4], J. Li[3], T. Thonhauser[2], Y. J. Chabal[1*]

[1]*Department of Materials Science & Engineering, University of Texas at Dallas, Richardson, TX, USA*
[2]*Department of Physics, Wake Forest University, Winston-Salem, NC, USA*
[3]*Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, NJ, USA*

[*]e-mail: chabal@utdallas.edu

The ability to incorporate metal atoms into nanoporous materials such as metal organic frameworks (MOFs) in a well-controlled fashion would provide new opportunities to prepare functionalized and modified materials for potential applications such as catalysis and gas separation. There are however new challenges that need to be overcome such as understanding the reaction mechanisms in order to develop structural and process optimization. MOFs possess three-dimensional structures, with a complex pore architecture, involving to a number of processes (gas transport, adsorption and reaction) that are much more complex than on flat surfaces.

To address these issues, we have combined in-situ infrared spectroscopy, X-ray-photoelectron spectroscopy and *ab initio* calculations to study the reaction of a number of common ALD precursors --trimethylaluminium (TMA), diethylzinc (DEZ), titanium tetrachloride ($TiCl_4$)-- with in several Zr-MOFs containing hydroxyl (OH) and water (H_2O) groups. Differentiating the reactivity with OH and H_2O groups is particularly interesting because it depends on both the chemical and structural (i.e. sterics) environments.

We find that the OH groups in the $Zr_6(\mu_3\text{-}OH)_4(\mu_3\text{-}O)_4(OH)_x(OH_2)_y$ cluster node do not all react at similar rates (i.e., the reaction pathway and energetics are highly dependent on their location, accessibility and chemical environment). For different OH-containing MOFs without H_2O groups, the activation temperatures for the TMA reaction with bridge OH of Zr_6 clusters decreases with the node connectivity (250℃, 150℃ and 24℃ for UiO-66-NH_2, Zr-abtc and MOF-808, respectively). Interestingly, the amine group in UiO-66-NH_2 is found to act as a catalytic site by anchoring TMA molecules and facilitating their reaction with nearby hydroxyl groups, which is not observed in un-functionalized UiO-66. This synergistic effect between -NH_2 and -OH is fully elucidated by first-principles calculations. In addition, we find that TMA easily reacts with water adsorbed on the external surfaces of wet MOFs crystals at room temperature, forming a thick Al_2O_3 blocking layer on the periphery of MOFs crystals. These findings provide a basis for the design and synthesis of new MOFs structures requiring ALD for new applications.

Innovative, Rapid Synthesis of NIR-Fluorescent Nanocrystals for Intravital Bioimaging Applications

S. Shashank Chetty[*], S. Praneetha, A. Vadivel Murugan

Advanced Functional Nanostructured Materials Laboratory, Centre for Nanoscience and Technology,
Madanjeet School of Green Energy Technologies, Pondicherry University (A Central University), Puducherry, India

[*]e-mail: shashankchetty@yahoo.com

Intravital fluorescence biomedical imaging (IVBI) has become imperative research methodology for tracking biological molecules and processes in living organism.[1] Unlike other imaging techniques, fluorescence imaging utilizes low excitation energy in the visible to near-infrared (NIR) spectrum for visualizing across the multi-spatial scale that includes cells, tissues and small animals with high detection sensitivity and selectivity.[2] Precisely, emission wavelengths from 650–900 nm, known as "biological-optical-window" are highly suitable for in vivo imaging applications owing to their reduced absorptions and scattering process within the living systems.[3] Herein, we demonstrate an innovative, efficient, hassle-free and scalable one-pot microwave–solvothermal synthesis of bright luminescent $CuInS_2$-ZnS nanocrystals (CIZS-NCs) within 5 min at 230°C, using 1-dodecanethiol as both ligand and solvent without requiring co-solvent and inert-gas atmosphere. The approach tailored optical band-gaps of "sustainable CIZS-NCs" with enhanced fluorescence and long-lived emission lifetime (~0.6 µs) with significant quantum yield up to 88%, without shell-coating strategies. The ensemble of results provide an facile and straightforward labeling platform for rapid visualization using CIZS-NCs explicitly in cellular cytoplasm within 20 min and zebrafish embryos in 3 h for myriad of intravital fluorescence bioimaging applications.

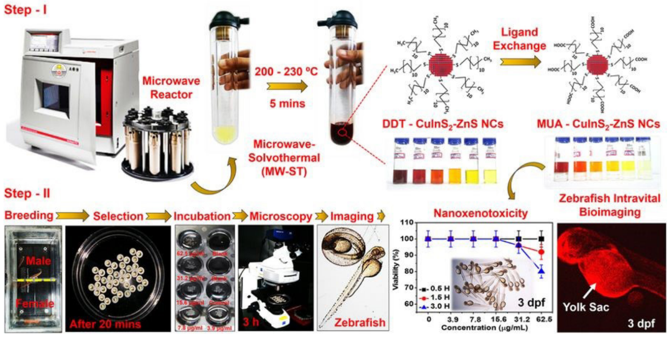


Figure 1. Schematic representation of MW-ST synthetic methodology, nano-xenotoxicity and intravital fluorescence bioimaging applications as illustrated in Steps I and II, respectively.

References

[1] "Substrate-Free Self-Assembled SiOx-Core Nanodots from Alkyalkoxysilane as a Multicolor Photoluminescence Source for Intravital Imaging", Lin, P. et al, Sci. Rep. 3, 1703–1708 (2013).
[2] "High-Quality CuInS2/ZnS Quantum Dots for In vitro and In vivo Bioimaging", Deng, D. et al., Chem. Mater. 24, 3029–3037 (2012).
[3] "Highly Luminescent CuInS2/ZnS Core/Shell Nanocrystals: Cadmium-Free Quantum Dots for In Vivo Imaging.", Li, L. et al., Chem. Mater. 21, 2422–2429 (2009).

The Role of Self-Assembly in Switching Phenomena in Molecular Tunneling Junctions

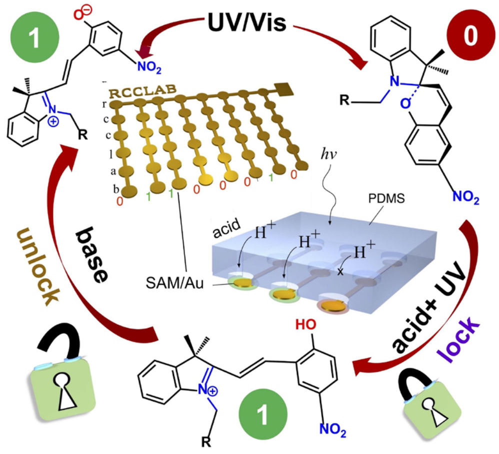
Ryan C. Chiechi[1,2*], Sumit Kumar[1,2], Wojciech Danowski[1], Saurabh Soni[1,2],
Isaac F. Leach[2], Shirin Faraji[2], Ben L. Feringa[1,2], Petra Rudolf[2]

[1]Stratingh Institute for Chemistry, University of Groningen, Groningen, The Netherlands
[2]Zernike Institute for Advanced Materials, Groningen, The Netherlands

[*]e-mail: r.c.chiechi@rug.nl

Unlike bulk transport, in Molecular Electronics, molecules span both electrodes and the dominant mechanism of transport is non-resonant tunneling. As a result, very small structural changes to the molecules can alter conductivity by orders of magnitude and it can be bias-dependant, allowing the tuning of rectification ratios. However, coupling these changes to external inputs and translating the phenomenology into stable device platforms is complicated by the fragility, nanoscale dimensions and thermodynamics of molecular switches. Soft lithography and other unconventional fabrication techniques are particularly well suited to address these problems.

In this talk, I will discuss our recent work on addressing the thermodynamic limits of surface-bound switches.[1] In the figure to the right, we combine light and chemical inputs to lock and unlock spiropyran-based switches in mixed monolayers, circumventing side-reactions and the thermodynamic instability of the merocyanine form of the switch, enabling the writing, erasing and rewriting of binary data on surface-bound switches. I will also discuss robustness of the switching process and the influence of the supramolecular structure of the molecular monolayer on the mechanism of the photoisomerization of spriopyran switches.



References

[1] "Chemical Locking in Molecular Tunneling Junctions Enables Nonvolatile Memory With Large On-Off Ratios" Kumar, Sumit; Merelli, Michele; Danowski, Wojciech; Rudolf, Petra; Feringa, Ben L; Chiechi, Ryan C. Adv. Mater., 1, 1807831 (2019).

Diamond Electronics with 2-D Transport Channel via Delta Doping

Aris Christou

Materials Science and Engineering Department, University of Maryland, College Park, MD, USA

e-mail: christou@umd.edu

Diamond transistors with surface 2D conduction channels are projected to be radiation hard with respect to neutrons. However, ionizing radiation hardness may be a problem due to the disruption of the 2D hole concentration. In this paper, the processing of three terminal devices with 2D surface conducting channels is presented as well as analysis of device transfer characteristics. The fabrication technology, surface preparation and testing, radiation induced defects and device characteristics of microwave power field effect transistors (FET) are reviewed. Devices built on 1) high quality diamond surfaces exploiting the 2 dimensional surface conductivity, and 2) the surface two dimensional "hydrogen terminated" conduction layer in diamond single crystals grown by CVD are analyzed. The emphasis is on the fundamental physics of radiation effects on two dimensional conduction layers in diamond materials. This is an unexplored area which could lead to new breakthroughs in the performance of high power microwave transistors in extreme environments such as high temperature and high radiation fields.

Single crystal diamond is projected to enable advanced semiconductor switches capable of operating at extremely high power and frequency.[1] Diamond exhibits ideal properties for such applications, including a 5.5 eV bandgap, >10 MV/cm breakdown strength, theoretical electron and hole mobilities exceeding 3800 cm^2/V^*sec, and an outstanding 22 W/cm·K thermal conductivity. However, achieving useful carrier densities in diamond is problematic, as typical dopants (boron, phosphorous) have activation energies exceeding 0.37 eV, leading to low activation efficiencies.[2] This limitation can be overcome by exploiting hole conductivity along 2D conducting channels to fabricate operational field effect transistors (FETs).

2D conducting channels have been created through hydrogen termination of diamond surfaces, or through delta-doping of diamond epitaxial layers. Hydrogen termination is achieved by exposing extremely clean diamond surfaces to a hydrogen plasma, creating a surface C-H dipole layer that significantly reduces the carrier ionization energy. Adsorbed species, such as atmospheric H_2O or NO_2, or high electron affinity oxides contact this dipole layer, and together generate a near-surface two-dimensional hole gas (2DHG) with carrier densities 1012-1014 holes/cm^2.[3] Incorporation of heavily-doped boron delta layers into intrinsic diamond epitaxial layers was also used to create 2D conducting channels with high hole density and mobility.

In this work, we will report on the fabrication, characterization, and optimization of diamond FETs with hydrogen-terminated and boron delta-doped 2D hole channels. Single crystal diamond substrates grown by high pressure high temperature (HPHT) synthesis have been prepared to produce ultra-smooth diamond surfaces, prior to hydrogen termination or chemical vapor deposition (CVD) epitaxy of boron delta layers. Fabrication and characterization methods will be discussed for devices with each 2D conducting channel type. In the case of hydrogen-terminated FETs, multiple processing routes for generation of the 2DHG will be compared, including simple atmospheric adsorbates, intentional NO_2 adsorption, and passivation with high electron affinity dielectrics such as Al_2O_3 and V_2O_5 deposited by atomic layer deposition (ALD). CVD growth techniques for creating boron delta layers used in the delta-doped FETs will also be reported.

Acknowledgements

Sponsored by the Department of Defense, Defense Threat Reduction Agency.

References

[1] M. Kasu, et al., Diam. Relat. Mater. 16, 1010 (2007).
[2] D.A.J. Moran, et al., IEEE Elect. Dev. Lett. 32(5), 599 (2011).
[3] M. Kubovic, et al., Diam. Relat. Mater. 18(5-8), 796 (2009).

Generalised Refraction with Microstructured Sheets

Johannes Courtial

University of Glasgow, UK
Physics and Astronomy, Kelvin Building, Glasgow, UK

e-mail: Johannes.Courtial@glasgow.ac.uk

Microstructured sheets can be used to change the direction of transmitted light rays in a controlled manner. An example of such a microstructured sheet is a telescope window (TW), an array of small telescopes, which act as the pixels of the sheet. The relationship between the incident and outgoing light-ray direction is a kind of law of refraction, significantly generalised from Snell's law. In this sense, such sheets perform pixellated generalised refraction.

My group has been working on different fronts to advance such sheets, in particular TWs, and I will summarise these efforts. Firstly, we have been constructing TWs, theoretically and experimentally, establishing their properties and imperfections. Secondly, we have been establishing the imaging properties of TWs and developing applications, which range from novel spectacles to invisibility cloaks, but to work well enough all of these still rely on the imperfections of TWs being removed. Thirdly, as a way of overcoming these imperfections we have started to consider the possibility of realising the same generalised refraction in the absence of pixels.

Investigations of Radiation Induced Effects in Nanostructured Ceramic Thin Films

D. Craciun[1], G. Dorcioman[1], M. D. Dracea[2], D. Pantelica[2], B. S. Vasile[3], C. Martin[4], M. Mogildea[5], V. Craciun[1, 6 *]

[1]National Institute for Lasers, Plasma and Radiation Physics, Măgurele, Romania
[2]Horia Hulubei Natl. Inst. for Physics and Nuclear Engineering, Măgurele, Romania
[3]Polytechnic University Bucharest, Bucharest, Romania
[4]Ramapo College, NJ, USA
[5]Institute for Space Sciences, Magurele, Romania
[6]Extreme Light Infrastructure-Nuclear Physics, Magurele, Romania

*e-mail: valentin.craciun@inflpr.ro

Thin films used for applications in advanced nuclear reactors, fusion installations or space exploration are exposed to a high level of radiation. It has been reported that nanostructured thin films, which possess very small crystal grains of the order of 10 nm exhibited better radiation resistance than large grain or single crystal films. The high density of grain boundaries present in these films could act as defects sinks, which will capture interstitials and vacancies formed during irradiation. Therefore, the structure and properties of these thin films will be less affected by exposure to radiation. Dislocations formed in such small crystalline grains will immediately diffuse towards grain boundaries and disappear. The increase of mechanical hardness after irradiation usually observed for single crystals or large grain films, which is caused by the generation of arrays of dislocations that become entangled and therefore immobile, is not observed in these nanostructured films.

To investigate in detail the radiation effects on properties, chemical composition and structure we used the Pulsed Laser Deposition (PLD) technique to grow ZrC and ZrN nanocrystalline thin films. By simply changing the deposition parameters, films possessing different chemical compositions and/or structures could be readily obtained. The effects of 800 keV Ar and 1.0 MeV Au ions on the properties of nanocrystalline ZrC and ZrN thin films were investigated using high resolution transmission electron microscopy, nanoindentation, optical reflectometry, X-ray specular and diffusive reflectivity, and X-ray diffraction investigations. The results confirmed that nanocrystalline films could withstand high irradiation fluences without degrading their crystalline structure, while the Si substrate was completely amorphized. Grazing incidence XRD investigations found that there is grain growth in ZrC films as an effect of ion irradiation, while a decrease of the grain size was observed under similar irradiation conditions for ZrN. A decrease of the carriers scattering rates was observed from IR optical reflectivity measurements for both films. The results are compared to those reported on polycrystalline or single crystal materials.

Acknowledgements

The work presented was funded by Nucleu –INFLPR program, and STAR 161/2017 and ELI 17/2017 projects.

Investigations of fs-Laser Irradiation Induced Defects in Oxide Thin Films

D. Craciun[1], A. M. Rostas[2], S. Irimiciuc[1], B. Hodoroaba[3], I. Anghel[1], G. Dorcioman[1], P. Garoi[1], V. Craciun[1*]

[1]National Institute for Lasers, Plasma and Radiation Physics, Măgurele, Romania
[2]National Institute for Materials Physics, Magurele, Romania
[3]Physics Faculty, University of Bucharest, Magurele, Romania
[4]Extreme Light Infrastructure-Nuclear Physics, Magurele, Romania

*e-mail: valentin.craciun@inflpr.ro

The physics of ultra-high power fs-laser interaction with matter has been a very active research topic lately, recognized by the award of the Nobel Prize for Physics last year to the pioneers of ultra-short laser pulse physics. There are now several PW-level laser installations already operational in Europe and world-wide, including two in Romania. To steer or focus high power fs-laser beams one needs high quality mirrors, which are fabricated using either dielectric layers/multilayers or metallic layers.

We investigated the use of the pulsed laser deposition technique (PLD) to obtain thin oxide films and multilayer structures that could be used for fs-laser mirrors. HfO_2 and ZrO_2 dielectric layers and multilayers were deposited on quartz, Si, and Ag covered Si substrates under oxygen atmosphere using a PLD installation with an ArF excimer laser. The 193 nm radiation is better absorbed in large band-gap oxide targets than the 248 nm wavelength of KrF lasers. After structural, compositional, electrical and optical characterization using X-ray reflectivity, grazing incidence X-ray diffraction, X-ray phototelectron spectroscopy and scanning electron microscopy, the deposited films were irradiated by fs-laser pulses to find the single pulse and multiple pulses laser damage threshold (LDT) values. The LDT values were obtained with the aid of two laser installations, which emits 400 fs pulses at kHz repetition rates and 25 fs pulses at a repetition rate of 100 Hz. Images of irradiated spots were investigated using optical and scanning electronic microscopy. The LDT values of around 0.8-1.0 J/cm^2 measured for the 25 fs laser pulses are comparable to those reported in the literature. The electron spin resonance investigations of irradiated films turned out to be the most sensitive technique to oxygen deposition conditions and defects induced by fs laser irradiation at fluences below the LDT values.

Acknowledgements

The work presented was funded by Nucleu –INFLPR program, and STAR 161/2017 and ELI 17/2017 projects.

Bulding 2D Graphene and N-Doped Graphene Nanowalls with Plasma

Uroš Cvelbar[1*], Gregor Filipič[1], Janez Zavašnik[1], Neelakandan Marath Santhosh[1,2],
Oleg Baranov[1,3]

[1]*Jozef Stefan Institute, Ljubljana, Slovenia, EU*
[2]*Jozef Stefan International Postgraduate School, Ljubljana, Slovenia, EU*
[3]*National Aerospace University, Kharkov, Ukraine*

[*]e-mail: uros.cvelbar@ijs.si

Plasmas find applications in various fields of nanomaterials science including the building of 2D carbon nanostructures like graphene nanowalls (GNW), which is an emerging field of material synthesis with some challenges related to its processing. Synthesis of GNW in a controlled manner with plasma-enhanced techniques opened future pathways for the large-scale, rapid functionalization of graphene for advanced applications. Plasma-supported methods enhance the possibility of processing (synthesis and functionalization) during the surface interactions between substrate and GNW offer the possibility for surface post-treatment. Among the important plasma-assisted methods for GNW synthesis, the most frequently used method is plasma-enhanced chemical vapour deposition (microwave assisted, inductively coupled, capacitively coupled PECVD), which can enable the grow GNW on the substrate even in the absence of a metal catalyst. The overall plasma processing of GNW is controlled by using specific gases and discharge parameters. Functionalization or doping of GNWs is correspondingly an important aspect in the plasma synthesis especially dealing with N-graphene.

This talk addresses the most important challenges associated with plasma-assisted mechanisms of GNWs dealing with the growth and doping of GNWs to create the optimal N-graphene. In these systems, plasma parameters including the densities of ions and radicals are extremely important, although they are regulated by the discharge parameters including power, gas mixture ratio, gas flow, and pressure. However, the main challenge is connected to understanding the role of plasma species in growth and their efficient control for improving the quality and selectively modifying properties of the synthesised GNW. Another challenge is material doping and understanding the mechanism of plasma doping form optimisation of specific bonds created. Nitrogen functionalization and doping are one of the potential directions on how to alter the electronic properties, whereas the oxygen plasma treatment, for example, helps to enhance surface morphological properties and widening band gaps, etc. In this perspective, the talk will highlight the recent progress in the field of building GNW and N-GNW including the building-up processes and future challenges that we have to address in GNW and N-GNW large-scale synthesis.

Ackowledgements

Supported by the European Union's Horizon 2020 research and innovation programme FET-Open under grant agreement No 766894 project PEGASUS. 332, 55 (2015)

Nanoporous Surfaces by Templateless Electropolymerization

Thierry Darmanin[1*], Sonia Amigoni[1], Frédéric Guittard[1,2]

[1]Université Côte d'azur, NICE Lab, IMREDD, Nice, France
[2]University California Riverside, Department of Bioengineering, Riverside, CA, USA

*e-mail: thierry.darmanin@unice.fr

Creating well-controlled surface nanostructures such as vertically aligned nanotubes is fundamental to well understand the relationships between surface structures and surface properties as well as for potential applications for example in photonic crystals, sensors, and surface adhesion. However, their preparation often required long and difficult processes such as the use of hard templates, AAO membranes for example, and many membranes are necessary to control nanotube parameters. The templateless electropolymerization is an excellent alternative to obtain easily and quicker controllable porous nanostructures. Gas bubbles produced directly in-situ during the process act as soft templates for the growth of the polymer. The electropolymerization of pyrrole directly in H_2O was intensively studied. In this process, H_2O can release O_2 and/or H_2 bubbles, which are responsible of the porosity of the nanostructures. A surfactant is necessary to stabilize the gas bubbles during the polymer growth. Very recently, we also explored the possibility to use organic solvent such as dichloromethane because most of the monomers are not soluble in H_2O.[1,2] Trace water naturally presents in solution are sufficient to produce O_2 and/or H_2 bubbles and as a consequence porous structures. By a judicious of the monomer, it is possible to obtain porous structures without surfactant. Exceptional results such as vertically aligned nanotubes were obtained with very rigid monomers such as 3,4-phenylenedioxythiophene, 3,4-naphthlenedioxythiophene and thienothiophene derivatives. Highly rigid substituents such as aromatic groups often gave better results. These substituents are also very interesting for fluorescence properties.

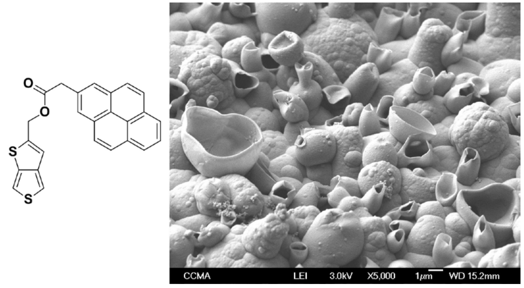


Figure 1. Coral-like structures obtained with a templateless electropolymerization approach.

References

[1] "A one-step electrodeposition of homogeneous and vertically aligned nanotubes with parahydrophobic properties (high water adhesion)", T. Darmanin, F. Guittard, J. Mater. Chem. A 4, 3197-3203 (2016).

[2] "A template-free approach to nanotube-decorated polymer surfaces using 3,4-phenylenedioxythiophene (PhEDOT) monomers", C. R. Szczepanski, I. M'Jid, T. Darmanin, G. Godeau, F. Guittard, J. Mater. Chem. A 4, 17308-17323 (2016).

Nanocrystal Engineering of Electrode Materials for Sustainable Solar Energy Harvesting and Storage Applications

George P. Demopoulos

Materials Engineering, McGill University, Montreal, QC, Canada

e-mail: george.demopoulos@mcgill.ca

We plan to provide an overview of our research in the area of sustainable energy materials spanning from nanostructured photo-electrodes for next generation photovoltaic applications to advanced Li-ion battery applications. Our recent solar energy material research has focused on new thin film structures featuring Cu_2ZnSnS_4 (kesterite) as light absorber.[1] The bulk of the presentation though will discuss our Li-ion battery work. This is driven by the strong demand for Li-ion batteries beyond the portable electronics sector into large format applications, namely EV batteries and stationary storage systems. With such demand it is not only necessary to design and develop new electrode materials but also do this in a sustainable manner from industrial production, scalability, economic, and environmental standpoints. In the meantime, the performance of electrode materials depends on the nanocrystal properties and preparation techniques. In this context our research puts equal emphasis on electrochemical materials performance as well as on electrode materials processing & engineering, searching to elucidate and control/optimize the intricate correlation between them. Herein, we report on the hydrothermal synthesis (@200℃) of defect-free Pmn21 lithium iron orthosilicate (Li_2FeSiO_4) mesocrystals,[2] their doping, mechanochemical activation, and their non-C coating leading to improve cathode performance. We have discovered high-energy milling to lead to crystal changes analogous to thermal annealing[3] activating obstructed diffusion channels for enhanced intercalation activity. In the meantime a novel self-assembly co-deposition method[4] will be described, involving in situ coating of reduced graphene oxide (redGO) onto 2D nanosheet-lithium titanate hydrates that upon conversion to 2D nano $Li_4Ti_5O_{12}$/graphene composites via reducing annealing can be built into high power Li-ion battery electrodes.

Acknowledgements

This work is supported by NSERC Canada, Hydro-Québec, and McGill's Sustainability Systems Initiative.

References

[1] Z. Wang et al., Lithium-Doped Cu_2ZnSnS_4 Superstrate Solar Cells with 5 % Efficiency – An Alternative to Thin film Kesterite Photovoltaics, Nano Energy, 53 (2018), 130-134.

[2] Yan Zeng et al., Hydrothermal Crystallization of Pmn21 Li_2FeSiO_4 Hollow Mesocrystals for Li-Ion Cathode Application, Chem. Eng. J., 359 (2019), 1592-1602.

[3] Majid Rasool et al., Mechanochemically-tuned structural annealing: a new pathway to enhancing Li-ion intercalation activity in nanosized βII Li_2FeSiO_4, J Mater. Chem. A (submitted).

[4] Marianna Uceda et al., Highly Conductive NMP-free Carbon-Coated Nano-Lithium Titanate/Carbon Composite Electrodes via SBR-Assisted Electrophoretic Deposition, Electrochimica Acta, 299 (2019), 107-115.

Magnetic, Chemical and Electrical Steering of Light at the Nanoscale

Alexandre Dmitriev

Department of Physics, University of Gothenburg, Gothenburg, Sweden

e-mail: alexd@physics.gu.se

A major challenge facing nanophotonics is the poor dynamic tunability. A functional adaptive nanophotonic element would feature the real-time large tunability of transmission and/or reflection of light's intensity and/or polarization, or the light's propagation direction over a broad range of wavelengths, and would be robust and easy to integrate. Several approaches have been explored so far including mechanical deformation,[1] thermal[2] or refractive index[3] effects, and all-optical switching.[4] Building on our previous advances in nanofabrication[5] and the combination of the plasmonic and ferromagnetic materials (magnetoplasmonics),[6] we devise an ultra-thin chiroptical surface, built on 2D nanoantennas, where the chiral light transmission is controlled by the externally applied magnetic field with tunability exceeding 100%. Using our previous advances in combining plasmon and molecular resonances,[7] we use a practical combination of the large array of magnetoplasmonic antennas and the thin layers of molecular photoswitches to explore the plasmon-molecular strong coupling and the associated polaritonic chemistry of phototransformations. We further use strongly-enhanced magneto-optics for sensing the sub-monolayer amounts of single-molecule-magnets with light.[8] Finally, in our latest work we visualize with atomic resolution the electrically-controlled reversible roomtemperature melting of the atomically thin outer layers of the optical antennas.[9]

References

[1] J. Y. Ou et al., Nature Nanotechnol. 8, 252 (2013).
[2] J. Y. Ou et al., Nano Lett. 11, 2142 (2011).
[3] Q. Wang et al., Nature Photon. 10, 60 (2015).
[4] M. Papaioannou et al., Light: Science & Applications 5, e16070; doi:10.1038/lsa.2016.70 (2016).
[5] H. Fredriksson et al., Adv. Mater. 19, 4296 (2007); K. Lodewijks et al., Sci. Rep. 6:28490, DOI: 10.1038/srep28490 (2016).
[6] I. Zubritskaya et al., Nano Lett. 15, 3204 (2015) ; N. Maccaferri et al., Ultrasensitive and label-free molecular-level detection enabled by light phase control in magnetoplasmonic nanoantennas, Nat. Commun. 6: 6150 (2015); K. Lodewijks et al., Nano Lett. 14, 7207 (2014); Z. Pirzadeh et al., ACS Photonics 1, 158 (2014) ; V. Bonanni et al., Nano Lett. 11, 5333 (2011).
[7] R. Toftegaard et al., Angew. Chem. Int. Ed. 47, 6025 (2008).
[8] F. Pineider et al., Mater. Horiz., 10.1039/C8MH01548A (2019).
[9] L. de Knoop et al., Phys. Rev. Mater., 2, 085006 (2018).

Modeling of Gas/Surface Interactions for Functional Polymers

Thomas Duguet[1*], Ghadi Dakroub[1,2], Stéphanie Roualdès[2], Vincent Rouessac[2], Corinne Lacaze-Dufaure[1]

[1]*CIRIMAT – CNRS, INPT, UPS, Toulouse, France*
[2]*IEM – CNRS, ENSCM, Université de Montpellier, Montpellier, France*

[*]e-mail: thomas.duguet@ensiacet.fr

Functional polymers are used in all industrial sectors for their low density, easy formability, low chemical reactivity, and compatibility with other materials to form composites or organic/inorganic hybrids. Due to the great variety of materials and their structural disorder, there are very few studies about their surface, although it seems strategic in many applications. In the present work, we show a methodology we developed in order to tackle this challenge; using both experiments and theoretical calculations. Two different examples will be detailed to illustrate our work.

The first example concerns the surface of polyepoxies used in the aerospace industry in order to lighten assemblies. Being for the electromagnetic shielding, for the limitation of permeability of liquid hydrogen tanks, or for the metallization of waveguides, a coating of metal is requested, with all the interfaces problems it implies. We will demonstrate how our methodology based on surface characterizations and modeling can contribute to a better design of these components. Noticeably, we are able to model and understand Cu chemisorption on the polyepoxy surface, and give hints on how to pretreat the surface to enhance the coating adherence.

In a second example, we will show how the same methodology applies to the understanding of the interaction of a BTEX gas (toluene) with organosilicon membranes synthesized by plasma-enhanced chemical vapour deposition (PECVD) in various conditions. Ultimately, we aim at tailoring the membranes composition and microstructure, in order to adjust its BTEX sorption properties.

Flexibility and Nanometer-Scale Rippling of Few-Layer Graphene

Traian Dumitrica[1*], Hao Xu[2], Chongze Hu[1]

[1]*Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN, USA*
[2]*Department of Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, MN, USA*

[*]e-mail: dtraian@umn.edu

We model bent few-layer graphene (FLG) as large-radii (up to 45 nm) infinitely-long multi-walled nanotubes in order to uncover its bending rigidity. Quantum calculations based on a density functional theory-based tight-binding model extended by Lennard-Jones interactions are carried out in an objective molecular framework, which accounts for the helical and angular symmetries exhibited by these large-diameter nanotube structures. Bending of ABA-stacked FLG simulated from different objective computational domains allow to evaluate the impact of interstitial defects and interlayer sliding onto FLG flexibility. We reveal a contrasting behavior: On one hand, inter-layer interstitials that bond to four carbon atoms located on two adjacent bent layers are stable and able to preserve the plate-like bending rigidity. Thus, introducing inter-layer interstitials can be an effective way to maintain the plate-like rigidity of FLG by preventing layer sliding. On the other hand, inter-layer sliding dramatically lowers the bending constant and makes FLG nearly as flexible as the on-atom thick graphene. We show that the layer-sliding gives rise to non-classical low-energy rippling modes characterized by wavelengths as small as a few nm and large local curvatures, which are distributed non-uniformly across the FLG thickness.

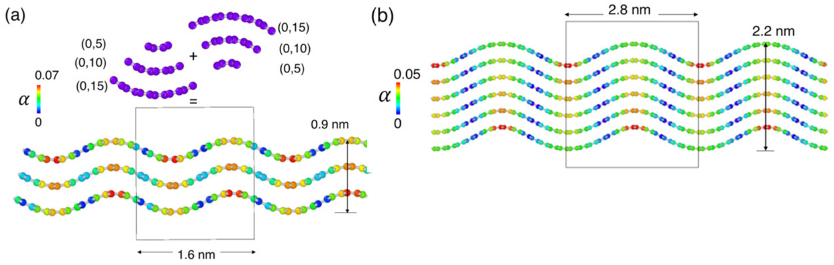


Figure 1. Nano-meter rippling of FLG. The unit cell is delineated by a rectangle. The color code reflects the distribution of the local curvature as measured by the modulus of the local pyramidalization angle (a) Ball-and-stick representation of 1.6 nm in wavelength ripple in 3-layer graphene. The schematics above the unit cell shows the construction of the periodic unit cell by joining together two objective domains of a (0,5) (0,10) (0, 15) nanotube. (b) A 2.8 nm in wavelength ripple in 6-layer graphene

Electrocatalysts for Polymer Electrolyte Membrane Fuel Cell

JeongHoon Lim, Junu Park, Chanwon Jung, Doosun Hong, EunAe Cho*

Department of Materials Science and Engineering, KAIST, Daejeon, South Korea

*e-mail: eacho@kaist.ac.kr

Polymer electrolyte membrane fuel cells (PEMFCs) are the most attractive power source for zero-emission vehicles owing to their environmental friendliness, high energy efficiency, and high power density. However, their high cost and low durability have prevented PEMFCs from being fully implemented and commercialized, mainly due to the use of platinum as a catalyst to overcome the sluggish kinetics of the oxygen reduction reaction (ORR) in the cathode. To reduce the use of Pt, extensive studies have been conducted and a large variety of ORR catalysts have been developed, such as Pt-M alloys as well as shape-controlled, dealloyed, and structurally ordered catalysts. Although those catalysts exhibited excellent intrinsic activity in aqueous environment, they have been hardly implemented in membrane-electrode assemblies (MEAs) for practical application.

In this talk, we report Pt-M intermetallic catalysts and M-doped PtNi octahedral nanoparticles on a carbon support (M-PtNi/C) that exhibit superior catalytic activity and stability in half-cell and MEA tests as an ORR catalyst for PEMFCs. To prevent agglomeration of Pt-M nanoparticles during heat treatment in which to transform the Pt-M alloy into Pt-M intermetallic structure, a facile synthetic process was conducted at low temperatures. Octahedral PtNi nanoparticles are known as one of the best ORR catalyst with its superior activity toward ORR. However, dissolution of Ni from the surface and collapse of the octahedral shape degrade the activity rapidly under the PEMFC operation conditions. To stabilize Ni and the octahedral shape, small amount of dopant was incorporated into the surface of octahedral PtNi. Electrochemical, chemical, and structural stability was thoroughly investigated through a harsh durability test. The effects of intermetallic structure and doping elements on the surface properties of Pt-based nanoparticles were examined by X-ray absorption fine structure (XAFS) analysis and density functional theory (DFT) calculation.

Advanced Theranostic Systems Based on Nanostructure Materials

Eleni K. Efthimiadou

Inorganic Chemistry Laboratory, Chemistry Department, National and Kapodistrian University of Athens, Panepistimiopolis, Zografou, Greece
National Center for Scientific Research "Demokritos", Aghia Paraskevi Attikis, Greece.

e-mail: efthim@chem.uoa.gr

Nanostructured delivery and diagnostic systems that induces specific targeting properties by exploiting the local physicochemical tumor characteristics will be evaluated is the present work.[1,2] It is well known that cancer cells have specific physicochemical characteristics,[3,4] 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 this 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.

References

[1] Tapeinos, C., et al., Colloids Surf B Biointerfaces, 148: p. 95-103 (2016)
[2] Torchilin, V., Eur J Pharm Biopharm, 71 (3): p. 431-44 (2009)
[3] Efthimiadou, E.K., et al., Int J Pharm, 461 (1-2): p. 54-63 (2014)
[4] Efthimiadou, E.K., et al., Mater Sci Eng C Mater Biol Appl, 37: p. 271-7 (2014)

Synthesis, Fundamental Studies and Applications of Colloidal TiO_2 and Complex Nanocrystals

M. Epifani

Consiglio Nazionale delle Ricerche, Istituto per la Microelettronica e Microsistemi (CNR-IMM), Lecce, Italy

e-mail: maurosalvatore.epifani@cnr.it

Titanium dioxide colloidal nanocrystals are usually prepared by high temperature routes that directly provide crystalline structures, in most cases in the anatase crystallographic phase. Hence, as for many other colloidal nanocrystals, the properties and evolution of related amorphous phases are scarcely known. In this work, a synthesis of anatase nanocrystals starting from amorphous precipitates will be illustrated. The possible advantages of processing amorphous structures will be described, on the basis of the underlying physico-chemical principles. Such principles were suggested by early crystallization studies of CdSe nanoparticles, so demonstrating the close entanglement of supposedly far apart fields of materials chemistry. Then the crystallization behaviour of the starting, sol-gel prepared amorphous titania nanoparticles, upon solvothermal treatment, will be discussed. The importance of surface composition in crystallization phenomena in such size regime will be evidenced. Hints about the shape control by oriented attachment will be provided. Finally, it will be shown that the involved sol-gel chemistry makes it possible the tailoring of the surface composition of titania nanocrystals and, hence, of the surface properties and reactivity. It will be shown that, while titanium dioxide is not really known in water purification or as a powerful gas-sensor, by suitable inorganic surface modification successful performances are possible in such scattered fields as chemical sensors, supercapacitors and water filtering. In particular, it will be shown that the surface modified TiO_2 nanocrystals are: powerful sensors of such reducing gases like acetone and ethanol; very efficient adsorbents of methylene blue and other contaminants; stable supercapacitors retaining both the advantages of pure V_2O_5 and pure TiO_2; selective blockers of visible light in electrochromic windows.

Optoelectronic Properties of Few-Layer Films of 2D Semiconductors

Vladimir Falko

National Graphene Institute, the University of Manchester, Manchester, UK

e-mail: vladimir.falko@manchester.ac.uk

The talk will overview the properties of electronic band structure and optical properties of few-layer films of transition metal dichalcogenides (TMDs: $MoSe_2$, MoS_2, WSe_2 and WS_2) and post-transition metal chancogenides (PTMCs: InSe and GaSe).

For PTMCs, we describe their properties based on ab initio DFT and related multi-orbital tight-binding model analysis of the electronic band structure and wave functions in the two-dimensional N-layer crystals, and compare those to the results of photoluminescence spectroscopy of this material[1-3] and their heterostructures.[4] In particular, we find that the band gap in InSe and GaSe strongly depends on the number of layers, with a strong (more than twice for InSe) reduction from the monolayer to crystals with N>6.

We also show that inter-subband transitions in the films of these materials as well as in the films of TMDs densely cover the spectral range from infra-red to THz optics. In particular, this is provided by the subband structure of the valence band that has the edge at the Γ-point in the TMD films and conduction band subbands in InSe and GaSe films which also have the edges at the Γ-point. The latter feature of few-layer transition metal dichalcogenide crystals also offers an opportunity to create material for high-efficiency light-emitting systems by combining them with PTMC crystals into type-II heterostructures with the band edges in the Brillouin zone centre.

References

[1] D. Bandurin, et al, Nature Nanotechnology 12, 223 (2017); S. Magorrian, et al, Phys. Rev. B 94, 245431 (2016)

[2] V Zolyomi, et al, Phys Rev B 89, 205416 (2014); ibid. B 87, 195403 (2013); Z. Ben Aziza, et al, Phys. Rev. B 98, 115405 (2018)

[3] G. Mudd, et al, Scientific Reports. 6, 39619 (2016)

[4] M. Hamer, et al, 2D Mater. 5, 041009 (2018)

[5] M. Danovich, et al, Phys. Rev. B 98, 035411 (2018); P. Schmidt, et al, Nature Nanotechnology (2018): doi.org/10.1038/s41565-018-0233-9

[6] S. Magorrian, et al, Phys. Rev. B 97, 165304 (2018)

Multiphoton Lithography: Principles, Materials and Applications

Maria Farsari

IESL-FORTH, Heraklion, Greece

e-mail: mfarsari@iesl.forth.gr

Multiphoton Lithography is a technique that allows the fabrication of three-dimensional structures with sub-100 nm resolution.[1] It is based on multi-photon absorption; when the beam of an ultra-fast laser is tightly focused into the volume of a transparent, photosensitive material, polymerization can be initiated by non-linear absorption within the focal volume. By moving the laser focus three-dimensionally through the material, 3D structures can be fabricated. The technique has been implemented with a variety of materials and several components have been fabricated such as mechanical metamaterials (Fig. 1a), and biomedical implants (Fig. 1b).

The unique capability of Multiphoton Lithography lies in that it allows the fabrication of computer-designed, fully functional 3D devices. In this talk, we summarize the principles of microfabrication, and present our recent research in materials processing and functionalization of 3D structures. Finally, we discuss the future applications and prospects for the technology.

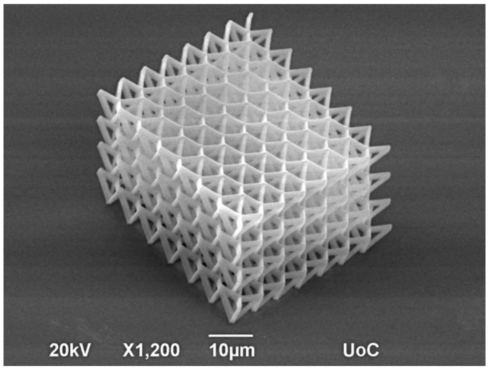


Figure 1. An auxetic material

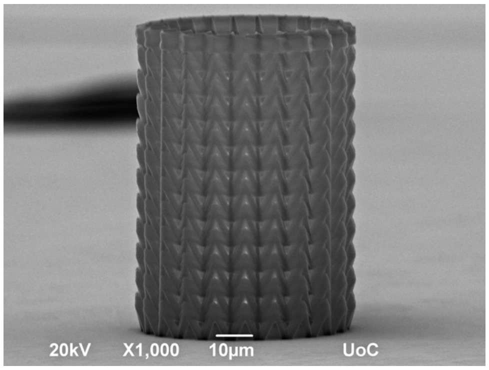


Figure 2. A stent

References

[1] Camposeo A, et al., Advanced Optical Materials, "Additive Manufacturing: Applications and Directions in Photonics and Optoelectronics", 7, 1800419 (2019).

