

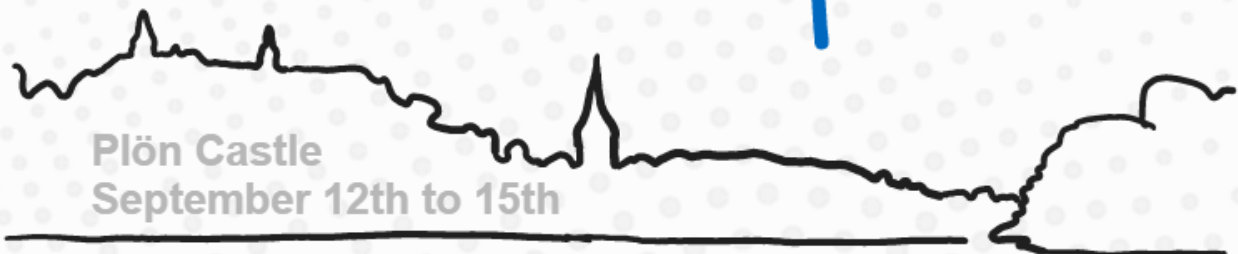
NANOWORKSHOP 2023

11th INTERNATIONAL WORKSHOP ON FUNCTIONAL NANOCOMPOSITES

12th - 15th September 2023 Plön Castle, Germany

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Nanoworkshop 2023



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Christian-Albrechts-Universität zu Kiel

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20 years after the 1st Nanoworkshop “International Workshop on Polymer/Metal Nanocomposites” 2003 in Kiel, the 11th Nanoworkshop “International Workshop on Functional Nanocomposites” will take place again in Germany near Kiel after being hosted in many countries all over the world. The workshop aims at bringing together material scientists, physicists, chemists, and engineers from academics and industries to share the latest developments in the field of functional nanocomposites. Topics range from advanced preparation techniques and new material properties to industrial applications and include computer simulations as well as theoretical work. While originally, the focus was put on polymer-based nanocomposites, over the years it was extended to functional nanocomposites in general.

The workshop will be held in the fascinating Plön Castle, the largest of its kind in Schleswig-Holstein, rich in history and with a breathtaking view over the Lake of Plön. It also offers on-site accommodation and many opportunities for touristic activities.

Contents

INVITED TALKS	1
Tuning Ag-Au structures at the nanoscale	2
Covadonga Álvarez, Yves Huttel, José Miguel García-Martín, Álvaro Mayoral, Alicia de Andrés, Lidia Martínez	
Functional Metal Oxide Surfaces: Photocatalytic, Self-Cleaning, Sensing, and Micro-/Nanostructuring Applications	3
Salih Veziroğlu, Josiah Shondo, Tim Tjardts, Franz Faupel, Oral Cenk Aktas	
Advanced (S)TEM investigations of nanomaterials for green energy production	4
Maria Chiara Spadaro	
Multifunctional plasma-enabled functional thin films low dimensional nanoarchitectures: from synthesis to devices	5
Ana Borrás	
The structural analysis of biobased materials by X-ray scattering characterization	6
Shun Yu, Jenny Bengtsson, Hanna Ulmefors, Omid Hosseinaei, Andreas Bengtsson, Jiliang Liu	
Exploration of the gap between classical and plasma polymers: fundamental and applied science opportunities	7
Jaroslav Kousal	
TALKS	8
Advances and challenges in the application of the post magnetron in a gas aggregation nanoparticle source	9
Daniil Nikitin, Jan Hanus, Tereza Kosutova, Pavel Pleskunov, Ondrej Kylian, Suren Ali-Ogly, Pavel Mares, Jiri Vyskocil, Andrei Choukourov, Hynek Biederman	
How to locate nanoparticles: Using in-situ diagnostics to understand growth and trapping dynamics	10
Jonas Drewes, Oguz Han Asnaz, Oleksandr Polonskyi, Stefan Rehders, Franko Greiner, Thomas Strunskus, Holger Kersten, Jan Benedikt, Franz Faupel, Alexander Vahl	
Operator Risk Assessment during Dismounting and Cleaning of a Gas Aggregation Nanocomposite Deposition Source	11
Harry Nizard, Eleonore Fröhlich, Carsten Kykal, Sigrun Klinkenberg, Dominic Hecker, Daniel Gloess	
Sputter-Based Synthesis of Group IV Transition Metal Nitride Nanoparticles and Nanofluids	12
Mariia Protsak, Kateryna Biliak, Pavel Pleskunov, Daniil Nikitin, Marco Tosca, Suren Ali-Ogly, Jan Hanuš, Miroslav Cieslar, Tereza Košutová, Anastasiya Sergievskaya, Stephanos Konstantinidis, David Cornil, Jérôme Cornil, Andrei Choukourov	
From sputtering onto liquids to functional nanoparticle - hydrogel composites	13
Stephanos Konstantinidis, Valentine Jauquet, France-Emmanuelle Bol, Anastasiya Sergievskaya, Polona Umek, Jeremy Odent	