Design and Synthesis of Electroactive Hierarchical Functional Materials

Charl FJ Faul

School of Chemistry, University of Bristol, Bristol, UK

e-mail: charl.faul@bristol.ac.uk

Use of synthetic organic approaches for the preparation of novel aniline-based materials allow us to exploit their tuneable conductive, redox and optical properties.[1] We are therefore designing new materials in key areas for further application:

Functional 1D Wires: We are exploiting this functional aniline-based platform to prepare novel redox-active cationic surfactants, and investigating their supramolecular organisation into self-assembled nanowires in solution,[2] and actively tuning their packing parameter to address assembly in a reversible fashion.[3] These activities fit well with related investigations into the formation and control of novel functional supramolecular polymers.[4]

Functional 3D Materials and Devices: Using 2-photon polymerisation-based direct laser writing (DLW), finely controlled 3D-printed conjugated structures can be prepared to form actively tuneable photonic crystals.[5] Using related principals, we also show initial results for the fabrication of macroscopic soft actuators,[6] and the preparation of fully 3D-printed soft energy storage devices.

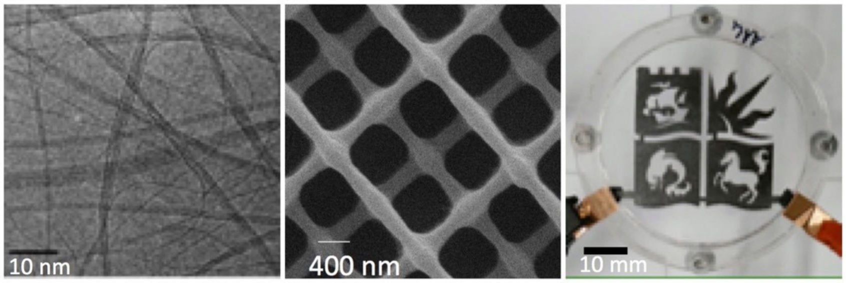


Figure 1. a) 3-nm self-assembled nanowires in solution; b) 3D-printed responsive photonic structure c).

References

[1] C. F. J. Faul, Acc. Chem. Res., 47, 3428 (2014)
[2] O. A. Bell et al., J. Am. Chem. Soc., 137, 14288 (2015)
[4] C. Jarret-Wilkins et al., Chem. Eur. J., 24, 15556 (2018)
[5] Y. Hu et al., Adv. Opt. Mater., 5, 1600458 (2017)
[6] D. T. Kuhnel, et al., Adv. Mater. Tech., 4, 1800232 (2019)

Fabrication and Applications of Nanocrystalline Diamond and Engineered Diamond Micro- and Nanocomponents

Hans Fecht

Ulm University, Institute of Functional Nanosystems, Germany

Nanocrystalline and ultrananocrystalline diamond combines the remarkable properties of conventional diamond, such as extreme hardness and wear resistance and a coefficient of friction of about 0.01. Here, we report on the correlation between grain size and relevant physical and chemical properties of phase pure NCD and UNCD layers synthesized by chemical vapour deposition on silicon single crystal wafers with diameters up to six inches. The UNCD films consist of ultra small (ca. 5 nm) equiaxed grains resulting in ultra smooth surfaces with surface roughness equivalent to the grain size. The mechanical properties show that due to the large number of grain boundaries with highly disordered atomic structure the Young's modulus is decreased from about 1010 to 500 -700 GPa and fracture strength is increased from 1 GPa to ca. 5 GPa. This makes the material very attractive for a number of applications.

As a step further, by a sophisticated combination of high-precision photolithographic masking techniques and controlled reactive ion etching processes (RIE) complex shaped microparts are designed and fabricated. A number of different examples and industrial applications will be discussed, such as lubrication-free microcomponents and hybrids for high-precision mechanical devices, sensors for harsh environments, MEMS components and ultra-sharp cutting tools for bio-applications.

Synthesis of Polystyrene-*b*-Poly(Solketal Methacrylate) Polystyrene-*b*-Poly(Glyceryl Methacrylate) Copolymers for Isoporous Membranes

Sarah Saleem[1], Sofia Rangou[1], Clarissa Abetz[1], Brigitte Lademann[1], Volkan Filiz[1*],
Volker Abetz[1,2]

[1]*Helmholtz-Zentrum Geesthacht, Institute of Polymer Research, Geesthacht, Germany*
[2]*University of Hamburg, Institute of Physical Chemistry, Hamburg, Germany*

Block copolymers are well known for the formation of many microphase separated morphologies depending on the architecture of the block copolymer(s) involved, molecular weight, composition and thermodynamic properties. Anionic living polymerization provides a way to the creation of well-defined block copolymers by the sequential addition of monomers. It is mostly used to synthesize block copolymers with controlled compositional and structural parameters such as molecular weight, narrow molecular weight distribution, copolymer composition, branching, and other architectural parameters.

In this work, we compare double hydrophobic polystyrene-b-poly(solketal methacrylate) (PS-b-PSMA) and amphiphilic polystyrene-b-poly(glyceryl methacrylate) (PS-b-PGMA) diblock copolymer membranes which are prepared by combining the block copolymer self-assembly in solution with a non-solvent induced phase separation (SNIPS).[1] Diblock copolymers (i.e., PS-b-PSMA) were synthesized by sequential living anionic polymerization, whereas PS-b-PGMA was obtained by acid hydrolysis of the acetonide groups of the PSMA blocks into dihydroxyl groups (PGMA), Fig.1.

Membrane structures and bulk morphologies were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM); respectively. The resulting PS-b-PGMA diblock copolymers produce an ordered hexagonal cylindrical pore structure during the SNIPS process, while membranes fabricated from the double hydrophobic (PS-b-PSMA) do not under similar experimental conditions. Membrane performance was evaluated by water flux and contact angle measurements.

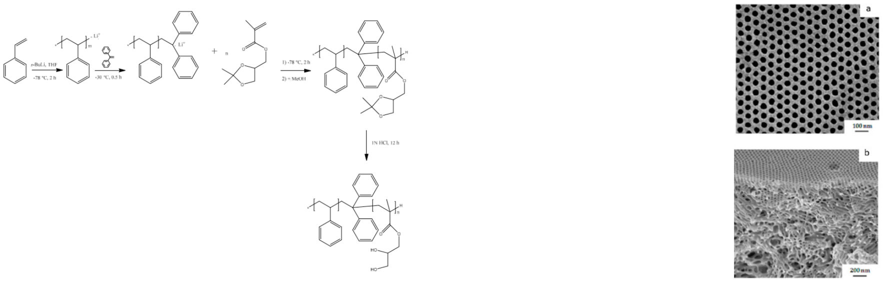


Figure 1. Route of synthesis for PS-b-PSMA and PS-b-PGMA by sequential anionic polymerization of styrene and isopropylidene glycerol methacrylate and subsequent hydrolysis. THF: tetrahydrofuran. SEM topography images of membranes prepared from 23 wt % PS81-PGMA19 in THF/DMF 50/50 wt % and the corresponding cross-section view.

References

[1] S. Saleem, S. Rangou, C. Abetz, B. Lademann, V. Filiz, V. Abetz, Polymers, 2017, 9, 216.

Photochemistry and Free Radicals in Organic Nanocrystals

Malcolm D. E. Forbes[1*], Natalia V. Lebedeva[2], Ryan C. White[2], Valery F. Tarasov[3],
Miguel Garcia-Garibay[4], Jin H. Park[4], Marino Resendiz[4], Vince M. Hipwell[4],
Edris Rivera[4]

[1]*Center for Photochemical Sciences and Department of Chemistry, Bowling Green State University, Bowling Green, OH, USA*
[2]*Caudill Laboratories, Department of Chemistry, University of North Carolina, Chapel Hill, NC, USA*
[3]*Semenov Institute for Chemical Physics, Kosygin St, Moscow, Russia*
[4]*University of California, Los Angeles, CA, USA*

*e-mail: forbesm@bgsu.edu

This lecture will begin with a brief history of the organic molecular triplet state, its connection to phosphorescence, and its detection by electron paramagnetic resonance spectroscopy. Comparison of steady–state and time-resolved EPR methods will be presented, as applied to triplet states created in single crystals as well as randomly oriented frozen glasses. The main structural parameter obtained from EPR spectroscopy of triplet states is the dipolar coupling D, an anisotropic parameter related to the distance between the unpaired electrons. The spincorrelated radical pair, normally observed in confined media such as micelles or reverse micelles, can be thought of as a weakly coupled triplet state, and its major spin–spin coupling is that from the isotropic exchange interaction J between the unpaired spins. Spectra from either triplet states or correlated radical pairs are often strongly spin polarized, i.e., they exhibit non-Boltzmann spin state populations (enhanced absorption (A) and/or emission (E)). This polarization carries valuable structural and mechanistic information about the triplet states themselves and any ensuing radicals they later form. The origins of these processes and analysis of spin-polarized TREPR spectra will be presented and discussed.

This background material will be presented as means of better understanding the time-resolved EPR spectra of transient, spin polarized radical pairs created in the interior of nanocrystals of dicumyl ketones in aqueous suspensions. The nanoparticles are created by the arrested growth technique, and are approximately 200 nm in diameter. Four dicumyl ketones were studied: the parent compound dicumylketone (DCK), the bis(p-dimethoxy) compound (DCKOMe), the fluorinated analog (p-F), and the bis(p-trifluoromethyl) analog (DCKF6). All four compounds form nanocrystals easily, and 308 nm photolysis with TREPR detection leads to spin-polarized (AAAEEE), broad, anisotropic spectra that resemble powder pattern triplet state EPR spectra with an approximate D value of 250 G. Direct comparison will be made to free solution spectra (highly resolved lines, net Nanocrystalline Radical Pairs from DCK. From Lebedeva, et al. J. Am. Chem. Soc., 2010, 132 (1), pp 82–84. A polarization, with a narrow spectral width).

For some compounds, comparison to frozen triplet state spectra of the parent compound will also be put forward (strongly spin polarized (AEAEAE) with D values of approximately 1000 G). The nanocrystal suspensions are created in aqueous surfactant solutions that are well below the critical micellar concentration of the surfactant (SDS), and no disproportionation products are observed, therefore it is concluded that the radical pairs do not exit the nanocrystal. Spectral simulation shows that the inter-radical separation in the nanocrystal is about 5 Å, and that they experience both dipolar and exchange couplings between the unpaired electrons. This is the first report of a spin polarized radical pair triplet state, and it is an unusual example of observation of a triplet state EPR spectrum at room temperature.

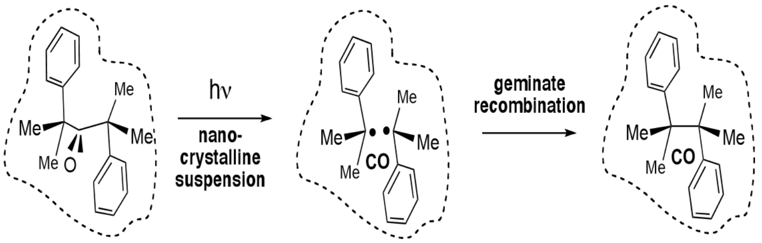


Figure 1. Nanocrystalline Radical Pairs from DCK. From Lebedeva, et al. J. Am. Chem. Soc., 2010, 132 (1), pp 82–84.

Surface Roughness Effects on Fluid Dynamics and Thermodynamic Properties of Liquids at Fluid/Solid Interfaces

Michael Frank[1*], Dimitris Drikakis[2]

[1]University of Strathclyde, Glasgow, UK
[2]University of Nicosia, Nicosia, Cyprus

The presentation concerns the effects of surface irregularities and imperfections on fluid dynamics and thermal resistance at a solid-liquid interface. The study has utilized molecular dynamics simulations for liquid argon confined between silver walls. The surface roughness was designed using fractal theory, introducing stochastic patterns of multiple scales that resemble realistic surface geometries. Contrary to most previous studies that show a monotonic decrease of the thermal resistance with increasing surface roughness, here we show a more complex behavior that depends on the strength of the solid-liquid interactions. The thermal resistance decreases with increasing roughness for weak interactions but it increases with increasing roughness depth for strong interactions. The above behavior is attributed to two competing phenomena, namely the area of the solid-liquid interface and the vibrational properties at the interface. Finally, we demonstrate that, for the same fractal parameters, randomly generated surfaces practically have the same thermal resistance and solid-liquid radial distribution function. Findings about the fluid dynamics behavior at the interface will also be discussed.

Reaction Mechanisms and Kinetics Studies with Molecular Nanocrystals

Miguel Garcia-Garibay*, Jin H. Park, Tim S. Chung, Vince M. Hipwell, Edris Rivera

University of California, Los Angeles, CA, USA

*e-mail: mgg@chem.ucla.edu

The use of spectroscopic methods to document detailed mechanistic and kinetic processes taking place in polycrystalline solids, dry powders, and other bulk materials has always been challenging due to their complex optical properties. Problems typically arise from their high scattering and optical densities and sometimes from their large birefringence and dichroism. This presentation will include the preparation of stable water suspensions of nanocrystalline compounds and demonstrate their use in the characterization of solid-state spectroscopic properties using simple transmission procedures. We selected well-known photophysical probes with characteristic solid state properties to illustrate the fact that nanocrystals are a state of matter in transition between supramolecular structures and bulk solids. We gathered conclusive experimental evidence that the nanocrystals used in these experiments have the same morphology as the macroscopic specimens grown from solution. Analysis of size and size distribution by polarized microscopy, dynamic light scattering (DLS) and probe microscopy methods (AFM, SEM) indicates that optimal samples should be of the order or 200 nm in size, which is below the wavelength of light used in most experiments, and a key parameter for the method to work well. Examples will be shown to illustrate the use of nanocrystals to obtain detailed mechanistic information of excited state processes and highly selective reactions in crystals, including a novel strategy for signal amplification with a gain based on a unusual excited state chain reactions.

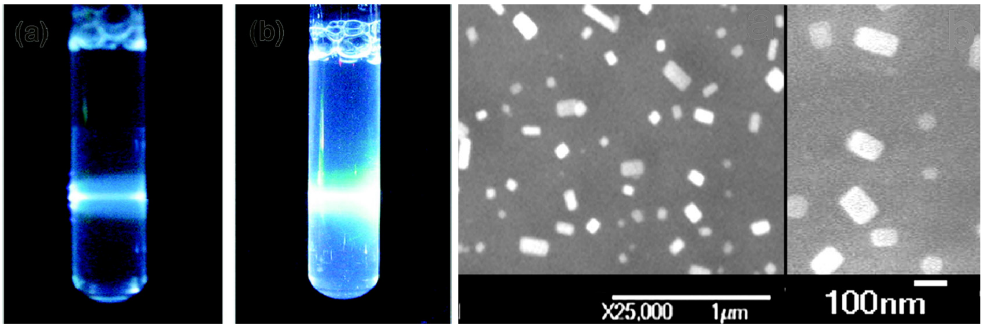


Figure 1. Room temperature phosphorescence of nanocrystalline benzophenone suspended in water and SEM images illustrating nanocrystals smaller than the wavelength of UV light.

References

[1] “Transient Kinetics and Quantum Yield Studies of Nanocrystalline α-Phenyl-Substituted Ketones: Sorting Out Reactions from Singlet and Triplet Excited States” Park, J. H.; Chung, T. S.; Hipwell, V. M.; Rivera, E. A.; Garcia-Garibay, M. A. J. Am. Chem. Soc., 140, 8192–8197 (2018).

Anisotropic Thermal Magnetoresistance in Radiative Heat Transfer

A. Garcia-Martin

IMN-Instituto de Micro y Nanotecnología (CNM-CSIC), Tres Cantos, Madrid, Spain

e-mail: a.garcia.martin@csic.es

The possibility to create and manipulate nanostructured materials encouraged the exploration of new strategies to control the electromagnetic properties without the need to modify its physical structure, i.e. by means of an external agent. An approach is the combination of magneto-optically active and resonant materials (e.g. plasmonic modes), where it is feasible to control the optical properties with magnetic fields in connection to the excitation of resonances[1] (magnetoplasmonics). It has been shown that these nanostructures can be employed to modulate the propagation wavevector of SPPs[2], which allows the development of label free sensors with enhanced capabilities[3-5] or to enhance the magneto-optical response in isolated entities as well as films, in connection with a strong localization of the electromagnetic field.[6-8]

Here we will show that they also play a crucial role in the active control of thermal emission and the radiative heat transfer (RHT).[9-11] In particular Near Field RHT between two MO particles can be efficiently controlled by changing the direction of the magnetic field, in the spirit of the Anisotropic Magneto Resistance in spintronics.[11]This phenomenon, which we term anisotropic thermal magnetoresistance (ATMR), stems from the anisotropy of the photon tunneling induced by the magnetic field. We discuss this effect through the analysis of the radiative heat exchange between two InSb particles, and show that the ATMR can reach amplitudes of 100% for fields on the order of 1 T and up to 1000% for a magnetic field of 6 T. These values are several orders of magnitude larger than in standard spintronic devices. More importantly, this thermomagnetic effect paves the way for exploring heat transfer physics at pico- and even subpicosecond time scales, which are even shorter than the relaxation time of heat carriers. Moreover, we show that the heat flux is very sensitive to the magnetic field direction, which makes this effect very promising for the development of a new generation of thermal and magnetic sensors.

References

[1] G. Armelles, et al., Adv. Opt. Mat. 1, 10 (2013)
[2] V.V. Temnov et al., Nat. Photon. 4, 107 (2010)
[3] B. Sepúlveda, et al., Opt. Lett. 31, 1085 (2006)
[4] M.G. Manera, et al., Biosens. Bioelectron. 58, 114 (2014)
[5] B. Caballero, et al., ACS Photonics 3, 203 (2016),
[6] N. de Sousa et al., Phys. Rev. B 89, 205419 (2014)
[7] N. de Sousa et al., Sci. Rep. 6, 30803 (2016)
[8] M. Rollinger et al., Nano Lett. 16, 2432-2438 (2016)
[9] E. Moncada-Villa, et al., Phys. Rev. B 92, 125418 (2015).
[10] R. M. Abraham Ekeroth, et al., Phys. Rev. B 95, 235428 (2017)
[11] R. M. Abraham Ekeroth, et al., ACS Photonics 5, 705 (2018).

3D Printing of Nanocomposites and Nanogels

Emmanuel P. Giannelis

Department of Materials Science and Engineering, Cornell University Ithaca, NY, USA

e-mail: epg2@cornell.edu

Despite extensive progress to engineer hydrogels for a broad range of technologies, practical applications have remained elusive. Stereolithography, SLA, has demonstrated extreme promise because of its ability to selectively create a desired structure layer-by-layer out of a liquid pre-gel solution under exposure to patterned light. As such SLA is an attractive manufacturing technique for rapid prototyping and the fabrication of customizable items like biomedical implants or scaffolds. In this presentation, I will review our efforts to develop ionic polymer nanocomposite systems and then focus on more recent work on systems for 3D printing. These new nanocomposite hydrogels and ionogels combine within a single platform tunable stiffness, toughness, extensibility, and resiliency. In addition to their excellent mechanical performance, they exhibit fast printing, conductivity, and fast osmotically-driven actuation. The tunable properties combined with the ability for 3D-printing into complex architectures, provide opportunities for a variety of practical applications such as artificial tissue, soft actuators, compliant conductors, and sensors for soft robotics.

Biomimetic NAD Analogs for Photochemical CO_2 Reduction

Ksenija D. Glusac

Department of Chemistry, University of Illinois at Chicago, Chicago, IL, USA
Department of Chemistry, Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH, USA

e-mail: glusac@uic.edu

In photosynthetic organisms, CO_2 reduction is achieved via hydride transfer from NADH cofactors, while the catalytic cycle is closed using photochemical reduction of NAD^+ by water. In our work, we mimic this chemistry using artificial NADH analogs adsorbed on photocathode surface for photochemical regeneration (Fig 1). In this biomimetic approach, the selectivity for methanol production will be achieved, while the undesired proton reduction will be suppressed by metal-free catalysts.

We present a study of the "dark" and "light-driven" halves of the catalytic cycle. Thermodynamic hydricities of organic hydride donors were obtained using experimental and computational methods, which enabled the development of the structure-property relationship and the discovery of NADH analogs that are capable of reducing CO_2 to formate. The photochemical recovery of NADH-analogs by mid- and wide-gap p-type semiconductors (GaP and NiO) was investigated using time-resolved laser spectroscopy. The kinetics of the interfacial charge transfer were found to be fast (the forward electron transfer and the subsequent charge recombination), possibly due to the presence of a large number of surface trap states. This work provides important proof-of-principle demonstrations of metal-free CO_2 reduction catalysis, and could have an impact on the development of a new generation of bio-inspired, earth-abundant materials for energy storage.

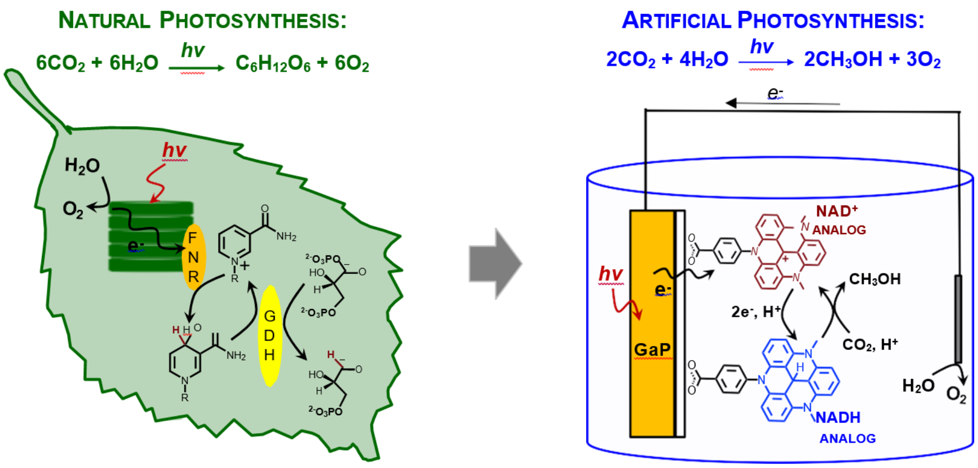


Figure 1. Representation of the natural and biomimetic CO_2 reduction by NADH analogs.

High Performance Solid Polymer Electrolytes for Energy Storage via Macromolecular Engineering

Emmanouil Glynos[1*], Emmanuel Giannelis[2], Georgios Sakellariou[3],
Spiros H. Anastasiadis[3]

[1]*Institute of Electronic Structure and Laser, Foundation for Research and Technology, Crete, Heraklion, Greece*
[2]*Department of Materials Science and Engineering, Cornell University, Ithaca, NY, USA*
[3]*Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou Athens, Greece*

[*]e-mail: eglynos@iesl.forth.gr

Solid polymer electrolytes (SPEs) could be a "real game-changer" as they hold the promise to solve most of the problems of liquid electrolytes. SPEs are inherently safe, nonflammable, and compatible with lithium metal anodes. Despite the considerable research effort in SPEs, the primary challenge is the development of solid materials with good mechanical properties without sacrificing ionic-conductivity. This talk will provide evidence that the use of complex macromolecular architectures holds the promise for the development of nanostructured materials with precise/desired morphologies that promotes SPEs properties to levels and temperature range not accessible before by conventional linear macromolecular systems. In particular, we will discuss the use of two difference polymer nanostructured nanoparticles, composed of high functionality star-shaped polymers, as additives to liquid electrolytes. In the first, when stiff/rigid polymer poly(methyl methacrylate), PMMA, nanoparticles, composed of high functionality star-shaped PMMA molecules, were incorporated to a liquid, ion-conducting, poly(ethylene oxide), PEO, doped with bis(trifluoromethane) sulfonamide (LiTFSI), the resulted SPEs exhibit two orders of magnitude higher conductivity and one order of magnitude higher mechanical strength compared to their linear PMMA blend analogues. Key to this phenomenon is the formation of highly interconnected, pure of liquid PEO, conducting regions as the result of PMMA nanoparticle dispersion within the liquid electrolyte. In the second, mikto-arm star copolymers composed of ion-conducting PEO arms that complement stiff insulating polystyrene arms, PS, were introduced to liquid PEO electrolytes and the resulted SPEs possess a shear modulus of G'~ 0.1 GPa and an ion conductivity σ ~ 10-4 S/cm. Noticeably, these SPEs show a strong decoupling between the mechanical behavior and ionic-conductivity. Due to their nanostructured morphology, these nanoparticles empower specific interactions with the liquid electrolyte, directing their self-assembly behavior into highly interconnected structures, promoting the decoupling of the antagonistic properties of conductivity and mechanical strength. As the synthesis of mechanical robust electrolytes with superior ion-conductivity has been the subject in a wide variety of solid-state electrochemical devices, this approach may significantly contribute to other applications, beyond lithium metal batteries, such as anion exchange membranes for fuel cells, efficient active layers in dye-sensitized solar cells, electrochromic devices and water desalination systems.

Using Artificial Intelligence and Computational Techniques yo Assist the Engineering of 2D Materials

Kuan Eng Johnson Goh

*Institute of Materials Research & Engineering, Agency for Science, Technology and Research (A*STAR), Innovis, Singapore*
Department of Physics, National University of Singapore, Singapore

e-mail: gohj@imre.a-star.edu.sg; phygkej@nus.edu.sg

The rise of two dimensional (2D) materials in the last two decades has been fueled by both scientific and technological interests. The unique opportunities to find 2D materials in stable monolayer form (e.g. graphene, transition metal dichalcogenides, hexagonal boron nitride, etc.) have spawned a large library of such materials, inspiring fundamental relooks into the material physics in such intrinsically 2D confined layers, but also the potential of combining hetero-layers in unique ways for novel applications. A key challenge though stifles the technological proliferation of such materials, namely, reproducible material quality. Even though exfoliated monolayers currently offer some of the best attainable samples, they are nevertheless imperfect, often with defects such as missing atom vacancies, or intercalated contaminant atoms. The understanding of these defects and their impact on the intended use of these 2D materials will have direct implications on how we go about engineering these materials into devices. One way to study such atom-level defects is to use the scanning tunneling microscope (STM) which offers atomic resolution imaging of the topographical and electrostatic potential landscape on 2D materials. The complete characterization of these defects however is time and labor intensive and can be instrument dependent. In addition, the analysis and interpretation of STM data is also a highly specialized skill set, making direct inferences difficult to access, even for experienced users. Comparison with literature data or results from multiple laboratories will often be necessary in order to avoid fallacious identification of features in STM images or spectroscopic data.

In this talk, I will share our recent efforts in using artificial intelligence combined with traditional computational method to assist in the identification of vacancy type defects in the STM images of 2D materials. The correct identification of such defects is an important first step in our efforts to use defect engineering to tailor the properties of 2D materials for specific applications.[1] The use of machine learning based on convolution neural networks for automating defect identification will be discussed, and preliminary training with a simulated data set, and the associated tests of the trained network using real experimental data will be presented.

References

[1] "Electrical Doping Effect of Vacancies on Monolayer MoS_2", J. Yang, H. Kawai, C. P. Y. Wong, and K. E. J. Goh, J. Phys. Chem. C 123. 5, 2933 (2019).

Laser Processing of Silicon Nanostructures for Optical Applications

Letian Wang[1], Matthew Eliceiri[1], Yoonsoo Rho[1], Heng Pan[2], Costas P. Grigoropoulos[1*]

[1]*Laser Thermal Laboratory, Department of Mechanical Engineering,University of California, Berkeley, CA, USA*
[2]*Department of Mechanical and Aerospace Engineering, Missouri University of Science and Technology, Rolla, MO, USA*

This talk presents recent research on the laser-enabled assembly and phase transformation of silicon nanostructures. Manipulating and tuning nanoparticles by means of optical field interactions is of key interest for nanoscience and applications in electronics and photonics. We report direct optically modulated writing of nanoparticle patterns (size, number and location) of high precision using a pulsed nanosecond laser. The nanoparticle arrangement and dimensions are modulated by the laser pulse energy and polarization. The fast cooling-rate induced phase switching of crystalline Si nanoparticles to amorphous state. Based on these effects, a multiscale laser programming method of Mie resonator arrays is proposed. The number of Mie resonators as well as the resonance peaks and dielectric constants of selected resonators can be programmed. Time-resolved optical probing and thermal modeling are utilized to understand the dynamic evolution of the phase transformation process. Furthermore, we show that nanoscale domains can be reversibly crystallized and amorphized upon laser irradiation. The programmable light-matter interaction serves as a mechanism to fabricate optical metasurfaces, structural color and multi-dimensional optical storage devices.

Head-to-Tail Bis-Coumarins, Conjoined Coumarins and Coronene Analogs

Daniel T. Gryko[1*], Marek K. Węcławski[2], Irena Deperasińska[2],
Marzena Banasiewicz[2]

[1]*Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland*
[2]*Institute of Physics, Polish Academy of Sciences, Warsaw, Poland*

[*]e-mail: dtgryko@icho.edu.pl

These π-Expanded coumarins have attracted considerable attention in recent years. The growing number of their possible applications, including two-photon fluorescence microscopy, OLEDs, dye-sensitized solar cells, energy and electron transfer systems and fluorescent probes, significantly accelerates the progress in the synthesis of coumarins. Noticeably, the extension of coumarin π-systems can be achieved through multiple methods.

The unique synthesis of two novel types of π-expanded coumarins will be presented. Modified Knoevenagel bis-condensation afforded 1,7-dioxa-perylene-2,8-diones. Subsequent oxidative aromatic coupling or light driven electrocyclization reaction led to dibenzo-1,7-dioxacoronen-2,8-dione. Unparalleled synthetic simplicity, straightforward purification and superb optical properties have a potential to bring these perylene and coronene analogs towards various applications. The proposed synthetic method is operationally simple and leads to analogs of perylene and pentacene in 2-3 steps. The examination of spectroscopic properties of all new compounds, showed that they displayed intense fluorescence. The smooth photochemical transformation of 1,7-dioxa-perylene-2,8-diones into dibenzopentacenes opens new possibilities towards the synthesis of large π-expanded heterocyclic analogs of PAHs. The use of presented approach can lead to a wide range of previously unknown heterocycles, which can serve as ideal platforms in such diverse areas as molecular electronics and fluorescent imaging.

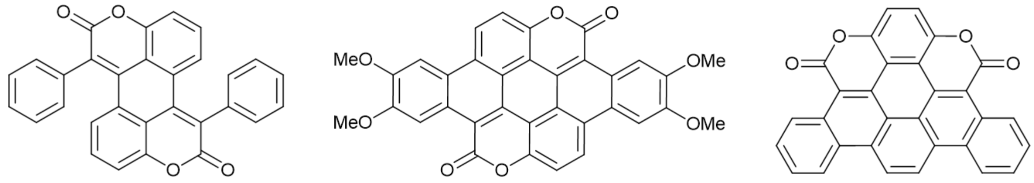


Figure 1. The structures of head-to-tail bis-coumarins and conjoined coumarins

---

References

[1] “π-Expanded Coumarins: Synthesis, Optical Properties and Applications”, Tasior, M.; Kim, D.; Singha, S.; Krzeszewski, M.; Ahn, K.; Gryko, D. T., J. Mat. Chem. C 3, 1421-1446 (2015).

[2] “Building Molecular Complexity from Quinizarin; Conjoined Coumarins and Coronene Analogs”, Węcławski, M. K.; Deperasińska, I.; Banasiewicz, M.; Young, D. C.; Leniak, A.; Gryko, D. T. Chem. Asian J. DOI: 10.1002/asia.201800757 (2019).

Porphyrins as Photoredox Catalysts

Dorota Gryko

Institute of Organic Chemistry PAS, Warsaw, Poland

e-mail: dorota.gryko@icho.edu.pl

> *"Look deep into nature, and then you will understand everything better."*
> *— Albert Einstein*

Our life depends on porphyrinoids and these tetrapyrroles are referred as pigments of life. Among them are chlorophylls, which in the first instance are responsible for transforming light energy into the chemical reactivity with the ultimate production of starch (photosynthesis). Following nature, we have been exploiting potential of porphyrinoids and the unlimited source of solar energy in catalytic reactions.

Over the years, impressively divers range of photochemical reactions has been developed, they are mainly catalyzed by ruthenium and iridium complexes. On the other hand organic dyes exhibiting considerable advantages have been also shown to act as photocatalysts with eosin Y being the most widely studied.

The presentation will highlight a successful application of porphyrinoids as photosensitizers and as photoredox catalysts for visible-light induced selective functionalizations, including photooxidation of aldehydes,[1] alkylation of carbonyl compounds,[2] arylation of heteroarenes.[3] We will also show that predictions about the reaction mechanism can be based on the analysis of PC structure – the presence of electron-withdrawing groups will favor reductive quenching cycle, whereas electron-donating substituents will stabilize $PC^{\bullet+}$ in oxidative quenching cycle.

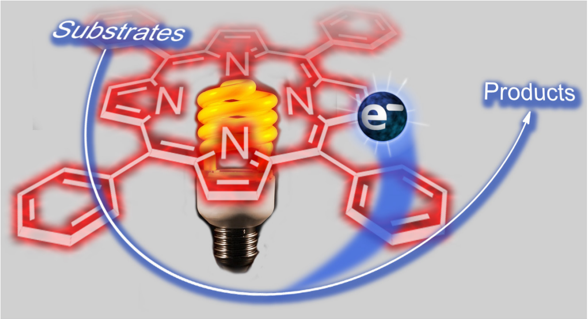


Figure 1. Porphyrins under light irradiation

References

[1] "Mechanistic Insights into Enantioselective C-H Photooxygenation of Aldehydes via Enamine Catalysis", D. J. Walaszek, K. Rybicka-Jasińska, S. Smoleń,M. Karczewski, D. Gryko Adv. Synth. Catal. 357, 2061 (2015).

[2] "Porphyrins as Photoredox Catalysts - Experimental and Theoretical studies" K. Rybicka-Jasińska, W. Shan, K. Zawada, K. M. Kadish, D. Gryko, J. Am. Chem. Soc. 138, 15451 (2016).

[3] "Porphyrin-catalyzed photochemical C-H arylation of heteroarenes" K. Rybicka-Jasińska, B. König, D. Gryko, Eur. J. Org. Chem. 2104, (2017)

Nano-Calcium Phosphate Coating and Self-Assembled Collagen Direct Enthesis Regeneration on Silk

Joseph Pearson, Mikayla Rahman, Joo Ong, Rena Bizios, Teja Guda*

Department of Biomedical Engineering, University of Texas at San Antonio, San Antonio, TX, USA

*e-mail: teja.guda@utsa.edu

Introduction: The inability of the ACL to heal is largely due to the synovial environment which is largely avascular and therefore lacks nutrients. Injuries to the ACL are often combined with surrounding tissue damage, due to the proximity of and attachment to those tissues. Our study examines the effects of a unique in vitro bioreactor for biophysical stimulation of bone:enthesis:ligament grafts with tissue specific nanomaterial matrices with vitamin supplementation to enhance directed tissue differentiation.

Methods: The base scaffolds were prepared from silk fibroin that was dissolved in hexfluoro-2-propanol. The salt-leached silk "bone" scaffolds were mineralized with nano-scale calcium phosphate coatings while the lyophilized silk "ligament" scaffolds were combined during lyophilization with Collagen I which self-assembled to create supporting fibrils between silk sheets (Fig 1). The scaffold materials were characterized with extensively and in vitro studies were carried out with mesenchymal stem cell seeding either under static, dynamic stimulation (Fig 2) or supplemented with calcitriol on the ligament portion and ascorbic acid on the bone portion.

Results and Conclusions: The silk bone dynamic mineralization process provided nanomaterial coatings with Ca:P ratios similar to hydroxyapatite. The silk:collagen ratio produced similar mechanics to the silk alone and enthesis scaffold mechanics were similar to the ligament. The combination of dynamic stimulation and addition of vitamins significantly increased scaffold mechanical properties and at the gene level resulted in bone, hypertrophic cartilage and ligament type phenotypes being produced in a gradient based manner across the graft.

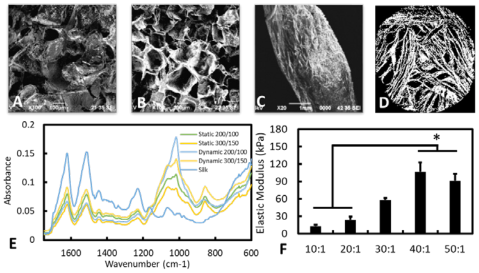


Figure 1. SEM of (a)static and (b)dynamic mineralized silk, (c)silk ligament and (d)µCT of silk-collagen ligament. (e)FTIR and (f) mechanical evaluation of silk:collagen ratios.

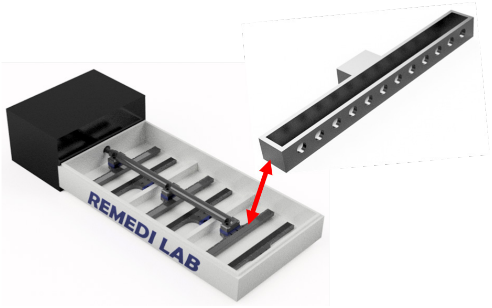


Figure 2. Dynamic stimulation system with the ligament graft clamped and the bone portion of the enthesis placed in the clamp (red callout).

Aromatic Singlet Fission Materials – Up- and Down-Converting Photons

Dirk M. Guldi

Department of Chemistry and Pharmacy & Interdisciplinary Center of Molecular Materials, Engineering of Advanced Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

e-mail: dirk.guldi@fau.de

The Shockley-Queisser limit places an upper bound on solar conversion efficiency for a single p-n junction solar cell at slightly more than 30%. To surpass this limit, multi-exciton generation is being explored in inorganic semiconductors, while singlet fission (SF) is being investigated in arrays of conjugated organic molecules. In an optimal SF process, the lowest singlet excited state of one molecule (S1) that is positioned next to a second molecule in its ground state (S0) is down-converted into two triplet excited states (T1) each residing on one of the two adjacent molecules. The two triplet states initially form a correlated pair state 1(T1T1), which then evolves into two separated triplet states (T1 + T1). As such, the energetic requirement for SF is E(S1) ≥ 2 × E(T1).

We have set our focus in recent years on intramolecular SF in molecular materials and their studies in solution rather than on intermolecular SF investigations in crystalline films.

Implicit in intramolecular SF is a resonant, direct excitation of the SF material. In pentacene dimers linked by a myriad of molecular spacers, SF takes place with quantum yields of up to 200%. In addition, all key intermediates in the SF process, including the formation and decay of a quintet state that precedes formation of the pentacene triplet excitons, have been identified. This approach is, however, limited to the part of the solar spectrum, where, for example, the pentacene dimers feature a significant absorption cross-section. To employ the remaining part of the solar spectrum necessitates non-resonant, indirect excitation of the SF materials via either up- or down-conversion. For example, the up-conversion approach is realized with singlet excited states in pentacene dimers, which are accessed by two-photon absorptions (TPA). TPA is then followed in the second step of the sequence by an intramolecular SF – similar to what is seen upon resonant, direct excitation. Quite different is the down-conversion approach, which is based on an intramolecular Förster resonance energy transfer (FRET) and thereby the (photo)activation of the SF material. FRET requires the use of a complementary absorbing chromophore and enables funneling its excited state energy unidirectionally to the SF performing pentacene dimer. Again, SF completes the reaction sequence.

Integration Process of Individual Single-Walled Carbon Nanotubes into Sensing Devices Monitored by Raman Spectroscopy

Miro Haluska*, Lalit Kumar, Laura Vera Jenni, Christofer Hierold

Micro and Nanosystems ETH Zürich, Zurich, Switzerland

*e-mail: haluska@micro.mavt.ethz.ch

In this contribution, we are focusing on sensors based on individual single-walled carbon nanotubes (SWCNTs). The differences in electrical characteristics of individual carbon nanotube field-effect transistors (iCNFETs) cannot be explained solely by the variation in intrinsic properties of different SWCNTs. They can be caused by impacts of device fabrication processes on SWCNTs too. To identify critical process steps we use various techniques including Raman spectroscopy. The latter is a powerful method for identifying and characterizing carbon nanostructures and for detecting changes in their properties.[1]

Our individual SWCNT based devices are fabricated either by standard photo- or electron-beam lithography, or by an additive manufacturing utilizing ultra-clean mechanical transfer from "growth chips" into the final devices.[2] SWCNTs used for iCNTFET are synthesized from ferritin-based Fe catalyst nanoparticles by CVD at 820 - 865°C in CH_4/H_2.[3] As-grown SWCNTs are inspected by Raman spectroscopy with laser energies below the level which can induce changes in the nanotube structure. The diameter and structural quality of the CNTs are estimated from the position of the Raman radial breathing mode (RBM) and from the ratio of D and G mode intensities, respectively. By Raman spectroscopy we determined, for example, a minimal thickness of sacrificial alumina layer required to protect SWCNTs from the impact of plasma ashing used for removing lithography resist residuals.[4] Finally, some of the devices with substrate-bound[4] as well as with suspended nanotubes[5] were characterized by electrical measurements to confirm the improve performance of iCNTFETs. Eight times reduction in variation of iCNTFET electrical resistance with substrate-bound nanotubes were achieved.[4]

References

[1] "Raman spectroscopy in graphene related system" Jorio, A., Dresselhaus M., Saito R., Dresselhaus G. F., s, Wiley-VCH (2011).

[2] "Transfer of carbon nanotubes onto microactuators for hysteresis-free transistors at low thermal budget", Muoth, M., Hierold, C., IEEE MEMS 2012, Paris, pp 1352-1355 (2012).

[3] "Narrowing SWNT diameter distribution using size-separated ferritin-based Fe catalysts", Durrer L., Greenwald, J., Helbling, T., Muoth, M., Riek, R., Hierold, C., Nanotechnology 20, pp 355601-7 (2009).

[4] "Enabling fabrication of clean electrical contacts to carbon nanotubes using oxygen plasma ashing", Liu, W., Chikkadi, K., Hierold, C., Miroslav Haluska, physica status solidi b, 253, pp 2417-2423 (2016).

[5] "Selective metallization and passivation of dry-transferred carbon nanotubes in field-effect transistors", Jenni L.V., Haluska M., Hierold C., IEEE MEMS 2018, Belfast, pp 479 – 482 (2018).

Manipulating Nanoparticles with Holographic Optical Tweezers: Nanotools and Nanofabrication

Simon Hanna

H H Wills Physics Laboratory, University of Bristol, Tyndall Ave, Bristol, UK

e-mail: s.hanna@bristol.ac.uk

Holographic optical tweezers are a flexible tool for manipulating colloidal particles with microscopic and sub-microscopic dimensions. As a development of conventional tweezers, they have been used widely for almost 20 years, as a means of applying forces to physical and biological systems. Much early work with optical tweezers was based on the manipulation of dielectric spheres. However, more recently, attempts have been made to manipulate both non-spherical particles, and particles that are substantially smaller than the wavelength of light being used. The small particle size introduces interesting challenges for optical trapping, while the symmetry-breaking gives rise to opportunities for controlling both the amplitude and direction of the force that can be applied. The challenges occur largely due to the significance of Brownian motion which, in the case of extended particles, can couple with the beam-shape to produce non-conservative and cyclic motion. The other implication of small particle size is, of course the challenge of imaging the particles during the experiment.

In this presentation, I will give an overview of the technique of holographic optical tweezing, and will illustrate its application in nanoscience, through two main application areas: nanotools and nanofabrication. A nanotool is defined as any tool that can be manipulated using optical tweezers on a nanometer scale to apply sub-nano Newton forces. Typically, the nanotool itself will be many-microns across and will require multiple optical traps in order to manipulate it. By judicious design, it is possible to use nanotools to probe systems with a resolution of a few nanometers, and forces in the femto- to pico-Newton range. In the realm of nanofabrication, the optical tweezers offer the opportunity to place particles in a predefined configuration, controlling both position and orientation. The challenges for achieving this in the case of nanoscale particles will be reviewed.

A Physical Model for Nanoscale GaN Based HEMTs

Jin He*, Yandong He, Xiaomeng He, Jun Pan, Xiaomeng Wang, Caixia Du, Yuan Ren

Peking University Shenzhen SoC Key Laboratory
PKU-HKUST Shenzhen-Hong Kong Institution

*e-mail: frankhe@pku.edu.cn

Gallium Nitride (GaN)-based high electron mobility transistors (HEMTs) are emerging as promising contenders to replace existing Silicon and Gallium Arsenide (GaAs) devices in the radio-frequency/microwave power amplifiers and high-power switching applications. Along with the fast development of Mirco- & Nano- device technology and circuit integration, compact predictive models for nanoscale GaN HEMTs are of great value for circuit design and simulation. This report is focused on developing a physical model to fulfill the gap between the nanoscale device technology and circuit designs for GaN HEMTs. In this report, a physics-based compact model for the drain currents and capacitances of GaN HEMTs is developed. First, a surface-potential-based compact model for the drain current is developed. Consistently, the charge and capacitance model is formulated to predict the terminal capacitances and trans-capacitances for transient simulations. Also, the parasitic capacitances are modeled with conformal mapping method and unified parameters. Then, the model is calibrated and validated with TCAD simulations, and the experimental DC I-V and S-parameter measurements of fabricated devices. Finally, the benchmarking tests and the typical circuit simulations are demonstrated in the model platform.

Materials Imaging Initiative: A New Paradigm for Functional Materials

S. Hong[*], S. Cho, G. Park, J. Yeom, S. Eom, A. Jetybeyava, J. Kim, S. Yun,
H. Kim, H. J. Kim, J. Ryu, P. Li, C. Oh, M. Chen-Glasser, H. K. Kim, Y. Han

Department of Materials Science and Engineering, KAIST, Daejeon, Korea

[*]e-mail: seungbum@kaist.ac.kr

Renaissance established the scientific method, a system by which both observation and reason are employed in order to test the proposed mechanisms for planetary motion. Descartes promoted science by first questioning everything and then building up a theory based on sound observational evidence. Materials science is no exception in the sense that visualization of order parameters or materials properties provides the solid ground on which materials theory and design can flourish. Here I will present our current research thrusts to visualize polarization, electrical charges and ionic transport to understand the emerging phenomena on materials surfaces as well as interfaces and how they help design future memory and energy storage devices.[1-5] Last but not least, I will discuss the vision of materials imaging initiative.

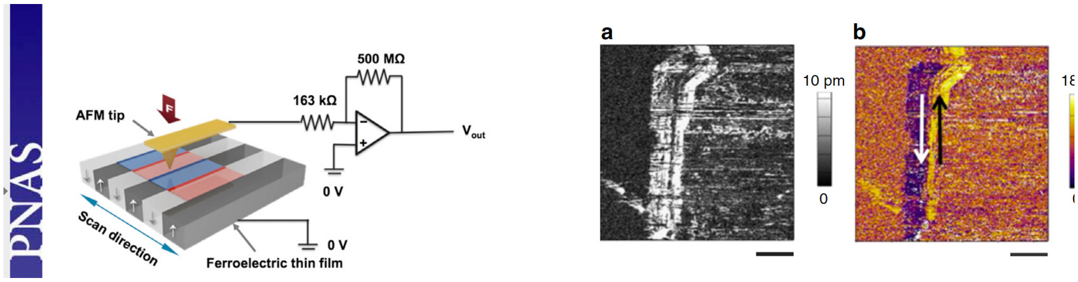


Figure 1. (left) Schematic of charge gradient microscopy (CGM)[1] and (right) piezoresponse force microscopy (PFM) (a) amplitude and (b) phase images of flexible ferroelectric organic crystals.[2]

References

[1] "Charge gradient microscopy," S. Hong, S. Tong, W. I. Park, Y. Hiranaga, Y. Cho, and A. Roelofs, Proc. Natl. Acad. Sci. USA 111, 6566 – 6569 (2014)

[2] "Flexible ferroelectric organic crystals," M. Owczarek, K. A. Hujsak, D. P. Ferris, A. Prokofjevs, I. Majerz, P. Szklarz, H. Zhang, A. A. Sarjeant, C. L. Stern, R. Jakubas, S. Hong, V. P. Dravid, and J. F. Stoddart, Nat. Comm. 7, 13108 (2016)

[3] "Screening Mechanisms at Polar Oxide Heterointerfaces," S. Hong, S. M. Nakhmanson, and D. D. Fong, Reports on Progress in Physics 79, 076501 (2016)

[4] "Scanning probe-type data storage beyond hard disk drive and flash memory," Y. Cho and S. Hong, MRS Bulletin 43, 365 – 270 (2018)

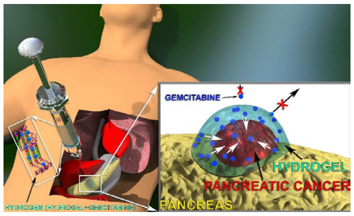
Multiresponsive Hydrogels for Targeted Delivery of Gemcitabine to Treat Pancreatic Cancer

Hermis Iatrou[1*], Panayiotis Bilalis[1], Dimitrios Skoulas[1], Anastasis Karatzas[1],
John Marakis[2], Athanasios Stamogiannos[3], Chrisida Tsimblouli[4], Evangelia Sereti[4],
Efstratios Stratikos[3], Konstantinos Dimas[4], Dimitris Vlassopoulos[2]

[1]*University of Athens, Department of Chemistry, Panepistimiopolis, Zografou, Greece*
[2]*FORTH, Institute for Electronic Structure and Laser, Greece and Department of Materials Science & Technology, University of Crete, Heraklion, Greece*
[3]*National Centre for Scientific Research Demokritos, Agia Paraskevi, Athens, Greece.*
[4]*Department of Pharmacology, University of Thessaly, Larissa, Greece*

[*]e-mail: iatrou@chem.uoa.gr

A novel, multifunctional hydrogel exhibiting a unique set of properties for the effective treatment of pancreatic cancer (PC) is presented. The material is comprised of a pentablock terpolypeptide of the type PLys-b-(PHIS-co-PBLG)-PLys-b-(PHIS-co-PBLG)-b-PLys which is a non-cytotoxic polymer. It can be implanted via the least invasive route and selectively delivers gemcitabine to efficiently treat PC. Simply mixing the novel terpolypeptide with an aqueous solution of gemcitabine within a syringe results in the facile formation of a hydrogel that can become liquid under the shear rate of the plunger. Upon injection in the vicinity of cancer tissue, it reforms into a hydrogel due to the unique combination of its macromolecular architecture and secondary structure. Due to its pH responsiveness, the hydrogel melts only close to PC, thus the drug can be delivered directionally towards the cancerous rather than healthy tissues in a targeted, controlled and sustained manner. The efficacy of the hydrogel was tested in-vivo on human to mouse xenografts using the drug gemcitabine. It was found that the efficacy of the hydrogel loaded with only 40% of the drug delivered in one dose, was equally or slightly better to the peritumoral injection of 100% of the free drug delivered in two doses, the typical chemotherapy so far. The results suggest that the hydrogel can direct the delivery of the encapsulated drug effectively in the tumor tissue. Enzymes lead to its biodegradation, avoiding removal by resection of the polymeric carrier after cargo delivery. The unique properties of the hydrogel formed can be predetermined through its molecular characteristics, rendering it a promising modular material for many biological applications.



Acknowledgements

The research was co-financed by the European Union and Greek national funds through the Operational Program Competitiveness and innovation, under the call RESEARCH – CREATE – INNOVATE (project code: T1EΔK-01612).

References

[1] P. Bilalis, et al Biomacromolecules, 19 (9), 3840–3852 (2018).

Tailoring the Properties of Polymers and Polymer Composites by Nano- Additives

Alojz Ivankovic[1*], Dong Quan[1], Chiara Mischo[1], Neal Murphy[1], Declan Carolan[2], Clemence Rounge[2]

[1]University College Dublin, Dublin, Ireland,
[2]FAC Technology, London, UK

[*]e-mail: alojz.ivankovic@ucd.ie

Nanomaterials, including core-shell rubber (CSR) nanoparticles, silica nanoparticles, multi-walled carbon nanotubes (MWCNTs), graphene nanoplatelets and their hybrid combinations were used to modify polymers (e.g. structural adhesives) and polymer composites (e.g. carbon fibre reinforced plastics, CFRPs) in an effort to improve their structural performance and functionality. CSR nanoparticles gave the most superior toughening performance, i.e. an over tenfold improvement in the fracture energy of adhesive joints was achieved by adding 30 wt.% CSR nanoparticles in to the epoxy resin.[1] However, the addition of CSR nanoparticles caused detrimental effects on the stiffness and strength of the epoxies. A good balance between the toughness and mechanical properties was achieved by the addition of silica/rubber hybrid nano-modifiers into the epoxies.[2] The toughening performance of MWCNTs/graphene was poor due to their poor dispersibility and weak adhesion to the epoxies.[3]

However, excellent electrical conductivity was achieved for adding only a small amount of MWCTNs/graphene (<0.5%) in the epoxies. Adding MWCNTs to epoxy and CFRPs moderately increased the mode-I fracture energy, but significantly increased the mode-II fracture energy.[4] The superior toughening performance of MWCNTs in mode-II fracture was attributed to: 1) increased MWCNT breaking and crack deflection mechanisms under shear load, and 2) large fracture process zone accompanied with extensive hackle markings and micro-cracks ahead of the mode-II crack tip of CFRPs. MWCNTs were also deposited on thermoplastic veils and used as interlayers in CFRPs, aiming to further improve the fracture toughness and impact strength. Additionally, the electrical conductivity of CFRPs was significantly enhanced. In parallel with the experimental work, multi-scale numerical models were developed in order to help understanding and quantifying the deformation and fracture mechanisms of nanomodified materials and hence in tailor-design of new advanced materials.

References

[1] "Fracture behaviour of epoxy adhesive joints modified with core-shell rubber nanoparticles." D. Quan, N. Murphy, and A. Ivankovic, Engineering Fracture Mechanics 182, 566-576 (2017)

[2] "Interaction of Toughening Mechanisms in Ternary Nanocomposites" D. Quan, R. Pearson, and A. Ivankovic, Polymer Composites 39, 3482-3496 (2018).

[3] "CNTs and core-shell rubber nanoparticles modified structural epoxy adhesives" D. Quan, D. Carolan, C. Rouge, N. Murphy, and A. Ivankovic, Journal of Materials Science 52, 4493-4508 (2017).

[4] "Enhancing mode-I and mode-II fracture toughness of epoxy and carbon fibre reinforced epoxy composites using multi-walled CNTs" D. Quan, J.L. Urdaniz and A. Ivankovic, Materials & Design 143, 81-92 (2018).

HRTEM and Oxidation Resistance Mechanism of Amorphous Hf-B-Si-C-N Coatings at High-Temperatures

J.C. Jiang[1*], Y. Shen[1], P. Zeman[2], V. Simova[2], J. Vlček[2], E. I. Meletis[1]

[1]Department of Materials Science and Engineering, The University of Texas at Arlington, Arlington, TX, USA
[2]Department of Physics and NTIS- European Centre of Excellence, University of West Bohemia, Plzeň, Czech Republic

*e-mail: jiangjc@uta.edu

In this talk, we present the microstructure evolution of a series hard amorphous Hf-B-S-C-N coatings at high temperatures and the high temperature oxidation mechanism. The amorphous coatings with a hardness of ~20 GPa were deposited by reactive pulse dc magnetron sputtering and annealed in air at temperatures from 1100℃ to 1500℃. In all annealed coatings, the amorphous structure was transformed into a two-layered structure comprising of an oxidized layer on the top followed by a bottom layer (Fig. 1a).[1] The top oxide layer possesses HfO_2 nanoparticles dispersed in an amorphous SiOx-based matrix. The microstructure of the bottom layer varies from the amorphous structure to a nano-crystallization layer being composed of HfB_2 and HfN nanoparticles separated by h-Si_3N_4 and h-BN boundaries (Fig. 1b)[2] depending on the annealing temperature. The oxidized/bottom layer interface exhibit fine HfO_2 nanoparticles surrounded by quartz SiO_2. The high-temperature oxidation resistance of the coatings is attributed to evolving microstructure of HfO_2 nanoparticles within a dense SiOx-based matrix and quartz SiO_2 in front of the bottom layer acting as a barrier for heat and O diffusion.

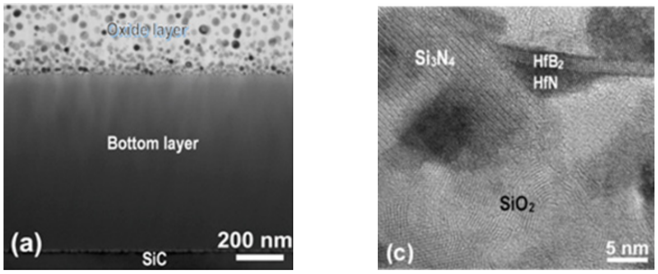


Figure 1. (a) XTEM of annealed $Hf_7B_{23}Si_{17}C_4N_{45}$, (b) HRTEM image of the bottom layer of annealed $Hf_7B_{23}Si_{22}C_6N_{40}$.

Acknowledgements

This work was supported by the U.S. National Science Foundation under Award NSF/CMMI DMREF-1335502 and by the Czech Science Foundation under Project No.17-08944S.

References

[1] Study of the high-temperature oxidation resistance mechanism of magnetron sputtered $Hf_7B_{23}Si_{17}C_4N_{45}$ film, M. Zhang, J. Jiang, P. Zeman, Š. Zuzjaková, J. Vlček, E.I. Meletis, Journal of Vacuum Science & Technology A 36(2), 021505 (2018).

[2] Microstructure evolution in amorphous Hf-B-Si-CN high temperature resistant coatings after annealing to 1500℃ in air, Y. Shen, J.C. Jiang, P. Zeman, V. Šímová, J. Vlček, E.I. Meletis, Scientific Reports 9(1), 3603 (2019).

$BaCO_3$ and $BaTiO_3$ Coatings on Ti Fabricated by Plasma Electrolytic Oxidation

Hsiao-Chien Wu, Jiechao Jiang*, Efstathios I. Meletis

Department of Materials Science and Engineering, The University of Texas at Arlington, Arlington, TX, USA

*e-mail: jiangjc@uta.edu

$BaCO_3$ and $BaTiO_3$ coatings on titanium substrate plates were fabricated by plasma electrolytic oxidation of titanium in an electrolyte of 0.5 M $Ba(CH_3COO)_2$ with 2 M NaOH using a current density of 10 mA/cm^2 processed for 1 hour and 4 hours, respectively. The surface morphology, composition and bonding states of the coatings were investigated by SEM, XPS and FTIR. The cross-sectional structure was studied using FIB. The microstructures of the coatings were examined using XRD, electron diffraction and HRTEM. The $BaCO_3$ costing possesses a loose structure with presence of numerous pores close to the Ti substrate and a well-condensed structure close to the surface (Fig. 1a). The $BaCO_3$ coating is composed of orthorhombic $BaCO_3$ nanorods that can be classified into two layers based on the orientation of nanorods: the nanorods at the bottom layer close to the Ti substrate are oriented vertically along the growth direction, while those on the top layer close to the surface are oriented horizontally within the surface plane (Fig. 1b). Such orientation variation of the $BaCO_3$ nanorods results in a density difference of the coating along the growth direction. A 60 nm thick sharp interface layer composed of nanocrystalline brookite TiO_2 was formed between the $BaCO_3$ bottom layer and the Ti substrate. The $BaCO_3$ coating was grown by decomposing $Ba(CH_3COO)_2$ into $BaCO_3$ and C_2H_6O followed by "physical" deposition on the substrate without any chemical reaction on the Ti. The $BaTiO_3$ coating exhibits a relatively dense structure and is composed of rutile and brookite TiO_2 nanostructures at the bottom layer followed by a dominant tetragonal $BaTiO_3$ on the top. Formation of the $BaTiO_3$ structure involves anodic reaction of the Ti to generate titanium ions and transformation of the $BaCO_3$ structure via substituting the C^{4+} with Ti^{4+} ion. Growth mechanism and structural evolution from $BaCO_3$ to $BaTiO_3$ will be addressed in detail.

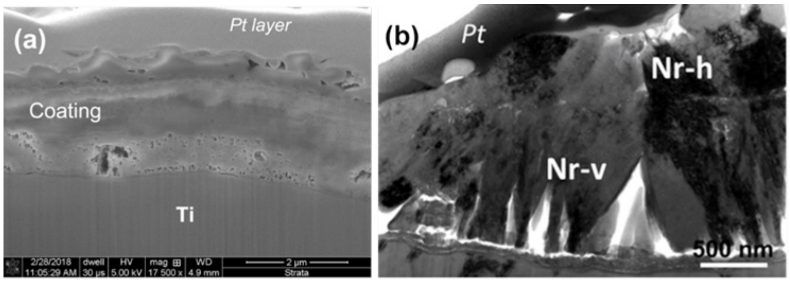


Figure 1. (a) X-SEM image of $BaCO_3$ coating cut by FIB. (b) XTEM of $BaCO_3$ coating.

Hybrid Quantum Photonic Integrated Circuits

A. W. Elshaari[1], I. Esmaeil Zadeh[2], A. Fognini[2], E. Büyüközer[1], T. Lettner[1], P. Zhao[3], E. Schöll[1], S. Gyger[1], D. Dalacu[4], P. J. Poole[4], M. E. Reimer[5], V. Zwiller[1], K. D. Jöns[1*]

[1] *Applied Physics Department, Royal Institute of Technology, Albanova University Centre, Stockholm, Sweden*
[2] *Delft University of Technology, Delft, The Netherlands*
[3] *Department of Electronic Engineering, Tsinghua National Laboratory for Information Science and Technology, Tsinghua University, Beijing, China*
[4] *National Research Council of Canada, Ottawa, Canada*
[5] *Institute for Quantum Computing and Department of Electrical & Computer Engineering, University of Waterloo, Waterloo, Canada*

[*] e-mail: klausj@kth.se

I will present our recent results on hybrid quantum photonic integrated circuits for quantum information processing. The hybrid approach allows us to harvest synergy effects between previously independent research fields, providing new functionalities and directions in the fascinating world of quantum photonic integrated circuits.

I will discuss our approach to integrate bright quantum light sources in complex on-chip quantum circuits. Currently, the most promising sources are based on III/V semiconductor quantum dots. However, complex photonic circuitry is mainly achieved in silicon photonics due to the tremendous technological challenges in circuit fabrication. We take the best of both worlds by developing a hybrid nanofabrication technique[1], allowing to integrate III/V semiconductor nanowire quantum dots[2] into silicon-based photonics. I will present on-chip generation, spectral filtering, and routing of single-photons from selected single and multiple nanowire quantum emitters all deterministically integrated in a CMOS compatible silicon nitride photonic circuit.[3] Using tunable ring resonators, we are able to de-multiplex emitted single photons from independent quantum emitters and route the photons to different ports on the photonic circuits. Our second generation chips are fabricated on piezoelectric substrates allowing to strain-tune the quantum dot properties as well as the ring resonator resonances.[4]

Our new approach eliminates the need for off-chip components, opening up new possibilities for large-scale quantum photonic circuits with different kinds of on-chip single- and entangled-photon sources.

References

[1] I. Esmaeil Zadeh et al., Nano Letters 16(4), 2289-2294 (2016).
[2] M. A. M. Versteegh et al., Nature Communications 5, 5298 (2014).
[3] A. W. Elshaari et al., Nature Communications 8, 379 (2017).
[4] A. W. Elshaari et al., Nano Letters 18(12), 7969-7976 (2018).

Parity-Time Symmetry in Chiral Metamaterials

Maria Kafesaki[1,2,*], Sotiris Droulias[1,2], Ioannis Katsantonis[1,2], Costas Soukoulis[2,3], Eleftherios Economou[2,4]

[1]*University of Crete, Dept. of Materials Science and Technology, Heraklion, Greece*
[2]*Foundation for Research and Technology Hellas (FORTH), Institute of Electronic Structure and Laser, Heraklion, Greece*
[3]*Ames Lab and Department of Physics and Astronomy, Iowa State University, Ames, IA, USA*
[4]*University of Crete, Department of Physics, Heraklion, Greece*

[*]e-mail: kafesaki@iesl.forth.gr

Optical systems respecting Parity-Time (PT) symmetry are receiving more and more attention in recent years; this is mainly due to their novel and unique physical phenomena involved and their associated great potential in applications. Such phenomena include unidirectional invisibility, simultaneous coherent perfect absorption and lasing, loss-induced transparency, asymmetric propagation and diffraction effects etc.

The practical realization of PT-symmetric systems and the demonstration of their related phenomena are greatly facilitated by the concepts and ideas of the metamaterials research field. Metamaterials (artificial materials with engineerable optical properties) and their designing rules enable the realization of structures with almost arbitrary values of optical parameters, e.g. permittivity and permeability, including the extreme parameters often required in the practical realization of PT-symmetric systems.

A category of metamaterials which, although important, is highly unexplored under the concept of PT-symmetry is chiral metamaterials, i.e. metamaterials where the structure cannot be superimposed with its mirror image. In chiral metamaterials, where magnetoelectric coupling plays a crucial role, not only the permittivity and permeability, but also the chirality parameter (the parameter which quantifies the magnetoelectric coupling) plays important role in the wave propagation, enabling giant in many cases polarization control.

The exploration of the fascinating combination of chirality and PT-symmetry is the main topic of the work discussed here.[1] In particular, in this work we examined (a) the possibility to combine chirality and PT-symmetry, which was not clear taking into account the currently known and reported required conditions, (b) the material parameter conditions necessary to achieve PT-symmetry in chiral media, and (c) the unique physical phenomena that become possible in PT-symmetric chiral systems. Such phenomena not only include all the effects that are possible in non-chiral PT-symmetric systems but also can combine them with waves of arbitrary polarization, from linear to circular. Moreover, direction dependent polarization and propagation effects were observed, which empower PT-symmetric chiral metamaterials with unique power in the wave propagation and polarization control.

References

[1] "Chiral metamaterials with PT symmetry and beyond", S. Droulias et. al., submitted to Phys. Rev. Lett.

Novel CVD Modified Nanoporous Separation and Catalytic Membranes and Their Applications

Nick Kanellopoulos

National Center for Scientific Research "Demokritos", Agia Paraskevi, Athens, Greece

e-mail: n.kanellopoulos@inn.demokritos.gr

Novel CVD methodologies have been developed for the growth of single – and multi-wall oriented carbon nanotubes with outside diameter ranging from 0.72 nm to 200 nm using different internal diameter templates. One of the major applications is to mimick the function of biological aquaporins and achieve their astonishing large water permeation rates. In addition low pressure and low energy demand forward osmosis and nanofiltration mixed-matrix polymeric hollow fibre membranes based on oriented graphene oxide or SWCNT are developed to replace the conventional high energy demand reverse osmosis systems. The same methodology is applied for the development of high and low CO^2 permeance membranes needed for the development of low energy demand multi-stage CO^2 capture membrane systems.

Another major application of the CVD methodologies is the development of carbon-nanotube catalytic membranes containing Single Atom Catalysts with tailored nanostructure to develop cost-effective membrane intensified systems for the cost-effective conversion of CO^2 to fuels.

Influence of Thermal Annealing and Nickel Addition on the Magnetic Properties of Co/CoO Multilayers

D. I. Anyfantis[1], N. Kanistras[1*], A. Barnasas[1], D. Trachylis[2], C. Politis[3], P. Poulopoulos[1]

[1]*Materials Science Department, University of Patras, Patras, Greece*
[2]*Buisiness Development, Patras Science Park, Patras, Greece*
[3]*Department of Materials Science and Engineering, University of Texas at Arlington, Arlington, TX, USA*

[*]e-mail: n.kanistras@upnet.gr

Cobalt-based multilayers are grown via radiofrequency magnetron sputtering with the use of one Co target and natural oxidation. They have shown excellent multilayer sequence down to a multilayer period of 2.1 nm. The Co layers are continuous, fully textured {111} and have the face centered cubic structure.[1]

In the present work, we investigate the influence of mild thermal annealing and of nickel addition on the magnetic properties of Co/CoO multilayers. Hysteresis loops are recorded to study the magnetic anisotropy. The experiments were performed primarily with a MOKE (Magneto-Optic Kerr Effect Magnetometry). Co/CoO multilayers were annealed up to 250℃ for maximum time of one and a half hour. They were mainly in-plain magnetized. Decreased remanence in the parallel geometry for multilayers with thin Co layers could be attributed to antiferromagnetic exchange. The interaction between CoO and Co at the CoO/Co interfaces results in the appearance of unusual magnetic loops with negative remanence (invert hysteresis effect) in the perpendicular measuring geometry. Such loops are not frequently encountered and their observation is attributed to the exchange coupling between a soft ferromagnetic phase and a hard antiferromagnetic phase at the Co/CoO interfaces

Acknowledgements

D.T. and P.P. acknowledge Patras Science Park and its Clean Tech Energy Innovation Hub.

References

[1] "Naturally Produced Co/CoO Nanocrystalline Magnetic Multilayers: Structure and Inverted Hysteresis", Francesca Santarossa et al., J. Nanosci. Nanotechnol. 16, 4960–4967, (2016).

Magnetic Metamaterials

Vassilios Kapaklis

Department of Physics and Astronomy, Uppsala University, Uppsala, Sweden

*e-mail: vassilios.kapaklis@physis.uu.se

Metamaterials are artificial materials with an engineered periodic structure aiming in properties which cannot be found in nature. Lithographically nano-patterned magnetic materials can result in fascinating behaviour exploiting the magnetic dipolar interactions between individual elements. The emergent properties in such systems are distinctly different from those of their constituent components, driven by the collective dynamics of the interacting elements and respond to external stimuli such as magnetic fields or temperature. Further enhanced functionality can be realised exploiting the fact that the periodicity and element size in such nano-patterned magnetic arrays matches well the wavelengths of visible light, thus providing an ideal setting for the investigation of the interaction of light with magnetic metamaterials, through plasmons. In my talk, I will present approaches for the fabrication of magnetic metamaterials using thin films. Recent works have demonstrated the creation of reconfigurable magnetic structures which undergo phase transitions and exhibit dynamics on adjustable length- and energy-scales.[1-4, 7-9] The interaction of visible light with such structures also reveals the opportunity of "steering" light and altering optical properties using such magnetically reconfigurable metasurfaces.[5,6]

References

[1] V. Kapaklis et al., New J. Phys. 14, 035009 (2012).
[2] A. Farhan et al., Nature Physics 9, 375 (2013).
[3] V. Kapaklis et al., Nature Nanotechnology 9, 514 (2014).
[5] E. Melander et al., Appl. Phys. Lett. 101, 063107 (2012).
[6] M. Rollinger et al., Nano Letters 16, 2432 (2016).
[7] M. S. Andersson et al., Scientific Reports 6, 37097 (2016).
[8] C. Nisoli et al., Nature Physics 13, 200 (2017).
[9] E. Östman et al., Nature Physics, 14, 375 (2018).

Tailoring Quantum Dots and Photonic Crystals for Integrated Photonics Applications

Eli Kapon

Laboratory of Physics of Nanostructures, Institute of Physics
Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

*e-mail: eli.kapon@epfl.ch

Emerging quantum technologies based on non-classical states of light are promising for applications such as quantum communications, computing and sensing. Basic building blocks in this platform are sources of single and entangled photons, as well as optical components for single photon manipulation and processing. This talk reviews an approach for producing integrated photonic chips for single photon generation, routing and switching, based on the monolithic integration of semiconductor quantum dots (QDs) and photonic crystal (PhC) waveguides and cavities.

The site controlled QDs are made by metallorganic vapor phase epitaxy (MOVPE) of (In)GaAs/(Al)GaAs heterostructures on GaAs susbstartes patterned with arrays of inverted pyramids. Besides positioning accuracy at the nm level, these pyramidal QDs can be tailored in emission wavelength and polarization. The PhC devices are made in thin (~200nm) GaAs membranes perforated with air-holes, which provides a means for tailoring the 2D effective index and hence the confined mode structure (near field patterens, resonance frequencies, …). This photonic mode tailoring is also essential for adjusting the light-matter interaction with QD-confined excitons integrated with these PhC structures.

We developed a scheme with which systems of site-controlled, pyramidal QDs can be monolithically integrated with membrane PhC cavities and waveguides. Relative alignment precision of better than 50nm between the ~20nm-sized QDs and the PhC mode features are demonstrated. Several integrated devices are demonstrated and investigated,[1,2] including: up to four QD systems coupled to the same PhC cavity mode, five QDs multiplexed into a common PhC waveguide for increasing the single photon flux, QDs coupled to a system of a PhC cavity coupled to a PhC waveguide for optimizing single photon extraction and transfer on chip, and Tilted-potential PhC cavities supporting Airy Bloch modes. Prospects for more complex functional single-photon devices based on ths approach will be presented.

References

[1] "Deterministic radiative coupling of two semiconductor quantum dots to the optical mode of a photonic crystal nanocavity", M. Calic, C. Jarlov, P. Gallo, B. Dwir, A. Rudra and E. Kapon, Scientific Reports 7, 4100 (2017).

[2] "Deterministic coupling of a system of multiple quantum dots to a single photonic cavity mode", A . Lyasota, C. Jarlov, P. Gallo, A. Rudra, B. Dwir and E. Kapon, Appl. Phys. Lett. 111, 053103 (2017)

[3] "Symmetry guide to ferroaxial transitions," J. Hlinka et al., Phys. Rev Lett, accepted (2016).

Nano-Scaled Activated Carbon as Potential Filler for CO_2 Selective Mixed Matrix Membranes

D.S. Karousos*, A.A. Sapalidis, E.P. Kouvelos, E.P. Favvas

Materials and Membranes for Environmental Separation Laboratory, Institute of Nanoscience and nanotechnology, NCSR "Demokritos", Aghia Paraskevi, Attica, Greece

*e-mail: d.karousos@inn.demokritos.gr

A coconut-shell derived activated carbon is preliminarily examined regarding its usability as filler material in mixed matrix polymeric membranes for CO_2/CH_4 and CO_2/N_2 gas separations. The CO_2-selective adsorption on the filler material is expected to have a beneficial effect on the overall gas separation factor of the polymeric membranes.

In particular, grains of the activated carbon were grinded to obtain a fine powder, in order to become miscible and dispersible in a polymer solution for mixed matrix membrane preparation. The as prepared powder microstructure was characterized by FESEM and LN_2-porosimetry and pore size distribution was then calculated by DFT-analysis. Single gas gravimetric adsorption was implemented to obtain adsorption isotherms of the filler material at the working conditions of the membranes for each gas. Adsorption isotherms were fitted using Toth and Sips models, which are semi-empirical equations that apply to heterogeneous adsorbent surfaces with different adsorption sites. Based on the above equations CO_2/N_2 and CO_2/CH_4 gas separation factors were calculated vs. pressure and found to decline starting from values up to 8 and 3, respectively. Heat of CO_2 adsorption was also predicted by regression of four adsorption isosteres (at temperatures 298, 323, 343, 373K) with the Virial equation and results showed that adsorption is physical, with heat of adsorption at zero loading reaching 27.3 kJ/mol. In addition, from the abrupt loading increase between pressure steps of the gravimetric measurements, it can be concluded that adsorption kinetics are very fast.

Overall, the examined nano-scaled activated carbon is a low-cost, CO_2-selective, physically and rapidly adsorbing material. Based on these characteristics it is a promising candidate material for use as filler in polymeric mixed matrix membranes.

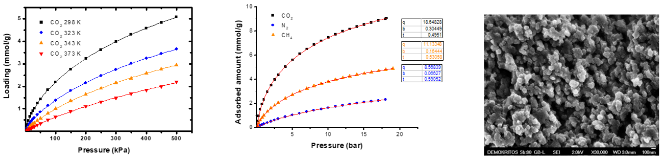


Figure 1. CO_2 adsorption isotherms at 298, 323, 343 and 373K (left), CO_2, N_2 and CH_4 adsorption isotherms at 298K (center), and SEM image of grinded activated carbon (right).

Acknowledgements

The project "CO_2 separation by using mixed matrix, based on nano-carbon membranes (GG-CO_2), T2ΔΓΕ-0183, is acknowledged for the financial support.

References

[1] D.S. Karousos et al., Separ. Sci. Techn. 51 (2016) 83–95; [2] E.P. Favvas et al., Sepur. Purif. Technol. 132 (2014) 336–345.

Enhanced and Metastable Magnetism Directly Probed in Individual Nanoparticles

Armin Kleibert

Swiss Light Source, Paul Scherrer Institute, Switzerland

e-mail: armin.kleibert@psi.ch

Magnetic nanoparticles show a variety of unique properties such as superparamagnetism, magnetic single domain states, enhanced magnetic moments and magnetic anisotropies, which are not found in their bulk counterparts. These phenomena make magnetic nanoparticles highly interesting for many applications ranging from medicine to data storage.[1] However, despite intense efforts a clear understanding of the size-dependent evolution of the magnetic properties of nanoparticles is still lacking even for nanoparticles of the canonical 3d transition metals. This is partly because most experiments average the properties of a large number of particles. However, even in mono-disperse samples, nanoparticles can exhibit considerable scattering on the magnetic properties, e.g., due to variations in size, shape and structure or due to particle-particle and/or particle-substrate interactions, which render a simple correlation between averaged ensemble properties and the size-dependent behavior of individual particles difficult.

To tackle this issue we have pushed X-ray photoemission electron microscopy for the magnetic characterization of individual nanoparticles and their distribution within large ensembles.[2-4] The magnetic properties of the particles are further correlated with their actual size and morphology by applying complementary scanning electron microscopy and atomic force microscopy on the very same nanoparticles. This approach revealed unexpected spiraling spin structures and metastable states with exceptionally high magnetic anisotropy in pure iron nanoparticles.[2,3] Similarly, we found strongly enhanced and metastable magnetic properties in cobalt nanoparticles irrespective of their size.[4] Our data suggest that the origin of this behavior has to be sought in the actual microstructure of the particles, which so far remained difficult to assess in nanoparticle magnetism studies. To address this issue we have developed an approach to combine X-ray photoemission electron microscopy with atomic resolution scanning transmission electron microscopy. Our first results using this approach on individual cobalt nanoparticles will be presented.

References

[1] "Magnetic nanoparticles: synthesis, protection, functionalization, and application", A. H. Lu et al., Angew. Chem. Int. Ed. 45, 1222 (2007).

[2] "Size-Dependent Spin Structures in Iron Nanoparticles", A. Fraile Rodríguez et al., Phys. Rev. Lett. 104, 127201 (2010).

[3] "Direct Observation of Magnetic Metastability in Individual Iron Nanoparticles", A. Balan et al., Phys. Rev. Lett. 112, 107201 (2014).

[4] "Direct observation of enhanced magnetism in individual size- and shape-selected 3d transition metal nanoparticles", A. Kleibert et al., Phys. Rev. B 95, 195404 (2017).

Cold-Electron Transport at Room Temperature for Energy-Efficient Electronics

Seong Jin Koh

University of Texas at Arlington, Arlington, TX, USA

e-mail: skoh@uta.edu

At non-zero temperatures, electrons are thermally excited in accordance with the Fermi-Dirac distribution. This electron thermal excitation is usually not a desirable phenomenon that obscures or wipes out novel low-temperature characteristics of various electron systems. For example, the Coulomb blockade in single-electron transport or spin-valve effect in spintronic systems could disappear when the temperature is elevated from low temperatures to room temperature. The Fermi-Dirac electron thermal excitation is also the root cause of the excessive heat dissipation (energy consumption) of the advanced metal-oxide-semiconductor field-effect transistors (MOSFETs). This talk presents a new approach that effectively suppresses the Fermi-Dirac electron thermal excitation at room temperature. This is accomplished using a discrete energy state of a quantum well, which filters out thermally excited electrons and allows only energy-filtered cold electrons to pass through. We find that the quantum well state effectively suppresses the electron energy distribution such that the effective electron temperature becomes ~45 K at room temperature without external cooling. We demonstrate this suppressed electron thermal distribution by investigating electron transport through CdSe quantum dots, where differential conductance measurements show extremely narrow peaks, with full widths at half maximum of only ~15 mV at room temperature. The suppressed electron thermal excitation also enables realization of single-electron transport at room temperature without external cooling. We observe clear Coulomb staircase and Coulomb oscillations at room temperature for single-electron transistors in which 10 nm Au nanoparticles are used as the Coulomb islands. The effective electron temperature of ~45K suggests that if such low-temperature electrons are implemented, transistors can be switched on and off with a subthreshold swing of ~10 mV/decade, allowing transistors to operate with extremely little energy. On-going effort to fabricate such transistors will be discussed.

Computationally Designed Amyloid Materials as Scaffolds for Biomedical and Environmental Uses

C. Kokotidou[1,2*], S.V.R. Jonnalagadda[3], A.A. Orr[3], M. Seoane-Blanco[4],
C.P. Apostolidou[1,2], M. J. van Raaij[4], A. Llamas-Saiz[5], P. Tamamis[3], A. Mitraki[1,2]

[1]Department of Materials Science and Technology, University of Crete, Heraklion, Greece
[2]Institute of Electronic Structure and Laser (IESL), FORTH, Heraklion, Greece
[3]Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX, USA
[4]Departamento de Estructura de Macromoleculas, CSIC, Madrid, Spain
[5]X-Ray Unit, RIAIDT, University of Santiago de Compostela, S. de Compostela, Spain

[*]e-mail: chkokotidou@materials.uoc.gr

Amyloid self-assembly refers to the conversion of specific proteins and peptides from their native functional states into long unbranched fibers that are characterized by a cross-beta sheet quaternary structure. Amyloid formation has been associated with a range of human disorders, including Alzheimer's disease, prion and Parkinson's disease. Fibrous amyloid structured aggregates are not only involved in misfolding and disease, but can also be exploited for the formation of novel functional amyloid biomaterials. Amyloid biomaterials have significantly advantageous properties, which among others include their easy fabrication, and the capacity to tune their properties by changes at their sequence level. Naturally occurring peptide sequences extracted from amyloid proteins or beta-sheet protein regions can self- assemble outside the context of the entire sequence into amyloid fibrils and can serve as scaffolds for novel biomaterials. Peptide sequences GAIIG and GAITIG are part of the amyloid-beta (Aβ) peptide, linked to Alzheimer's disease, and the adenovirus fiber shaft, respectively.

In this study, we took advantage of their unique self-assembling properties and with the aid of computational methods we applied suitably selected modifications at flexible positions, to tune the properties of amyloid forming peptides in order to discover novel functional biomaterials in two different applications. In the first application, our computational and experimental results suggest interaction of a designed beta-breaker peptide GAIPIG with Alzheimer's Aβ peptide, delaying the aggregation of the peptide Aβ1-40 in vitro and considering it as a potential inhibitor of amyloid formation. In the second application, we present novel amyloid biomaterials that are capable of binding and capturing cesium ions at neutral and low pH conditions, enabling their use as scaffolds for the removal of cesium ions from nuclear waste or blood.

References

[1] "A novel amyloid designable scaffold and potential inhibitor inspired by GAIIG of amyloid beta and the HIV-1 V3 loop". C. Kokotidou, S.V. Jonnalagadda et al. FEBS Letters 592 1777-1788 (2018)
[2] "Computational Design of Functional Amyloid Materials with Cesium 2 Binding, Deposition, and Capture Properties" S.V. Jonnalagadda, C. Kokotidou et al, J. Phys. Chem. B, 122 (30), 7555–7568 (2018)

Effect of Rotation on the Adsorption Process

Ramonna I. Kosheleva[1,2*], Athanasios C. Mitropoulos[1], Thodoris D. Karapantsios[2], Margaritis Kostoglou[2]

[1]Hephaestus Advanced Laboratory, Eastern Macedonia & Thrace Institute of Technology, Kavala, Greece
[2]Division of Chemical Technology, School of Chemistry, Aristotle University, Thessaloniki, Greece

*e-mail: kosheleva.ramonna@gmail.com

Rotation can intensify a number of industrial processes resulting in an increase in production efficiency and a decrease in energy consumption and environmental footprint. Although, several studies have focused on rotating packed beds, only a few have examined the effect of rotation on the adsorption process.

In this work, CO_2 adsorption on activated carbon under rotation is investigated. To this end, a special device has been developed allowing rotation at a maximum speed of 5,000 rpm while the pressure difference is recorded by a pressure transducer at constant temperature. An amount of 3.6 g of commercially available activated carbon with surface area of ~1000 m^2/g is used as an adsorbent. A vacuum of 10^{-3} mbar is achieved and CO_2 is introduced at a starting pressure of 5,665 mbar to the system. A long equilibration time of 95h, at room temperature of 25℃±1℃ is allowed. After that, the system is rotated at maximum speed for 60s and left to rest for 52 hours. A new rotation is conducted under the same conditions and further 27 hours rest is attained. Figure 2 shows the result. Rotation facilitates an additional adsorption of more than 11%. Lower temperatures are expected to enhance the process.