Plasma polymer and composite nanoparticles from gas aggregation sources: Rebounding upon impact on the substrate	14
Katerina Skorvankova, Pavel Solar, Alexander Vahl, Tim Tjardts, Lucia Bajtosova, Anna Kuzminova, Ondrej Kylian, Franz Faupel	
Electrostatic manipulation of charged nanoparticles for deposition of tailored surfaces... 15	
Pavel Čurda, David Kaftan, Tomáš Kozák, Sanjay Kumar, Petr Sezemský, Vítězslav Straňá	
Nanostructured iron oxides thin film catalysts developed by RF sputtering for the solar photo-Fenton degradation of methylene blue dye	16
Antonella Milella, Regina Del Sole, Danilo Benedetti, Savino Cosmai, Francesco Fracassi, Fabio Palumbo	
Structure control during in situ printing of functional nanocomposite films for solar cell applications	17
Peter Müller-Buschbaum	
Surface-Grafted Atom Transfer Radical Polymerization on Superparamagnetic Iron Oxide Superparticles	18
Lea Regina Klauke, Michael Kampferbeck, Andreas Meyer, Tobias Vossmeier	
Aerosol assisted atmospheric pressure plasma deposition of nanocomposite coatings for organic water pollutant abatement	19
Fabio Palumbo, Regina Del Sole, Chiara Lo Porto, Danilo Benedetti, Savino Cosmai, Francesco Fracassi, Antonella Milella	
Inorganic-organic hybrid nanostructures based on biopolymer templating for thermoelectric application.....	20
Linus Huber, Peter Müller-Buschbaum	
Anti-corrosion polymer gel sheet containing liquid-phase synthesized layered double hydroxide (LDH) nanoparticles	21
Minoru Mizuhata, Kota Kamon, Yun Yang, Hideshi Maki, Hiro Minamimoto	
Plasma-enabled nanocarbons and nanocomposites for zero-carbon world: recent updates	22
Kostya {Ken} Ostrikov	
Highly Porous Activated Carbon Electrodes Prepared from The Bio-Wastes – for High-Performance Supercapacitor Applications	23
Amarjeet Kaur	
Memsensor Devices: An innovative approach to bio-inspired sensing	24
Rohit Gupta, Roshani Madurawala, Niko Carstens, Maik-Ivo Terasa, Thomas Strunskus, Abdou Hassanien, Sören Kaps, Franz Faupel, Rainer Adelung, Alexander Vahl	
Wet-coated sensors for virus detection	25
Jungui Zhou, Yingjian Guo, Constantin Harder, Peter Müller-Buschbaum, Peng Zhang, Stephan V. Roth	
Polarizonics: Earth-Abundant Nanocomposites for Colored Solar Absorbers that Outshine Black	26
Mady Elbahri, Mhd Adel Assad, Amirhossein Azari, Moheb Abdelaziz	

Boosting effect of Ag-Cu nanoparticle-built surfaces for LSPR detection of pathogens	27
Sanjay Kumar, Hana Maskova, Pavel Curda, Anna Kuzminova, Pavel Pleskunov, Ryan Rego, Jan Sterba, Ondrej Kylian, Vitezslav Stranak	
CdS/ZnS core/shell nanostructures based broadband Photodetector.....	28
Tania Kalsi, Pragati Kumar	
Broadband Solar Absorbers Based on Plasmonic Metal-Dielectric Nanocomposites	29
Moheb Abdelaziz, Mhd Adel Assad, Kevin Rogall, Jonas Drewes, Nanda Perdana, Torge Hartig, Thomas Strunskus, Carsten Rockstuhl, Franz Faupel, Alexander Vahl, Mady Elbahri	
Electron Transport in Discontinuous Thin Metal Films	30
James Eliot Morris	
Self-organized Nanoparticle Network Retains Brain-like Critical Dynamics after Covering with an Insulating Matrix.....	31
Blessing Oluwasayo Adejube, Niko Carstens, Ole Gronenberg, Florian Ziegler, Jonas Drewes, Oguz Han Asnaz, Ulrich Schürmann, Thomas Strunskus, Jan Benedikt, Simon Anthony Brown, Lorenz Kienle, Alexander Vahl	
A Stretchable and Flexible Neuromorphic Device for in-Materia Adaptive Computing.....	32
Francesca Borghi	
The matrix matters: field-driven phenomena in Ag-based nanofluids prepared by cluster-beam deposition.....	33
Daniil Nikitin, Kateryna Biliak, Jonathan Lemke, Mariia Protsak, Pavel Pleskunov, Marco Tosca, Suren Ali-Ogly, Blessing Adejube, Lucia Bajtošová, Zulfiya Černočová, Franz Faupel, Alexander Vahl, Andrei Choukourov	
Relationship between structure, mechanical properties and function in locust cuticle, a functional nanocomposite.....	34
Chuchu Li, Hamed Rajabi, Stanislav Gorb	
Controls of Visible-Light Driven Reduction Reaction at Plasmonic Cathode Electrode.....	35
Hiro Minamimoto, Yuto Tajiri, Minoru Mizuhata	
Cellulose-based smart hybrid materials.....	36
Stephan Volkher Roth	
Facile Scalable Single Step Multi-Level Structure Engineering Makes TNO₄/Carbon Nanohybrids a New Promising Lithium-Ion Battery Anode.....	37
Zhuijun Xu, Yonggao Xia, Yajun Cheng, Peter Müller-buschbaum	
In-situ GISAXS/GIWAXS investigation of dcMS and HiPIMS deposited gold onto polymers	38
Yusuf Bulut, Benedikt Sochor, Kristian Reck, Jonas Drewes, Suzhe Liang, Tianfu Guan, Thomas Strunskus, Franz Faupel, Peter Müller-Buschbaum, Stephan V. Roth	
Morphology changes at the organic-metal interface: effects on the structure, electronic and thermoelectric performance.....	39
Benedikt Sochor, Simon Schraad, Tanny Chavez, Guanhua Hao, Eric Roberts, Anna Lena Oechsle, Marie Betker, Yusuf Bulut, Tzu-Yen Huang, Anton Le Brun, Tim Laarmann, Peter Müller-Buschbaum, Stephan Roth	