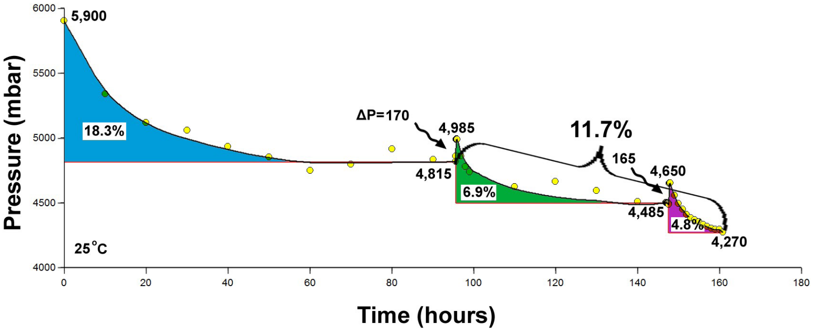


Figure 1. Effect of rotation on gas adsorption. The blue area shows the adsorption achieved without rotation (18,3%). Green area corresponds to additional adsorption (6,9%) achieved after first rotation. Magenta area corresponds to even further adsorption (4,8%) after second rotation. Please note that the given percentages are differential (not cumulative). ΔP peaks are attributed to temperature increase due to rotation friction.

References

[1] "A rotating sample cell for in situ measurements of adsorption with x-rays", Ramonna I. Kosheleva et al, Rev. Sci. Instrum. 89, 123113 (2018).

Vapor Adsorption in Conjunction with SAXS Under a Rotational Field

Ramonna I. Kosheleva[1,2*], Thodoris D. Karapantsios[2], Margaritis Kostoglou[2],
Evangelos P. Favvas[3], Athanasios C. Mitropoulos[1]

[1]Hephaestus Advanced Laboratory, Eastern Macedonia & Thrace Institute of Technology, Agios Lukas, Kavala, Greece
[2]Division of Chemical Technology, School of Chemistry, Aristotle University, Thessaloniki, Greece
[3]Institute of Physical Chemistry, NCSR Demokritos, Agia Paraskevi Attikis, Greece

*e-mail: kosheleva.ramonna@gmail.com

The effect of rotation of vapor adsorption on porous glass is examined by in-situ measurements of small angle x-ray scattering (SAXS). The experiment was conducted and analyzed for both static and rotating conditions. The rotation of the sample was achieved by a specially designed rotating cell described elsewhere; maximum rotational speed was 2,150 rpm.[1] In order to reveal the impact of rotation, a contrast matching technique was applied. Vycor 7930 was used as the adsorbent and CH_2Br_2 as adsorbate having the same electron density with the solid. Pores are partially filled at relative pressure of 0,4. Results obtained from SAXS measurements are presented in Fig.1.

As it is shown, rotation increases the adsorption capacity of the porous matrix by more than 14%. The result confirms that rotation leads to adsorbate contraction and vapor molecules rearrangement; that is, more free space is gained through the mechanism presented in Fig.2. The most interesting outcome is that the specific mechanism is irreversible; the new arrangement of molecules is preserved after rotation (see wet-static after rotation curve in Fig.1).

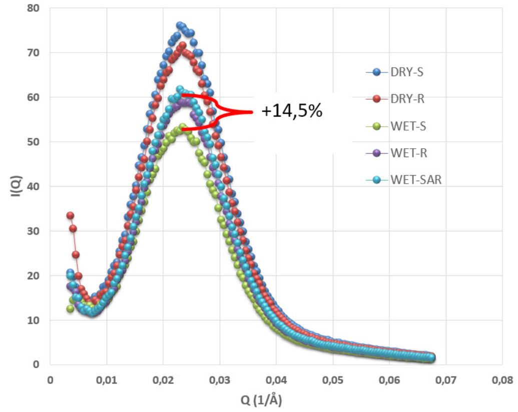


Figure 1. SAXS spectra of five cases: DRY-S (static); DRY-R (rotating); WET-S, WET-R and WET-SAR (static after rotation).

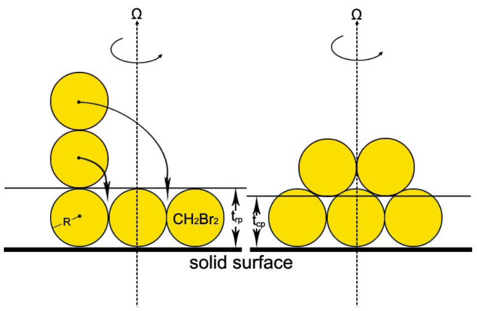


Figure 2. The proposed mechanism of vapor molecules rearrangement.

References

[1] "A rotating sample cell for in situ measurements of adsorption with x-rays", Ramonna I. Kosheleva et al., Rev. Sci. Instrum. 89, 123113 (2018).

Multi-Sensitive Nano-Containers as Potential Drug Delivery Systems Against Cancer

Theodora S. Koutsikou[1,2*], Elias Sakellis[1], N. Boukos[1], G. Mitrikas[1], E. K. Efthimiadou[1,2]

[1]*Institute of Nanoscience and Nanotechnology, National Center for Scientific Research "Demokritos", Athens, Greece*
[2]*Department of Chemistry, National and Kapodistrian University of Athens, Athens, Greece*

[*]e-mail: d-koutsikou@hotmail.com

Within the most recent decade, progress in the design of controlled drug delivery systems (DDSs) has resulted in tremendous development in the treatment of numerous diseases. In this study, a kind of 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 small size of this structure allows nano-carriers to overwhelmed various biological barriers and accomplish passive targeting through the enhanced permeability and retention (EPR) effect, which facilitates the delivery of drugs particularly to the intended tissues without provoking unfavorable reactions in cancer therapy. 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.

Acknowledgements

We acknowledge support by the project MIS 5002567, under the “Action for the Strategic Development on the Research and Technological Sector,” funded by the Operational Program “Competitiveness, Entrepreneurship and Innovation” (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

References

[1] E.K. Efthimiadou, C. Tapeinos, P. Bilalis, G. Kordas, Journal of Nanoparticle Research, 13 (2011) 6725-6736.

Microbubble Agents for Biomedical Applications: Focus on Nanomechanics and the Nanoshell

Vasileios Koutsos

Institute for Materials and Processes, School of Engineering, The University of Edinburgh, Edinburgh, UK

Stable, haemodynamically inert, hollow, micrometer-size spheres composed of an ultrathin nanoscale biocompatible shell (nanoshell) which encapsulates an inert gas are used as ultrasound contrast agents and are normally referred to as microbubbles. They are smaller than the smallest blood vessel of a human body to allow improved visualization of the vascular bed and differentiate vascular patterns of tumours non-invasively. Such nanoshelled microstructures can be used as carriers for drug/gene delivery, which is a topic of much current interest in biomedical research. Furthermore, with appropriate surface modification such microbubbles can acquire targeting capability for certain cell types (e.g. cancerous cells). Their nanomechanical properties are extremely important since they have to be stable for considerable time until they rupture/degrade under specific conditions in order to release their load in the right place and at the right time. Moreover, materials at the nanoscale (such as thin-shell structures) may behave differently to those on the macroscale, so predicting their mechanical properties presents a challenge. We have conducted a systematic study of both hard-shelled, polymeric-based and soft-shelled, phospholipid-based microbubbles employing nanocompression by performing atomic force microscopy (AFM) force-distance curves. Individual microbubbles of different diameter were compressed from few nanometres up to approx. 50% of their initial diameter. We have performed multiple compressions on individual microbubbles to assess their mechanical robustness and measured their stiffness. Furthermore, we used different mechanical theories to estimate the elastic modulus of the microbubble shell. In the case of phospholipid-based shells, we have also estimated the effective elastic modulus of the whole microbubble as (if it was) a homogenous object. We compare and discuss our results with other phospholipid systems, namely supported lipid membranes, vesicles, cells and other recent AFM studies of lipid-coated microbubbles. Furthermore, as microbubble science is expanding to biological targeting and drug/gene delivery, we investigated the characteristics of molecular targeting using modified lipid-shelled microbubbles (biotin–avidin chemistry and the CD31 antibody) to probe individual Sk-Hep1 hepatic endothelial cells. The modified (targeted) microbubbles provide a single distribution of adhesion forces with a median of 93 pN. This interaction was assigned to the CD31 antibody–antigen unbinding event and proves the capability of single microbubbles to target cell lines. Moreover, we will present an investigation on the structure and thickness of the phospholipid-based nanoshell based on measurements obtained by using AFM and cryogenic scanning electron microscopy (cryo-SEM).

Hybrid Inorganic Nanomaterials for (Photo) Electrochemical Energy Conversion, Generation of Fuels and Charge Storage

Pawel J. Kulesza*, Iwona A. Rutkowska, Ewelina Szaniawska, Justyna Lubera

Faculty of Chemistry, University of Warsaw, Warsaw, Poland

*e-mail: pkulesza@chem.uw.edu.pl

Our research interests aim at establishing structure/property relations leading to rational designs of functionalized materials for efficient electrocatalysis and electrochemical energy conversion and storage. Graphene is, in principle, a promising material for consideration as component of electrocatalytic materials, particularly with respect to reduction of oxygen, an electrode reaction of importance to low-temperature fuel cell technology. Different concepts of utilization, including nanostructuring, doping, admixing, preconditioning, modification or functionalization of various graphene-based systems for catalytic electroreduction of oxygen are considered.

There has been growing interest in the electrochemical reduction of carbon dioxide, a potent greenhouse gas and a contributor to global climate change. Given the fact that the CO_2 molecule is very stable, its electroreduction processes are characterized by large overpotentials. To optimize the hydrogenation-type electrocatalytic approach, we have proposed to utilize nanostructured metallic centers (e.g. Cu, Pd or Ru) in a form of highly dispersed and reactive nanoparticles generated within supramolecular network of various polytungstate systems. Among important issues are the mutual completion between hydrogen evolution and carbon dioxide reduction and specific interactions between coordinating centers and metallic sites. Another possibility to enhance electrocatlytic reactions is to explore direct transformation of solar energy to chemical energy using transition metal oxide semiconductor (WO_3, Cu_2O) materials (e.g. toward water splitting or photoelectrochemical reduction of carbon dioxide mostly to methanol).

The potential materials for solid-state electrochemical applications including charge storage are expected to contain three-dimensionally distributed highly concentrated redox centers between which fast electron self-exchange (hopping) is feasible. The applicable materials also must host mobile counter-ions that are capable of providing charge balance during electron transfers, thereby serving the same purpose as the supporting electrolytes in conventional electrochemistry. The emphasis is on the elements of dynamics for the efficient delivery of charge and on reactivity of the 'redox conducting' (certain polyoxometallates or metal oxide) materials.

We will also consider nanoelectrocatalytic systems permitting effective operation of the iodine-based charge relays in dye sensitized solar cells. The ability of palladium or platinum nanostructures to induce splitting of I-I bonds in the iodine (triiodide) molecules is explored here to enhance electron transfers in the triiodide/iodide-containing 1,3-dialkylimidazolium room-temperature ionic liquids.

Carbon Microspheres from Agricultural Wastes

Efstathios V. Liakos, Athanasios C. Mitropoulos, George Z. Kyzas*

Hephaestus Advanced Laboratory, Eastern Macedonia and Thrace Institute of Technology, Kavala, Greece

*e-mail: kyzas@teiemt.gr

In this study, the synthesis of carbon microspheres were investigated via direct pyrolysis of agrofood wastes from restaurants. Potato peels (PP) were used as precursors and mineral oil as reagent for the preparation of carbon spheres. Briefly, the PP were washed with distilled water in order to remove dust and impurities and thereafter carbonized at 500℃. Then, the yielded amorphous carbon from PP was impregnated with H_3PO_4 under stirring for 24 h. In addition, the obtained activated carbon was dried in an oven furnace in order to evaporate the larger amount of H_3PO_4 and then oven carbonized in a porcelain crucible for the second activation process at high temperature. Thereafter, the obtained activated carbon was grounded in a mortar and sieved with a 400 mesh screen (37 μm) to obtain the powder form of activated carbon from PP. In addition, the process contains the closure of powder form activated carbon in a 316 stainless steel tube with 3% mineral oil. The closure process of powder form activated carbon and mineral oil was achieved by welding the top and bottom of 316 stainless steel tube. Finally, the process contains the pyrolysis of 316 stainless steel tube in an oven where only at 1100℃ was achieved the decomposition of activated carbon in carbon microspheres as it is clearly confirmed with SEM microscopy (Fig. 1). The initial sample characterization was achieved with SEM-EDX, XRD, BET and FTIR.

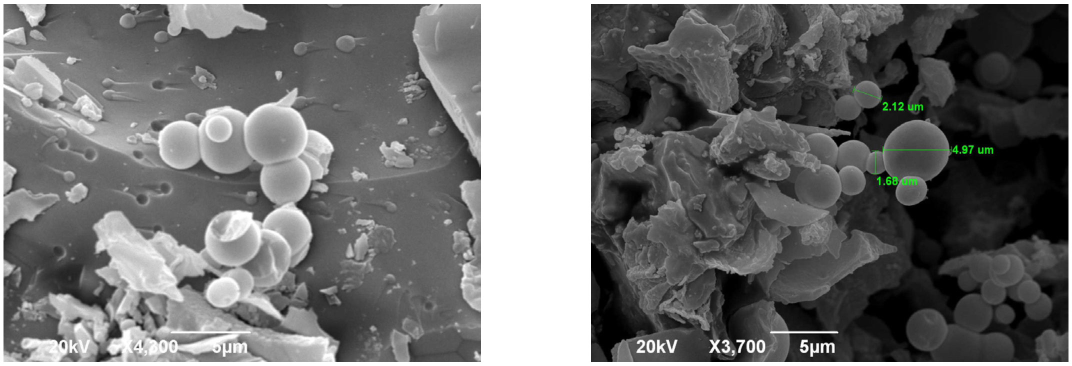


Figure 1. SEM images after decomposition of activated carbon and transformation in carbon microspheres at 1100℃

Acknowledgements:

This research was co-financed by the project "Development of NAnotechnology-enabled "next-generation" MEmbranes and their applications in Low-Energy, zero liquid discharge Desalination membrane systems"/NAMED, Τ2ΔΓΕ-0597.

Curvilinear Magnetism

Denys Makarov

Helmholtz-Zentrum Dresden-Rossendorf e.V., Dresden, Germany

e-mail: d.makarov@hzdr.de

There is one aspect, which is in common to the majority of fundamentally appealing and technologically relevant novel magnetic materials, namely their non-collinear magnetic textures like spin spirals, chiral domain walls or skyrmions.[1] These textures are typically driven by the Dzyaloshinskii-Moriya interaction (DMI). Recently, curvature effects emerged as a novel mean to design chiral magnetic properties by relying on extrinsic parameters, e.g. geometry of thin films.[2] In particular, novel effects occur when the magnetization is modulated by curvature leading to new magnetization configurations and is implications on the spin dynamics due to topological constraints. Advances in this novel field solely rely on the understanding of the fundamentals behind the modifications of magnetic responses of 3D-curved magnetic thin films[3,4] and nanowires.[5] The lack of an inversion symmetry and the emergence of a curvature induced effective anisotropy and DMI are characteristic of curved surfaces, leading to curvature-driven magnetochiral effects and topologically induced magnetization patterning.[6,7] The application potential of 3D-shaped objects is currently being explored as mechanically reshapeable magnetic field sensorics[8] for flexible interactive electronics,[9,10] spin-wave filters and high-speed racetrack memory devices.[11] The fundamentals as well as application relevant aspects of curvilinear nanomagnets will be covered in this presentation.

References

[1] "The 2017 Magnetism Roadmap", D. Sander et al., J. Phys. D 50, 363001 (2017).

[2] "Magnetism in curved geometries", R. Streubel, et al., J. Phys. D 49, 363001 (2016).

[3] "Curvature Effects in Thin Magnetic Shells", Y. Gaididei et al., Phys. Rev. Lett. 112, 257203 (2014).

[4] "Multiplet of Skyrmion States on a Curvilinear Defect: Reconfigurable Skyrmion Lattices", V. Kravchuk et al., Phys. Rev. Lett. 120, 067201 (2018).

[5] "Mesoscale Dzyaloshinskii-Moriya interaction: geometrical tailoring of the magnetochirality", O. M. Volkov et al., Scientific Reports 8, 866 (2018).

[6] "Coupling of Chiralities in Spin and Physical Spaces: The Möbius Ring as a Case Study", O. V. Pylypovskyi et al., Phys. Rev. Lett. 114, 197204 (2015).

[7] "Curvature-Induced Asymmetric Spin-Wave Dispersion", J. A. Otalora et al., Phys. Rev. Lett. 117, 227203 (2016).

[8] "Shapeable magnetoelectronics", D.Makarov et al., Appl. Phys. Rev. 3, 011101 (2016).

[9] "Magnetosensitive e-skins with directional perception for augmented reality", S. Canon Bermudez et al., Science Advances 4, eaao2623 (2018).

[10] "Electronic-skin compasses for geomagnetic field driven artificial magnetoreception and interactive electronics", S. Canon Bermudez et al., Nature Electronics 1, 589 (2018).

[11] "Beating the Walker Limit with Massless Domain Walls in Cylindrical Nanowires", M. Yan et al., Phys. Rev. Lett. 104, 057201 (2010).

The Impact of Imaging Technology in Shaping Current Neuroscience Research and Medical Practice

Nikos Makris

Center for Morphometric Analysis, Department of Psychiatry
Harvard Medical School Boston, MA, USA

Recent developments in neural systems conceptualization and characterization using current neuroimaging technology has advanced considerably our understanding of brain structure and function in humans. The integration of structure and function is a critical goal in basic and clinical neuroscience and multimodal neuroimaging offers a unique possibility to achieve this objective. Importantly, recent neuromodulatory therapeutic interventions applied in neurology, psychiatry and neurosurgery such as transcranial magnetic stimulation (TMS) and deep brain stimulation (DBS) use cutting edge diffusion MRI (dMRI) tractography and other neuroimaging modalities to outline precisely neural systems and thus tailor treatments more precisely to the individual subject. Current automated methodologies are very useful in routine neuroimaging work given their capability in making big data analyses and multimodal imaging feasible and, most importantly, cost efficient.

Multiple Fluorophores in the Emission of Cesium Lead Bromide Perovskite Nanocrystals

Y. Zhang[1,2], T. Guo[4], H. Yang[1], R. Bose[4], L. Liu[3], J. Yin[1], Y. Han[3], O. M. Bakr[3], O. F. Mohammed[1], A. V. Malko[4*]

[1]*Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia*
[2]*Institute for Advanced Interdisciplinary Research (iAIR), University of Jinan, Jinan, Shandong, China*
[3]*KAUST Catalysis Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia*
[4]*Department of Physics, The University of Texas at Dallas, Richardson, TX, USA*

[*]e-mail: anton.malko@utdallas.edu

Perovskite nanocrystals (PNCs) have attracted a lot of scientific interest in the recent years due to the extraordinary optical and electronic properties such as compositional and structural versatility, tunable bandgap, high photoluminescence (PL) quantum yield (QY) and facile chemical synthesis. Among them, all inorganic Cs_nPbX_m perovskites have attracted particular attention due to enhanced light emission and photo/thermal stability. Lower dimensionality polymorphs can be formed by manipulation of chemical- synthesis conditions where Cs^+ can stabilize 3D $[PbX_6]$ framework, resulting in 2D (nanosheet), 1D (nanowire) and 0D (nanodot) internal octahedra arrays within the bulk of the perovskite. The gamut of available experimental approaches are further expanded in colloidal PNCs where both external size quantization and internal 0D structure may combine to achieve “multidimensional” electronic properties that are engineered both on atomic scale and nanoscale. In this work, we explore the photon emission statistics from individual 3D ($CsPbBr_3$) and 0D (Cs_4PbBr_6) PNCs in order to address the origin of their PL emission. Using time-correlated, time-stamped single photon counting (TCSPC) we obtain PL intensity trajectories and extract PL lifetimes and second–order correlation functions at different excitation levels. Blinking traces show “burst-like” intensity behavior, with large bin-to-bin fluctuations, akin to molecular fluorophores. Recorded single photon emission statistics indicate that some of the measured PNCs are single photon emitters, others contain several emissive centers with very similar lifetimes. Few of the PNCs exhibited effects of photobrightening – superlinear increase of PL emission intensity due to the activation of an additional number of emissive centers within the PNC. Such emission behavior, independent of the confinement effects afforded by quantization in the medium/large sized Cs-based PNCs, supports theoretical framework that points towards Br-vacancy states localized within isolated octahedra.

Control of Nanoparticle Ferroelectric Vortex-Like Polarization States

John Mangeri[1*], Daopei Zhu[2,3], Krishna Pitike[3], S. Pamir Alpay[3], Serge Nakhmanson[3], Olle Heinonen[4]

[1]*Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic*
[2]*School of Civil Engineering, Wuhan University, Wuhan, China*
[3]*Department of Materials Science and Engineering, University of Connecticut, Storrs, CT, USA*
[4]*Material Science Division, Argonne National Laboratory, Lemont, IL, USA*

[*]e-mail: mangeri@fzu.cz

Recent developments in chemical synthesis techniques have enabled creation of monodisperse perovskite ferroelectric nanoparticles of various shapes and sizes that can be embedded in a dielectric medium[1] to form novel functional microscale architectures. The on-going effort to harness these nanomaterials for a wide range of applications has shown promising new pathways such as engineering multiferroicity, flexible electronics, to improvements in photovoltaic efficiencies among others. Using an open-source real-space finite element approach based on Landau's theory of the phase transition, an analysis of the polarization topology of these structures is performed. It is found that the equilibrium polarization at room temperature is greatly affected by the particle size, shape, and choice of embedded matrix environment.[2,3] Specifically, we observe the presence of skyrmionlike vortex states at a specific size regime. This leads to radically different polarization vs. electric field response loops that can be controlled by tuning the material parameters. In addition to the high dispersed case, we conducted an investigation of an interacting dimer system of these structures. The nonlinear polarization switching is shown to be strongly tunable on the interparticle spacing and applied electric field geometry. The physical origin of this effect lies in the long-range elastic strains that propagate between the particles.[4] Surprisingly, the anisotropy of the field response reveals precise control of the ordering of the vortex-like polarization patterns.

Acknowledgements

J. M. acknowledges funding from the IOP researchers mobility (CZ.02.2.69/0.0/0.0/16_027/0008215)

References

[1] "Solvothermal synthesis and controlled self-assembly of monodisperse titanium-based perovskite colloidal nanocrystals", D. Caruntu, T. Rostamzadeh, T. Costanzo, S. Salemizadeh Parizi, and G. Caruntu, Nanoscale 7, 12955 (2015).
[2] "Topological phase transformations and intrinsic size effects in ferroelectric nanoparticles", J. Mangeri, Y. Espinal, A. Jokisaari, S. Pamir Alpay, S. Nakhmanson, O. Heinonen, Nanoscale 9, 1616-1624 (2017).
[3] "Size, shape, and orientation dependence of the field-induced behavior in ferroelectric nanoparticles", D. Zhu, J. Mangeri, R. Wang, S. Nakhmanson Journal of Applied Physics 125, in-press (2019).
[4] "Electromechanical control of polarization vortex ordering in an interacting ferroelectric-dielectric composite dimer", J. Mangeri, S. Pamir Alpay, S. Nakhmanson, O. Heinonen, Applied Physics Letters 113, 092901 (2018).

Impact of Alloying and Interfaces on Fracture Toughness of Transition Metal Nitrides and Borides

Paul H. Mayrhofer

Institute of Materials Science and Technology, TU Wien, Vienna, Austria

e-mail: paul.mayrhofer@tuwien.ac.at

As the demands on tools and components continuously increase, protective coatings are increasingly important. Whenever mechanical attack is dominating the loading profile of materials, the combination of high strength and fracture toughness is required. Nitrides but especially diborides are excellent candidates for exceptionally high strength (with hardnesses even above 40 GPa) to withstand high mechanical loading. However, their fracture resistance is rather limited, with typical K_{IC} values of ~3 MPa√m for nitrides and ~1 MPa√m for diborides (obtained by in-situ micromechanical bending tests of free-standing coating materials).

By applying alloying and architecture concepts (e.g., composition and/or phase modulated layers) to transition metal nitrides and borides, their fracture resistance can be increased significantly, while still keeping their high strength. The coatings were prepared by physical vapor deposition (magnetron sputtering as well as arc evaporation) and investigated by X-ray diffraction, transmission electron microscopy, nanoindentation (for hardness and indentation modulus), and in-situ micromechanical bending tests (for fracture toughness). This allowed the development of Ti-Al-Ta-N coatings with H ~35 GPa combined with KIC ~4.7 MPa√m, Ti-Si-N coatings with H ~38 GPa combined with K_{IC} ~4.5 MPa√m, and W-Ta-B_2 coatings with H ~42 GPa combined with K_{IC} ~4.0 MPa√m.

The individual concepts allow the design of materials to meet the ever-growing demand for protective coatings tailor-made for specific applications.

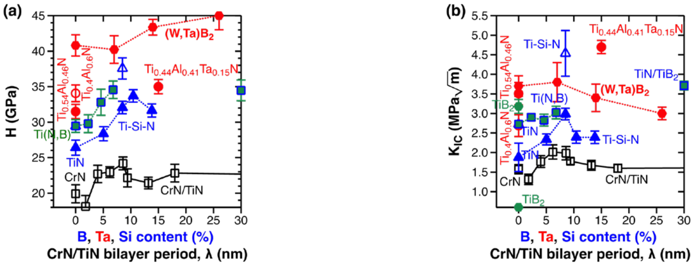


Figure 1. (a) Hardness, H, and (b) fracture toughness, KIC, of various nitrides and borides.[1-3]

References

[1] "Superlattice effect for enhanced fracture toughness of hard coatings," R. Hahn, M. Bartosik, R. Soler, C. Kirchlechner, G. Dehm, P.H. Mayrhofer, Scripta Mat. 124 (2016) 67

[2] Fracture toughness of Ti-Si-N thin films, M. Bartosik, R. Hahn, Z.L. Zhang, I. Ivanov, M. Arndt, P. Polcik, P.H. Mayrhofer, Int. J. Ref. Met. Hard Mat. 72 (2018) 78

[3] Influence of Ta on phase stability and mechanical properties of WB2, C. Fuger, V. Moraes, R. Hahn, H. Bolvardi, P. Polcik, H. Riedl, P.H. Mayrhofer, MRS Commun. 9(1) (2019) 375

In Vitro Evaluation of NBs@O_2 and NBs@Air Induced Toxicity

Elisavet D. Michailidi[1,2*], E. P. Favvas[2], E. K. Efthimiadou[1,2]

[1]Institute of Nanoscience and Nanotechnology, NCSR Demokritos, Athens, Greece
[2]Department of Chemistry, National and Kapodistrian University of Athens, Athens, Greece

[*]e-mail: e.michailidi@inn.demokritos.gr

Nanobubbles (NBs) are defined as "nanoscopic gaseous cavities, which diameter is less than 1 μm. Over the last few years they have attracted significant attention due to their properties; longevity, high mass transfer efficiency as a result of large surface/volume ratio, high oxygen dissolution rate, negative surface charge and generation of free radicals during their collapse make them promising for medical applications.[1,2]

In this study, the effect of NBs@O_2 and NBs@air on cell lines is investigated. NCTC, healthy human keratinocyte cells, and M6, human melanoma cells were used to assess the effect of the NBs on the migration ability of cells by the wound healing assay. In the case of M6 cell line, it was observed that treatment with NBs@O_2 inhibits the proliferation by 41.93% in comparison with the control; while for NBs@air is only 5.34%. On the healthy NCTC cell line, the reduction is 18.74% for NBs@O_2 and 2.38% for NBs@air. Clearly, M6 cells are much more affected than NCTC cells by the treatment of NBs@O_2.

Moreover, the cytotoxicity of NBs@air and NBs@O_2 was evaluated via the MTT assay. NCTC and M6 cell lines were used. In order to inhibit the effect of endogenous ROS, 2,2'-bipyridine and thiourea were used; as a solution in water enriched with NBs@air and NBs@O_2. 2,2'-bipyridine is a chelator which forms complexes with endogenous iron cation, blocking the Fenton reaction; while thiourea is used as a scavenger for the endogenous ROS. By the MTT cytotoxicity assay, it is confirmed that the treatment with NBs lead the cells to apoptosis due to oxidative stress caused by exogenous ROS formed by the collapse of NBs.[3] The free radical formation is confirmed by EPR spectroscopy. According to EPR measurements the radical concentration was at 1^{*}μM. Finally, Rhodamine B was used to determine the localization of NBs in the cells by fluorescence microscopy. It was observed that NBs@air are localized to the cell nucleus while NBs@O_2 are localized to the cytoplasm.

References

[1] Takahashi, M., K. Chiba, and P. Li, *Free-radical generation from collapsing microbubbles in the absence of a dynamic stimulus*. The Journal of Physical Chemistry B, 2007. 111(6): p. 1343-1347.

[2] Liu, S., et al., *Effects of nanobubbles on the physicochemical properties of water: The basis for peculiar properties of water containing nanobubbles*. Chemical Engineering Science, 2013. 93: p. 250-256.

[3] McCord, J.M., *The evolution of free radicals and oxidative stress*. The American journal of medicine, 2000. 108(8): p. 652-659.

A Novel Method of Bulk NBs Production: Evaluation of the Physicochemical Properties

E.D. Michailidi[1,2*], E.K. Efthimiadou[1,2], A.C. Mitropoulos[3], E.P. Favvas[2]

[1]Institute of Nanoscience and Nanotechnology, NCSR Demokritos, Athens, Greece
[2]Department of Chemistry, National and Kapodistrian University of Athens, Athens, Greece
[3]Department of Petroleum and Mechanical Engineering, Eastern Macedonia and Thrace Institute of Technology, St. Lucas, Kavala, Greece

[*]e-mail: e.michailidi@inn.demokritos.gr

Over the last few years, nanobubbles (NBs) have attracted great scientific attention thanks to their unique physicochemical properties and a significant number of potential applications. The term "nanobubbles" (NBs) refers to nanoscopic gaseous cavities, which diameter is less than 1μm[1]. The extraordinary longevity, along with the fact that NBs systems have special physicochemical properties, such as high specific surface, mass transfer ability, low surface tension and contact angle make, especially the bulk, NBs solutions promising a wide range of applications.[2,3]

In this study, a novel type of NBs generator, which operates at low pressure, is designed, constructed and discussed. Air nanobubbles (NBs@air) and oxygen nanobubbles (NBs@O_2) were evaluated in terms of size and colloidal behaviour. Moreover, their important physicochemical properties such as: contact angle (CA), vapour pressure (VP) and density were investigated. As the results show all these properties are affected from the presence of bulk NBs into the water. Dynamic Light Scattering measurements showed that the nanobubbles' size, diameter, is fluctuated from 190 to 680 nm and depends on the gas type, the generator processing time, the water salinity and pH. It was shown that NBs have an effect on the vapor pressure value, since from 28mbar was shifted at 33mbar and 35mbar for NBs@air and NBs@O_2 respectively. These differences were stronger at 60℃ where from 142mbar for untreated water the vapor pressure increased at 157 and 160mbar for NBs@air and NBs@O_2 respectively. It is also observed that both NBs@air and NBs@O_2 have a significant effect on the CA value. In the case of NBs@air, the CA is 26.94℃(SD=±1.5), showing a reduction of 49.79% while in the case of NBs@O_2 the value is 31.27° (SD=± 0.87) and the reduction is 41.72%. Finally, a small but yet observable decrease at the density measurement was noted at high temperature (60℃). It is obvious that the existence of NBs into bulk water phase change dramatically its physicochemical properties as a two phase specific colloidal system is created.

These results are particularly promising for attractive future technological applications. Preliminary results indicate that NBs could potentially be used as green surfactants for surface cleaning.

References

[1] Alheshibri, M., Qian, J., Jehannin, M. & Craig, V.S. A history of nanobubbles. *Langmuir* 32, 11086-11100 (2016).
[2] Liu, s., Kawagoe, y., Makino, y., Oshita, S. Effects of nanobubbles on the physicochemical properties of water: The basis for peculiar properties of water containing nanobubbles. *Chem. Eng. Sci.* 93, 250 (2013).
[3] Azevedo, A., Etchepare, R., Calgaroto, S. & Rubio, J. Aqueous dispersions of nanobubbles: Generation, properties and features. *Minerals Engineering* 94, 29-37 (2016).

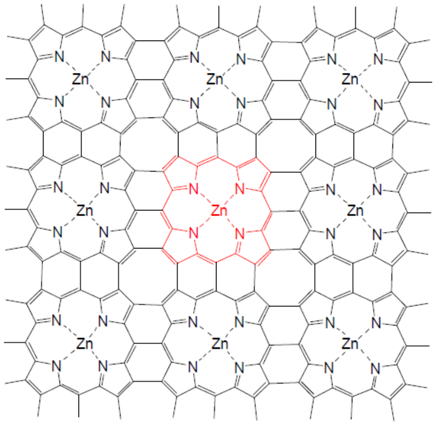
Porphene - A Heterocyclic Analog of Graphene

Thomas F. Magnera[1], Josef Michl[1,2*]

[1]Department of Chemistry, University of Colorado, Boulder, CO, USA
[2]Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Prague, Czech Republic

[*]e-mail: josef.michl@colorado.edu

Controlled oxidative coupling of zinc porphyrin on the surface of an aqueous subphase in a Langmuir-Blodgett trough yields a bilayer of porphene, a fully conjugated two-dimensional polymer with fourfold symmetry. Its structure was proven by in-situ grazing incidence X-ray diffraction and is analogous to that of graphene, but porphene is composed of fused porphyrin rings while graphene is composed of fused benzene rings. The synthesis yields large (>0.1 mm across) sheets of a porphene bilayer. Investigations of porphene formation mechanism and its spectroscopic, structural, electrical, chemical, and mechanical properties, as well as exfoliation to single sheets and construction of twisted multilayer sheets using bidentate ligands, are currently underway. The ability of the porphyrin macrocycle to bind many different kinds of metal cations carrying two, one, or no additional ligands promises that porphene will not be a single polymer but rather, a large family of two-dimensional polymers with tunable properties. Here, porphene differs from graphene in that its functionalization does not require taking any of its π-electron centers out of conjugation, and merely involves insertion of metal ions into its macrocycles and attachment of arbitrary ligands. It is therefore expected that it will be at least as versatile as graphene.



Self-Nanoemulsifying Drug Delivery Systems (SNEDDS) for the Oral Delivery of Lipophilic Drugs

Tianjing Zhao[1,2], Devid Maniglio[1], B. Chen[2], J. Chen[2], Claudio Migliaresi[1*]

[1]*BIOtech Research Center, University of Trento, Trento, Italy*
[2]*School of Environmental and Chemical Engineering, Shanghai University, China*

[*]e-mail: claudio.migliaresi@unitn.it

The increasing number of lipophilic drug candidates in development in the pharmaceutical industry calls for advanced drug delivery systems that are able to increase their bioavailability. Many of these drug candidates possess insufficiently water solubility but high permeability, thus the solubility or dissolution rate in the gastrointestinal tract are the limiting steps for their adequate absorption following oral administration.

Self-emulsifying drug delivery systems (SEDDS) and in particular self-nanoemulsifying drug delivery systems (SNEDDS) have attracted increasing for the improvement of the availability of drugs. SNEDDS comprised oil, surfactant, drug and/or co-surfactant, have a unique ability of forming fine o/w emulsions on mild agitation followed by dilution in aqueous media, such as GI fluids.

The present work will present the preparation of novel self-nanoemulsifying drug delivery systems to overcome the shortages of conventional SNEDDS.

Secondly, pH-sensitive stimulus was combined with self-emulsification technique to explore the release of drug in the GI tract.

According to the results obtained, SNEDDS shows great potential in improving the solubility, enhancing bioavailability and reducing inter/intra subject variability. To conclude, we claim that these SNEDDS would offer the most beneficial outcome in augmenting the bioavailability of poorly soluble and highly metabolized drugs.

References

[1] "Design and optimization of self-nanoemulsifying formulations for lipophilic drug", Zhao T., Maniglio D., Chen J., Chen B., Motta A., Migliaresi C., Nanotechnology 26(12), 2015.

[2] "Development of pH-sensitive self-nanoemulsifying drug delivery systems for acid-labile lipophilic drugs", Zhao T., Maniglio D., Chen J., Chen B., Migliaresi C., Chemistry and Physics of Lipids, 196, 81-8, 2016.

Highly Sensitive Planar Photo-Detectors for the Ultra-Violet to the Near Infrared Wavelength Range Based on a Silicon-on-Insulator Substrate

Vissarion Mikhelashvili*, Gadi Eisenstein

Department of Electrical Engineering, Technion, Haifa, Israel

*e-mail: beso@ee.technion.ac.il

Various materials including Silicon and wide band gap (WBG) semiconductors have been examined and reported in different photodetector (PD) structures. However, in some applications Silicon based PDs have advantages over WBG materials as they can be fabricated by common CMOS technologies. The Metal-Insulator-Semiconductor-Metal (MISM) devices we report used a Silicon-on-Insulator (SOI) substrate with a silicon device layer having a thickness of 450 nm. The active area of the PDs was covered by an insulator stack comprising a 3.5 nm thermal SiO_2 layer and a 19 nm thick HfO_2 deposited by atomic layer deposition. We used electrode configurations which were circular.

Table 1 lists the geometrical parameters of the inter electrode space, gate and back electrodes widths. Fig. 1 (a) and (b) show electrodes configuration of device #C4. In all configurations, gate was deposited on the insulator stack and the back electrode on the Silicon device layer. PDs were characterized in a wavelengths range: from 245 to 880 nm.

A responsivity (R) of 1.77 A/W was achieved at 405 nm independent of the illumination intensity, while at 245 nm, the R was found to be nonlinear and at an intensity of 8 μW/cm², it reached a record value of 30.5 A/W (see Fig. 1 (c)). The inset in Fig. (c) shows the shift (about of 90 nm) of the spectral responsivity to the short wavelength side with reduction of the Si device layer thickness. Local fringing electric fields across asymmetric MIS and MS junctions, stemming from the insulator stack and a reduction of the effective barrier height under illumination are assumed to cause the high R at wavelengths longer than 285 nm. The super linear rise in responsivity for wavelengths shorter than 285 nm is due to deep trap states which are charged by the injected electrons. Finally, the dramatic increase of the R is achieved for small optical window areas (basically at small spaces) due to an enhancement of the electric field fringing effect.

Sample number	Space, μm	Gate electrode's width, μm	Back electrode's width, μm
C1	2	2	2
C2	4	2	2
C3	6	2	2
C4	2	4	4
C5	2	6	6
Big circle	35	15	70

Table 1. Inter electrodes space and electrodes width of the "circle" type devices.

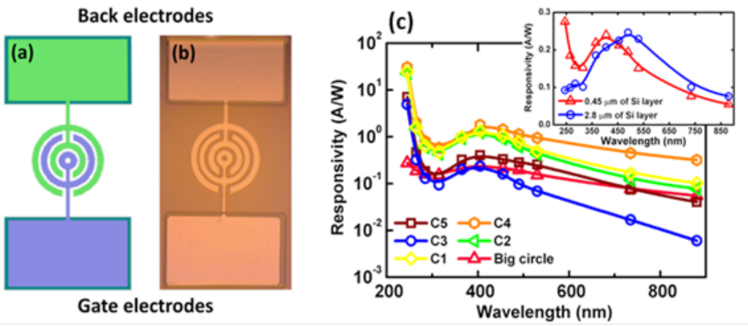


Figure 1. (a) A plan view of the design and (b) implementation for device #C4. (c) Comparison of the R spectra of the devices. Inset show R spectra of "big circle" devices with different thicknesses of the Si layer.

A Bigger, Better Inverted Region

John R. Miller[1*], Tomoyasu Mani[2], Marshall D. Newton[1], Andrew R. Cook[1]

[1]*Brookhaven National Laboratory, Upton, NY, USA*
[2]*University of Connecticut, Mansfielf, CT, USA*

[*]e-mail: jrmiller@bnl.gov

A principal theme will be that we can more deeply understand the Inverted Region of the Marcus Theory and use to it control and improve energy conversion. Here we focus on the role of electronic coupling between diffusing donor and acceptor molecules. Figure 1 depicts bimolecular electron transfer (ET) rate constants, ket, for large and small electronic couplings. For small electronic couplings highly-exoergic ET, typical for charge recombination (CR) reactions, ket is slowed three decades by the inverted effect. But with large electronic couplings (red curve) CR is barely slowed and is almost as fast as moderately exoergic charge separation (marked CS); there is a long, flat region with rates at the diffusion-controlled limit. We will discuss test of how realistic this idealized example is and how we might lean to exert control over electronic couplings to achieve conditions like those of the blue curve in Figure 1. We hope to understand how the inverted region is often absent[1,2] and sometimes present.[2,3]

We will also describe results finding very high charge mobility along conjugated polymer chains and note how high mobilities 4 could assist both in better organic photovoltaic devices and might enhance the inverted region, and briefly note new approaches to redox potentials.

References

[1] “Kinetics of Fluorescence Quenching by Electron and H-Atom Transfer",Rehm, D.; Weller, A. Isr. J. Chem, 8, 259-271,(1970); "The Rehm-Weller Experiment in View of Distant Electron Transfer",Rosspeintner, A.; Kattnig, D. R.; Angulo, G.; Landgraf, S.; Grampp, G. Chem. Eur. J., 14, 6213-6221,(2008).

[2] “Solvent Effects on Photoinduced Electron-Transfer Reactions",Niwa, T.; Kikuchi, K.; Matsusita, N.; Hayashi, M.; Katagiri, T.; Takahashi, Y.; Miyashi, T. J. Phys. Chem., 97, 11960-11964,(1993).

[3] “Driving Force Dependence of Intermolecular Electron-Transfer Reactions of Fullerenes",Fukuzumi, S.; Ohkubo, K.; Imahori, H.; Guldi, D. M. Chemistry – A European Journal, 9, 1585-1593,(2003); "Pressure Tuning of Electron Attachment to Benzoquinones in Nonpolar Fluids: Continuous Adjustment of Free Energy Changes",Holroyd, R.; Miller, J. R.; Cook, A. R.; Nishikawa, M. J. Phys. Chem. B, 118, 2164-2171,(2014).

[4] “High Intrachain Hole Mobility on Molecular Wires of Ladder-Type Poly(p-Phenylenes)",Prins, P.; Grozema, F. C.; Schins, J. M.; Patil, S.; Scherf, U.; Siebbeles, L. D. A. Phys. Rev. Lett., 96, 146601,(2006); "Electron Transport with Mobility, μ > 86 cm2/(V s), in a 74 nm Long Polyfluorene",Cook, A. R.; Asaoka, S.; Li, X.; Miller, J. R. J. Phys. Chm. Lett., 10, 171-175,(2019).

Amyloid Designable Peptide Bionanomaterials and Their Applications

Chrysoula Kokotidou[1,2], Graziano Deidda[1,2], Sai Vamshi R. Jonnalagadda[3],
Asuka A. Orr[3], Anthi Ranella[2], Phanourios Tamamis[3], Anna Mitraki[1,2 *]

[1]*Department of Materials Science and Technology, University of Crete, Heraklion, Greece*
[2]*Institute of Electronic Structure and Laser (IESL), FORTH, Heraklion, Greece*
[3]*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX, USA*

[*]e-mail: mitraki@materials.uoc.gr

Our work focuses on the design, engineering, production and characterization of novel bionanomaterials based on natural fibrous proteins and peptides. We aim to take advantage of their unique self-assembling properties and develop functional biomaterials for uses in the area of biomedicine, environmental protection etc. These biomaterials can be used as scaffolds for the insertion of additional functionalities, such as metal binding sites, tissue-targeting motifs, or enzymatic subunits. We have been using a combination of computational and experimental approaches towards rational self-assembling peptide designs. The designer peptides self-assemble into fibrils that are structurally characterized with Transmission Electron Microscopy, Scanning Electron Microscopy and X-ray fiber diffraction; these fibrils were previously targeted to bind to metal nanoparticles, silica, and more recently, calcium[1] and cells.[2] More recently, we took advantage of their unique self-assembling properties and with the aid of computational methods we applied suitably selected modifications at flexible positions, to tune the properties of amyloid forming peptides in order to discover novel functional biomaterials.[3] Using this approach, we identified novel amyloid biomaterials that are capable of binding and capturing cesium ions at neutral and low pH conditions, enabling their use as scaffolds for the removal of cesium ions from nuclear waste or blood.[4]

References

[1] "Self-Assembly of an Aspartate-Rich Sequence from the Adenovirus Fibre Shaft: Insights from Molecular Dynamics Simulations and Experiments" P. Tamamis et al., J. Phys. Chem. B., 118, 1765 (2014)
[2] "Self-assembled amyloid peptides with Arg-Gly-Asp (RGD) motifs as scaffolds for tissue engineering", G. Deidda et al., ACS Biomaterials Sci. and Engineering 3, 1404 (2017)
[3] "A novel amyloid designable scaffold and potential inhibitor inspired by GAIIG of amyloid beta and the HIV-1 V3 loop." C. Kokotidou, S.V.Jonnalagadda et al., FEBS Letters 592, 1777 (2018)
[4] "Computational Design of Functional Amyloid Materials with Cesium 2 Binding, Deposition, and Capture Properties" S.V.Jonnalagadda, C. Kokotidou et al, J. Phys. Chem. B, 122, 7555 (2018)

The Effect of Nanobubbles on Heavy Metal Ions Adsorption by Activated Carbon

George Z. Kyzas, Athanasios C. Mitropoulos*

Hephaestus Advanced Laboratory, Eastern Macedonia and Thrace Institute of Technology, Kavala, Greece

*e-mail: amitrop@teiemt.gr

It is fact that apart from the adsorption capacity of each material used in wastewater treatment, another important factor is the optimum contact time. The shorter the adsorption time (until equilibrium) is, the more cost effective is the whole process. The whole process is conducted in aqueous phase, given that the wastewaters are in a water medium. Water decontamination is of high importance issue and many different technologies have been developed for this purpose. A promising one is the adsorption of pollutants (dyes, heavy metals, pharmaceutical compounds, phenols, etc.) onto porous materials. This wastewater treatment method is considered the most cost effective, especially when low cost adsorbents are selected. In this work, Nanobubbles (NBs) enriched deionized water is suggested for the investigation of heavy metal removal efficiency. Lead ions (Pb(II)) were selected as model pollutants. As model adsorbent material, activated carbon was synthesized using a novel source. Lignite (from Greek power industry) was supplied and after appropriate modifications was transformed to activated carbon with very high yield percentage (67%). The main scope of the present study is to examine how NBs affects the adsorption capacity or kinetics. The adsorption capacity of Pb(II) was found to be approximately similar either in the presence (Qmax = 171 mg/g) or absence of NBs in water (Qmax = 167 mg/g). On the contrary, the major effect of NBs was to accelerate the adsorption process by 366%. A mechanism was proposed too.[1]

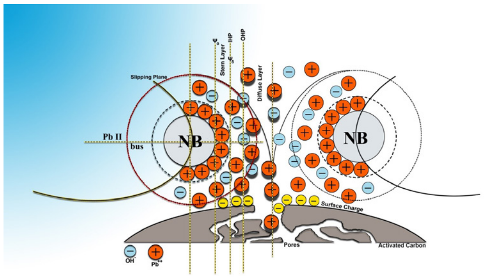


Figure 1. Illustration of the effect of NBs on adsorption kinetics of Pb^{2+} by activated carbon.

Acknowledgements

This research was co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code: T1EDK-02692, entitled: Nanoreinforced Concrete for Pavement Deicing).

References

[1] G.Z. Kyzas, et al. Chem. Eng. J. 356, 91-97 (2019).

Real-Space Imaging of Charge Carrier Dynamics in Solar Cell Materials

Omar F. Mohammed

Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, KSA

e-mail: omar.abdelsaboor@kaust.edu.sa

The collection of light-generated charge carriers in all optoelectronic devices is limited by the losses and ambiguous carrier dynamics at the surfaces and interfaces of the absorber layers, which are ultrafast in nature. These dynamical processes can only be visualized in space and time by scanning ultrafast electron microscopy (the sole technique capable of surface-selective visualization of light-triggered carrier dynamics at nanometer scale) along with ultrafast electronic and vibrational spectroscopies. In additional to our state-of-the-art femtosecond laser spectroscopic techniques, we established and developed the second generation four-dimensional (4D) scanning ultrafast electron microscopy (S-UEM) and demonstrate the ability to take time-resolved electron images (snapshots) of nanoscale material surfaces with 650 fs and 3 nm temporal and spatial resolutions, respectively. In this method, the surface of the photoactive materials is excited by a clocking optical pulse and the photo-induced changes will be directly imaged using a pulsed electron beam as a probe pulse, generating secondary electrons with a couple of electron volts energy, which are emitted only from the very top surface of the material in a manner that is extremely sensitive to the localization of the electron and hole on the surface and interfaces of the optoelectronic device. This method provides direct and controllable ultrafast dynamical information in many photoactive materials commonly used in solar cells, photodetectors and photo-catalysis. For instance, we have clearly demonstrated in space and time how the surface morphology, surface passivation, thickness of the absorber layer, grains, surface orientation & termination, surface defects and nanostructured features can significantly impact the overall dynamical processes of the charge carriers on the surface of absorber layers.[5-9] Finally, charge carrier dynamics at the interface of semiconductor quantum dots and perovskite materials using femtosecond laser spectroscopy will also be presented and discussed.

References

[1] O. M. Bakr, O. F. Mohammed., Science 355, 1260 (2017).
[2] A. O. El-Ballouli, E. Alarousu, M. Bernardi, S. M. Aly, A. P. Lagrow, O. M. Bakr, O. F. Mohammed., J. Am. Chem. Soc. 136, 6952 (2014).
[3] R. Begum, M. R. Parida, A. L. Abdelhady, B. Murali, N. Alyami, G. H. Ahmed, M. N. Hedhili, O. M. Bakr, and O. F. Mohammed., J. Am. Chem. Soc. 139, 731 (2017).
[4] O. F. Mohammed, D.-S. Yang, S. Pal, A. H. Zewail, J. Am. Chem. Soc. 133, 7708 (2011).
[5] J. Sun, V. A. Melnikov, J. I. Khan, O. F. Mohammed, J. Phys. Chem. Lett. 6, 3884 (2015).
[6] R. Bose, J. Sun, J. I. Khan, B. S. Shaheen, A. Adhikari, T. K. Ng, V. M. Burlakov, M. P. Parida, D. Priante, A. Goriely, B. S. Ooi, O. M. Bakr, O. F. Mohammed, Adv. Mater. 28, 5106 (2016).
[7] B. S. Shaheen, J. Sun, D-S Yang, and O. F. Mohammed, J. Phys. Chem. Lett. 8, 2455 (2017).
[8] R. Bose, A. Bera, M. R. Parida, A. Adhikari, B. S. Shaheen, E. Alarousu, J. Sun, T. Wu, O. M. Bakr, O. F. Mohammed, Nano Lett. 16, 4417 (2016).
[9] R. Bose, A. Adhikari, V. M. Burlakov, G. Liu, M. A. Haque, D. Priante, M. N. Hedhili, N. Wehbe, C. Zhao, H. Yang, T. K. Ng, A. Goriely, O. M. Bakr, T. Wu, B. S. Ooi, O. M. Bakr, O. F. Mohammed, ACS Energy Lett. 3, 476–481 (2018).

Nanoscale Architectures for Applications in Electrocatalysis and Photoelectrosynthesis

G. F. Moore

School of Molecular Sciences and the Biodesign Institute Center for Applied Structural Discovery (CASD), Arizona State University, Tempe, AZ, USA

*e-mail: gary.f.moore@asu.edu

The chemical modification of (semi)conducting surfaces with electrocatalysts provides a strategy to develop nanomaterials that convert sunlight to fuels and other value-added chemical products. However, the realization of this approach remains a major challenge and advancements are constrained by the availability of effective methods to interface the requisite components. In addition, there is an incomplete understanding of fundamental factors limiting performance of the integrated constructs. In this presentation I will discuss efforts to develop heterogeneous-homogeneous architectures that combine the form factors of underpinning solid-state supports with polymeric surface coatings used to direct, template, and assemble molecular fuel-forming catalysts.[1-5] Thermodynamic and kinetic models pertinent to these types of assemblies will also be discussed.

References

[1] "Polymeric Coatings for Applications in Electrocatalytic and Photoelectrosynthetic Fuel Production", B. L. Wadsworth, D. Khusnutdinova, G. F. Moore, J. Matter. Chem. A. 6. 44, 21654–21665 (2018).

[2] "Electrocatalytic and Optical Properties of Cobaloxime Catalysts Immobilized at a Surface-grafted Polymer Interface", B. L. Wadsworth, A. M. Beiler, D. Khusnutdinova, S. I. Jacob, G. F. Moore, ACS Catal. 6. 12, 8048–8057 (2016).

[3] "Metalloporphyrin-modified Semiconductors for Solar Fuel Production", D. Khusnutdinova, A. M. Beiler, B. L. Wadsworth, S. I. Jacob, G. F. Moore, Chem. Sci. 8. 1, 253–259 (2017).

[4] "Cobalt Porphyrin-polypyridyl Surface Coatings for Photoelectrosynthetic Hydrogen Production", A. M. Beiler, D. Khusnutdinova, B. L. Wadsworth, G. F. Moore, Inorg. Chem. 56. 20, 12178–12185 (2017).

[5] "Electrocatalytic Properties of Binuclear Cu(II) Fused Porphyrins for Hydrogen Evolution", D. Khusnutdinova, B. L. Wadsworth, M. Flores, A. M. Beiler, E. A. Reyes Cruz, Y. Zenkov, G. F. Moore, ACS Catal. 8. 10, 9888–9898 (2018).

Formation of Superlubricious Layers on Hard Carbon Coatings

Michael Moseler

Fraunhofer Institute for Mechanics of Materials IWM, Freiburg, Germany
Physics department, University of Freiburg, Freiburg Germany

e-mail: mos@iwm.fhg.de

Superlubricity of tetrahedral amorphous carbon (ta-C) coatings under boundary lubrication with organic friction modifiers is important for industrial applications, but the underlying mechanisms remain elusive. Here, combined experiments and simulations unveil a universal tribochemical mechanism leading to superlubricity of ta-C/ta-C tribopairs. Pin-on-disc sliding experiments show that ultra- and superlow friction with negligible wear can be achieved by lubrication with unsaturated fatty acids or glycerol, but not with saturated fatty acids and hydrocarbons. Atomistic simulations reveal that, due to the simultaneous presence of two reactive centers (carboxylic group and C=C double bond), unsaturated fatty acids can concurrently chemisorb on both ta-C surfaces and bridge the tribogap. Sliding-induced mechanical strain triggers a cascade of molecular fragmentation reactions releasing passivating hydroxyl, keto, epoxy, hydrogen and olefinic groups. Similarly, glycerol's three hydroxyl groups react simultaneously with both ta-C surfaces, causing the molecule's complete mechano-chemical fragmentation and formation of aromatic passivation layers with superlow friction.

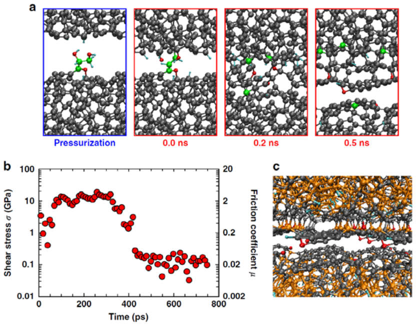


Figure 1. Quantum MD simulation of two ta-C surfaces lubricated with a glycerol molecule. a Snapshots of the 1-ns sliding simulation. b Evolution of the shear stress σ and friction coefficient μ. c Shear-induced aromatic passivation of both ta-C surfaces. 3- and 4-fold coordinated C atoms are represented in grey and orange spheres, respectively.

References

[1] "Mechano-chemical decomposition of organic friction modifiers with multiple reactive centres induces superlubricity of ta-C", T. Kuwahara, P.A. Romero, S. Makowski, V. Weihnacht, G. Moras, M. Moseler, Nature Communications 10, 151 (2019).

[2] "Friction Regimes of Water-Lubricated Diamond (111): Role of Interfacial Ether Groups and Tribo Induced Aromatic Surface Reconstructions", T. Kuwahara, G. Moras, M. Moseler, Phys. Rev. Lett. 119 096101 (2017).

Silks as Materials for Biomedical Use

Y. Yang[1], G. Greco[2], D. Maniglio[1], B. Mazzolai[3], C. Migliaresi[1], N. Pugno[2], A. Motta[1*]

[1]Department of Industrial Engineering and BIOtech Research Center, University of Trento, Trento, Italy
[2]Laboratory of Bio-Inspired & Graphene Nanomechanics, Department of Civil, Environmental and Mechanical Engineering, University of Trento, Italy
[3]Center for Micro-BioRobotics@SSSA, Istituto Italiano di Tecnologia, Italy

[*]e-mail: antonella.motta@unitn.it

Silk form silkworms have acquired increasing interest in the last 10-15 years for applications in medicine and namely in tissue engineering.

In addition to silkworms, other animals produce materials commonly named “silk”, as spiders, wasps, bees, and other insects.

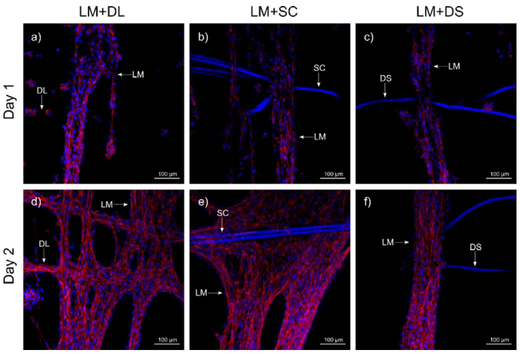
Silkworms make filaments with constant composition in the cocoons, while spiders in the same web make silks with different composition, properties and role. Moreover, the difficult procurement did not allow the practical exploitation of the interesting physical and biological properties of silks from spiders.

In this presentation, silks from *Bombyx mori* (SC, before degumming and DS, after degumming) silkworm, *Linothele megatheloides* (LM) spider, and of the web-dragline of *Cupiennis salei* (DL) spider, isolated in our spider farm, have been compared in terms of aminoacidic composition, mechanical properties, morphology and biological properties in cell cultures.

In particular, biological properties have been assessed comparatively in competitive arrays of couples of fibers to evidence the biological antagonism between the different types of silks. In addition, samples of nets or web have been used, to better determine cell adhesion and metabolism.

The confocal images of competitive NIH 3T3 cell culture tests on couples of fibers are reported in the figure. Well evident is the much larger preferential early adhesion of cells on the LM silk filament with respect to the DL, SC and DS silks at day one, persisting at day 2 for the silkworm silks.

Properties of the investigated silks and cell culture results on the above setups and nets will be presented and commented.



Dimpled SiO_2 Nanostructures Decorated With Magnetic Iron Oxide Nanoparticles for as Detection and Removal in Aqueous Medium

S. Mourdikoudis[1*], S. Deeprasert[1], L. Wang[1], K. Simeonidis[2], E. Duguet[3], T. Nguyen[1]

[1]*Healthcare Biomagnetics Laboratory-University College London, Department of Physics & Astronomy, The Royal Institution of Great Britain, London, UK*
[2]*Department of Chemical Engineering, Aristotle Univ. of Thessaloniki, Greece*
[3]*Institut de Chimie de la Matiere Condensee de Bordeaux, Pessac Cedex, France*

[*]e-mail: s.mourdikoudis@ucl.ac.uk

Nowadays, iron oxide nanoparticles are gaining their popularity also in the environmental domain by having favorable advantages of being non-toxic, biocompatible and superparamagnetic. Fe-oxide NPs are often used to detect and remove heavy metals including arsenic, and tackle other issues (microbes, organic pollutants) in potable water or wastewater. In this research work, pre-synthesized Fe-oxide NPs were modified with 3-amino-propyltrimethoxysilane (APS) to obtain an amino group on their surface and for the formation of a carboxylic group, succinic anhydride was added, together with triethylamine (TEA). The carboxylic acid-modified Fe-oxide NPs were grafted onto amine-functionalized silica nanostructures (Fig. 1) where different combinations of Fe-oxide NPs and SiO_2 dimples were investigated. Successful growth of other nanomaterials (gold NPs) has been already published by Duguet's group.[1] The γ-Fe_2O_3-NPs-decorated silica dimples were studied by techniques such as TEM, FTIR and DLS to characterize the product morphology as well as the composition and charge of the surface coating. The hybrid material is employed for the removal of arsenic from water in a user-friendly and environmentally benign method which involves simple magnetic separation means to control the NPs fate.

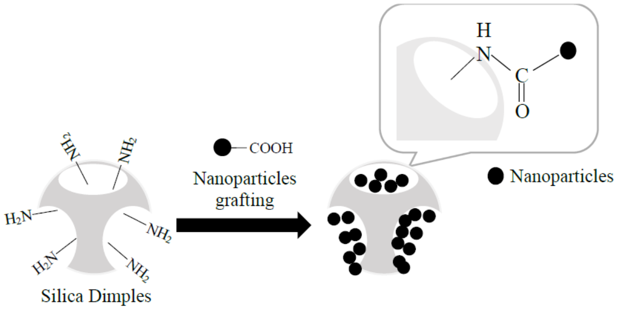


Figure 1. The process of grafting nanoparticles onto the silica dimples.

References

[1] "Templated growth of gold satellites on dimpled silica cores", C. Chomette, E. Duguet, S. Mornet, E. Yammine, V. N. Manoharan, N. B. Schade, C. Hubert, S. Ravaine, A. Perro and M. Treguer-Delapierre, Faraday Discuss., 191, 105 (2016).

Challenges and Opportunities in Nanostructured Materials for Clean Energy Conversion and Storage

S. Praneeth, A. Vadivel Murugan*

Pondicherry University (A Central University), Pondicherry, India

*e-mail: avmrajeshwar@gmail.com

Rapid depletion of fossil fuels, increasing greenhouse gas emissions and growing environmental concerns demand the development of alternative, sustainable clean energy technologies. In this regard, nanostructured materials play an important role in advancing the electrochemical energy storage and conversion technologies such as such as Solar cells and high energy density batteries are appealing for a variety of clean energy needs ranging from portable electronics to automobiles to stationary power as they provide clean energy. Design and development of new materials that can lower the cost, increase the efficiency, and improve the durability can have a significant impact in making these technologies commercially viable. In this regard, nanostructured materials and nanotechnology offer great promise because of the unusual properties endowed by confining their dimensions and the combination of bulk and surface properties to the overall behavior. However, solution-based synthesis approaches and the associated processing play a critical role in controlling the particle composition, size, morphology, and the overall electrochemical properties and performances. I present here an overview of some of the recent progress in our laboratory on how nanomaterials and nanotechnology can impact the development of high performance, affordable materials for clean energy technologies and I also address what are the issues and challenges in the nano-materials and correlation between structure-properties-performance relationships.

References

[1] "The Chemistry of Nanomaterials, Synthesis, properties, and applications", A. Vadivel Murugan, and K. Vijayamohanan, Book entitled: "Applications of Nanostructured Hybrid Materials for Supercapacitors", WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, publishers, Germany, pp 219-248 (2007) ISBN: 978-3-527-31664-9, Edited by Prof. C. N. R. Rao, A. Müller, & A. K. Cheetham.

[2] "Nanostructured electrode materials for electrochemical energy storage and conversion", A. Manthiram, A. Vadivel Murugan, T. Muraliganth, A. Sarkar, Energy. Environ, Sci., 1, 62 (2008).

[3] "Comparison of Microwave Assisted Solvothermal and Hydrothermal Syntheses of $LiFePO_4$/C Nanocomposite Cathodes for Lithium Ion Batteries", A. Vadivel Murugan, T. Muraliganth, and A. Manthiram, J. Phys. Chem. C 112, 14665 (2008).

[4] "Unveiling the Co^{2+} Ion Doping-Induced Hierarchical Shape Evolution of ZnO: In Correlation with Magnetic and Photovoltaic Performance",R. Krishnapriya, S. Praneetha, A.Vadivel Murugan, ACS Sustainable Chem. Eng, 5, 9981-9992 (2017).

Moose, Ferret and Other Furry Animals: Simulating Complex Behavior of Electroactive Materials at Mesoscale

Lukasz Kuna[1], John Mangeri[2], Daopei Zhu[3,4], Krishna Pitike[4], S. Pamir Alpay[1,4],
Olle G. Heinonen[5], Serge Nakhmanson[1,4*]

[1]*Department of Physics, University of Connecticut, Storrs, CT, USA*
[2]*Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic*
[3]*School of Civil Engineering, Wuhan University, Wuhan, China*
[4]*Department of Materials Science and Engineering, University of Connecticut, Storrs, CT, USA*
[5]*Material Science Division, Argonne National Laboratory, Lemont, IL, USA*

[*]e-mail:serge.nakhmanson@uconn.edu

Ferret is an open-source highly scalable real-space finite-element-method (FEM) based code for simulating transitional behavior of materials systems with coupled physical properties at mesoscale. This code is built on MOOSE, or Multiphysics Object Oriented Simulation Environment, that is being maintained by Idaho National Laboratory. MOOSE allows efficient solving of coupled-physics problems, has a proven record of scaling of execution on modern supercomputers, and is easily extendable to include new physics and couplings. Real-space FEM approach allows treatment of materials systems possessing complicated geometry and morphology, and evaluation of property dependencies on the system shape, size, microstructure and applied conditions. In this presentation, we provide an overview of computational approach utilized by the Ferret code and showcase some of its modeling capabilities. The highlighted projects conducted with Ferret include (a) modeling of size and shape effects in semiconducting piezoelectric nanostructures; (b) simulations of piezo-force microscopy (PFM) characterization of perovskite-ferroelectric nanoislands, and (c) calculations of light transmission, as well as the action of electro- and elasto-optic effects in polycrystalline piezoelectrics.

Acknowledgements

J.M. acknowledges funding support from the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists, Office of Science Graduate Student Research (SCGSR) program. The SCGSR program is administered by the Oak Ridge Institute for Science and Education (ORISE) for the US Department of Energy. ORISE is managed by ORAU under contract number DE-SC0014664. US National Science Foundation (award DMR 1309114) is also acknowledged for partial funding of some activities related to the development of the Ferret code. Nanoparticles Research, 15, 2139-2152

Spatially and Time-Resolved X-Ray Detected Ferromagnetic Resonance to Study Dynamic Magnetic Properties of Micro-Magnets

D.S. Pile[1], T. Feggeler[2], T. Schaffers[1], R. Meckenstock[2], M. Buchner[1], D. Spoddig[2], V. Ney[1], M. Farle[2], H. Wende[2], R. Narkowicz[3], K. Lenz[3], J. Lindner[3], H. Ohldag[4], K. Ollefs[2], A. Ney[1*]

[1]*Solid State Physics Division, Johannes Kepler University, Linz, Austria*
[2]*Faculty of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Duisburg, Germany*
[3]*Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany*
[4]*Stanford Synchrotron Radiation Laboratory, SLAC, Menlo Park, CA, USA*

[*]e-mail: andreas.ney@jku.at

By using lithographically fabricated micro resonators it is possible to measure ferromagnetic resonance (FMR) of micron-sized samples with a detection sensitivity of down to 106 spins.[1] These micro resonators allow combining scanning transmission x-ray microscopy (STXM) and FMR, using a time synchronization scheme between the x-ray pulses of the synchrotron and the microwave excitation (STXM-FMR). The STXM-FMR setup enables the visualization of the high frequency magnetization dynamics in the GHz regime with a high lateral resolution of nominally 35 nm and a time resolution down to 17.4 ps.[2] In this contribution we present the results for two perpendicular Permalloy (Py) micro stripes 5x1x0.03 µm3 each.[3] The samples were pre-characterized using conventional FMR to identify the excited modes in the Py stripes in combination with micro-magnetic simulations. The STXM-FMR technique enables to directly observe uniform and inhomogeneous magnetic excitation modes of the Py stripes. The observed spatial distribution of the excitations matches the simulations rather well. In addition some modes were found to be moving at velocities up to 30 km/s and the direction of movement could be influenced by the mutual positioning of the stripes.

Acknowledgements

Financial support by the Austrian Science Fund (FWF), Project No. I-3050, ORD-49 and the German Research Foundation (DFG), Project No. 321560838 is gratefully acknowledged.

References

[1] "Visualization of spin dynamics in single nanosized magnetic elements", A. Banholzer, R. Narkowicz, C. Hassel, R. Meckenstock, S. Stienen, O. Posth, D. Suter, M. Farle, J. Lindner, Nanotechnology 22, 295713 (2011).
[2] "Microwave soft x-ray microscopy for nanoscale magnetization dynamics in the 5–10 GHz frequency range", S. Bonetti, R. Kukreja, Z. Chen, D. Spoddig, K. Ollefs, C. Schöppner, R.Meckenstock, A. Ney, J. Pinto, R. Houanche, J. Frisch, J. Stöhr, H. Dürr, H. Ohldag, Rev. Sci. Instrum. 86, 093703 (2015).
[3] "The combination of micro-resonators with spatially resolved ferromagnetic resonance", T. Schaffers, R. Meckenstock, D. Spoddig, T. Feggeler, K. Ollefs, C. Schöppner, S. Bonetti, H. Ohldag, M. Farle, A. Ney, Rev. Sci. Instrum. 88, 093703 (2017).

Artificial Magnetic Elements Based on High Entropy Alloys as Building Blocks for Novel Magnetic Phases

Dimitrios Niarchos

INN, NCSR Demokritos, Athens, Greece
AMEN Technologies, Athens, Greece

e-mail: d.niarchos@inn.demokritos.gr

Many developments in modern technology are based in permanent magnets (PMs), including a plentiful of critical applications in the fields of energy, automotive, robotics and more.[1] The most powerful PMs are based on $Nd_2Fe_{14}B$ with small addition of Dy and (BH)max >400 kJ/m^3 that can operate at temperatures up to 200℃. However, as with other RE-based PMs, they are expensive. For higher temperature applications $SmCo_5$ -type magnets are used but with moderate energy products (BH)max ~ 240 kJ/m^3.

Today, there is an urgent need for the discovery of rare earth lean/free permanent magnets due to the critical strategic character of these metals.[2] A novel family of alloys of the type $ThMn_{12}$ –tetragonal structure is rare-earth lean and very promising for applications.[3] All these magnets are very brittle that prohibits them for wider applications. On the other hand the new classes of High Entropy Alloys (HEAS) have excellent mechanical properties that might –if incorporated in permanent magnets – will make them less fragile and cheaper.

In this work we will present our efforts first to synthesize Rare-Earth based HEAs (RE-HEAs), second to synthesize Transition Metal HEAS (TM-HEAs) and subsequently the successful efforts to prepare $\{RE\text{-}HEAs\}_{x-}(TM\text{-}HEAs)_y$ alloys with the same or better properties compared to the parent alloys of $SmCo_5$, $Nd_2Fe_{14}B$ and $(Nd,Sm)\text{-}Fe_{12-x}Tx$ (T=Ti,Mo) at much lower materials cost. We will present and confirm that such an approach provides extra degrees of freedom to manipulate the crystallographic and magnetization data as well the microstructure, opening up a new pathway towards novel permanent magnet alloys.

References

[1] Magnetic materials and devices for the 21st century: Stronger, lighter, and more energy efficient, Gutfleisch, O. et al.,. Advanced Materials, 23(7), pp.821–842 (2011).
[2] ERECON 2014; European Commission 2017
[3] Nanocrystalline High Entropy Alloys: A new Paradigm in High-Temperature Strenght and Stability, Yu Zou, et al., Nano Lett. 2017, 17, 1569−1574

Effect of PEO-Treated Dome Diaphragms on Acoustic Performance of High Frequency Compression Drivers

Christian Zung[1,2], Jingzeng Zhang[1], Igor Levitsky[3], Xueyuan Nie[1*]

[1]*Faculty of Engineering, University of Windsor, Windsor, Ontario, Canada*
[2]*College of Engineering, University of Michigan, Ann Arbor, MI, USA*
[3]*Radian Audio Engineering, Ontario, Canada*

[*]e-mail: xnie@uwindsor.ca

Plasma electrolytic oxidation (PEO) is a technology that enables to prepare nanostructured surfaces on materials to give enhanced mechanical properties like hardness, stiffness, wear resistance and corrosion resistance. In this project, PEO coatings were applied to 6 aluminum speaker domes to study what effects PEO coatings could offer. Three were processed to have a thin coating and the others processed to have a thicker coating. Afterwards, the six speaker domes were conducted with several tests and measurements. From the experiment at 12 kHz - 14 kHz the PEO coating provides benefits to the speaker dome that could improve sound quality. From the SPL (sound pressure level) test the coated speaker domes had demonstrated mostly the same effects. When dealing with low frequencies from 200 Hz to 5k kHz the coatings had shown no adverse effects to the sensitivity of the speaker domes. However, when reaching frequencies between 5 kHz to 12 kHz the sensitivity of the coated domes shows a slight decrease in sensitivity. The last result from SPL test showed that at the high frequency from 12 kHz to 14 kHz the dome actually had improved in sensitivity. It also is important to notice that at this high frequency range the thicker coating of DPH #5 had actually performed better. From the impulse response test, there was very little to no change showing that the PEO coating neither impedes nor improves its response to input signal. From the CSD (cumulative spectral decay) graph the decay is mainly the same till once again we reach frequencies of 12 kHz to 14 kHz due to the stiffness of the coating. Lastly, from the multitoned distortion test there was little to no change. Thus, the PEO coating has very few adverse effects besides the decreased sensitivity at the mid frequency range. The PEO coating has many beneficial effects from increased wear resistance, sensitivity and dampening effects to the speaker dome. Overall, this PEO coating can be very beneficial when applying it to low frequencies as well as high frequencies so as to help get better sound quality and increased lifetime.

Figure 1. Al speaker dome after coating

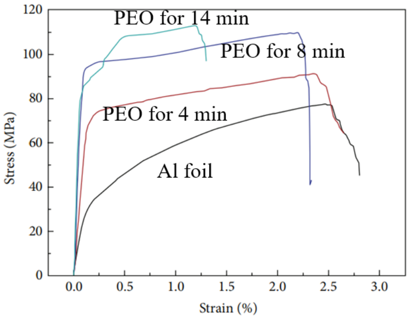


Figure 2. Graph of stress vs. strain

Charge Transfer and Energy Conversion Using Synthetic Protein/Porphyrin Ensembles

David L. Officer[1*], Christopher J. Hobbs[1], Nicholas Roach[1], Klaudia Wagner[1], Pawel Wagner[1], Holly van der Salm[2], Jonathan E. Barnsley[2], Keith C. Gordon[2], Goutham Kodali[3], Christopher C. Moser[3], P. Leslie Dutton[3]

[1]ARC Centre of Excellence for Electromaterials Science and the Intelligent Polymer Research Institute, University of Wollongong, Wollongong, Australia
[2]Department of Chemistry, University of Otago, Dunedin, New Zealand
[3]The Johnson Research Foundation and Department of Biochemistry and Biophysics, University of Pennsylvania, Philadelphia, PA, USA

[*]e-mail: davido@uow.edu.au

The emulation of the photoinduced charge transfer and energy conversion processes in photosynthesis could not only provide a new generation of economical photovoltaic devices but also lead to sustainable hydrogen production through water splitting as well as fuel and food production through carbon dioxide fixation.

The challenge in building a useful ‘artificial photosynthetic’ assembly is not in simply mimicking the natural photosynthetic apparatus but utilizing new materials to create and, if possible, improving the structural properties and functionality of the biological system. In 1994, Dutton et al. developed the methodology for the facile production of de novo synthetic protein helices (maquettes), structurally simpler analogs of natural redox proteins, which have proved extremely useful for the study of porphyrin behaviour and interactions in proteins. It has been demonstrated that not only is a maquette-bound porphyrin more efficiently photo oxidized than a free porphyrin but also that light induced electron transfer between the porphyrin complex and an acceptor is faster and higher yielding. As the maquettes can be assembled on a variety of surfaces such as gold or titanium dioxide, they provide a unique platform on which to build and study photosynthetic-like charge transfer and energy conversion processes.

With the aim of developing light-harvesting porphyrin array protein ensembles (Fig. 1), we have synthesized and incorporated amphiphilic porphyrins into maquettes and studied the charge transfer and energy conversion characteristics of these ensembles on titanium dioxide. We have demonstrated efficient photoinduced electron injection into the semiconducting acceptor to give photovoltaic devices as well as the ability to vary the injection with metallated porphyrins. We will discuss these results and the potential of these ensembles for the development of photosynthetic-like catalytic systems.

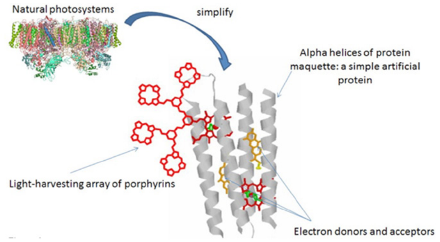


Figure 1. Proposed synthetic protein/porphyrin ensemble

Tuning Electronic Properties of Well-Defined Nanoscale Objects by Locking-in π-Conjugated Superstructures

Jean-Hubert Olivier[*], Adam Ashcraft, Victor Paulino, Kaixuan Liu

Department of Chemistry, University of Miami, Cox Science Center, Coral Gables, FL, USA

[*]e-mail: jh.olivier@miami.edu

As a product of the dynamic equilibrium between solubilized building blocks and self-assembled structures, supramolecular architectures are fragile compositions where minor changes in temperature, solvent dielectric, and building-block concentration can trigger the dismantlement of superstructures and concomitant loss of the emergent properties associated with them. We posit that developing molecular strategies to covalently polymerize superstructures can provide entirely new nanoscale platforms with which to elucidate structure-function properties that remain elusive by current supramolecular methodologies. We will introduce the design principles to reticulate 1-dimensional supramolecular polymers following a 1,3-dipolar cycloaddition "click-chemistry" (Figure 1A-C). Confirmed by atomic force microscopy and transmission electron microscopy, organic nanomaterials created in this manner are best characterized by a nanowire morphology. These findings confirm that conformation of supramolecular 1D assemblies can be captured using the unveiled lock-in strategy. Investigation of the electronic properties of length-sorted nanowires exploiting electrochemical measurement methods reveals a non-negligible stabilization of the energy of the conduction band with respect to that of parent, non-polymerized self-assembly (Figure 1D). It is important to note that the presented strategy opens new avenues to not only capture conformation of supramolecular assemblies but also to enforce the formation of emergent electronic properties not accessible in pristine, non-covalent assemblies.

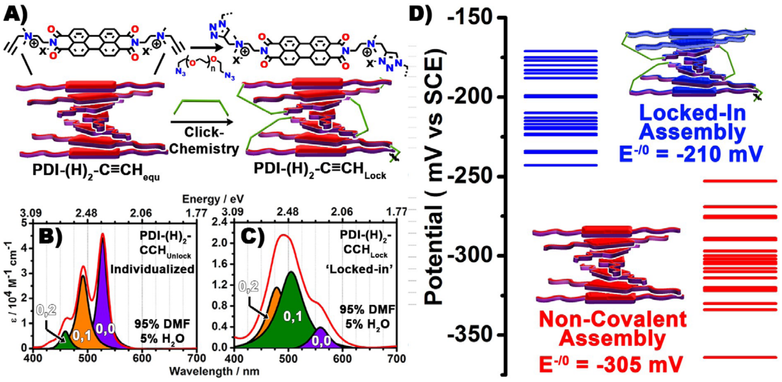


Figure 1. A) Design strategies to lock in superstructure conformation. (B-C) Spectroscopic evidences of superstructure locking. (D) Statistical potentiometric properties of locked-in and non-covalent assembly.

DFT Study on Carrier Transport in Electronic Devices

Tomoya Ono*, Arqum Hashmi, Kenta Nakanishi

Center for Computational Sciences, University of Tsukuba, Tsukuba, Japan

*e-mail: ono@ccs.tsukuba.ac.jp

First-principles studies based on the density functional theory are conducted to understand the spin-polarized transport property in magnetic tunnel junctions (MTJs), in which 2D material is sandwiched between ferromagnetic transition-metal(TM) electrodes. We vary the thickness of the graphene (Gr) or hexagonal boron nitride (h-BN) spacer region between two TM electrodes. We investigate the junctions where one side is Ni and the other is Co (non-symmetric junctions) as well as the junctions with Ni electrodes on both sides (symmetric junctions). In addition to the spin-resolved density of states, transmission spectrum is calculated by the nonequilibrium Green's function method implemented in RSPACE code[1-3] to show tunneling behavior. Although magnetic exchange couplings between the electrodes and spacer region are low, it is found that spin filtering strongly depends on electrode material and number of atomic layers in the spacer region. Symmetric junctions exhibit broad transmission spectra, while the non-symmetric junctions have narrow transmission peaks. It is found that the monolayer junctions exhibit low contact resistance. When the thickness of the spacer region is changed, the bilayer junctions show high contact resistance. It is noteworthy that the transport property of the bilayer junctions is significantly spin polarized, which is robust and independent of the electrode material compared to the monolayer junctions. Furthermore, the tunneling magnetoresistance (TMR) ratios of Gr-based MTJs are drastically affected by the Fermi surfaces of electrodes and the localized transmission spectra. On the other hand, the TMR ratios of h-BN-based ones depend on the stacking order, local density of states, and super exchange interaction between the atoms in the electrodes and spacer region. Our calculation reveals that multilayers of Gr or h-BN are promising candidates for the spacer region of MTJs.

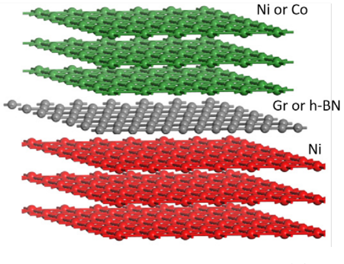


Figure 1. Computational model for MTJ.

References

[1] "Timesaving Double-Grid Method for Real-Space Electronic-Structure Calculations", T. Ono and K. Hirose, Phys. Rev. Lett. 82, 5016 (1999).

[2] "Real-space electronic-structure calculations with a time-saving double-grid technique", T. Ono and K. Hirose, Phys. Rev. B 72, 085115 (2005).

[3] "First-Principles Calculations in Real-Space Formalism: Electronic Configurations and Transport Properties of Nanostructures", K. Hirose, T. Ono, Y. Fujimoto, and S. Tsukamoto, (Imperial College Press, London, 2005).

Long-Range Antiferromagnetic Order in Epitaxial Mn$_2$GaC Thin Films from Neutron Reflectometry

A. Ingason[1], G. Palsson[2*], M. Dahlqvist[1], J. Rosen[1]

[1]*Department of Physics, Chemistry and Biology, Linkoping, Sweden*
[2]*Department of Physics & Astronomy, Uppsala, Sweden*

*e-mail: gunnar.palsson@physics.uu.se

The nature of the magnetic structure in magnetic so-called MAX phases is a topic of some controversy. Here we present unpolarized neutron-diffraction data between 3.4 and 290.0 K and momentum transfer between Q = 0.0 and 1.1 Å−1, as well as complementary x-ray-diffraction data on epitaxial thin films of the MAX phase material Mn$_2$GaC. This inherently layered material exhibits neutron-diffraction peaks consistent with long-ranged antiferromagnetic order with a periodicity of two structural unit cells. The magnetic structure is present throughout the measured temperature range. The results are in agreement with first-principles calculations of antiferromagnetic structures for this material where the Mn-C-Mn atomic trilayers are found to be ferromagnetically coupled internally but spin flipped or rotated across the Ga layers. The present findings have significant bearing on the discussion regarding the nature of the magnetic structure in magnetic MAX phases.

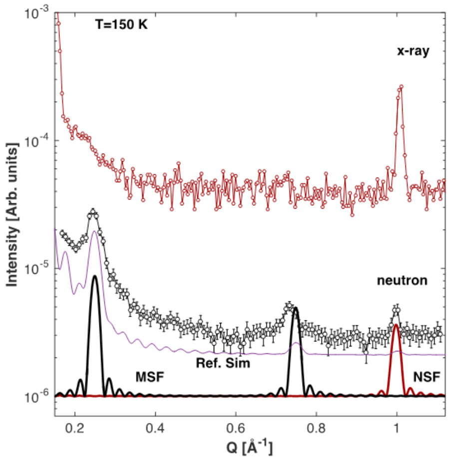


Figure 1. Cx-ray diffraction from 50 nm Mn$_2$GaC (red circles), and unpolarized neutron diffraction (open black circles). Pure magnetic peaks appear at momentum transfer below 1.0 Å-1, originating from long-ranged antiferromagnetic order.

References

[1] “Long-range antiferromagnetic order in epitaxial Mn$_2$GaC thin films from neutron reflectometry”, A. S. Ingason, G. K. Palsson, M. Dahlqvist, and J. Rosen, Physical Review B 94, 024416 (2016).