POSTER ABSTRACT	40
Gas Sensing Behavior of Different Two Dimensional Nanostructured Materials for Hydrogen Gas: A Comparative Study	41
Nutan Sharma, Sheetal Charan, Arjun Kumawat, Sachin Saini, Subodh Srivastava	
Synthesis and Self-Assembly of Titania Nanoplatelets and Their Subsequent Encapsulation in a Polystyrene Shell via Surface-Grafted Controlled Radical Polymerization.....	42
Jana Struck, Laura Ronja Franzen, Sophia Caroline Bittinger, Tobias Vossmeier	
Nanoparticles of plasma polymerized hexane as targets for laser-driven proton-boron fusion	43
Marco Tosca, Pavel Pleskunov, Mariia Protsak, Katherina Biliak, Daniil Nikitin, Anna Macková, Romana Mikšová, Giovanni Ceccio, Daniele Margarone, Antonino Cannavò, Zdeňka Kolská, Lorenzo Giuffrida, Andrei Choukourov	
Biopolymer-Templated Deposition of Hierarchical 3D-Structured Graphene Oxide/Gold Nanoparticle Hybrids for Ultrasensitive Surface-Enhanced Raman Scattering.....	44
Yingjian Guo, Constantin Harder, Shouzheng Chen, Yusuf Bulut, Benedikt Sochor, Elisabeth Erbes, Peter Müller-Buschbaum, Stephan V. Roth	
One-step synthesis of hybrid ZrN/Ag nanoparticles with tunable optical properties	45
Mariia Protsak, Suren Ali-Ogly, Pavel Pleskunov, Kateryna Biliak, Daniil Nikitin, Miroslav Cieslar, Marco Tosca, Andrei Choukourov	
Memristive planar devices based on a tunable nanostructured Au/ZrOx composite film ...	46
Filippo Profumo, Francesca Borghi, Andrea Falqui, Paolo Milani	
Observation of early stages of HiPIMS film formation on polymers with GISAXS	47
Kristian Amand Reck, Yusuf Bulut, Thomas Strunskus, Alexander Vahl, Stefan Schröder, Jonas Drewes, Peter Müller-Buschbaum, Stephan V. Roth, Franz Faupel	
Forming process and electrical-structural properties of 2D and 3D nanostructured Au resistive switching networks.....	48
Giacomo Nadalini, Francesca Borghi, Andrea Falqui, Tereza Kosutova, Nicola Ludwig, Paolo Milani	
Exploring the potential of magnetic, reactant-free nickel nanofluids: a preliminary study .	49
Kateryna Biliak, Mariia Protsak, Marco Tosca, Daniil Nikitin, Pavel Pleskunov, Jan Prokleška, Andrei Choukourov	
Tailored polymer thin films enabled by initiated chemical vapor deposition (iCVD).....	50
Torge Hartig, Joschka Paulsen, Jonas Drewes, Julia Piehl, Oleg Lupan, Alexander Vahl, Thomas Strunskus, Franz Faupel, Stefan Schröder	

INVITED TALKS

Tuning Ag-Au structures at the nanoscale

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Silver and gold nanostructures are subject of intensive research due to their interesting properties at the nanoscale, which make them particularly suitable for many different applications ranging from catalysis, nanomedicine, optics, sensing, etc [1,2]. Like the formation of alloys that combines the properties of different elements resulting in novel materials, the combination of different shapes and dimensions also leads to materials having novel properties, especially at the nanoscale. In this talk we will present different combinations of silver and gold nanostructures. In particular, nanocolumns (NCs) fabricated by Glancing Angle Deposition with magnetron sputtering [3], nanoparticles (NPs) fabricated by means of a Multiple Ion Cluster Source (MICS) [4] as well as combinations of NCs with NPs [5]. We will first briefly present the ultra-high vacuum physical methods used to grow the NCs and NPs, highlighting the control over chemical composition, shape and dimensions of the fabricated nanostructures. Later, we will present some examples of application of these systems, including photo-induced self-cleaning surfaces [5], antibacterial coatings [6], controlled wettability or catalysis.

Keywords: *nanoparticles, nanocolumns, gas-phase synthesis, glancing angle deposition, dual scale roughness*

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Functional Metal Oxide Surfaces: Photocatalytic, Self-Cleaning, Sensing, and Micro-/Nanostructuring Applications

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Titanium oxide (TiO₂) is one of the most used photocatalytic materials for various applications such as environmental remediation, (solar)water splitting, and self-cleaning due to its high activity, low cost, and high chemical, and physical stability. However, the photocatalytic activity of TiO₂ is limited by the wide energy of the bandgap, low quantum efficiency, and rapid recombination of photogenerated charge carriers (electrons and holes). During the last decades, numerous approaches, such as tailoring the morphology (nanoparticles, thin film, etc.), and combining with a metal, noble metal, and metal oxide micro/nanostructures, have been demonstrated to enhance the photocatalytic activity of TiO₂. However, it is still a major challenge to find the best photocatalytic combination for specific applications. Recent studies have revealed that particle size plays a considerable role in the photocatalytic activity of TiO₂. Reducing the particle size (increasing active surface area) indicates a higher photocatalytic activity. Nevertheless, the use of photocatalytic nanoparticles in continuous flow systems (such as water remediation, water splitting, etc.) has some practical limitations such as reusing and splitting them up from the reaction media. Hence, the use of robust and stable thin film photocatalysts becomes more suitable rather than nanoparticle systems for practical applications. Nevertheless, thin films are restricted by low surface area in contrast to nanoparticles and they show extremely limited photocatalytic activity. Here we present some case studies on enhancing the photocatalytic performance of TiO₂ thin film by modification with metallic [1,2] and oxide [3,4] nanostructures for practical applications such as water purification, self-cleaning, selective oil absorption [5], and organic molecule sensing [6].

Keywords: metal oxide, functional surfaces, photocatalysis, self-cleaning, PIERS

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Advanced (S)TEM investigations of nanomaterials for green energy production

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The development and optimization of growth processes, that allow to control shape and size of the produced nanostructures, is an aspect of major interest in material science and nanotechnology. Nanostructures with desired morphological, structural and chemical features exhibit specific properties that can be exploited in several research fields, such as catalysis, photovoltaics and so on. Transmission electron microscopy (TEM) is ideal thanks to the possibility to obtain information on nanostructures with high spatial resolution, down to the atomic scale. To unambiguously investigate specific TEM or STEM image characteristic features, 3D atomic modelling and EM image simulation are required.

Here some of our results for nanoparticles and nanowire structures. By combining scanning transmission electron microscopy in high angle annular dark field (HAADF-STEM) mode, with modelling and simulation we could recognize the presence of specific features that need to be deeply investigated and addressed to unveil their formation mechanism and their effects reflected in the final device electronic properties.