Hollow pH Sensitive Polymeric Nanospheres Modified With Quantum Dots for Theranostic Applications

Athina Papadopoulou[1,2*], Eleni Efthimiadoul[2]

[1]Institute of Nanoscience and Nanotechnology, National Center for Scientific Research "Demokritos", Athens, Greece
[2]Department of Chemistry, National and Kapodistrian University of Athens, Athens, Greece

Nowadays, in nanomedicine field, nanomaterials are widely used as carriers for theranostic applications. The advantages of using polymers in nanomedicine include biocompatibility, structural flexibility, low toxicity, and low cost.[1]

In this work, we focus on a strategy, where first prepared polymer nanospheres are subsequently 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. With the ease to provide simultaneous therapy and imaging under controlled delivery, polymer nanoparticles have great potentials in biomedical research and applications.[2] This work describes the synthesis of hollow pH sensitive polymer nanospheres (NS) modified with quantum dots, which have important properties, for drug loading and release to the target cells. In detail, the hybrid NS will be synthesized in two steps procedure. In the first step, NS developed by using radical emulsion polymerization and in the second step doping with QDs will be taken place.

Their colloidal stability, structural and morphological characterization will be evaluated by DLS, FT-IR, SEM and TEM. Furthermore, hemolysis, wound healing and MTT assay, will be assessed in order to evaluate their biocompatibility. Fluorescent microscopy will be used to investigate the hybrid NS uptake and localization in different cell cultures.[3]

References

[1] "Recent Advances in pH-Sensitive Polymeric Nanoparticles for Smart Drug Delivery in Cancer Therapy", Lim, Eun-Kyung, Chung, Bong H., Chung, Sang J., Current Drug Targets 19(4), 300-317 (2018).
[2] "Quantum dots: Applications and safety consequences", Reshma, V. G. Mohanan, P. V., Journal of Luminescence 205, 287-298 (2019).
[3] "Multifunctional nanoparticles for drug delivery and molecular imaging", Bao, G. Mitragotri, S. Tong, S., Annu Rev Biomed Eng 15, 253-82 (2013).

Spintronics and THZ Radiation: Probing Ultrafast Spin and Charge Current Dynamics

Evangelos Papaioannou

Fachbereich Physik and Landesforschungszentrum OPTIMAS, Technische Universität Kaiserslautern, Kaiserslautern, Germany

e-mail: papaio@rhrk.uni-kl.de

The conversion mechanism of spin to charge currents and vice versa, with the help of the spin Hall and the inverse spin Hall effect plays currently a central role in the research field of spintronics. The target is to realize future spintronic devices operated at THz frequencies based on the ultrafast generation and conversion of charge and spin currents.

Here, we present experiments using femtosecond laser pulses to trigger ultrafast spin and charge dynamics in magnetic bilayers composed of ferromagnetic (FM) /non-magnetic (NM) layers where the NM layer features a strong spin-orbit coupling. Such heterostructures are novel sources for the generation of THz radiation based on the spin-to-charge conversion in magnetic films.[1-3] The key technological and scientific challenge of THz spintronic emitters is to increase their low intensity and frequency bandwidth. In this presentation it will be demonstrated the way to engineer both factors by taking into account the scattering lifetime and the interface transmission of spin polarized, non-equilibrium electrons. It will be resolved the role of the electron-defect scattering lifetime on the spectral shape and of the interface transmission on the THz amplitude and how this is linked to the structural properties of bilayer emitters. The enhanced performance of spintronic terahertz emitters based on bulk and interface defect density will be revealed. The presented results will define a roadmap[4] of the properties of the emitted as well as the detected THz-pulse shapes and spectra that is essential for future applications of spintronic emitters in THz technology.

References

[1] "Efficient terahertz generation using Fe/Pt spintronic emitters pumped at different wavelengths", E. T. Papaioannou et al., IEEE Transactions on Magnetics 54, 1 (2018).

[2] "Optimized spintronic terahertz emitters based on epitaxial grown Fe/Pt layer structures", G. Torosyan et al., Sci. Rep. 8, 1311 (2018).

[3] "Efficient metallic spintronic emitters of ultrabroadband terahertz radiation", T. Seifert et al., Nat. Photon. 10, 483 (2016).

[4] "Enhanced performance of spintronic terahertz emitters based on defect engineering", S. Keller et al., Arxiv: http://arxiv.org/abs/1901.10011 (2019).

Sensitization of Semiconductor Single Crystals with Quantum Confined Semiconductors

K. Watkins, L. Kubie, M. Spitler, B. A. Parkinson*

Department of Chemistry, University of Wyoming, WY, USA

*e-mail: bparkin1@uwyo.edu

We report studies of the fundamentals of electron injection by molecules, quantum dots, quantum confined nanoplatelets and semiconducting nanotubes into large bandgap metal oxide semiconductors and gallium phosphide. We have been testing a theoretical model that predicts that the photocurrent yields and photocurrent-voltage behavior are controlled by the doping density that then determines the field gradient of the Schottky barrier at the electrode/electrolyte interface. The model was shown to be applicable to sensitization by both thiacyanine and ruthenium based sensitizing dyes with the difference of the behavior between the two classes of dyes being attributed to the different distance of the photogenerated hole on the dye from the injected electron that influences the rate of the back reaction. We have extended these studies to monolayers of adsorbed CdSe quantum dots (QDs) of various sizes on well-characterized TiO_2 single crystals with varying doping densities. We are also building on our previous work where we were able to observe sensitized photocurrent quantum yields >1 from multiple exciton generation and collection from PbS quantum dots adsorbed on single crystal anatase electrodes and are working on preparation of InSb QDs that may be capable of producing 3 excitons per high energy photon.

We have also discovered that hot injection synthesis of silver sulfide (Ag_2S) nanoparticles forms nanoplatelets with a height of only 3.5±0.2 Å and are quantum-confined with a 1S exciton Bohr diameter resulting in a confinement ratio of ~12.6. The growth of these NPLs is quantized by layer thickness as indicated by UV-vis spectra and steady-state fluorescence spectra. TEM, XRD and AFM analyses of these NPLs support platelet formation along the (202) plane of the Ag_2S structure. Unlike previous Ag_2S studies, the sensitized photocurrent spectroscopy measurements mimic the distinct absorption spectral shapes of the nanoplatlets.

We have also shown that photoexcited single wall semiconducting nanotubes (SWSNTs) can produce sensitized photocurrents on n-TiO_2, n-SnO_2 and n and p-GaP single crystal electrodes. The key to this success appears to be the use of cholate to solubilize the nanotubes that then provides a carboxylate group to bond directly to the oxide surface that increases the electronic coupling to the semiconductor. In addition to sensitization we see photocurrents due to SWSNTs can also be produced with the semiconductor under accumulation and the SWSNTs acting as a semiconducting absorber.

Exploring Magnetic Disorder at the Nanoscale

D. Peddis[1,2*], N. Yaacoub[3], R. Mathieu[4], K. N. Trohidou[5], D. Fiorani[1]

[1]*Istituto di Struttura della Materia-CNR, 00015 Monterotondo Scalo (RM), Italy*
[2]*DCCI, Università di Genova, Genova, Italy*
[3]*IMMM, UMR CNRS 6283, Le Mans Université, Le Mans Cedex 9, France*
[4]*Department of Engineering Sciences, Uppsala University, Uppsala, Sweden*
[5]*Institute of Nanoscience and Nanotechnology, NCSR "Demokritos," Aghia Paraskevi, Attiki, Greece*

[*]e-mail: davide.peddis@unige.it

Magnetic nanoparticles (MNPs) show many interesting phenomena due to their unusual physical properties strongly correlated with their size and morphology. Among the relevant features of the size reduction of MNPs, the occurrence of surface magnetic disorder deserves a special attention as it strongly modifies the magnetic properties of the materials. In the case of magnetic nanoparticles with surface to volume ratio (S/V) higher than 1 (i.e. for spherical nanoparticle with diameter below 5 nm) the fraction of spins lying at/or near the surface produces a great enhancement of surface anisotropy and magnetic frustration due to the spin disorder. In this frame, this communication will present two kinds of nanoparticle systems with high S/V ratio, highlighting the effect molecular coating and peculiar magnetic structure in hollow nanoparticles with R > 1. We investigated the effect of coating 5 nm $CoFe_2O_4$ particles by diethylene glycol (DEG) and oleic acid (OA). An unexpected increase of the saturation magnetization and the blocking temperature, and a decrease of the coercive field was observed DEG coated $CoFe_2O_4$ nanoparticles with respect to nanoparticles coated by OA. This can be attributed to the larger atomic magnetic moments and to the lower magnetocrystalline anisotropy of the DEG sample as was demonstrated by DFT calculations1. Starting from these results and having in mind the exploration of "the no man's land" of system with very high value of R > 1 hollow iron oxide nanoparticles with external diameter ~9.4 nm has been investigated. High-resolution transmission electron microscopy images confirmed the crystalline structure and the presence of an ultrathin shell thickness of ~1.4 nm, implying, to the best of our knowledge, the highest value of R observed in the literature (R ≈ 1.5). These hollow nanoparticles have been investigated by AC/DC magnetization measurements and using zero-field/in-field 57Fe Mössbauer spectrometry. The in-field hyperfine structure suggests presence of a complex magnetic structure that can be fairly described as due to two opposite pseudo speromagnetic sublattices attributed to octahedral and tetrahedral iron sites. Such an unusual feature, observed for the first time in crystalline materials.[2]

Acknowledgements

This work was partially supported by the FET-Proactive MAGENTA Project (Contract N. 731976).

References

[1] Vasilakaki, M., D. Peddis et al. Nanoscale 2018, 21244–21253.
[2] Sayed, F.; D. Peddis, et alJ. Phys. Chem. C 2018, 122, 7516–7524.

Detection of Molecular Nanomagnet Thin Films with Plasmon-Enhanced Magneto-Optics

F. Pineider[1,2 *], E. Pedrueza de Villalmanzo[3], A. Mekonnen Adamu[3], M. Serri[2],
E. Smetanina[3], V. Bonanni[2], G. Campo[2], L. Poggini[2], M. Mannini[2],
C. de Julián Fernández[4], C. Sangregorio[5], M. Gurioli[6], A. Dmitriev[3], R. Sessoli[2]

[1]Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa, Italy,
[2]Department of Chemistry 'Ugo Schiff', University of Florence, Sesto Fiorentino (FI), Italy
[3]Department of Physics, University of Gothenburg, Göteborg, Sweden
[4]CNR-IMEM, Parma, Italy
[5]CNR-ICCOM, Sesto Fiorentino (FI), Italy
[6]Department of Physics and Astronomy, University of Florence, Sesto Fiorentino (FI), Italy

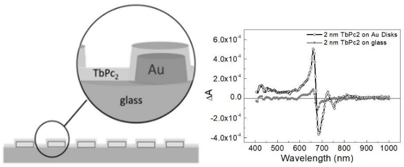
[*]e-mail: francesco.pineider@unipi.it

Accessing the behavior of molecular nanomagnets deposited on surfaces is challenging but highly important, in view of the technological development of molecule-based electronics. To date, synchrotron radiation-based x-ray magnetic circular dichroism is considered the most suited technique to this aim;[1,2] however, more flexible, laboratory scale experiments represent a welcome addition.

Here we propose plasmon-enhanced magnetic circular dichroism in the visible range to study thin films (2 nm) of the TbPc2 single-molecule magnet deposited on gold nanodisks. The significant boost in magneto-optical response afforded by the nanoantennas (see Figure 1) allows obtaining spectroscopic and magnetometric information of the molecular deposit.

To accurately interpret the magneto-optical response of the molecular-plasmonic hybrid structure, the magnetoplasmonic behavior of the gold nanodisks was modelled quantitatively.[3,4] We found that such contribution is far from negligible, and it is mandatory to and take it into account to understand the optical and magneto-optical processes taking place in the hybrid nanostructure.

With this proof of concept, which we believe is the first reported case of plasmon enhanced magneto-optics on molecular nanomagnets, we suggest that with appropriate tuning of the plasmon resonance of the nanoantenna to the molecular absorption bands this could become a general method to study reduced amounts of magnetic materials on surface.



Acknowledgements

This work has been financed by the EC through grant 737093, "FEMTOTERABYTE" H2020-FETOPEN-2016-2017.

References

[1] M. Mannini et al., Nature Mater., 2009, 8, 194.
[2] M. Mannini et al., Nature, 2010, 468, 417.
[3] F. Pineider et al., Nano Lett., 2013, 13, 4785.
[4] B. Sepulveda et al., Phys. Rev. Lett. 2010, 104, 147401.

Preparation, Characterization and Magnetic Properties of Fe-Ni Alloys

I. G. Pitsakis[1*], V. Karoutsos[1], P. Poulopoulos[1], M. Angelakeris[2], C. Politis[3]

[1]Department of Materials' Science, University of Patras, Patras, Greece
[2]Department of Physics, Aristotle University of Thessaloniki, Thessaloniki, Greece
[3]Department of Materials Science and Engineering, University of Texas at Arlington, Arlington, TX, USA

[*]e-mail: johnpitsakis@gmail.com

Two different Fe-Ni alloys were prepared using the electric arc voltage method: $Fe_{50}Ni_{50}$ and $Fe_{60}Ni_{40}$. Unlike commercial alloys, which always contain impurities, our samples were synthesized by using high quality powders (99.99 wt. %) in an argon gas atmosphere.

The samples were heated up to 650℃ and were then cooled at a very slow rate of 0.8℃/h down to a temperature of 250℃ in order to approach thermal stability as close as possible. Before and after the heat treatment, the samples' structure was examined using scanning electronic microscopy (Zeiss Evo MA10) Energy Dispersive X-ray Spectroscopy (EDS) and X-ray diffraction spectroscopy (XRD). The magnetic properties of the samples were determined using a vibrating-sample magnetometer.

The EDS measurements show that there are few dispersed localized particles in the γ-disordered FCC phase of the $Fe_{60}Ni_{40}$ sample where Fe-Ni composition is close to 50-50 (weight %). Furthermore, the magnetic hysteresis curves reveal an increase in coercivity of the heat treated samples (especially for the $Fe_{50}Ni_{50}$ sample) compared to the same samples before heat treatment.

These results suggest that, during a slow-rate cooling process, a phase transition takes place transforming, to a minor extent, from the γ-disordered phase of our Fe-Ni alloys to the L10 ordered phase.

Unusual Magnetic Response of Au in a Plasmonic Material

P. Poulopoulos[1*], A. Stamatelatos[1], A. Goschew[2], P. Fumagalli[2], E. Sarigiannidou[3], L. Rapenne[3], C. Opagiste[4], S. Grammatikopoulos[5], F. Wilhelm[6], A. Rogalev[6]

[1]Materials Science Department, University of Patras, Patras, Greece
[2]Institut für Experimentalphysik, Freie Universität Berlin, Berlin-Dahlem, Germany
[3]Univ. Grenoble-Alpes, CNRS, Grenoble INP, LMGP, Grenoble, France
[4]Institut Néel, CNRS, UGA, Grenoble INP, Grenoble - France
[5]Department of Mechanical Engineering, Technological Educational Institute (T.E.I.) of Western Greece, Patras, Greece
[6]European Synchrotron Radiation Facility (ESRF), Grenoble, France

[*]e-mail: poulop@upatras.gr

Thin films of noble nanoparticles, usually Ag or Au, embedded in a dielectric matrix produce nowadays quite some scientific interest. Their optical absorption spectra in the visible light are dominated by localized surface plasmon resonance(s) (LSPR). Plasmonic thin films find advanced technological applications such as in clean energy, enhanced- efficiency solar cells, photocatalysis, gas sensing etc., see e.g.[1]

Recently, we have developed Au-Ni-O plasmonic thin films with intense LSPRs starting from a precursor fully disordered Au-Ni-O alloy.[2] In this work, we focus on the magnetic response of Au in such a material. The technique of choice is the element-specific X-Ray Magnetic Circular Dichroism (XMCD). Magnetic measurements, performed at room temperature with fields as large as 17 T, show, surprisingly, a paramagnetic behavior of Au. Au, in bulk form, is a diamagnet. High Resolution Transmission Electron Microscopy (HRTEM) reveals the existence of tiny Au nanoparticles with a size of a few atomic layers. Charge transfer from Au to oxygen is revealed with the help of X-Ray Absorption (XAS) spectra. Our experiments show a way to establish and probe Au paramagnetism in alloys.

Acknowledgements

We thank the ESRF crew for the excellent operational conditions. This work was partially co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code:T1EDK-04659).

References

[1] "Combined effects of small gold particles on the optical gas sensing by transition metal oxide films", M. Ando, T. Kobayashi, M. Haruta, Catal. Today 36, 135 (1997).

[2] "Growth of Au Nanoparticles in NiO via Short Annealing of Precursor Material Thin Film and Optimization of Plasmonics", S. Grammatikopoulos et al., Phys. Status Solidi A 214, 1700303 (2017).

A Novel Microwave Assisted Hydro/Solvothermal Method to Prepare $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ and $LiFePO_4$ for Lithium Batteries

Selvarasu Praneetha*, A. Vadivel Murugan

Pondicherry University(A Central University), Pondicherry, India

*e-mail: praneethaselvarasu@gmail.com

Development of low-cost, environmentally friendly system has proven to be a safe and effective cathode material for a lithium-ion rechargeable battery. $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ (LRMR) and $LiFePO_4$ (LFP) were captured wide research interest in recent years as they offer high capacities of around ~250 $mAhg^{-1}$ and 170 $mAhg^{-1}$ with a significant reduction in materials cost and improvement in safety, compared to the $LiCoO_2$ cathode. A major limitation with $LiFePO_4$ arises due to its poor electronic and ionic conductivities. Moreover, layered solid-solutions exhibit a huge IRCL loss due to side-reaction on cathode surface with the electrolyte. We present here, innovative and energy efficient low-cost processes namely microwave assisted hydrothermal and solvothermal solid-solutions cathodes with hierarchical micro-/nanostructure surface modifications using GNS, Al_2O_3, $MgPO_4$ and $FePO_4$. The obtained products were characterized by powder XRD, XPS, Raman spectroscopy and TEM analysis Electrochemical characterization were also demonstrated, which exhibits a discharge capacity of ~ 164 $mAhg^{-1}$ for LFP and ~ 300 $mAhg^{-1}$ for 1.5 wt.% $MgPO_4$ + 2.5 wt.% Al_2O_3-coated LRMR sample with spherical morphology with excellent columbic efficiency of 92% upon 100 cycles. We believe that above said innovative processes could be considered as an efficient way to synthesize cathode materials for lithium batteries.

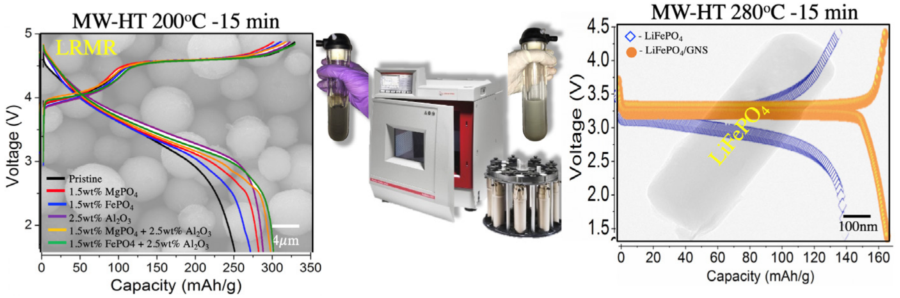


Figure 1. Schematic illustration of MW- HT/ST process to synthesize $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ & GNS/$LiFePO_4$ nanohybrid and their electrochemical studies.

References

[1] "High capacity double-layer surface modified $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ cathode with improved rate capability", QY Wang, Jun Liu, A. Vadivel Murugan, Arumugam Manthiram, J.Mater.Chem., 19, 4965-4972 (2009).

[2] "A rapid, one-pot microwave-solvothermal synthesis of a hierarchical nanostructured graphene/$LiFePO_4$ hybrid as a high performance cathode for lithium ion batteries", S. Praneetha and A. Vadivel Murugan, RSC Advances, 3, 25403-25409 (2013).

Iron Oxide Magnetic Nanoparticles Modified with Biomolecules for Theranostic Applications

Danai Prokopiou[1,2*], Elias Sakellis[1], Beata Kalska-Szostko[4], Michael Pissas[1], Nikos K. Boukos[1], Anna Laurenzanna[3], Eleni K Efthimiadou[1,2]

[1]*Institute of Nanoscience and Nanotechnology, National Center for Scientific Research "Demokritos", Athens, Greece*
[2]*Department of Chemistry, National and Kapodistrian University of Athens, Athens, Greece*
[3]*Department of Biomedical and Clinical Science, University of Florence, Florence, Italy*
[4]*Institute of Chemistry, University of Bialystok, Bialystok, Poland*

Iron Oxide Magnetic Nanoparticles (IONPs) attract great interest on the scientific community due to their broad spectrum of applications. As theranostic agents can be used aiming to improve cancer diagnosis and treatment in early stage, reducing simultaneously the side effects on normal tissues (magnetic drug targeting).[1] One of the most known therapeutic approach is hyperthermia on the site of tumor by using alternate magnetic field. Furthermore, the IONPs used as contrasts agents *(in vivo)* in MRI, in gene transformation, biosensors, enzyme immobilization, immunoassays, purification *(in vitro)* and so on.[2]

In this work, we synthesized magnetic nanoparticles modified with tri-sodium citrate and sodium borohydride, as reducing and coating agents in one step synthesis aiming at improving their colloidal behavior and targetability.[1] In order to improve the hydrophilicity and biocompatibility of the IONPs coated with PEG-co-PLA copolymer. This synthesis was carried out in two steps in presence with PVA and PVP polymers.

The evaluation of cytotoxicity in IONPs coated with organic molecules, was performed by using the MTT assay in different cell lines, healthy and diseased. As healthy cells were used NCTC and HEK and as cancerous A375-M6 and U87MG cells. According to our results it is observed that IONPs are not toxic after incubation to healthy cells. To investigate the cellular uptake of IONPs we used Prussian Blue stain to identify the mNPs localization. And it is observed that the mNPs penetrate the cells' membrane and localized on their nucleus. To study the integrity of the cell (NCTC, A375-M6) cytoskeleton after treatment with mNPs fluorescent microscopy was used and we observed that after treatment with mNPs, the cancer cells led to apoptosis. Finally, an additional biological examination of cell cytotoxicity was carried out in epidermal cells after treatment with mNPs. The used assay called wound healing let us to evaluate how the cells' growth affected by the treatment.

References

[1] "Magnetic nanoparticles: synthesis, protection, functionalization, and application.", Lu, A.H., E.L. Salabas, and F. Schuth, Angew Chem Int Ed Engl, 46(8): p. 1222-44, 2007.

[2] "Interaction of metal oxide nanoparticles with lung surfactant protein A." Schulze, C., U.F. Schaefer, C.A. Ruge, W. Wohlleben, and C.M. Lehr, Eur J Pharm Biopharm, 77(3): p. 376-83, 2011.

Metal and Charge-Transfer Complexes of the Color Chromophores of Fruits, Flowers and Wine

Frank H. Quina[1*], Cassio P. Silva[1], Gustavo T. M. Silva[1], Karen M. Silva[1],
Adilson A. Freitas[2], Farhan Siddique[3], Xue Li[3], Juanjuan He[3], Adelia J. A. Aquino[3]

[1]*Instituto de Química, Universidade de São Paulo, São Paulo, Brazil*
[2]*Instituto Superior Técnico, Universidade Nova de Lisboa, Lisbon, Portugal*
[3]*School of Pharmaceutical Science and Technology, Tianjin Univ., Tianjin, China*

[*]e-mail: quina@usp.br

The colors of anthocyanins, the natural plant pigments responsible for most of the red, purple and blue colors of flowers, fruits and leaves, are modulated by pH, substitution and complexation with metal ions and/or colorless organic molecules (copigments) such as hydroxycinnamic acids or esters.[1,2] Anthocyanins and their synthetic analogs (hydroxyflavylium cations) are very efficient at absorbing and dissipating light energy via excited state proton transfer or charge-transfer mediated internal conversion without appreciable excited triplet state formation. Circumventing the ultrafast energy dissipation pathways that contribute to the photostability of these pigments is key to the rational design of fluorescent pigments or probes, photoredox catalysts and novel PDT sensitizers based on pyranoflavylium cation chromophores.[1] During the maturation of red wine, the anthocyanins of grapes are transformed into pyranoanthocyanins, which have a pyranoflavylium cation chromophore. The relatively facile synthesis of substituted pyranoflavylium cations permits manipulation of the redox properties and the nature of the lowest excited state (TICT, charge-transfer or localized).[3] Synthetic pyranoflavylium cations can be quite fluorescent and form charge-transfer complexes with colorless molecules but, unlike anthocyanins, form long-lived triplet states and singlet oxygen in acidic acetonitrile solution.[4] A combination of experimental and ab initio quantum chemical methodology is currently being employed to elucidate structure/property/color relationships for flavylium and pyranoflavylium cation chromophores and their metal ion and charge-transfer complexes.

References

[1] "Chemistry inspired by the colors of fruits, flowers and wine", F. H. Quina; E. L. Bastos, Anais Acad. Bras. Ciênc., 90, 681 (2018).
[2] "Quantum Chemical Investigation of the Intramolecular Copigmentation Complex of an Acylated Anthocyanin", He et al.. J. Braz. Chem. Soc., 30, 492 (2019).
[3] "The electronic transitions of analogs of red wine pyranoanthocyanin pigments", Siddique et al., Photochem. Photobiol. Sci., 18, 45 (2019).
[4] "Triplet Excited States and Singlet Oxygen Production by Analogs of Red Wine Pyranoanthocyanins", Silva et al., Photochem. Photobiol., 95, 176 (2019).

Microbial Poly-γ-Glutamic Acid (γ-PGA)-Based Micro/Nanoparticles as Delivery Systems

Iza Radecka[1*], Martin P. Khechara[1], Marek Kowalczuk[1,2], Mariastella Scandola[3], Maria Letizia Focarete[3], Ibrahim R. Khalil[1]

[1]*Faculty of Science and Engineering, University of Wolverhampton, Wulfruna Street, Wolverhampton, UK*
[2]*Polish Academy of Sciences, Centre of Polymer and Carbon Materials, Zabrze, Poland*
[3]*Department of Chemistry 'G. Ciamician' and National Consortium of Materials Science and Technology (INSTM, Bologna RU), Alma Mater Studiorum – Università di Bologna Bologna, Italy*

[*]e-mail: i.radecka@wlv.ac.uk

Poly-γ-glutamic acid (γ-PGA)-based micro/nanoparticles have gathered significant attention as antimicrobial agents and for drug delivery.[1] γ-PGA is a naturally occurring biodegradable, non-toxic and non-immunogenic biopolymer produced by several gram-positive bacteria. Moreover, due to the presence of carboxylic groups on the side chains it offers an attachment point for various therapeutic agents.

Recently, there has been an increasing interest in an oncolytic adenoviral vector as an alternative anti-cancer therapy.[2] Therefore, significant research efforts have been focused on the development of biodegradable polymer poly-gamma-glutamic acid (γ-PGA)-based nanoparticles used as a vector for safe anti-cancer therapy. In addition, there has been an increasing interest in oncolytic adenoviral (Ad) vector anti-cancer therapy due to their ability to efficiently infect a variety of both dividing and non-dividing cells. However, the major barrier towards Ad vector applications is the induction of an immune response. Our study introduces a specific antibody blind polymer coated-viral vector into cancer cells using γ-PGA and chitosan (CH). Adenovirus was successfully encapsulated into the biopolymer particles using the ionic gelation method.[1,2] Moreover, only 3.1% of encapsulated adenovirus was detected by anti-adenovirus antibodies compered to naked adenoviruses. The unique characteristics of γ-PGA based particles have a promising future for pharmaceutical applications and in anti-cancer therapy.

References

[1] "Bacterial-Derived Polymer Poly-γ-Glutamic Acid (γ-PGA)-Based Micro/Nanoparticles as a Delivery System for Antimicrobials and Other Biomedical", Khalil, I. R.; Burns, A. T. H.; Radecka, I.; Kowalczuk, M.; Khalaf, T.; Adamus, G.; Johnston, B.; Khechara, M.P., International Journal of Molecular Sciences, 18, page 313 (2017)

[2] "Poly-Gamma-Glutamic Acid (γ-PGA)-Based Encapsulation of Adenovirus to Evade Neutralizing Antibodies", Khalil, I.R., Khechara, M., Kurusamy, S., Armesilla, A., Gupta, A., Mendrek, B., Khalaf, T., Scandola, M., Focarete, M., Kowalczuk, M., Radecka, I. Molecules, 23, page 2565 (2018)

Fuel from the Sun: Where is That Pot of Gold?

Krishnan Rajeshwar

The University of Texas at Arlington, Arlington, TX, USA

e-mail: rajeshwar@uta.edu

Impressive advances have been made in our fundamental understanding of semiconductor/electrolyte interfaces, both in the dark and under illumination. Yet it must be said that no viable commercial processes exist, at least to date, for generating energy-rich products from reducing CO_2 or by splitting water. No better yardstick is needed from two sciences of comparable vintage: namely, high Tc superconductors and Li-ion batteries. It is beyond debate that both these sciences have evolved into mature technologies that have seen the light of day in terms of commercialization. What will it take to move photoelectrochemical solar fuels generation into the commercial space? The materials challenges will be discussed in this talk.

Deterministic Nanofabrication of Quantum-Dot Based Single-Photon Sources for Applications in Quantum Communication

Stephan Reitzenstein

Technische Universität Berlin, Berlin, Germany

e-mail: stephan.reitzenstein@physik.tu-berlin.de

Non-classical light sources are major building blocks for photonic quantum networks and for photonic quantum information technology. In this context, significant progress has been achieved regarding the development of efficient single-photon sources based of self-assembled quantum dots (QDs) with superb optical and quantum optical properties. However, the position and emission energy of these nanostructures is random, which leads to low processing yield and poor device performance if standard nano-processing schemes are used to realize quantum devices with single QDs acting as quantum emitters. These issues have strongly limited the applicability of single QD based non-classical light sources beyond proof-of-principle experiments.

In order to realize highly efficient and scalable QD based non-classical light sources I will introduce a nanotechnology platform based on in-situ electron-beam lithography (EBL). This technique allows us to integrate pre-selected QDs into nanophotonic devices such as microlenses and waveguide systems with nm-accuracy, flexible device design and high process yield.[1,2] Using 3D in-situ EBL we realize deterministic QD-microlenses (see Fig. 1) which feature excellent properties in terms of broadband photon extraction efficiency, single photon purity and photon indistinguishability.[3] Moreover, I will present that deterministic QD-microlenses allow us to explore the limits of photon indistinguishability by delay-time and temperature dependent Hong-Ou-Mandel experiments,[4] and to path the way towards entanglement swapping.[5] Beyond that, QD-microlenses are model systems for the coherent control of the QD's biexciton-exciton cascade[6] and for the efficient generation of polarization entangled photon pairs.

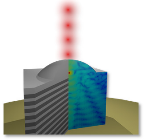


Figure 1. Schematic view of a single-QD microlens.

References

[1] "In situ electron-beam lithography of deterministic single-quantum-dot mesa-structures using low-temperature cathodoluminescence spectroscopy", M. Gschrey et al., Appl. Phys. Lett. 102, 251113 (2013)

[2] "Deterministic Integration of Quantum Dots into on-Chip Multimode Interference Beamsplitters Using in Situ Electron Beam Lithography", P. Schnauber et al., Nano Letters 18, 2336 (2018)

[3] „Highly indistinguishable photons from deterministic quantum-dot microlenses utilizing three-dimensional in situ electron-beam lithography", M. Gschrey et al., Nat. Commun. 6, 7662 (2015)

[4] "Exploring Dephasing of a Solid-State Quantum Emitter via Time- and Temperature-Dependent Hong-Ou-Mandel Experiments", A. Thoma et al., Phys. Rev. Lett. 116, 033601 (2016)

[5] "wo-photon interference from remote deterministic quantum dot microlenses", A. Thoma et al., Appl. Phys. Lett. 110, 011104 (2017)

[6] "Path-Controlled Time Reordering of Paired Photons in a Dressed Three-Level Cascade", S. Bounouar et al., Phys. Rev. Lett. 118, 233601 (2017)

Creation and Manipulation of Magnetic Topological Textures by Electrical Means

Davi Röhe Rodrigues[1*], Artem Abanov[2], Jairo Sinova[1, 3], Karin Everschor-Sitte[1]

[1]Institute of Physics, Johannes Gutenberg – Universität, Mainz, Germany
[2]Department of Physics & Astronomy, Texas A&M University, College Station, TX, USA
[3]Institute of Physics ASCR, v.v.i, Czech Republic

[*]e-mail: davrodri@uni-mainz.de

We present methods to control the creation and motion of magnetic nanostructures by electrical means. Inspired by the ideas of the 2007 and 2016 Physics' Nobel prize awarded projects on electrical resistance dependence on magnetic textures and topology applications in condensed matter, we study the current-driven dynamics of topological magnetic textures. The (meta)stability of these structures provided by topological properties and their manipulation by current allows for their use in fast and efficient nanosized memory and logic devices.

By exploring the fundamental principles of the highly complex model for ferromagnetic materials, we present methods with minimal requirements to create topological objects and obtain an effective theory to describe their motion. We show that it is possible to controllably create magnetic domain walls and skyrmions by currents in materials with engineered inhomogeneities.[1,2] Above a critical current strength defined by the material properties, the creation period obeys a universal power law. We show that these magnetic textures can be created even without the aid of "twisting terms". We propose methods to decrease the magnitude of the critical current for more efficient applications. Moreover, despite the infinite degrees of freedom within the underlying model, we obtain an effective description of the current and field-driven motion of topological textures in terms of a finite set of soft modes.[3,4] These modes correspond to pairs of variables whose dynamics can be determined independently of the material properties and specific textures' profiles. These powerful and general results pave the way for conceiving spintronic devices with a broad range of materials and configurations.

References

[1] "Current-driven periodic domain wall creation in ferromagnetic nanowires", M.Sitte, K.Everschor-Sitte, T.Valet, D.R.Rodrigues, J.Sinova, A.Abanov, Phys.Rev.B 94, (2016)
[2] "Skyrmion production on demand by homogeneous DC currents", K. Everschor-Sitte, M.Sitte, T.Valet, Ar.Abanov, and J.Sinova, New Journal of Physics 19, (2017)
[3] "Spin texture motion in antiferromagnetic and ferromagnetic nanowires", D.R. Rodrigues, K.Everschor-Sitte, O.A.Tretiakov, J.Sinova, Ar.Abanov, Phys.Rev.B 95, (2017)
[4] "Characterizing breathing dynamics of magnetic skyrmions and antiskyrmions within the Hamiltonian formalism", B.F. McKeever, D.R. Rodrigues, D.Pinna, Ar.Abanov, J.Sinova, K.Everschor-Sitte, Phys.Rev.B 99, (2019)

Nano-Structured Photocatalytic Surfaces Prepared by Sputtering for Infections Prevention in Hospital Facilities: Non-Noble Metals for a Noble Aim

Sami Rtimi

Swiss Federal Institute of Technology at Lausanne, EPFL, Lausanne, Switzerland

During the last few decades, the increase of infections by toxic pathogens/biofilms leading to hospital-acquired infections (HAIs) has motivated many scientists in the area. More advanced antibacterial films presenting uniform nano-particulates distribution, high adhesion to the substrate, mechanical resistance and faster bacterial/biofilm inactivation under light or in the dark are needed due to health concerns. Cu-, Ag-, Fe-based nanostructured thin films have been used under actinic light (λ< 387 nm) and reported to generate highly oxidative radicals leading to fast antibacterial action (Gram+ and Gram-) as shown in Scheme 1. Moreover, TiO_2-based thin films have been reported to inactivate bacteria under UV light. The restricted absorption of the indoor visible/actinic light has motivated workers to dope TiO_2 with metal oxides or to use bimetal coated surfaces (i.e. Cu, Ag or Fe) to shift the absorption of the films to the visible region. In this talk, I will show the coupling of TiO_2 with copper oxide, silver oxide or iron oxide killing bacteria in the minute range and a brief illustration of the bactericidal activity of Ag-Cu bimetal/oxides system. The potential for practical applications of these innovative nanostructured 2D films and 3D sputtered medical devices in health-care facilities are accounted for in the present talk.

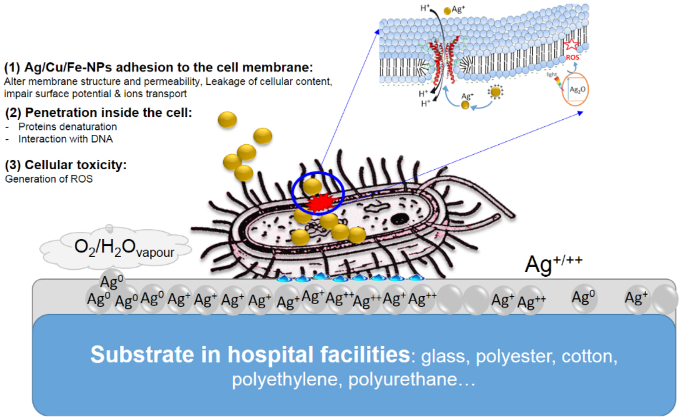


Figure 1. Schematic illustration of bacterial inactivation on nanostructured sputtered surfaces/substrates.

Nanoreactors of Metal-Oxide Supported Combinations of Noble Metal Catalytic Nanoparticles: Electrooxidation of Simple Organic Fuels

Iwona A. Rutkowska*, Pawel J. Kulesza

Faculty of Chemistry, University of Warsaw, Warsaw, Poland

*e-mail: ilinek@chem.uw.edu.pl

There has been growing interest in utilizing small (simple) organic molecules, as alternative fuels to hydrogen, in electrochemical energy conversion systems. In addition to ethanol (biofuel), that can be ideally oxidized to carbon dioxide thus delivering twelve electrons, recent important systems include dimethyl ether as well. But realistically the respective reaction is rather slow at ambient conditions. Obviously, there is a need to develop novel electrocatalytic materials.

Platinum has been recognized as the most active catalytic metal towards oxidation of ethanol at low and moderate temperatures. But Pt anodes are readily poisoned by the strongly adsorbed intermediates, namely by CO-type species, requiring fairly high overpotentials for their removal. To enhance activity of Pt catalysts towards methanol and ethanol oxidation, additional metals including ruthenium, tin, molybdenum, tungsten or rhodium are usually introduced as the alloying component. More recently it has been demonstrated that catalytic activity of platinum-based nanoparticles towards electrooxidation of ethanol has been significantly enhanced through interfacial modification with ultra-thin monolayer-type films of metal oxo species of tungsten, titanium or zirconium.

We pursue a concept of utilization of mixed metal (e.g. zirconium/tungsten or titanium/tungsten) oxide matrices for supporting and activating noble metal nanoparticles (e.g. PtRu) during electrooxidation of methanol and ethanol. Among important issues is incorporation of Rh nanostructures capable of weakening, or even breaking, the C-C bond in the ethanol molecules. On the other hand, rhodium itself is not directly electrocatalytic toward oxidation of ethanol. The oxides and noble metal nanoparticles have been deposited in a controlled manner using the layer-by-layer method. Remarkable increases of electrocatalytic currents measured under voltammetric and chronoamperometric conditions have been observed. The most likely explanation takes into account possibility of specific interactions of noble metals with transition metal oxide species as well as existence of active hydroxyl groups in the vicinity of catalytic noble metal sites. In addition, formation of "nanoreactors" where ethanol is partitioned (at Rh) to methanolic residues further oxidized at PtRu cannot be excluded.

Our recent interests concern dimethyl ether (CH_3OCH_3), a gas commonly used in aerosol propellants, solvents and coolants, as a possible alternative fuel for low temperature fuel cells. Dimethyl ether (DME) is non-toxic, non-teratogenic, non-mutagenic and non-carcinogenic gas. When oxidized to CO_2, a CH_3OCH_3 molecule releases 12 electrons. In this respect, we are going to consider combination of Pt or PtRu with the other metal (Pd) or metal (W, Mo) oxo nanostructures.

Microwave Detection of Free Charge Generation in Sensitized Molecular Thin Films

Garry Rumbles*, Obadiah Reid

[1]NREL, Golden, CO, USA
[2]Department of Chemistry and RASEI, University of Colorado, Boulder, CO, USA

*e-mail: garry.rumbles@nrel.gov

This presentation will discuss the microwave detection of free carriers generated in molecular thin films using judiciously chosen, dilute electron acceptors for both singlet and triplet states generated from a singlet fission process.

Understanding the photo-induced electron transfer processes in condensed phase systems, such as in molecular thin films, is an intriguing problem. Unlike studies of isolated, molecular dyads and triads in fluid solution, the product of the electron transfer system is not a bound charge-separated (CS) state, but state of unbound, separate charges that can drift under the influence of an applied field. Calculating the driving force of this process is similar to the well-established Weller equation for generating the CS state, but omits the coulomb term as the charges of free of this binding energy. However, we have found that this simplified version of the driving force is remarkably effective at identifying appropriate acceptors to disperse in the molecular films to generate high yields of long-lived free carriers. And yet it is unclear why a simple two-state description ($D^* + A \rightarrow D^+ + A^-$) of the system is appropriate.

In recent studies, where we have used transient microwave conductivity to detect the mobile charges in the molecular films, we have identified acceptors not only with an optimum reduction potential, but also low yields for acceptors whose reduction potentials are both lower and higher than the optimum. These results appear consistent with the inverted and normal regions of the Marcus formulation for photo-induced electron transfer theory. Yet it remains unclear which step in the charge generating process for which this formulation is appropriate, or why it is not always observed. A discussion of this interpretation of the data will form the focus of this presentation.

Atomic-Scale View on Thin-Film and Nanostructure Growth on Weakly-Interacting Substrates

K. Sarakinos

Nanoscale Engineering Division, Department of Physics, Chemistry and Biology, Linköping University, Linköping, Sweden

e-mail: kostas.sarakinos@liu.se

Growth of thin metal films and nanostructures with controlled morphology on weakly-interacting 2D material (e.g., graphene and MoS_2) and oxide (e.g., SiO_2, TiO_2, ZnO) substrates is an essential step in the fabrication of high-performance optoelectronic and sensing devices. This requires a universal understanding of the atomic-scale processes that govern the dynamics of film morphological evolution, from island nucleation through formation of a continuous film.

We use atomistic kinetic Monte-Carlo (kMC) simulations to study nucleation and growth of single Ag island on weakly-interacting fcc(111) surfaces.[1] The results show that 3D nuclei are first formed due to facile adatom ascent at single-layer island steps, followed by the development of sidewall facets bounding the islands, which in turn facilitates upward diffusion from the base to the top of the islands. The limiting atomic process which determines the island height, for a given number of deposited atoms, is the temperature-dependent rate at which adatoms cross from sidewall facets to the island top. The latter results in an increased top-layer nucleation probability with increasing temperature. This finding explains multiple experimental observations for film growth on weakly-interacting substrates, which show that film roughness increases with increasing growth temperature, contrary to morphological evolution data available for homoepitaxial film/substrate systems.