Multifunctional plasma-enabled functional thin films low dimensional nanoarchitectures: from synthesis to devices

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Abstract. In this presentation, we will present our last advances in the exploitation of plasma and vacuum deposition methods for the nanoengineering of thin films and supported low-dimensional materials. A key step in the development of such nanoarchitectures is the implementation of a soft-template procedure based on the use of single-crystal small-molecule nanowires grown on processable substrates under mild conditions. We will demonstrate the application of vacuum and plasma-assisted deposition techniques to develop complex nanowires (NWs) and nanotubes (NTs) with a core@multishell morphology where each shell adds functionality or multifunctionality to the system. The steps required for the integration of these nanomaterials as supported or in-device applications will be presented. Two final applications will drive the presentation, namely, the development of multisource energy harvesters (piezo, solar, pyro and triboelectric) and novel approaches for smart surfaces and efficient de-icing by acoustic waves. The universal character of vacuum and plasma methods allows for the deposition of an unprecedented variety of possibilities, including, organic (small-molecules, organic nanocomposites, polymeric layers), inorganic (metal and metal oxides), hybrid (hybrid perovskite) materials acting as conducting, semiconducting, dielectric, photo-absorbent, piezoelectric or plasmonic components in a multilayer or radial configuration. We will share the results accomplished during the last years in the field of energy harvesting (solar cells,[1-4] piezoelectric and triboelectric nanogenerators[5-7]), semi-transparent nanoelectrodes,[8] wetting [9], de-icing and anti-icing.[10-11]

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The structural analysis of biobased materials by X-ray scattering characterization

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The sustainable development goal calls for the materials transition from fossil-based polymeric materials to ones from renewable resources. Novel biobased materials derived from forests and agricultural plants are emerging for this purpose and have demonstrated the potential to substitute fossil-based counterparts in many applications, such as packaging, textile, energy storage, electronics, etc. Despite the bright future, some fundamental challenges of developing biobased materials remain in manipulating the heterogeneity of their components and the hierarchy of their structure, as well as handling the inherent complex interaction between biobased macromolecules and water[1]. To address these challenges, advanced X-ray scattering techniques, especially at synchrotron radiation facilities, provide many possibilities to investigate the structure variation of the material in real-time and with good spatial information, shown in Fig. 1. In this presentation, we summarize some of our recent works to investigate the water-lignocellulose interaction by coupling X-ray scattering with relative humidity/mechanics-controlled tests[2] and decipher the distribution of different biocomponents by using micro-focused scanning X-ray scattering imaging techniques[3]. In addition, we will discuss the development of the hierarchical structure of carbonaceous materials derived from biobased materials in the perspective of X-ray scattering characterization[4].

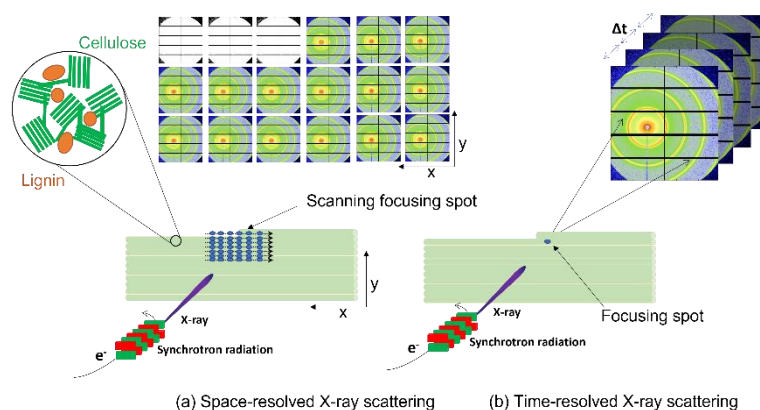


Fig. 1. Schematics of the characterization of lignocellulose material by X-ray scattering

Keywords: cellulose, lignin, SAXS/WAXS, water, hierarchical structure

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Exploration of the gap between classical and plasma polymers: fundamental and applied science opportunities

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Plasma polymerization (plasma-enhanced chemical vapour deposition) is a well-known method for depositing organic thin films. One of its drawbacks is typically a limited molecular complexity of the films compared to those obtained from classical chemistry. This is partially caused by the need to use the precursors with sufficient vapour pressure and, therefore, a limited molar mass. To overcome this limitation, plasma-assisted vapour thermal deposition (PAVTD) has been developed [1].

PAVTD uses a solid polymer in a crucible to obtain oligomers through thermal degradation/evaporation, which are then re-polymerized in RF plasma. Using heavy (several monomeric units, 10^2 - 10^3 g/mol) building blocks, the chemical structure of the original polymer is largely preserved, even with plasma-induced fragmentation and crosslinking. In this way, PAVTD utilizes both top-down and bottom-up processes. This approach allows control of the properties like biodegradability and hydrolyzability in a very broad range, as was demonstrated using polylactic acid (PLA) [2, 3]. Effectively, PAVTD films bridge the gap between the classical and plasma polymers.

The batch process is limited in deposition duration (~2h) and stability due to temperature- and history- sensitivity of the deposition rate. However, Yasuda-like scaling law was already reproduced in PAVTD [4].

Recently, a continuous-PAVTD setup was developed, utilizing common FDM 3D printing filaments and a modified off-the-shelf filament heater/extruder (Fig. 1, inset). The filament feed rate is slower than in 3D printing (several g/h), but this is a significant material input for plasma polymerization (RF power 0-32W, argon, 0.4 Pa). The continuous feed of the material significantly improves the stability of the process and the deposition rate (up to several nm/s) while increasing the running time (over 7 hours was demonstrated, limited only by the filament storage) [5]. The continuous-PAVTD setup was successfully operated with various polymer filaments (like PLA or PVA), alone or in combination with other deposition techniques, to produce nanocomposites. Additionally, the higher controllable evaporation (and thus deposition) rate allows to shift the deposition process to lower energy-per-mass ratios and to study the plasma polymerization in a new way (Fig. 1, spectra). With improved stability and deposition rate, PAVTD can become both a practical deposition method and a tool for studying plasma polymerization processes.

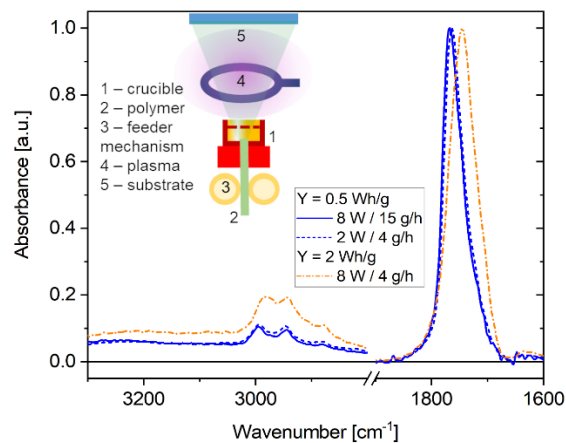


Fig. 1. Infrared spectra of PLA-like films prepared using PAVTD. Inset: Simplified scheme of the PAVTD setup with continuous feed.

Keywords: Plasma polymer, plasma-assisted vapour thermal deposition

Acknowledgements: This contribution was supported by the grant GA22-21007S of the Czech Science Foundation.

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TALKS

Advances and challenges in the application of the post magnetron in a gas aggregation nanoparticle source

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Gas Aggregation Sources (GAS) of nanoparticles (NPs) have become very popular in recent years usually following the Haberland's original design [1]. The GAS systems can be easily combined with other plasma sources for in-flight treatment/coating of NPs and thus enable the fabrication of NPs with more complex structure (e.g., [2, 3]). At present GAS are equipped with planar magnetrons [1], however, they suffer mainly from inefficient target material utilization, NP loss because of uncontrollable re-deposition on the target surface and escape to the walls. In addition in some cases they have a high Ar gas consumption. In this report, a post-cylindrical magnetron [4] has been placed in the GAS instead of a planar magnetron. At first in-line (in axis) configuration has been tested with the Cu cylindrical target, in which the magnetic circuit rotates at a frequency of several rotations per minute up to about 30 RPMs. Working gas Ar pressure from 20 to 160 Pa, flow 10 to 100 sccm and magnetron currents from 0.5 to 2 A have been used. In further study a new magnetic circuit so called closed loop endless arch has been applied. In addition to Cu the Cu + Ag composite target has been examined that allowed bimetallic NPs, e.g. Ag/Cu preparation. In the following experiments the post magnetron was placed perpendicularly to the GAS axis. This has an advantage that the NPs trajectory through plasma zone is decreased that suppress nanoparticle capture and size increase. The measurement of size distributions confirmed this finding. The SEM investigation showed that with the increasing magnetron current the average size of NPs decreases. In addition to these investigations we started to mix nitrogen with argon that ended in reactive sputtering and Cu₃N nanoparticle production. At a relative concentration 0.3 of N₂ in the gas Ar + N₂ mixture the occurrence of Cu₃N was confirmed by EDX analysis while XRD confirmed that Cu₃N NPs possess crystalline structure. Further perspectives are outlined.

Keywords: nanoparticles, gas aggregation, cluster source, post magnetron

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How to locate nanoparticles: Using in-situ diagnostics to understand growth and trapping dynamics

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Among the variety of nanoparticle (NP) beam deposition methods, gas phase synthesis of NPs via a Haberland-type gas aggregation source (GAS) attracts a substantial research interest due to its capability of depositing surfactant-free, highly pure NPs and being compatible with both, a range of other vapor phase deposition methods and a large variety of different substrates. The concept of a magnetron-based GAS dates back to its introduction in the early 1990s [1], and a broad theoretical framework on the condensation of NPs from supersaturated vapors in GAS has since evolved [2]. Triggered by the *in-situ* observation of a distinct population of large NPs very close to the target by means of small-angle x-ray scattering techniques [3], the interplay between NP growth and transport and the dynamic trapping of NPs within the aggregation zone have become an active research topic in the recent years.

In this contribution, photon-based *in-situ* diagnostics are applied to investigate dynamic trapping processes inside a GAS at the example of Ag-based NPs. The selection of Ag NP combines the benefit of a high deposition rate with a plasmon absorption peak of AgNPs in the UV-Vis range. As a first approach, UV-Vis spectroscopy is applied to locate the NPs in the aggregation zone of the GAS with a time resolution in the range of 100 ms. A shift of aggregation length and relative position of the UV-Vis light beam is induced by a change in the magnetron-to-beam distance, i.e. by moving the magnetron in and out of the GAS chamber. By this approach it was found that the plasmon absorption peak crucially depends on the magnetron-to-beam-distance, showing a maximum close to the magnetron [4]. While UV-Vis spectroscopy has proven to be capable of monitoring the plasmon resonance of NPs within its beam path and giving indications for NP trapping close to the magnetron, it does not provide information on the exact location of the NPs. Thus, in addition, laser light scattering from a green laser (532nm, outside of the plasmonic absorption peak of Ag NPs) was applied to obtain 2D information on trapping locations. With this method it was possible to obtain spatially- and temporally resolved information on NP trapping, indicating the inherent dynamics in the trapping processes [5]. In general, uncontrolled and unidentified trapping of NPs inside the GAS is detrimental to the gas phase synthesis of NPs and impacts the release of NPs into the NP beam. However, gaining a deeper understanding and better control of NP confinement is a promising pathway to broaden the range of obtainable NPs from GAS. In this contribution, it is shown how NPs from a GAS can also be captured and modified in a secondary radio-frequency plasma. To showcase the applicability of *in-situ* diagnostics to monitor the growth of a dielectric shell on GAS-derived NPs, the confinement of Ag NPs and the controlled addition of a SiO₂ shell will be presented [6].

Keywords: nanoparticles, gas phase synthesis, UV-Vis, laser scattering, trapping

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Operator Risk Assessment during Dismounting and Cleaning of a Gas Aggregation Nanocomposite Deposition Source

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This work investigates the operator risk during the dismounting and cleaning phases of vacuum-based nanocomposite deposition equipment. The equipment has been described in detail in previous publications [i, ii, iii, iv, v] and utilizes a "safe-by-design" approach, which ensures minimal external release of nanoparticles during normal operation. The study aims to assess whether nanoparticles remain attached to internal surfaces or disperse into the surrounding environment when the equipment is opened. The adherence of nanoparticles to internal surfaces is influenced by factors such as nanoparticle size and surface properties. The research also evaluates operator exposure to airborne nanoparticles and proposes guidelines for safe handling practices.

The measures presented in this work establish a NP exposure in the range of 0.5 to 2 $\mu\text{g}/\text{m}^3$ in the normal conditions with mask, and possibly up to 40 $\mu\text{g}/\text{m}^3$ for accidental sniffing of the NP aggregates. Potential effects of the inhaled particles are determined by the extent of particle deposition in the lung, permeation through fluid and airways and penetration into the cells lining the respiratory tract [vi]. The extrapolation of those measures for other metals is discussed.

The results indicate that proper containment measures and personal protective equipment can minimize operator exposure. Overall, the study contributes to establishing guidelines for safe equipment maintenance and ensuring operator safety in nanocomposite deposition processes.