We confirm, experimentally, that Ag and Cu films deposited onto SiO_2 and a-C substrates exhibit a pronounced 3D morphology, using in situ growth monitoring and ex situ real-space imaging. Our data show that morphological evolution is controlled by either island nucleation or island coalescence, depending on the interplay between vapor arrival and adatom diffusion rates.[2,3] This interplay results in distinct scaling behaviors of the film thicknesses at which characteristic morphological transitions occur as function of synthesis conditions. Using these scaling laws, it is shown that it is possible to determine atomic-scale diffusion rates during the early-film formation stages.

References

[1] "Formation and morphological evolution of self-similar 3D nanostructures on weakly-interacting substrates", B. Lü, G.A. Almyras, V. Gervilla, J.E. Greene, and K. Sarakinos, Phys. Rev. Mat. 2, 063401 (2018).

[2] "Dynamic competition between island growth and coalescence in metal-on-insulator deposition", B. Lü, V. Elofsson, E.P. Münger, and K. Sarakinos, Appl. Phys. Lett. 105, 233113 (2014).

[3] "Atomic-scale diffusion rates during growth of thin metal films on weakly-interacting substrates", A. Jamnig, D.G. Sangiovanni, G. Abadias, and K. Sarakinos, Sci. Rep., under review (2019).

Nanostructure Dynamics by Means of a Multifractal Theory of Motion

Alexandra Saviuc[1], Vlad Ghizdovat[2], Maricel Agop[3, 4]

[1] "Alexandru Ioan Cuza" University of Iaşi, Faculty of Physics, Iaşi, Romania
[2] "Grigore T. Popa" University of Medicine and Pharmacy, Faculty of Medicine, Biophysics and Medical Physics Department, Iaşi, Romania
[3] Physics Department, "Gheorghe Asachi" Technical University, Iaşi, Romania
[4] Academy of Romanian Scientist, Bucuresti, Romania

Assimilating any nanostructure with a complex system, and assuming that the complex systems structural units motions take place on multifractal curves, some dynamics are analysed in the framework of a multifractal theory of motion.

In such context, in order to describe nanostructure dynamics, while remaining faithful to the differentiable and integrable mathematical procedures, it is necessary to explicitly introduce scale resolution in the expression of the described physical variables, and also in the fundamental equations which govern nanostructure dynamics. This leads to the fact that any physical variable, dependent, in a "classical sense", only on spatial coordinates and time depends, in the new, non-differentiable mathematical structure, on scale resolution. In other words, instead of "working" with a single physical variable described by a strict non-differentiable function, we can "work" only with approximations of this mathematical function obtained by averaging it on different scale resolutions. As a consequence, any physical variable meant to describe nanostructure dynamics will function as the limit of a family of mathematical functions, it being non-differentiable for null scale resolutions, and differentiable otherwise.

A specific example of our model is described.

2D Thermoelectric Materials: Role of the Lattice Thermal Conductivity

Udo Schwingenschlogl

King Abdullah University of Science and Technology (KAUST),
Physical Science and Engineering Division (PSE), Thuwal, Saudi Arabia

e-mail: udo.schwingenschlogl@kaust.edu.sa

The presentation gives an overview of ab-initio calculations[1-3] addressing the thermoelectric performance of MXenes. Specific examples include a comparison of Ti_2CO_2, Zr_2CO_2, and Hf_2CO_2 in order to evaluate the role of the metal atom. The lattice thermal conductivity is demonstrated to grow along the series Ti-Zr-Hf in the temperature range 300-700 K, resulting in the highest figure of merit in the case of Ti_2CO_2. Flat conduction bands promote the thermopower in the case of n-doping. Functionalization effects are studied for Sc_2C, which is semiconducting for various functional groups, including O, F, and OH. The lowest lattice thermal conductivity is found for OH functionalization. Despite a relatively low thermopower, $Sc_2C(OH)_2$ therefore and due to a high electrical conductivity can be interesting for intermediate-temperature thermoelectric applications. We also discuss results on heterostructures built of MXenes and transition metal dichalcogenide monolayers. Low frequency optical phonons are found to occur as a consequence of the van der Waals bonding. They contribute significantly to the thermal transport and compensate for reduced contributions of the acoustic phonons (strong scattering in heterostructures), such that the thermal conductivities become similar to those of the constituent MXenes.

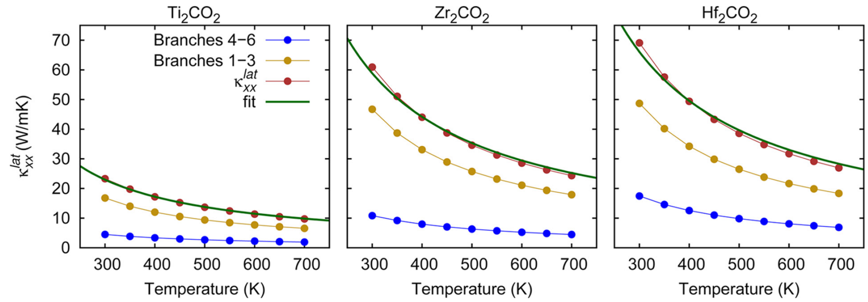


Figure 1. Lattice contributions to the thermal conductivity as functions of the temperature.[1]

References

[1] "Thermoelectric performance of the MXenes M_2CO_2 (M = Ti, Zr, or Hf)", A. N. Gandi, H. N. Alshareef, and U. Schwingenschlögl, Chem. Mater. 28, 1647 (2016).

[2] "Thermoelectric performance of functionalized Sc_2C MXenes", S. Kumar and U. Schwingenschlögl, Phys. Rev. B 94, 035405 (2016).

[3] "Thermal response in van der Waals heterostructures", A. N. Gandi, H. N. Alshareef, and U. Schwingenschlögl, J. Phys.: Condens. Matter 29, 035504 (2017).

Steering of Magnetic Domain Walls by Single Ultrashort Laser Pulses

Yasser A. Shokr[1, 2], Oliver Sandig[1], Mustafa Erkovan[3], Bin Zhang[1*], Matthias Bernien[1], Ahmet A. Unal[4], Florian Kronast[4], Umut Parlak[5], Jan Vogel[6], Wolfgang Kuch[1]

[1]*Institut für Experimentalphysik, Freie Universität Berlin, Berlin, Germany*
[2]*Faculty of Science, Department of Physics, Helwan University, Cairo, Egypt*
[3]*Karasu Vocational School, Sakarya University, Sakarya, Turkey*
[4]*Helmholtz-Zentrum Berlin fur Materialien und Energie, Berlin, Germany*
[5]*Gebze Technical University, Physics Department, Kocaeli, Turkey*
[6]*Université Grenoble Alpes, CNRS, Institut Néel, Grenoble, France*

We present a magnetic domain-imaging study by x-ray magnetic circular dichroism photoelectron emission microscopy on a Co/$Fe_{75}Gd_{25}$ bilayer under exposure to single focused ultrashort (100 fs) infrared laser pulses. Magnetic domain walls experience a force in the intensity gradient of the laser pulses away from the center of the pulse, which can be used to steer domain walls to move in a certain direction. Maximum domain-wall displacements after individual laser pulses close to 1 μm in zero external field are observed. Quantitative estimates show that electronic spin currents from the spin-dependent Seebeck effect are not strong enough to explain the effect, which we thus attribute to the torque exerted by magnons from the spin Seebeck effect that are reflected at the domain wall.

Robotic Manufacturing of Hierarchical Materials for Energy and Sensing Applications

Konstantinos A. Sierros

Mechanical and Aerospace Engineering, Statler College of Engineering, Evansdale Campus, West Virginia University, Morgantown, WV, USA

e-mail: kostas.sierros@mail.wvu.edu

There is currently a burgeoning interest to study new hierarchical materials that can be additively manufactured for a range of applications spanning from energy and sensing to biomedical. Additive manufacturing is an enabler of new shapes and structures with minimum material waste but the materials that can be printed remain limited and specific to commercial platforms. This represents a major constraint to the widespread use of additive manufacturing in new applications.

In this talk, we will present some of our latest work to address the need for new additive manufacturing materials used in innovative applications. We will demonstrate robotic manufacturing, through direct ink writing, of multifunctional hierarchical materials for energy and sensing applications. Direct ink writing is a versatile approach to pneumatically extrude inks, at digitally pre-defined substrate locations, through a nozzle attached to a robotically-controlled arm. We will discuss our recent studies on nanomaterials-based solutions and foam emulsion inks (based on metal, metal oxides and 2D materials) for the direct writing of hierarchical structures for applications in energy storage, photocatalysis, and gas sensing. In particular, we will address ink engineering, characterization, and printing parameters as important parts of the process since they determine the printing fidelity of the designed pattern. Typically, inks should exhibit shear-thinning behavior as a pre-requisite for successful printing. In addition to successful printing, which enables structural hierarchy across length scales, the ink components, their interactions and post-processing are very important for realizing the desired functionality of the printed structure. Here we will discuss about the functionality of the printed patterns and how it is related to ink components and post-processing methods.

The proposed robotic manufacturing approach exhibits great flexibility in realizing functional 3D structures with controlled hierarchy across scales and may hold the key to address current needs and challenges in many technological fields such as in energy, environmental, and biomedical.

Photocatalytic Activity of CNTs/ZnO Nanostructures Prepared via Atomic Layer Deposition

Inês E. Oliveira[1], Ana V. Girão[1], Ricardo M. Silva[1], Joaquim L. Faria[2], Cláudia G. Silva[2], Rui F. Silva[1*]

[1]CICECO - Aveiro Institute of Materials, Department of Materials and Ceramic Engineering, University of Aveiro, Aveiro, Portugal
[2]Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE – LCM), Chemical Engineering Department, Faculty of Engineering, Porto University, Porto, Portugal

[*]e-mail: rsilva@ua.pt

Industrial wastewaters typically contain high amounts of organic pollutants, so it is necessary to have ways to remove and dispose them. One of the most effective methods used to degrade this compound is through photocatalytic processes with semiconductors acting as catalysts. On the other end, nanostructures comprised of carbon nanotubes (CNTs) with metal oxide semiconductors have also shown interesting photocatalytic activity, by inducing synergies and cooperative effects between the two materials, boosting the overall efficiency of the photocatalytic processes. One of the most used photocatalytic semiconductor is the zinc oxide (ZnO) mainly due to its low toxicity, chemical stability and relatively high photocatalytic activity and band gap with 3.2 eV.

Herein, we present the controlled deposition of ZnO thin film via atomic layer deposition (ALD) on high surface area supports, such as CNTs arrays. The obtained nanostructures are highly suitable for photocatalytic degradation of organic pollutants. As a proof-of-concept different ZnO/CNTs nanostructures (25, 50, 100, and 200 ALD cycles of ZnO) were tested as photocatalysts in the degradation of rhodamine B (RhB). From Figure 1 it is possible to observe that the highest loading of ZnO onto the CNTs results in approximately 77% degradation of the RhB after 420 min. This finding highlights the hybrid combination of carbon nanotubes with photocatalytic active materials (ZnO) for the enhancing the overall photocatalytic activity of the final nanostructure.

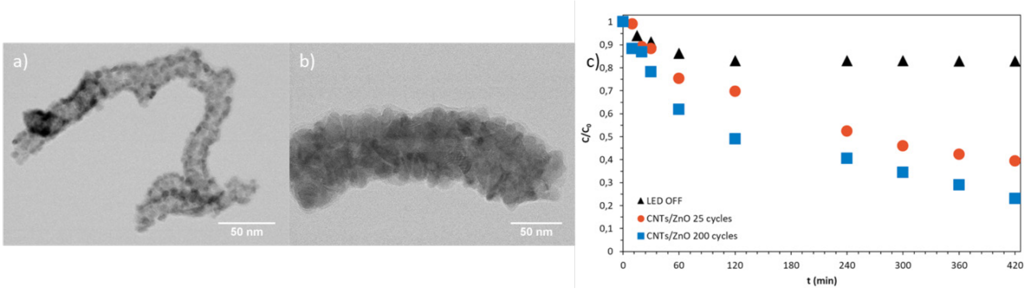


Figure 1. BF-TEM-STEM mode images of one nanotube coated with ZnO after: (a) 25 and (b) 200 ALD cycles; (c) evolution of the normalized concentration (C/C0) of RhB under UV (365 nm)-LED irradiation of the CNTs/ZnO nanostructures and the adsorption process with the LED-OFF, for comparison purpose.

Vibrational Control of Molecular Electron Transfer Processes

Spiros S. Skourtis

Department of Physics University of Cyprus, Nicosia Cyprus

e-mail: skourtis@ucy.ac.cy

Molecular electron transfer reactions where an electron (or hole) is transferred from an electron donor to an electron acceptor state through a molecular bridge are ubiquitous in chemistry and biology (photosynthesis, respiration, sensing, disease creation and control). Understanding the ET mechanisms and achieving the control of molecular ET rates is important for fundamental molecular science as well as for molecular technologies such as molecular electronics, energy materials and sensors. In molecular and biomolecular electron-transfer (ET) reactions vibrations are very important for the control of the ET rate.[1] Molecular vibrations may influence the donor, bridge and acceptor electronic-state energies, as well as the electronic couplings between these states. Such ET-active motions may be very localized high-frequency quantum vibrations and/or collective low-frequency breathing motions. These vibrations can be non-specifically excited by changing the temperature. The idea of driving specific ET-active vibrational motions by external Terahertz or Infrared (IR) fields in order to control ET rates has been around for some time but recent experiments clearly demonstrate that such control is possible at least for IR driving.[3] We describe the current status and future prospects of this field. We discuss design principles and optimal parameter regimes for achieving vibrational control of ET rates given the constraints imposed by the molecule-solvent environments and by the experimental setups.

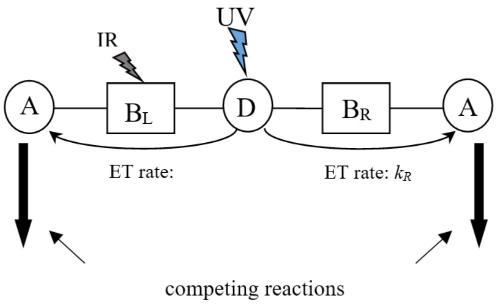


Figure 1. IR excitation of ET-active vibrations can influence the relative yields of competing ET reactions.

References

[1] “Fluctuations in biological and bioinspired electron transfer reactions”, S.S. Skourtis, D.H. Waldeck, and D.N. Beratan, Ann. Rev. Phys. Chem. 61, 461 (2010)

[2] “Vibrational control of molecular electron transfer”, S. Valianti and S.S. Skourtis, Molecular Physics, DOI: 10.1080/00268976.2018.1504997 (2018)

Determination of Magnetic Moment Profile of EuS/Co/Ni/Co Multilayers for Spintronics

A. Stamatelatos[1*], A. Goschew[2], P. Fumagalli[2], Th. Kehagias[3], B. Lindgren[4], V. Kapaklis[4], F. Wilhelm[5], A. Rogalev[5], P. Poulopoulos[1]

[1]*Materials Science Department, University of Patras, Patras, Greece*
[2]*Institut für Experimentalphysik, Freie Universität Berlin, Berlin-Dahlem, Germany*
[3]*Physics Department, Aristotle University, Thessaloniki, Greeece*
[4]*Department of Physics and Astronomy, Uppsala University, Uppsala, Sweden*
[5]*European Synchrotron Radiation Facility (ESRF), Grenoble, France*

[*]e-mail: alkstamatelatos@gmail.com

Recent studies have demonstrated significant room-temperature magnetic polarization of EuS in EuS/Co multilayers.[1] In addition, evidence of successful spin-injection from EuS/Co multilayers into (100) GaAs at low temperature has been observed by electroluminescence measurements. A circular polarization of 5% at 8 K at zero external magnetic field was found.[2] By replacing Co by Ni, we were able to reduce the roughness at the EuS/Ni interface and suppress the mixed-valence in EuS.[3]

Because of the previous study, we prepared a EuS/Co/Ni/Co multilayer in order to improve the growth quality while keeping the high magnetic moment of Co. We performed measurements of X-Ray Reflectivity (XRR) and High-Resolution Transition Electron Microscopy (HRTEM). The XRR patterns were fitted by means of the GenX code.[4] Combination of HRTEM with XRR allows us to deduce information on the multilayer growth aspects. X-Ray Magnetic Circular Dichroism (XMCD) measurements have been done on the L2-edge of Eu yielding the temperature dependence of the EuS magnetization. Furthermore, element specific hysteresis curves were probed as a function of temperature. From X-Ray Magnetic Scattering (XRMS) measurements, the magnetic moment profile of EuS could be derived.

We thank the ESRF crew for the excellent operational conditions.

References

[1] "Direct evidence for significant spin-polarization of EuS in Co/EuS multilayers at room temperature", S.D. Pappas et al., Scien. Rep. 3, 1333 (2013).

[2] "Spin injection from EuS/Co multilayers into GaAs detected by polarized electroluminescence", A. Goschew et al., IEEE Transactions on Magnetics pp(99):1-4, (2019).

[3] "Induced spin-polarization of EuS at room temperature in Ni/EuS multilayers", P. Poulopoulos et al., Appl. Phys. Lett. 104, 112411 (2014).

[4] "GenX: an extensible X-ray reflectivity refinement program utilizing differential evolution", M. Björck and G. Andersson, J. Appl. Cryst. 40, 1174-1178, (2007).

Development of Novel Antimicrobial Orthopaedic Medical Surfaces

Artemis Stamboulis

School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham, UK

e-mail: A.Stamboulis@bham.ac.uk

Despite the wide interest and intensive investigations on the use of antimicrobial peptides as promising active agents against bacterial and fungal microorganisms, clinical applications and commercial development of these compounds is still limited. Recent developments have focused on non-antibiotic anti-biofilm agents to help disrupt undesired biofilm formation on orthopaedic surfaces. These include surface modifications of orthopaedic implants and the use of all sorts of novel material alloys or nano-patterning of already existing materials. Examples include specific metal alloys such as titanium, polyethylene oxide, hydrophobic polycationic surfaces, intrinsically bioactive materials such as silver and copper, bioactive antibacterial coatings etc. This paper will give an overview of recent developments on the use of antimicrobial peptides and will focus on surface modifications of metal alloys and polymers to achieve antimicrobial medical surfaces with short- and long-term activity.

Nanomaterial-Based Antimicrobial Therapies: Principles, Limitations, and Potential

Svenja Siemer[1], Shirley K. Knauer[2], Roland Stauber[1*]

[1]*Department of Nanobiomedicine/ENT, University Medical Center of Mainz, Mainz, Germany*
[2]*Department of Molecular Biology II, Centre for Medical Biotechnology (ZMB), University of Duisburg-Essen, Germany*

[*]e-mail: rstauber@uni-mainz.de

Nanomaterials (NMs) have dramatically increased in functionality and complexity, potentially allowing also unprecedented control over microbial pathogens, such as bacteria, fungi, or viruses. From these advances arises the prospect of novel nanomaterial-based antimicrobial therapies, which clearly differ from their bulk counterparts. Yet, a rational understanding of NMs' physico-chemical characteristics and parameters at the nano-bio interface that impact their antimicrobial activity is required to overcome practical constraints for nanoantibiotics. We here define the most important NM parameters and biological outputs enabling controllable antimicrobial activity, while minimizing the complexity of designs. We present the problematic of nanomaterial resistance and mechanistic strategies to overcome these current limitations for next-generation practical applications. The presented insights will inspire NM designs that maximize functionality and safe translatability as new nanoantibiotics, and deepened our understanding on the biomedical and ecological relevance of nanomaterial-microbiota cross-talk in general.

References

[1] Westmeier, D. Proc Natl Acad Sci U S A, 7087, doi:10.1073/pnas.1804542115 (2018).
[2] Westmeier, D. Chem Soc Rev, 5312, doi:10.1039/c6cs00691d (2018).
[3] Siemer, S. Materials Today, doi:doi.org/10.1016/j.mattod.2018.10.041 (2018).
[4] Siemer, S. Nature publishing journal Science of Food, doi:doi.org/10.1038/s41538-018-0030-8 (2018).

Modification of Gold Nanoparticles with Small Molecules for Targeting Tyrosine Kinase

Anastasia Stavropoulou*, Maria Theodosiou, Eleni K. Efthimiadou

National and Kapodistrian University of Athens, Athens, Greece

*e-mail: astav@chem.uoa.gr

Angiogenesis is the formation of new networks of blood vessels from existing ones and is considered to promote the progression of cancer, in conjuction with tumor growth and metastasis.[1] Vascular endothelial growth factor (VEGF) which is critical for angiogenesis, acts through signaling by a family of tyrosine kinase receptors (VEGFR). Vascular endothelial growth factor receptor-2 has been proven to be key modulator, thus, blocking the VEGFR-2 pathway should be a potential way to distort the angiogenesis process, and to suppress tumor growth. Recently, a number of small molecules with quinazoline ring on the basis have been addressed to act as VEGF receptor inhibitors.[2] In this study, we synthesized several small molecules with quinazoline moiety conjugated with amino acids to produce potential tyrosine kinase inhibitors. The amino acids also act as binding units of the quinazoline ring to the nanoparticles, which are used in order to target the tyrosine kinase. Lately, nanoparticles are drawing more and more attention in medical nanotechnology since they are able to overpass biological barriers and invade the cells, guided by the enhanced permeability and retention effect (EPR effect) in the tumor.[3] Gold nanoparticles are excellent drug delivery system because of their distinctive characteristics, including high biocompatibility and facile conjugation to biomolecules as well as the optical properties provided by their localized surface plasmon resonance and the enhanced ability to bind amine and thiol groups tolerating surface modification.[4] The liking of anticancer drugs to colloidal AuNPs constitutes a potential strategy as long as the viability of the system is tested. They can decrease the dose of chemotherapy's drug, thence decrease its side effects. Therefore, we conjugated the synthesized small molecules with the quinazoline core on the surface of the gold nanoparticles and assessed their antiproliferative activity in vitro using U87 cell lines.

References

[1] "Mechanisms of angiogenesis", Risau, W., Nature 386, 671 (1997).

[2] "Design, synthesis and antitumor activity of 4-aminoquinazoline derivatives targeting VEGFR-2 tyrosine kinase." Yu, B., et al, Bioorganic & medicinal chemistry letters 22, 110114 (2012).

[3] "Role of cell cycle on the cellular uptake and dilution of nanoparticles in a cell population." Kim, J.A., et al. Nature nanotechnology 7, 62 (2012).

[4] "Enhancing proteasome-inhibitor effect by functionalized gold nanoparticles." Coelho, S.C., et al. Journal of biomedical nanotechnology 10, 717-723 (2014).

Lessons Learnt with Donor: Acceptor Photovoltaic Blends: Can They Be Applied to Doped Polymer Systems?

Natalie Stingelin

Georgia Institute of Technology, Atlanta, GA, USA

e-mail: natalie.stingelin@gatech.edu

We first discuss here the long-standing question of how free charges are generated in donor:acceptor blends that are used in organic solar cells. For this, we need to take into account that organic photovoltaic active layers are generally comprised of a complex phase morphology where intermixed and neat phases of the donor and acceptor material co-exist. We show that the fate of photogenerated electron-hole pairs – whether they will dissociate to free charges or geminately recombine – is determined at ultrafast times, despite the fact that their actual spatial separation can be much slower. The local arrangement of the donor and acceptor plays thereby a critical role in this phenomena as we demonstrate on a series of donor polymer:fullerenes binaries by combining 2D-NMR data with time-resolved ultra-fast spectroscopy results as well as detailed structural data. Our insights are important as similar considerations seem to apply to other organic blend systems, such as organic semiconductor:dopant binaries that can lead to highly conductive systems. Indeed we will discuss how the spatial arrangement, manipulated through intercalation and co-crystal formation with dopants in analogy to the photovoltaic donor:acceptor systems, affects charge transport. We will conclude with providing a tentative picture of the complex correlation of structure and electronic landscape for the understanding of organic photovoltaic cells as well as doped, conducting "plastics" of metallic-type transport.

Development of Graphene-Based μ-Electrodes for Bioelectronic Devices

A. Pylostomou[1,2], A. Salam Sarkar[2], K. Savva[2], M. Pervolaraki[2], E. Stratakis[1,2*]

[1] *Department of Materials Science and Technology, University of Crete, Heraklion, Greece*
[2] *Institute of Electronic Structure and Laser (IESL), Foundation for Research and Technology (FORTH), Heraklion, Greece*

[*] e-mail: stratak@iesl.forth.gr

During the last decades, the field of bioelectronics is becoming increasingly important due to the demand for clinical detection of various diseases. Epilepsy is a common neurological disorder, affecting millions of people around the world. It is known that metabolic disturbances are often associated with the seizures of epilepsy. Amongst other biomarkers, glucose level is often used for the prediction of incoming seizures, therefore, the creation of specific bioelectronic devices, such as biomolecular sensors, is of great importance. For neurological disorder detection, there is a huge need for hydrophilic, biocompatible and highly conductive electrodes in biosensors. Two-dimensional (2D) graphene based nanomaterials (NMs) exhibit promising physical, optical and electrochemical properties for ultrasensitive bioelectronic devices.

In this work, we developed two dimensional (2D) reduced graphene oxide (rGO) based μ-electrodes for biomolecular sensor. The GO films were fabricated by the vacuum filtration and spray gun techniques. The topography and the composition of the GO films were studied by various microscopic and spectroscopic techniques, respectively. For the enhancement of the electronic properties, an ultrafast pulsed laser was used for the reduction of the GO material. Electrical investigation was carried out in order to understand the enhancement in the electronic behavior of the fabricated electrodes. Finally, the μ-electrodes were developed via direct fs laser patterning towards the microelectronic sensor device realization.

Figure 1. Epilepsy affecting neurons in brain[1]

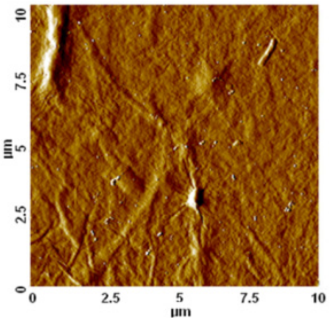


Figure 2. Top view AFM image of a GO film.

References

[1] "Surgeon Puts a Laser Focus on Epilepsy", Matt Wood, Science Life, December 17, (2013).

Novel Hybrid Iron Oxide@Gold Nanoflowers as a Potential Theranostic Agent for Cancer

Maria Theodosiou[1,2*], Elias Sakellis[2], Beata Kalska-Szostko[3], Michael Pissas[2],
Nikos K. Boukos[2], Eleni K Efthimiadou[1,2]

[1]Department of Chemistry, Laboratory of Inorganic Chemistry, National and Kapodistrian University of Athens, Department of Chemistry, Athens, Greece
[2]Institute of Nanoscience and Nanotechnology, National Centre for Scientific Research, "Demokritos", Athens, Greece
[3]Institute of Chemistry, University of Bialystok, Bialystok, Poland

*e-mail: mtheodoss@chem.uoa.gr

Hybridization of iron oxide nanoparticles with gold has attracted much interest in recent nanomedicine related literature, due to the wide range of theranostic applications in cancer research that stem from the combination of their physicochemical properties.

On one hand, maghemite iron oxide nanoflowers (IONfs) are superparamagnetic and have been reported for their potential in both magnetic resonance imaging (MRI) and magnetic hyperthermia treatment (HT) in cancer. Gold nanoparticles on the other hand are biocompatible, can be easily functionalized with biomolecules and exhibit the intrinsic optical phenomenon of surface plasmon resonance (SPR) that allows for a variety of biomedical applications, such as computed tomography (CT) or confocal fluorescence imaging and photothermal therapy (PT).

Herein, γ-Fe_2O_3 nanoflowers (IONfs) have been synthesized through a revised polyol method which produced a colloidally stable monodisperse aqueous ferrofluid. Following, for the synthesis of hybrid IONFs@gold (GIONfs), gold coating was achieved through the direct reduction of Au^{3+} on the surface of IONfs via a modified iterative seeding method using a strong reducing agent. For comparative purposes plain gold nanoparticles (GNps) have been synthesized in aqueous medium. The isolated GIONfs, IONfs and GNps have been thoroughly characterized morphologically, structurally and for their magnetoplasmonic response. Biological evaluation has been conducted in vitro in different cancer and healthy cell lines in order to determine their cytotoxicity and their bioimaging potential.

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 14650.

References

[1] "Gold coated magnetic nanoparticles: from preparation to surface modification for analytical and biomedical applications" Silva et al., Chem.Commun., 52, 7528-7540 (2016)
[2] Cooperative Organization in Iron Oxide Multi-Core Nanoparticles Potentiates Their Efficiency as Heating Mediators and MRI Contrast Agents", Lartigue et al., ACS Nano, 6, 10935-10949 (2012)

Tailoring the Properties and Predicting the Energy Gap of 2D Materials: A View from First Principles

Lara Kühl Teles

Instituto Tecnológico de Aeronáutica, São José dos Campos, SP, Brazil

The set of new two-dimensional (2D) materials is a unique platform to explore new possibilities for optical, electronic and mechanical properties, making them the next frontier in advanced materials for optical and electronic thin flexible devices applications based solely on 2D layers. Therefore, considerable effort has recently been directed to the synthesis and modification of 2D materials for band gap engineering. On the other hand, while 2D systems open possibilities for new physics and applications, they also present a greater challenge for electronic structure calculations, especially concerning excitations. In this talk, I discuss two different aspects, by means of first-principles electronic structure calculations: the application of the method DFT-1/2 for energy gap calculation for a set of 2D materials, and the possibilities of tailoring the graphene oxide properties by removal or addition of certain oxygen groups. In this context, the following systems are systematically discussed:

(i) The chemically tunable properties of under stoichiometric graphene oxide as a function of the growth temperature and the amount of hydroxyl and epoxy groups adsorbed on graphene. The structural disorder is modeled within a statistical approach based on a cluster expansion. A complete scenario of energetics and phase stability is developed, yielding insight into the structure and electronic properties of graphene oxide. Our results show that the tendency to agglomeration of oxygen-containing groups is independent of their relative proportion and indicate the favorable formation of a unique oxygen-rich phase with both groups. The chemical composition and atomic arrangements also significantly influence the average fundamental energy gap and the band gap bowing. In the case of a full oxidation with equal concentration of −OH and −O− groups a strong antibowing is found. Finally, we discussed the dependence of the optical absorbance on composition and temperature of a fully oxidized GO phase and demonstrated a strong influence of the relative amount of −OH and −O− groups on the calculated absorption spectra.

(ii) The performance of the fast-free parameter DFT-½, as an accurate practical model that incorporates approximate quasiparticle corrections. Our results show that the performance of DFT-½ method is comparable with state of art GW and superior of the HSE06 hybrid functional in the majority set of the 34 different 2D materials studied, with the same computational cost as standard DFT calculations. We provide criteria to predict the small number of cases in which the method is not adequate. The success of the DFT-½ method is associated to the atomic orbital character of the states at the top of the valence band and bottom of conduction band.

[*] in collaboration with F. Bechstedt, M. Marques, I. Guilhon, and D.S. Koda

Opto-electronic and Excited-State Dynamical Properties of Chiral, Semiconducting Polymer-Wrapped Carbon Nanotube Superstructures

George Bullard, Yusong Bai, Jean-Hubert Olivier, Pravas Deria, Jaehong Park, Michael J. Therien*

Department of Chemistry, French Family Science Center, Duke University, Durham, NC, USA

*e-mail: michael.therien@duke.edu

Highly charged, chiral anionic semiconducting polymers helically wrap single-walled carbon nanontubes (SWNTs) at periodic and constant morphology (Fig. 1A). These polymers can be used as tools to modulate SWNT electronic properties, provide expansive solubility, or organize functional organic moieties at predefined intervals along the SWNT surface. We detail (SWNT)-based nanohybrid compositions based on (6,5) chirality-enriched SWNTs ([(6,5) SWNTs]) and chiral semiconducting polymers that feature repeat units that contain electron acceptors. Such helically wrapped polymer-SWNT superstructures, for example, feature perylene diimide (PDI) electron acceptor unit positioned at 3 nm intervals along the nanotube surface, thus controlling rigorously SWNT–electron acceptor stoichiometry and organization. Potentiometric studies determine driving forces for photoinduced charge separation (CS) and thermal charge recombination (CR) reactions, as well as spectroscopic signatures of SWNT hole polaron and PDI radical anion states. Femtosecond pump-probe transient absorption spectroscopic experiments detail driving force- and solvent-dependent photoinduced CS and thermal CR dynamics, and provide insights into the factors that govern photoinduced charge transfer reactions at soft matter-hard matter interfaces defined by polymers and SWNTs (Fig. 1C). Related experiments probe the transient absorptive and dynamical properties of positively and negatively charged excitons (i.e., hole- and electron-trions) in these semiconducting polymer-wrapped SWNT superstructures; these studies determine trion transient absorptive signatures and dynamics as functions of absolute electron- or hole-doping levels (Fig. 1B). Global analysis of these data over the entire vis-NIR spectral domain, where these systems display characteristic transient absorptive spectral signatures, provide fundamental new understanding of trion formation and decay mechanisms in semiconducting SWNTs essential for developing electro-optic and photonic materials.

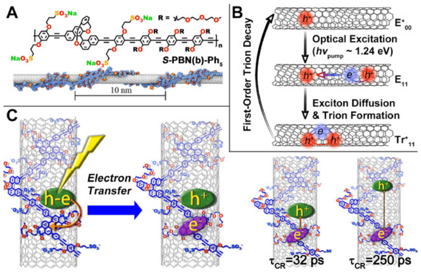


Figure 1. (A) Prototypical chiral semiconducting arylenethynylene polymer-wrapped SWNT assembly and MD simulation. (B) Schematic of hole trion formation in hole-doped, optically-excited semiconducting SWNTs. (C) Light-driven e-/h+ pair generation in a polymer-wrapped SWNTs composition, and subsequent CR dynamics.

X-ray Characterization of Thin-Film Catalyst Structures Used in the Artificial Leaf and Dye-Sensitized Interfacial Charge Transfer

David M. Tiede[1*], Gihan Kwon[2], Alex B. Martinson[3], Karen L. Mulfort[1]

[1]*Chemical Sciences and Engineering and 3Materials Science Divisions, Argonne National Laboratory, Lemont, IL, USA*
[2]*National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY, USA*

[*]e-mail: tiede@anl.gov

A key challenge for the design of efficient photoelectrochemical devices that employ nanoscaled interfacial designs for solar energy-to-fuels conversion lies in resolving atomic structures and dynamics at the active interfaces, and relating these to the complex cascade of events which includes excited-state charge separation, charge-accumulation, and multi-step energy conversion and catalysis. Our research programs have been developing in-situ, time-resolved X-ray techniques aimed at the resolution of atomic scale structures that underlie interfacial charge transfer and photo-driven water-splitting catalysis under conditions relevant to photoelectrochemical function for both interfacial thin-films and molecular photosensitizers and catalysts bound to semiconductor surfaces.

This presentation will show how high energy (>50 keV) X-ray scattering and pair distribution function (PDF) analysis provides atomic structure characterization that usefully complements electronic structure characterization derived from a combination of soft X-ray absorption (XAS), resonant X-ray emission (RXES), resonant inelastic X-ray scattering (RIXS) techniques for structure-function analysis of transition metal semi-conductor and catalyst thin films. Microporous high surface area electrodes were designed that allowed PDF analysis to be accomplished 0.2 Å spatial resolution for amorphous transition metal oxide thin films having thickness of down to 60 nm. The combined electronic and structural analyses demonstrate that hole transfer to catalytic sites in amorphous cobalt oxide thin films is the rate-limiting step for electrochemical water-splitting rather than the multi-step catalytic events themselves. The macroscopic catalytic properties of the thin films were found to be correlated to the electronic structures measured at the atomic scale for the metal-oxo cluster domains. These results show the interplay between intrinsic catalytic activity and charge transport properties of semiconductor thin-film catalysts.

We have extended this approach by the development of nanoporous electrode architectures which enable the use of combined PDF and X-ray spectroscopy analyses to resolve differences in coordination structures for molecular photosensitizers and catalysts in solution and when bound to semiconductor oxide surfaces. Measurements on ruthenium photosensitizer complexes bound to the TiO_2 surface resolve distortions in the surface-coordinating ligand structures. On-going work is investigating the correlation between ligand structural distortion and the metal-to-ligand charge-transfer (MLCT) states with ultrafast interfacial charge injection function.

Development of Neuromplants Based on Porous Collagen-Based Scaffolds

Dimitrios Tzeranis[1*], Constantina Georgelou[2], Alexandra Kourgiantaki[1],
Kanelina Karali[1,2], Maria Savvaki[1,2], Domna Karagogeos[1,2],
Ioannis Charalampopoulos[1,2], Achille Gravanis[1,2]

[1]*Foundation for Research and Technology - Hellas, Heraklion, Greece*
[2]*University of Crete, Heraklion, Greece*

[*]e-mail: dimitrios_tzeranis@imbb.forth.gr

Despite significant research efforts, very few treatments have demonstrated ability to induce regeneration in injured organs. In particular, there are no clinical treatments for devastating central nervous system (CNS) injuries that affect millions of patients worldwide.[1] Emergent technologies based on pluripotent stem cells, including Neural Stem Cells (NSCs), have demonstrated impressive effects, yet much remains for their clinical translation.[2,3] Biomaterials have been shown to be a key component of emerging NSCs treatments. This study describes the development of neuroimplants, novel treatments for CNS injuries based on NSCs and porous collagen-based scaffolds (PCS).

Porous collagen-based scaffolds have demonstrated significant regenerative ability in severely-injured skin and peripheral nerves.[4] This ability, originating from PCS effects on several elementary processes of wound healing, depends strongly on PCS physicochemical properties.[5] So far, little is known about PCS effects on NSCs and their ability to regulate wound healing after CNS injury. This study summarizes experimental observations on the effects of PCS-based grafts in two kinds of CNS injury in mouse: spinal cord dorsal column crush and optic nerve crush. Results suggest that PCS can safely deliver NSCs at CNS injury sites, enabled NSC differentiation in vivo towards both neural and glial lineages, and significant axonal elongation at the injury site leading to statistically significant improvement in functional assays. Ongoing research focuses on developing more effective neuroimplants by exploiting novel 3D micro/nano fabrication methods and by integrating PCS with optimal NSCs and effective small molecule compounds.

References

[1] "From basics to clinical: a comprehensive review on spinal cord injury", Silva, N.A., Sousa, N., Reis, R.L. and Salgado, A.J. Prog Neurobiol. 114, 25-57, (2014).
[2] "Cell transplantation therapy for spinal cord injury", Assinck, P., Duncan, G.J., Hilton, B.J., Plemel, J.R., Tetzlaffm W. Nat Neurosci. 20, 637-647 (2017).
[3] "Long-distance growth and connectivity of neural stem cells after severe spinal cord injury.Lu, P. et al. Cell 150, 1264-1273 (2012).
[4] "Biologically active collagen-based scaffolds: advances in processing and characterization", Yannas, I.V., Tzeranis, D.S., Harley, B.A., So, P.T, Philos Trans A Math Phys Eng Sci. 368, 2123-2139 (2010).

High Resolution Biological Imaging Across Scales for Fundamental Research and Translational Applications

Srigokul Upadhyayula

Harvard Medical School, Boston, MA, USA

e-mail: gokul@tklab.hms.harvard.edu

Direct physiological observation of subcellular features is now feasible using the Lattice Light-Sheet Microscopy. It is a transformative imaging technology that spans the relevant scales in space and time because of the wide resolution range and large volumetric acquisition capability. This new imaging method allows us to record dynamics at a scale of nanometers and milliseconds, determine their consequences at a scale of microns and hours, and visualize their long-term outcome at a scale of up to several millimeters over several days. I'll briefly present our past work on combined lattice light sheet microscopy with adaptive optics to achieve (Science, 2018), across large multicellular volumes, noninvasive aberration-free imaging of subcellular dynamics in vivo. Next, I'll discuss the combination of lattice light-sheet with the physical expansion of samples (Expansion Microscopy) that enables scalable super-resolution volumetric imaging of large tissues (Science, 2019) including the complete fly brain, columns of mouse brain – datasets spanning several hundred terabytes. Finally, I will introduce our next-generation microscope design– dubbed the "Swiss army knife microscope," which combines at least ten different modes of imaging and is designed to alleviate the tradeoffs related to resolution, speed, invasiveness and imaging depth, which precludes any single optical microscopy to function optimally for a diverse set of biological specimens. Broadly, I'm interested in how we can leverage the powerful combination of artificial intelligence tools with the next-generation multimodal imaging systems to accelerate the pace of discoveries in both fundamental and translational sciences. Furthermore, I am interested in discussing any strategies that allow (1) development and dissemination of robust 5D (x,y,z,t,c) image processing, data analysis, and visualization tools / platforms that are scalable to terabyte and petabyte datasets; (2) infrastructure access to keep up with increased data generation rates and support data processing, storage, and handling; and (3) open-access repositories to host terabyte to petabyte-scale imaging datasets from published papers for community investigation and reuse.

References

[1] Gao, R., Asano, S., Upadhyayula, S., Pisarev, I., Milkie, D., Liu, T., Singh, V., Graves, A., Huynh, G., Zhao, Y., Bogovic, J., Colonell, J., Ott, C., Zugates, C., Tappan, S., Rodriguez, A., Mosaliganti, K., Megason, S., Lippincott-Schwartz, J., Hantman, A., Rubin, G., Kirchhausen, T., Saalfeld, S., Aso, Y., Boyden, E., Betzig, E.; "Cortical Column and Whole Brain Imaging of Neural Circuits with Molecular Contrast and Nanoscale Resolution," Science, 2019, 363:6424, 245.

[2] Liu, T, Upadhyayula, S*., Milkie, D., Singh, V., Wang, K., Swinburne, I., Mosaliganti, K., Shea, J., Dambournet, D., Forster, R., Hockemeyer, D., Drubin, D., Martin, B., Matus, D., Koyama, M., Megason, S., Kirchhausen, T., Betzig, E.; "Observing the Cell in Its Native State: Imaging Subcellular Dynamics in Multicellular Organisms," Science, 2018, 360:6386, 284.