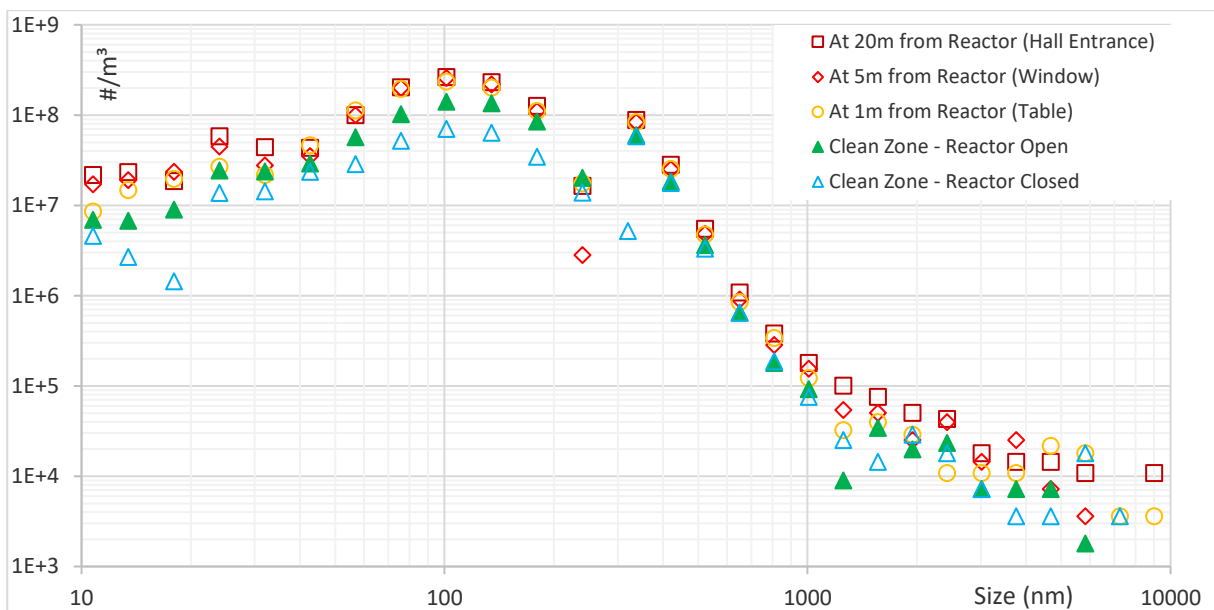


Fig. 1. Particle size distributions collected in (□) Pt.3, (◇) Pt.5, (○) Pt.4, (▲) Pt.6 reactor open, and (△) Pt.6 reactor closed.)

Keywords: Nanocomposite deposition, Safe-by-design, Nanoparticle adherence, nanotechnology, Operator risk

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Sputter-Based Synthesis of Group IV Transition Metal Nitride Nanoparticles and Nanofluids

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Group IV transition-metal nitrides (MeN, Me = Ti, Zr, and Hf) have been extensively studied as refractory plasmonic materials, predominantly in the form of thin films prepared by reactive magnetron sputtering [1]. Often, if not always, deposition on heated substrates and/or post-deposition annealing in NH₃ are required to produce films of high quality. Nanoparticles (NPs) of these nitrides have also been reported but to a lesser extent, and their synthesis also requires the use of aggressive compounds and elevated temperatures [2]. This work established a goal of using reactive magnetron sputtering of Ti, Zr, and Hf in mixtures of Ar and N₂ in the configuration of a gas aggregation cluster source to produce MeN NPs avoiding high temperatures and toxic chemicals. The second goal was to investigate the one-step loading of MeN NPs into vacuum-compatible liquids to produce linker- and residual-free plasmonic nanofluids.

Reactive sputtering was found to proceed in accordance with a thin-film deposition phenomenology, revealing a hysteresis loop in the deposition rate and magnetron bias upon an increase/decrease in the concentration of N₂ in the working gas. Sub-stoichiometric (sub-MeN) NPs are produced in the metallic mode, while the reactive mode leads to close-to-stoichiometric MeN NPs, although at the expense of a low deposition rate. MeN NPs are found to be of cubic morphology, which replicates the translational symmetry of fcc lattice determined by XRD. STEM-EDX and *in-situ* XPS measurements reveal partial surface oxidation with the formation of a 2-nm oxynitride shell on the NPs. Nevertheless, the MeNO shell is too thin to deteriorate the electrical conductivity of MeN, which was proven by single-particle conductive AFM measurements and supported by DFT calculations. Beams of MeN were loaded into vacuum-compatible liquids (polyethylene glycol, pentaphenyl trimethyl trisiloxane, and paraffin) to prepare nanofluids that are colorful in transmittance and show a bluish tint. UV-Vis measurements showed that the color is given by strong absorption due to interband transitions at $\lambda < 500$ nm and due to a broad plasmonic absorbance in the red/near-IR range. Although dry MeN NPs did not show photoluminescence, they were found to enhance photoluminescence of organic host liquids. The enhancement intensity depends on the chemical character of the organic molecule, and the phenomenon is presumably related to the different charge-transfer efficiency from MeN to organics. Thus, our method offers an environmentally benign, annealing-free route to MeN NPs and nanofluids with attractive optoelectronic properties.

Keywords: reactive sputtering, gas aggregation cluster source, transition metal nitride, plasmonic nanoparticles

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From sputtering onto liquids to functional nanoparticle - hydrogel composites

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In this work, multifunctional hydrogel-metal nanoparticles composites were synthesized in a two-step process. First, colloidal solutions of silver nanoparticles (Ag-NPs) were prepared by sputtering a silver target onto a liquid substrate. In the present case, the host liquids are vacuum – proof polymerizable poly(ethylene glycol) methacrylates which can subsequently be used to synthesize hydrogel - nanoparticles metal composites with interesting optical properties. The electrical power applied (P) to the sputtering plasma and the processing time (T) were varied to modify the concentration of the nanoparticles. Ex situ Transmission Electron Microscopy (TEM) data highlight the presence of two populations of NPs. The largest populations comprises small, few nm in diameter, nanoparticles. The second population is comprises a smaller number of bigger Ag-NPs having a diameter in the range of several tens of nm. Electron diffraction studies highlight that the Ag-NPs are crystallized. Interestingly, the viscosity of the colloidal solutions increases with the energy (E) delivered to the plasma, with $E = P \times T$. This observation would suggest plasma-induced polymerization of the liquid substrate for high E conditions. In the second step, the as-prepared colloidal solutions were polymerized by radical photopolymerization in the presence of a crosslinking agent (ethylene glycol dimethacrylate) and a photoinitiator (diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide). Scanning electron microscopy observations show that silver nanoparticles are well dispersed inside the hydrogels but also that the morphology of the gel changes with the working conditions, i.e. with the energy E delivered to the plasma during the elaboration of the colloidal suspensions. Finally, the hydrogel-silver nanoparticle composites were tested for the detection of Hg^{2+} cations in aqueous solutions. The detection was enabled by monitoring the UV-Vis absorption spectrum of the composite. Absorbance decreased as a function of the concentration of Hg^{2+} metal cations and immersion time (Fig. 1).

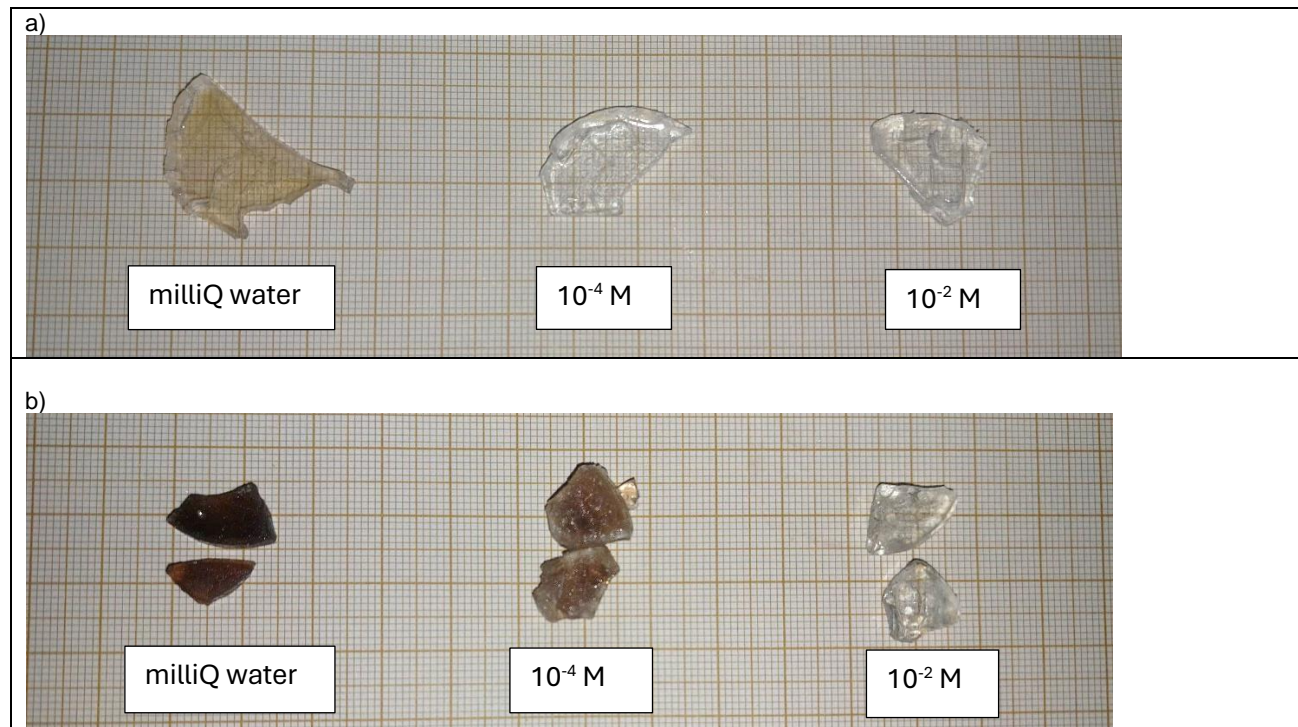


Fig. 1. The color of hydrogel - silver nanoparticle composites after immersion for 24 hours in milliQ water (left), 10⁻⁴ M (center) and 10⁻² M (right) mercury (II) nitrate aqueous solutions. The composites were synthesized by applying a) 10W of sputter power for 5 minutes and b) 80W for 5 minutes.

Keywords: Magnetron sputtering, liquid substrate, nanoparticles, hydrogel, composite

Plasma polymer and composite nanoparticles from gas aggregation sources: Rebounding upon impact on the substrate

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Gas aggregation sources (GAS) are commonly employed for the preparation of nanoparticles (NPs). However, like any other method, GAS encounter challenges in efficiency. One such challenge is the efficiency of NPs collection on substrates. After NPs are synthesised, they exit the GAS into the deposition chamber, where they are deposited on a substrate. Several phenomena may occur upon impact. Particles may be adsorbed on the surface, be implanted into the surface, or undergo reflection. Our study focuses especially on the last mentioned one – the reflection of plasma polymer and plasma polymer-containing NPs upon impact. This effect may be (depending on the deposition conditions) very strong since these types of NPs bear structural similarities to rubber balls.

Deposition rate is one of the most important parameters for optimization of NPs production process. This parameter describes how many NPs accumulate on the surface per unit of time and determine whether the process has any potential of practical application. In our study, we have studied the deposition rate both in the direct beam and in the reflected beam (see Figure 1).

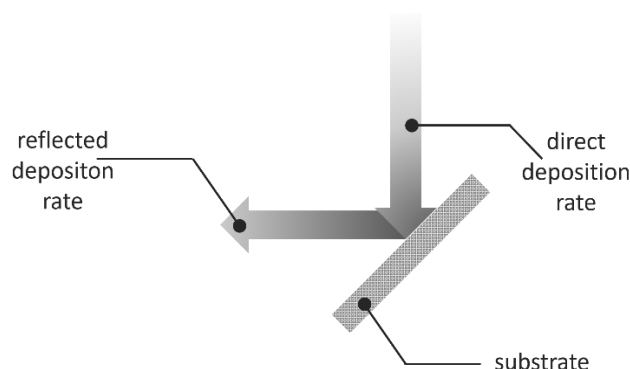


Fig. 1. Schematics of the investigation of NPs reflection from substrate upon impact

Our goal is to investigate the dependence of the rebounding effect on the speed of the NPs, on the type of the substrate and on the type of the NPs. A series of experiments was performed for NPs from RF sputtered nylon and for Ag@HMDSO core@shell NPs. Investigation of reflection was complemented with the measurements of NPs velocity in the deposition chamber before their interaction with the substrate using a mechanical time-of-flight filter [1]. Finally, we propose methods to suppress the reflection of the NPs and enhance their collection on the substrate.