Innovative, $TiO_2|Co_3O_4$ Photoanode Nanostructures for Hydrogen Production by Solar Water Splitting

Adeline Miquelot[1], Olivier Debieu[1], Stéphanie Roualdes[2], Christina Villeneuve-Faure[3],
Nathalie Prud'homme[4], Jeremy Cure[5], Vincent Rouessac[2],
Vassilios Constantoudis[6], George Papavieros[6], Constantin Vahlas[1*]

[1]CIRIMAT, CNRS/Université de Toulouse, Toulouse, France
[2]IEM, CNRS/Université de Montpellier/ENSCM, Montpellier, France
[3]LAPLACE, CNRS/Université de Toulouse, Toulouse, France
[4]ICMMO, CNRS/Université Paris Sud/Université Paris-Saclay, Orsay, France
[5]LAAS, CNRS/Université de Toulouse, Toulouse, France
[6]NCSR Demokritos and Nanometrisis, Athens, Greece

[*]e-mail: constantin.vahlas@ensiacet.fr

Production of "green" hydrogen by water splitting in a photo-electrochemical cell (PEC) through solar absorption in a redox reaction is a potential contribution to the future energy mix. In this perspective, we report recent results towards the tuning of a p-Co_3O_4/n-TiO_2 heterojunction as the PEC photo-anode (Figure 1). In such architecture, the UV light efficient TiO_2 PEC photo-anode is improved by the addition of the lower band-gap Co_3O_4 layer though (a) the broadening the spectral photocatalytic efficiency to the visible spectrum, (b) the formation of a p-n heterojunction that enhances excitons creation, charges separation, and extend their lifetimes. Co_3O_4 and TiO_2 films are processed by metalorganic and plasma enhanced chemical vapor deposition. The presentation will focus on the correlation among the electric and opto-electronic properties of the two individual layers, TiO_2 anatase and Co_3O_4, their nano- and micro-structure, and ultimately their performance in terms of H_2 photogeneration (Figure 2). The ultimate objective of this collaborative project is the development of new all-solid multilayered PEC for H_2 production/separation including innovative vacuum-deposited photo-anode and electrolyte membrane materials.

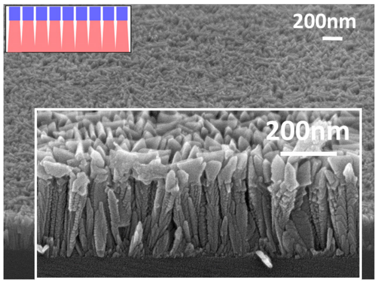


Figure 1. SEM cross section of a TiO_2/Co_3O_4(top) bilayer stack.

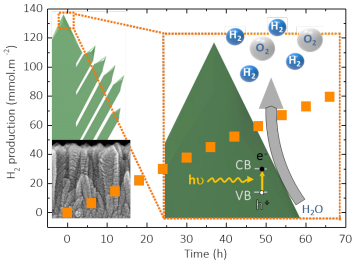


Figure 2. 66 h cumulative H_2 production of 79 mmol.m-2 for a nanotree-like columnar TiO_2 structure and schematic of the involved photocatalytic mechanism.

Amplification of Magneto-Optical Activity with Dark Plasmons in Magnetoplasmonic Nanocavities

Paolo Vavassori[1,2*], Alberto López-Ortega[1], Mario Zapata Herrera[1],
Nicolò Maccaferri[3], Matteo Pancaldi[4], Mikel Garcia[1], Andrey Chuvilin[1,2]

[1]*CIC nanoGUNE, Donostia–San Sebastian, Spain*
[2]*IKERBASQUE, Basque Foundation for Science, Bilbao, Spain*
[3]*Physics and Materials Science Research Unit, Université du Luxembourg, Luxembourg, Luxembourg*
[4]*Department of Physics, Stockholm University, Stockholm, Sweden*

[*]e-mail: p.vavassori@nanogune.eu

The rapidly developing field of magnetoplasmonics merges the concepts from plasmonics and magneto-optics to realize novel phenomena and functionalities for the manipulation of light at the nanoscale.[1] The intertwined optical and magneto-optical properties offer a smart toolbox for actively tunable optical ultrathin surfaces and metasurfaces.[2,3] Enhancing magneto-optical effects is crucial for size reduction of key photonic devices based on non-reciprocal propagation of light and to enable active nanophotonics. Here, we disclose an approach that exploits dark plasmons to achieve an unprecedented amplification of magneto-optical activity.[4] We designed and realized a symmetry broken non-concentric magnetoplasmonic-disk/plasmonic-ring nanocavity by e-beam lithography. The nanocavity is made of a ferromagnetic disk-shaped nanoantenna placed inside a ring-shaped gold nanoresonator. The broken symmetry enables the excitation of dark multipolar modes in the plasmonic-nanoring and their hybridization with the dipolar plasmonic resonance of the magnetoplasmonic nanoantenna. Such hybridization gives rise to a multipolar resonance that, when excited, produces a large amplification of the magneto-optic response of the nanocavity, ~1-order of magnitude higher than the amplification provided by localized plasmons in a bare magnetoplasmonic nanoantenna. Such large amplification is explained as due to the peculiar and enhanced electrodynamics of the nanocavity, yielding a large magnetically-activated radiant magneto-optical dipole driven by the low-radiant multipolar resonance mode, as confirmed by detailed numerical simulations and a modal decomposition of the density charge dynamics in the cavity

---

References

[1] "Tuning the magneto-optical response of nanosize ferromagnetic Ni disks using the phase of localized plasmons", N. Maccaferri et al., Phys. Rev. Lett. 111, 167401 (2013).
[2] "Magnetoplasmonic Design Rules for Active Magneto-Optics", K. Lodewijks et al., Nano Lett. 14, 7207 (2014).
[3] "Magnetic control of the chiroptical plasmonic surfaces", I. Zubritskaya et al., Nano Lett. 18, 302 (2018).
[4] "Magnetoplasmonics in nanocavities: Dark plasmons enhance magneto-optics beyond the intrinsic limit of magnetoplasmonic nanoantennas", A. López-Ortega et al., submitted

Amphiphilic Protein-Polymer Nanocarriers – Design, Synthesis and Drug Delivery

Kelly Velonia[1*], Alexis Theodorou[1], Charis Gryparis[1], Athina Anastasaki[2]

[1]Department of Materials Science and Technology, University of Crete, Heraklion, Crete, Greece
[2]Department of Materials, ETH Zurich, Zurich, Switzerland

[*]e-mail: velonia@materials.uoc.gr

Designed to mimic natural multifunctional assemblies, synthetic protein-polymer conjugates exhibit interesting aggregation properties and enormous potential in bio and nanotechnology. Such chimeric biohybrids have been previously prepared through direct or bioaffinity couplings,[1] while more recently, quantitative synthesis was achieved via in situ grafting from protein biomacroinitiators.[2] Nevertheless, the stringent anaerobic conditions required in most conventional controlled polymerization approaches, necessitate specialized equipment and limit their applicability in bioconjugate synthesis. Herein we present our studies on oxygen tolerant living polymerization approaches which, in the absence of external additives, overcome synthetic challenges and allow the quantitative synthesis of an unprecedented variety of amphiphilic bioconjugates. The assembling properties of novel bionanocarriers, their functionalization (e.g. enzyme encapsulation) and application in drug delivery will be comparatively discussed.[3]

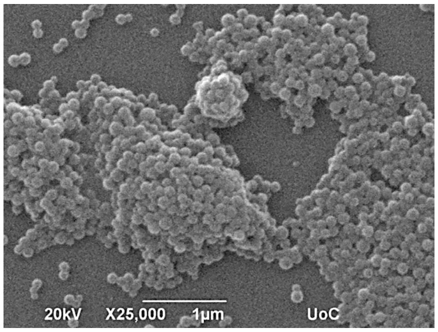


Figure 1. Uniform spherical protein-polymer nanocarrier superstructures

---

References

[1] "Lipase Polystyrene Giant Amphiphiles", K.Velonia, A. E. Rowan, R. J. M. Nolte, J. Am. Chem. Soc. 124, 4224 (2002).
[2] "In Situ ATRP-Mediated Hierarchical Formation of Giant Amphiphile Bionanoreactors", B. Le Droumaguet, K. Velonia, Angew. Chem. Int. Ed. 47, 6263 (2008).
[3] "Copper-Mediated Polymerization without External Deoxygenation or Oxygen Scavengers", E. Liarou, R. Whitfield, A. Anastasaki, N. G. Engelis, G. R. Jones, K. Velonia, D. M. Haddleton, Angew. Chem. Int. Ed 57, 8998 (2018). A. Theodorou et al. submitted.

Biodegradable Polymers from Food Waste

Kelly Velonia[1*], Alexis Theodorou[1], Elina Koi[1], Sophia Koutantou[1],
Ioannis Daliakopoulos[2], Aggeliki Maragkaki[2], George Daskalakis[2], Nikolaos Markakis[2],
Ioannis Sabathianakis[2], Christos Tsompanidis[3], Thrassyvoulos Manios[2]

[1]Department of Materials Science and Technology, University of Crete, Heraklion, Greece
[2]Department of Agriculture Technological Educational Institute of Crete, Heraklion, Crete, Greece
[3]ENVIROPLAN SA, Gerakas - Athens, Greece

[*]e-mail: velonia@materials.uoc.gr

Each person, each day in the EU produces approximately 350 to 450 gr of avoidable and unavoidable food wastes that need to both be reduced and utilized as part of a circular economy. Aiming to develop a holistic approach for the prevention of food waste, herein we present our studies on bioplastic production from municipal food waste. More specifically, we designed a bioplastic pilot bio-refinery for the production of compostable bags and evaluated a food-waste recycling system proposed by Sakai et al.[1] in terms of raw material quality and energy consumption by studying all parameters involved in the production of PLA via fermentation followed by tin (II) 2-ethylhexanoate catalyzed ring opening polymerization (ROP) of the produced lactic acid.[1]

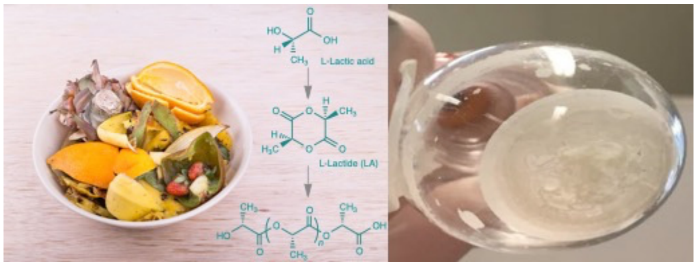


Figure 1. Transforming food waste into bioplastic.

References

[1] "Making Plastics from Garbage - A Novel Process for Poly-L-Lactate Production from Municipal Food Waste", K. Sakai, M. Taniguchi, S. Miura, H. Ohara, T. Matsumoto, Y Shirai, Journal of Industrial Ecology 7(3-4), 63 (2003).

Friction on Aperiodic Atomic Structures

M. Srbulović[1,2], K. Gkagkas[3], A. Vernes[1,2*]

[1]*AC2T research GmbH, Wiener Neustadt, Austria*
[2]*Technische Universität Wien, Vienna, Austria*
[3]*Advanced Material Research Division, Toyota Motor Europe NV/SA, Zaventem, Belgium*

*e-mail: vernes@ac2t.at

Aperiodic structures are frequently occurring in nature, such as the spiraling pattern within the seed pod of sunflowers.[1] All these discrete arrangements can be seen as perfect evolutionary accommodations of plants' leaves and seeds to external tribo-rheological conditions.[2] Accordingly, it can be expected that by mimicking these patterns on interacting surfaces in tribological systems, these could yield similar performances as observed in nature.[3] Exactly this hypothesis motivated the present work, namely to numerically predict the frictional regimes on aperiodic atomic structures, before these are created, for example, by nano-mechanical machining[4] or nano-coating and then tested in laboratory using, e.g., an atomic force microscope (AFM).

In this contribution, various nature-inspired aperiodic atomic structures will be computer generated and numerically studied with respect to their frictional characteristics towards the development of design rules for surfaces of given nano-tribological performance. These goals are achieved, on one hand, by applying and generalizing a proper cut-and-project methodology for creating the atomic structures and then by using adequate Prandtl-Tomlinson models, on the other hand, to compute the friction force along various sliding paths.

References

[1] "Phyllotaxis, Pushed Pattern-Forming Fronts, and Optimal Packing", M. Pennybacker and A. C. Newell, Phys. Rev. Letts. 110, 248104 (2013).
[2] "Plant Surfaces: Structures and Functions for Biomimetic Innovations", W. Barthlott, M. Mail, B. Bhushan, and K. Koch, Nano-Micro. Lett. 9, 23 (2017).
[3] "Nanomanufacturing of bioinspired surfaces", J. Sun and B. Bhushan, Tribol. Intl. 129, 67 (2019).
[4] "Recent advances in AFM tip-based nanomechanical machining", Y. Yan, Y. Geng, and Z. Hu, Int. J. Mach. Tools & Manu. 99, 1 (2015).

Molecular Electrets: What Do We Learn from Them and How to Interface Them with Halide Perovskites?

Jesse Tamayo[1], Macej Krzeszewski[2,3], Eli Espinoza[1], Daniel Gryko[2], Val Vullev[1,3*]

[1]Department of Chemistry, University of California, Riverside, CA, USA
[2]Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland
[3]Department of Bioengineering, University of California, Riverside, CA, USA

*e-mail: vullev@ucr.edu

Charge transfer (CT) represents nanometer-scale processes with the largest socioeconomic impacts. Via photosynthesis and cellular respiration, CT sustains life on Earth. Concurrently, CT in electronics and photonics makes our modern ways of living possible. Therefore, the importance of understanding CT and the developing capabilities to control it cannot be overstated.

Electric dipoles are ubiquitous and they present incomparable, but largely underutilized, paradigms for guiding CT.[1] We develop molecular electrets that, in addition to possessing large permanent dipoles, efficiently mediate CT.[2] In their abilities to rectify CT, the molecular electrets reveal (1) unprecedented synergy between dipole effects and the donor-acceptor electronic coupling,[3] and (2) the need for lowering media polarity to accelerate CT rates in the presence of dipoles.[4]

Interfacing electrets (or any organic CT-active moieties) with solid semiconducting materials presents the next level of organization for attaining utilizable functionalities. Focusing on modifying halide perovskites with auxiliary electron donors, we determine that similar to their interior, the perovskite interfaces are dynamic and the CT efficiency is limited by the binding propensity of the organic conjugates, rather than by the CT driving forces. These findings will set new paradigms not only for interfacing perovskite materials, but also for designing hybrid organic-inorganic nanostructures.

References

[1] "Dipole-Induced Effects on Charge Transfer and Charge Transport. Why Molecular Electrets Matter?", Derr, J.; Tamayo, J.; Espinoza, E. M.; Clark, J.; Vullev, V. I., Can. J. Chem. 96, 843-858 (2018).

[2] "From Biomimesis to Bioinspiration: What's the Benefit for Solar-Energy-Conversion Applications?", Vullev, V. I., J. Phys. Chem. Lett. 2, 503-508 (2011).

[3] "Dipole-Mediated Rectification of Intramolecular Photoinduced Charge Separation and Charge Recombination", Bao, D.; Upadhyayula, S.; Larsen, J. M.; Xia, B.; Georgieva, B.; Nuñez, V.; Espinoza, E. M.; Hartman, J. D.; Wurch, M.; Chang, A.; Lin, C.-K.; Larkin, J.; Vasquez, K.; Beran, G. J.; Vullev, V. I., J. Am. Chem. Soc. 136, 12966-12973 (2014).

[4] "Dipole Effects on Electron Transfer are Enormous", Krzeszewski, M.; Espinoza, E. M.; Červinka, C.; Derr, J. B.; Clark, J. A.; Borchardt, D.; Beran, G. J. O.; Gryko, D. T.; Vullev, V. I., Angew. Chem. Int. Ed. 57, 12365 -12369 (2018).

Flow-Regulated Growth of Titanium Dioxide Nanotubes in Microfluidics

J. Wan*, R. Fan, X. Chen, Z. Wang, D. Custer

University of California Davis, Davis, CA, USA

*e-mail: jdwanl@ucdavis.edu

Electrochemical anodization of titanium (Ti) in a static, bulk condition has been used widely to fabricate self-organized TiO_2 nanotube arrays. Such bulk approaches, however, require extended anodization time to obtain long TiO_2 nanotubes and produce only vertically-aligned nanotubes. To date, it remains challenging to develop effective strategies to grow long TiO_2 nanotubes in a short period of time and control the nanotube orientation. Here, we show that the anodic growth of TiO_2 nanotubes is significantly enhanced (~16-20 times faster) under flow conditions in microfluidics.[1] Flow not only controls the diameter, length, and crystal orientations of TiO_2 nanotubes but also regulates the spatial distribution of nanotubes inside microfluidic devices. Strikingly, when a Ti thin-film is deposited on silicon substrates and anodized in microfluidics, both vertically- and horizontally-aligned (relative to the bottom substrate) TiO_2 nanotubes can be produced. Our results demonstrate previously unidentified roles of flow in the regulation of growth of TiO_2 nanotubes and provide powerful approaches to effectively grow long oriented TiO_2 nanotubes and construct hierarchical TiO_2 nanotube arrays on silicon-based materials.

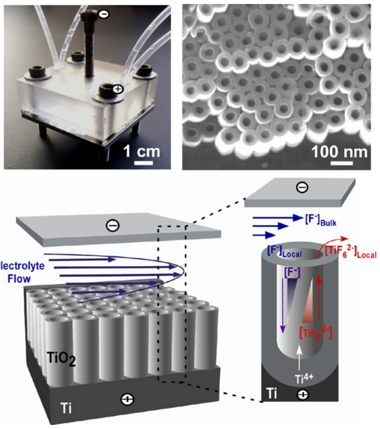


Figure 1. 1 (upper) A bright-field image of the assembled microfluidic device with a representive SEM image of fabricated nanotubes; (below) Schematics of the regulatory roles of flow in the anodic growth of TiO_2 nanotubes. Flow at high *Pe* reduces the thickness of the diffusion layer on the top of the nanotube and thus enhances ion flux inside the nanotube. In this case, $[F^-]$Local ≈ [F-]Bulk and $[TiF_6^{2-}]$Local ≈ 0.

References

[1] Flow-regulated growth of titanium dioxide (TiO_2) nanotubes in microfluidics. Fan, R., Chen, X., Wang, Z., Custer, D., Wan, J. Small, 13, 1701154 (2017).

2D Light Emitting Devices for Silicon Photonics

Yue Wang[1*], Thomas Krauss[1], Hanlin Fang[2], Juntao Li[2]

[1]Department of Physics, University of York, York
[2]State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-Sen University, Guangzhou, China

*e-mail: yue.wang@york.ac.uk

The missing piece of the jigsaw that is silicon photonics is a light source that can be easily incorporated into the standard silicon fabrication process. Molybdenum ditelluride ($MoTe_2$) is one of the most promising gain materials for this purpose,[1] with monolayer $MoTe_2$ having a direct bandgap of 1.13 eV (i.e. emission at 1130 nm). Here, I discuss our recent work using few-layer $MoTe_2$ and sandwiched $MoTe_2$ heterostructures as gain materials in silicon photonic crystal nanocavities. Firstly, we have demonstrated an optically pumped $MoTe_2$-on-silicon emitter by employing an L3 photonic crystal cavity, operating at 1305 nm, i.e. at the center of the "O-band" of optical communications, at room temperature with a threshold power density of 1.5 kW/cm^2.[2] Secondly, we have reported narrow emission from a sandwiched $MoTe_2$ heterostructure, consisting of a layer of $MoTe_2$ sandwiched between thin films of hexagonal boron nitride (hBN), on a silicon topological resonator. The topological photonic crystal nanocavity laser design allows us to better control the cavity mode and as such we have been able to demonstrate single mode operation with a wide free spectral range. We have achieved a Q-factor of 4,500. These results lend further support to the paradigm of 2D material-based integrated light sources on the silicon platform. Finally, it is worth noting that the carrier mobility of $MoTe_2$ is several times larger than that of doped silicon, which makes this material suitable for electrical injection devices as we move into the future.[3]

References

[1] Y Li, J Zhang, D Huang, H Sun, F Fan, J Feng, Z Wang, C Z Ning, Nature Nanotechnology 12, 987 (2017)
[2] H Fang, J Liu, H Li, L Zhou, L Liu, J Li, X Wang, TF Krauss, Y Wang, Laser & Photonics Reviews 12, 1800015 (2018)
[3] Y Bie, G Grosso, M Heuck, MM Furchi, Y Cao, J Zheng, D Bunandar, E Navarro-Moratalla, L Zhou, DK Efetov, T Taniguchi, K Watanabe, J Kong, D Englund and P Jarillo-Herrero, Nature Nanotechology 12, 1124 (2017)

Application of Positron Annihilation Induced AES to Characterize Single and Multi-Layered Graphene

A.H. Weiss*, A. J. Fairchild, V. A. Chirayath, R. W. Gladen, A. R. Koymen

The University of Texas at Arlington, Arlington, TX, USA

*e-mail: weiss@uta.edu

We have employed positron annihilation induced Auger electron spectroscopy[1] (PAES) to selectively characterize the surface of single and multilayered graphene. Our data provides a clear demonstration of the ability of positron spectroscopy to characterize 2-D materials with single atomic layer specificity[1] due to the trapping of positrons in an image correlation well just outside the surface prior to annihilation. PAES measurements were made on three samples; single layer graphene on copper,[2] multilayer graphene on copper and highly oriented pyrolytic graphite. The were collected using the advanced positron beam at University of Texas at Arlington. The ability of the beam optics to deposit ~ 1eV positrons on the sample allowed for the measurement of Auger spectrum from 600eV down to 0 eV without any secondary electron background.[1] We analyze the low energy part of the spectra to obtain information on the 2-D density of states of the surface.

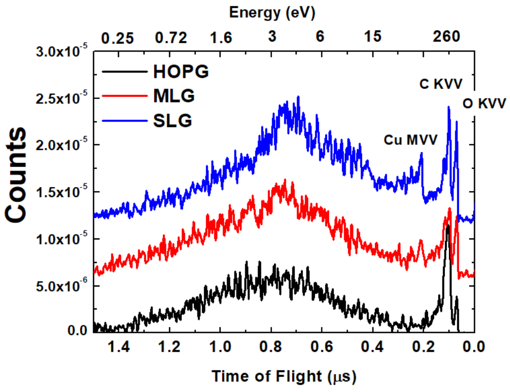


Figure 1. Time of flight positron annihilation induced Auger spectra collected from: highly oriented pyrolytic graphite (HOPG), multilayered graphene on Cu (MLG) and single layer graphene on Cu (SLG). The spectra have been shifted by a constant for clarity.

References

[1] "Auger-electron emission resulting from the annihilation of core electrons with low-energy positrons," A. H. Weiss et al., Phys. Rev. Lett., 61, 2245 (1988).

[2] "Auger electron emission initiated by the creation of valence-band holes in graphene by positron annihilation," V. A. Chirayath et al., Nature Communications, 8, 16116 (2017).

Element-Specific Characterization of Co:FePt Nanocomposites Magnet Films

F. Wilhelm[1*], V. Dupuis[2], D. Le Roy[2], N. Dempsey[3], A. Rogalev[1]

[1]*European Synchrotron Radiation Facility (ESRF), Grenoble, France*
[2]*Institut Lumière Matière, UMR5306/UCBL/CNRS, Villeurbanne, France*
[3]*Institut Néel, CNRS/UGA UPR2940, Grenoble, France*

[*]e-mail: wilhelml@esrf.fr

Nanocomposite magnets consisting of a mixture of a hard magnetic material and a high saturation magnetization ferromagnet are promising systems to overpass performances of the best permanent magnets. Theoretical descriptions of nanocomposite magnets[1] revealed the necessity of confining a soft magnetic material in clusters of typically less than 10 nm. Yet standard fabrication processes do not permit to produce such microstructures in a controllable manner. In this context a cluster-dedicated synthesis could permit to realize model films to experimentally explore underlying mechanisms that govern magnet performances in such nanocomposite magnets[2] We have been able to synthesize Co:FePt nanocomposite films (mass-selected soft magnetic Co clusters embedded in hard magnetic L10-FePt matrix) by combining low energy cluster beam deposition (LECBD) technique and e-beam evaporation. Doing so, the soft magnetic phase is restricted to clusters of nanometer size, selected from 2 to 8 nm while the volume fraction of nanoclusters in L10-FePt matrix was varied up to 30%. We will present results of standard structural (e.g. XRD, SEM, TEM) and magnetic characterizations (SQUID magnetometry, MFM) performed on these nanocomposite samples. Macroscopic characterization was then complemented with more sophisticated element selective approaches, i.e. X-ray linear dichroism (XLD) and X-ray magnetic circular dichoism (XMCD) spectroscopies at the K-edges of Fe and Co. Firstly, a high degree of texture in composite films is confirmed on microscopic level. Secondly, XLD signals at both Co and Fe sites are found to be nearly identical in amplitude and spectral shape. The latter is nearly identical to those measured on a pure L10-ordered FePt film. This observation is a very good indication that the Co clusters do not keep fcc structure as expected but rather adopt a tetragonal L10 structure. Microscopic magnetic characterization with XMCD has revealed that Co magnetic moments are aligned ferromagnetically with Fe moments in the L10-FePt matrix. Moreover, both are exhibiting the same magnetization curves that demonstrates that the Co:FePt nanocomposite behaves like a single magnetic phase material.

Acknowledgements

Funding by the ANR-SHAMAN (ANR-16-CE09-0019) is acknowledged.

References

[1] "Giant energy product in nanostructured two-phase magnets", R. Skomski and J. M. D. Coey, Phys. Rev. B 48, 15812 (1993).

[2] "Magnetic nanostructuring and overcoming Brown's paradox to realize extraordinary high temperature energy products", B. Balasubramanian, P. Mukherjee, R. Skomski, P. Manchanda, B. Das and D. J. Sellmyer, Scientific Reports 4, 6265 (2014).

Topological Spin Textures As Spin Wave Emitters

Sebastian Wintz

Paul Scherrer Institut, Villigen PSI, Switzerland

e-mail: sebastian.wintz@psi.ch

The study of spin-wave phenomena, also referred to as magnonics, plays an important role in present magnetism research[1,2] [Fig. 1]. This holds true, in particular, as spin waves are envisioned as signal carriers for future spintronic information processing devices, with a high potential to outperform present charge-based technologies in terms of energy efficiency and device miniaturization. Yet an implementation of magnonic technology will require the usage and control of spin waves with nanoscale wavelengths.

Here we will show that ferromagnetic spin textures in metallic systems can be used as nanoscale spin-wave emitters and waveguides. In particular, topological spin vortex cores prove to act as efficient and tunable generators for sub-100 nm spin waves[3,4] [Fig. 2(a,b)], while domain walls can be utilized as quasi one-dimensional channels for spin-wave propagation and routing[5] [Fig. 2(c)].

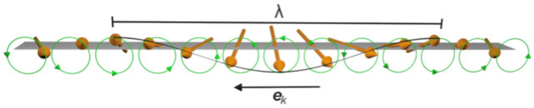


Figure 1. Schematics of a propagating spin wave.[3]

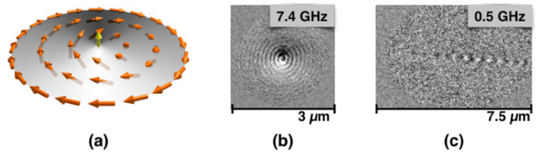


Figure 2. (a) Spin vortex. (b) Vortex core spin-wave emission. (c) 1D domain wall waveguide.

References

[1] "Magnetic oscillations and waves", A. G. Gurevich, and G. A. Melkov, New York CRC (1996).
[2] "Magnon spintronics", A. V. Chumak, V. I. Vasyuchka, A. A. Serga, and B. Hillebrands, Nat. Phys. 11, 453 (2015).
[3] "Magnetic vortex cores as tunable spin-wave emitters", S. Wintz et al., Nat. Nanotech. 11, 948 (2016).
[4] "Coherent excitation of heterosymmetric spin waves with ultrashort wavelengths", G. Dieterle et al., Phys. Rev. Lett. 122, 117202 (2019).
[5] "Emission and propagation of 1D and 2D spin waves with nanoscale wavelengths in anisotropic spin textures", V. Sluka et al., Nat. Nanotech. 10.1038/s41565-019-0383-4 (2019).

In-Situ Graphene Liquid Cell Electron Microscopy

Jong Min Yuk

Department of Materials Science and Engineering, KAIST, Daejeon, Korea

e-mail: jongmin.yuk@kaist.ac.kr

In-situ electron microscopy enables us to visualize directly chemical, physical or microstructural dynamics of nanomaterials under the external stimuli such as bias voltage, temperature, stress, or environments. Among various in-situ electron microscopy techniques, liquid-phase electron microscopy has been most difficult to realize due to the lack of containers to protect liquid evaporation in the high vacuum electron microscopy chamber. In this talk, we will introduce graphene liquid cells, two graphene layers encapsulating solution between them.[1] The graphene liquid cell facilitates real-time imaging of target materials in solution at high-resolution. Employing this cell into colloidal platinum nanocrystal system, we demonstrate site-selective coalescence, structural reshaping after coalescence, and surface faceting in atomic resolution. Furthermore, we will introduce a method for determining three-dimensional structures of individual nanoparticles in solution.[2] Tomography images of a nanoparticle with random orientations are acquired from a nanoparticle randomly rotating in solution. Using the tomography images, three-dimensional structure of a nanoparticle is reconstructed and we analyze the grain boundary structures. Lastly, we apply graphene liquid cell to battery electrode materials to demonstrate compositional and morphological evolution in real electrolyte during lithiation.[3] We directly visualize the generation of non-uniform composition field in core-shell SnO_2-Sn nanoparticles. The graphene liquid cell electron microscopy technique opens the way to explore the nanoscale regime previously inaccessible with conventional characterization tools.

References

[1] "High-Resolution EM of Colloidal Nanocrystal Growth Using Graphene Liquid Cells", J. M. Yuk et al., Science 336, 61 (2012).
[2] "3D Structure of Individual Nanocrystals in Solution By Electron Microscopy", J. Park et al., Science 349, 290 (2015).
[3] "Strong Stress-Composition Coupling in Lithium Alloy Nanoparticles", H. K. Seo et al., Submitted (2019).

In Vitro Study of Doxorubicin Encapsulation into Arsonoliposomes

Paraskevi Zagana[2*], Spyridon Mourtas[2], Anastasia Basta[2], Sophia G. Antimisiaris[1,2]

[1]*Department of Pharmacy, University of Patras, Greece*
[2]*Institute of Chemical Engineering Sciences (FORTH/ICE-HT), Patras, Greece*

[*]e-mail: voulazagana@yahoo.gr

Arsonoliposomes are liposomes that incorporate arsonolipids in their membranes and have been studied previously, in terms of their stability and antitumor activity.[1,2] They demonstrate significant toxicity towards cancer cells while being less toxic towards normal cells. Doxorubicin (DOX), is a commonly used anti-cancer drug which is currently used in the clinic as in the form of PEG-liposomes.

In this study, we sought to investigate the possibility to encapsulate DOX into arsonoliposomes and arsonoliposomes that are modified with a curcumin derivative (TREG), in order to study at a latter step, if the DOX-arsonoliposome combined system demonstrates additive or even synergist anticancer activity. PEGylated arsonoliposomes and TREG-arsonoliposomes composed of DSPC/Chol/PEG-2000-DSPE/Arsonolipid/TREG (in some cases) were prepared and the loading of DOX was attempted by applying the active loading method protocol. A drug/lipid ratio (D/L) of 1/7 (w/w) was always used, while the effect of using different temperatures (40℃ and 60℃) and different time periods of incubation (15, 30, 60 and 90 min), on the DOX encapsulation in arsonoliposomes and TREG-arsonoliposomes, was tested. In all cases, liposomes were purified after the loading process and the % DOX entrapment efficiency was calculated based on initial/final D/L ratio.

Results show that the active-loading protocol succeeds to encapsulate high percents of DOX into arsonoliposomes (up to 99%) and TREG-arsonoliposomes (up to 89%); Maximum loading was demonstrated when the incubation was carried out at 40℃, for arsonoliposomes and 60℃ for TREG-arsonoliposomes. Considering the duration of incubation, in both cases DOX encapsulation was highest after 90 min. DOX-loaded arsonoliposomes and TREG-arsonoliposomes are currently tested for their anticancer activity towards different types of cancer cells, in vitro, and the first results are interesting.

Acknowledgements

This research is 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 in the context of the project "Innovative Drug and Imaging agent Delivery Systems [SYSTOFAR]" (MIS 5004447)."

References

[1] Zagana P, et al. (2009) Arsonoliposome interaction with cells in culture. Effect of pegylation and lipid composition. J Mol Nutr Food Res 53:592–599
[2] Gortzi O, et al. (2002) Arsonoliposomes, a Novel class of arsenic-containing liposomes: effect of palmitoyl-arsonolipid-containing liposomes on the viability of cancer and normal cells in culture. Pharm Res 19:79–86

Superior High-Temperature Behavior of Amorphous Coatings from Quinary Hf-B-Si-C-N System

Petr Zeman[1*], Efstathios I. Meletis[2], Jaroslav Vlcek[1]

[1]*University of West Bohemia, Plzen, Czech Republic*
[2]*University of Texas at Arlington, Arlington, TX, USA*

[*]e-mail: zemanp@kfy.zcu.cz

Multielement ceramic coatings are appropriate candidates for high-temperature applications due to their excellent behavior at temperatures exceeding 1000℃. When the excellent oxidation resistance is combined with the thermal stability of a high optical transparency, they can be applied for high-temperature passive protection of optical and optoelectronical devices. On the other hand, a combination of the high oxidation resistance and the thermal stability of the electrical conductivity makes them suitable for capacitive pressure, vibration or tip clearance sensors in severe oxidation environments.

The present work focuses on systematic investigation of high-temperature behavior of two amorphous Hf-B-Si-C-N coatings with different electrical and optical properties. The coatings were prepared by reactive pulsed dc magnetron co-sputtering of a B_4C-15%Hf-20%Si target in two Ar+N_2 mixtures (15% and 20% N_2 fractions). Particular attention is paid to thermogravimetric analysis and differential scanning calorimetry of the coatings in air and Ar, and to the evolution of the film structure, microstructure and elemental composition with increasing annealing temperature from 1100℃ to 1700℃.

The coating prepared at the 15% N_2 fraction has an elemental composition of $Hf_7B_{23}Si_{22}C_6N_{40}$ and is electrically conductive, while the coating prepared at the 20% N_2 fraction has an elemental composition of $Hf_7B_{23}Si_{17}C_4N_{45}$ and is optically transparent. Both coatings are sufficiently hard (≈ 20 GPa) and exhibit a superior oxidation resistance up to 1600℃ due to the formation of a nanocomposite diffusion barrier surface layer consisting of HfO_2 nanocrystallites surrounded by a borosilicate amorphous matrix. A small difference in the composition results, however, in a different thermal stability of the amorphous structure of the coatings above 1400℃. While the $Hf_7B_{23}Si_{17}C_4N_{45}$ coating underneath the oxide layer retains its amorphous structure, the $Hf_7B_{23}Si_{22}C_6N_{40}$ coating crystallizes into different phases (Si_3N_4, B(C)N, HfCN, HfB_2) with a unique self-organized structures.[1,2]

References

[1] "Superior high-temperature oxidation resistance of magnetron sputtered Hf–B–Si–C–N film", P. Zeman, S. Zuzjakova, P. Mares, R. Cerstvy, M. Zhang, J. Jiang, E.I. Meletis, J. Vlcek, Ceram. Int. 42, 4853 (2016).

[2] "Microstructure evolution in amorphous Hf–B–Si–C–N high temperature resistant coatings after annealing to 1500℃ in air", Y. Shen, J. C. Jiang, P. Zeman, V. Simova, J. Vlcek, E. I. Meletis, Sci. Rep. 9, 3603 (2019).

Ions Colliding with Clusters of Fullerenes and Polycyclic Aromatic Hydrocarbons

Henning Zettergren

EDepartment of Physics, AlbaNova University Center, Stockholm University, Sweden

e-mail: henning@fysik.su.se

Molecular clusters bridge the gap between isolated (gas phase) molecules and condensed matter. In this talk, I will give an overview of recent advances in the understanding of how such weakly bound clusters of fullerenes and Polycyclic Aromatic Hydrocarbons (PAHs) respond to energetic ion impact. I will highlight results from experimental and theoretical studies demonstrating how the cluster environment plays a crucial role for the fate of the individual molecules, and how the projectile charge, mass, and velocity of the ion may be tuned to study a rich variety of molecular destruction and formation pathways. In this talk, the focus will be on exotic bond-forming reactions occurring on very fast (sub-picosecond) timescales inside the clusters. These molecular growth processes are ignited by prompt atom knockout processes, where individual atoms are permanently displaced from molecules through Rutherford type scattering processes. The key molecular property determining the cross sections for such reactions is the threshold displacement energy, which we have recently measured for isolated fullerenes[5] and PAHs.[6] These results will be discussed in view of those reported for graphene.[7] The studies discussed in this talk may advance the understanding of energetic processing and formation of complex molecules in space, where PAHs and fullerenes are believed to be key players.[8]

References

[1] M. Gatchell and H. Zettergren, J. Phys. B 49, 162001 (2016)
[2] R. Delaunay et al, Carbon 129, 766 (2018)
[3] R. Delaunay et al, J. Phys. Chem. Lett. 6, 1536 (2015)
[4] H. Zettergren et al, Phys. Rev. Lett. 110 185501 (2013)
[5] M. H. Stockett et al., Carbon, 139 906 (2018)
[6] M. H. Stockett et al., J. Phys. Chem. Letters 6, 4504 (2015)
[7] J. C. Meyer et al., Phys. Rev. Lett. 108, 196102 (2012)
[8] A. G. G. M Tielens, Rev. Mod. Phys. 85, 1021 (2013)

Interface Engineering on 1D ZnO Nanomaterials and Their Applications

Yue Zhang

State Key Laboratory for Advanced Metals and Materials, School of Materials Science and Engineering,
University of Science and Technology Beijing, Beijing, China
Key Laboratory of New Energy Materials and Technologies, University of Science and Technology Beijing, Beijing, China

e-mail: yuezhang@ustb.edu.cn

Energy and sensing technology are two significant scientific research fields. Their development has substantially reduced human's dependence on traditional resources, and pushed forward the progress of human society. ZnO is a unique piezoelectric semiconductor, and ZnO nanostructures are treated as important candidates for construction of high performance micro-nano functional devices. This report presents a systematic review of engineered 1D ZnO applications in the field of energy conversion and sensing system, summarizes a series of research results in structure design, performance optimization and system integration of 1D ZnO nanostructure functional devices. For applications in energy conversion field, we mainly talk about the research results on engineered 1D ZnO based light emitting diodes, solar cells, and photochemical water splitting systems. For applications in sensing field, the investigations of engineered 1D ZnO based self-powered photodetector, biosensor, and stress/strain sensor will be mainly introduced. The comprehensive understanding, summary and review of such interface engineering protocols may provide novel and effective approaches for designing of energy conversion devices and sensing systems.

Rapid Construction of Metal Phosphate Anodes of Li-Ion Batteries via Plasma-Assisted Electrolytic Deposition

Jingzeng Zhang*, Tao Li, Ran Cai, Xueyuan Nie

Department of Mechanical, Automotive & Materials Engineering, University of Windsor, Windsor, Ontario, Canada

*e-mail: jzzhang@uwindsor.ca

The lithium-ion battery (LIB) as an energy storage system has been increasingly used in automotive industry, portable electronic devices and other applications. Besides preformance enhancement of the cathode materials, the advancced anode materials are also expected to further improve the capacity of LIBs. Most studies emphasize the powder-based active electrode materials. However, the powder-based electrode materials need to be mixed with a binder in the manufacturing of the electrodes, which leads to the long production line, big manufacturing foorprint, and high cost. Additionally, the fabrication and recycling of powder materials are the time-comsuming and pollutants-containing process. Therefore, it is necessary to develop a clean technology to synthesize binder-free electrodes with a minium cost. In this presentation, a plasma assisted-electrolytic deposition (PAED) technique, which was evolved from the traditional plasma electrolytic oxidation (PEO), was used to sythesize a low-cost metal-phosphate anode of LIBs. During the PAED, the metal phosphate coating directly grew on a titanium (Ti) foil wthin 2-3 minutes. For instance, a Ni$_3$(PO$_4$)$_2$ binder-free anode was successfully systhesized using the PEAD (Fig.1).[1] As shown in Fig.2, the capacity of Ni$_3$(PO$_4$)$_2$ anode can reach 1400 µAh/cm^2 and remained 750 µAh/cm^2 after 40 cycles, which is higher than the capacity of most of repoted anode materials in LIBs.[1-3] The high capacity of Ni$_3$(PO4)$_2$ indicates that the PAED is a potential clean technology to rapid construct the high performance anodes for LIBs.

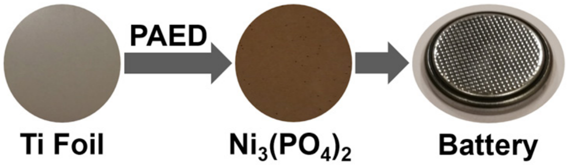


Figure 1. PAED synthesized Ni$_3$(PO$_4$)$_2$

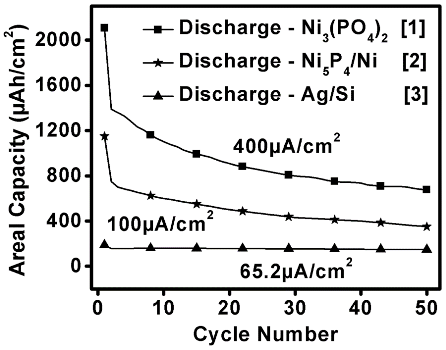


Figure 2. Cycling performance of Ni$_3$(PO$_4$)$_2$ anode

References

[1] T. Li, R. Cai, X. Nie and J. Tjong, J. Electroanal. Chem., 2019, 835, 81-85
[2] J. Ma, S. Ni, X. Lv, X. Yang and L. Zhang, Mater. Lett., 2014, 133, 94-96.
[3] P. Wang, L. Tong, R. Wang, A. Chen, W. Fang, K. Yue, T. Sun and Y. Yang, RSC Adv., 2018, 8, 41404-41414.

Index

BOOK OF ABSTRACTS

6th International Conference from Nanoparticles &
Nanomaterials to Nanodevices & Nanosystems

IC4N SPONSORS

UNIVERSITY OF SCIENCE AND TECHNOLOGY BEIJING

KIT
Karlsruher Institut für Technologie

UNIVERSITY OF TEXAS ARLINGTON | COLLEGE OF ENGINEERING

UNIVERSITY OF PATRAS

MAVS OPEN PRESS

Available electronically at:
http://hdl.handle.net/10106/28271