Acknowledgement:

This work was supported by grant GACR 20-15405Y from the Grant Agency of the Czech Republic.

Keywords: Nanoparticles, Gas Aggregation Source, Plasma polymer, Reflection of nanoparticles upon impact

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Electrostatic manipulation of charged nanoparticles for deposition of tailored surfaces

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This study combines numerical simulation with an experimental investigation of high-level designed nanostructured surfaces built from metal nanoparticles (NPs). The goal of this research is to prepare highly designed isotropic surfaces with high purity, defined size, homogeneous surface coverage, and high deposition rate, i.e., the properties appreciated in the precise fabrication of biosensors and/or nanoelectronics [1-3]. The approach is based on the manipulation of electrically charged nanoparticles, produced by a gas aggregation cluster source (GAS) [4] equipped with a quadrupole mass filter (QMF) and a pair of two parallel electrodes mounted at the QMF output orifice. As the used mass filter is not able to affect neutral species (according to mass to charge ratio), other approaches for investigation were employed. At first, quartz crystal microbalance-based measurement with the voltage-biased electrode, roughly estimated that only about half of the total mass flux in the beam is ionized. Furthermore, the electrostatic voltage bias modulates the trajectories of ionized nanoparticles according to Lorentz's force.

A numerical simulation calculating the electric field distribution (by the finite difference method applied to the Poisson equation) and tracking the movement of charged nanoparticles in it (by the Monte Carlo method) was employed to support the experiment. The effect of the distribution of charged nanoparticles on the electric field is accounted for iteratively using a self-consistent field algorithm. The simulation enables us to predict the distribution and properties of the NPs across the (x, y) substrate plane as a function of the electrical potential superimposed by the charged NPs in the volume and the

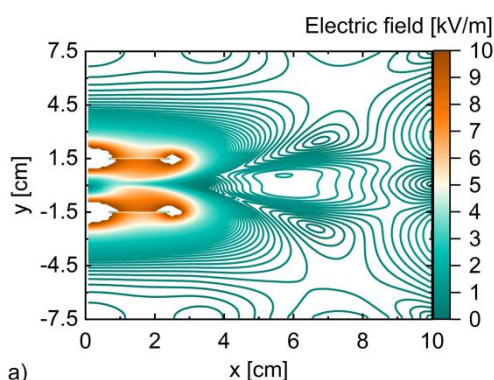


Fig. 1. Electric field created by biased deflection electrodes and beam of moving charged nanoparticles. The simulation of the complex electric field distribution including a contribution of charged NPs. external electrical field.

A good qualitative agreement was found between the model and the properties of GAS-deposited NPs onto the Si substrate. The external electric field acts as a beam splitter, where neutral species are not affected and their distribution on the substrate is determined by conventional diffusion. The trajectories of charged NPs are determined by the electric field, which finally enables to calculate size/mass ratio with respect to (x, y) substrate position. The NPs surface density can be easily controlled by deposition time, which is rather short; deposition of NPs monolayer takes approximately 30 - 60 s in our experimental condition. Our future challenge is to tailor and optimize the deposition of nanoparticles (shape, geometry, surface coverage density) as agents responsible for SERS, MALDI, LSPR detection of (bio)molecules and/or bio-complexes. This fundamental research supports fabrication of defined nanostructured sensor transducers build of nanoparticles.

Keywords: Nanoparticles, Electrostatic manipulation, Gas aggregation, Nanostructure tailoring

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Nanostructured iron oxides thin film catalysts developed by RF sputtering for the solar photo-Fenton degradation of methylene blue dye

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Advanced oxidation processes (AOPs) are promising water treatment technologies, capable to remove a wide spectrum of organic pollutants from water with high levels of mineralization, under optimized conditions, or at least to transform them into converted to readily degradable small organic molecules. A variety of technologies belong to AOPs, having in common the progressive oxidative degradation of the organic contaminants accomplished by highly reactive and oxidizing transitory species (e.g., hydroxyl radical, superoxide radical) generated in situ. Among AOPs, Photo-Fenton reaction is considered a cost effective and efficient process to remove several classes of contaminants such as pesticides, dyes, pharmaceuticals and phenols, in presence of H₂O₂ and metal cations. A major advantage of photo-Fenton over other AOPs, such as direct photolysis of H₂O₂ and photoexcitation of TiO₂, is the possibility to use visible light instead of high intensity UV light. However, homogeneous photo-Fenton reaction, mostly performed with inorganic iron salts presents some limitations preventing its widespread application to wastewater treatment: a narrow pH range around 3 is required to ensure that Fe(II) and Fe(III) species exert their catalytic role. Heterogeneous photo-Fenton methods aim to overcome these drawbacks, proceeding at neutral pH and without producing any sludge at the end of the treatment by using iron-based solid catalysts. Therefore, the synthesis of supported catalysts by environmentally friendly preparation methods is a constantly evolving research area.

In this contribution, we address the deposition of iron oxide thin films with different composition and morphology, through RF-sputtering of an iron target in argon/oxygen plasma mixtures, and their application as the solar photo-Fenton degradation of methylene blue as model pollutant. In particular, we present three different routes for the preparation of the iron oxides thin film catalysts with good efficiency and recyclability, all based on RF sputtering. Nanostructured iron films deposited in pure argon were converted to Fe₂O₃ upon thermal annealing in oxygen atmosphere, obtaining different morphologies depending on the thickness. These nanostructured materials resulted to be efficient catalysts for the photo-Fenton degradation of methylene blue dye (photodegradation percentage up to 90%). In order to avoid the cost and time consuming annealing step, hematite films were also deposited by deposition in Ar/O₂ mixtures, reaching a quite good dye removal efficiency (photodegradation above 80%). In order to increase the photocatalytic performances, double-step deposition processes were also explored. In optimized conditions, a degradation of 97% was accomplished and the reusability of the catalyst over ten cycles was demonstrated.

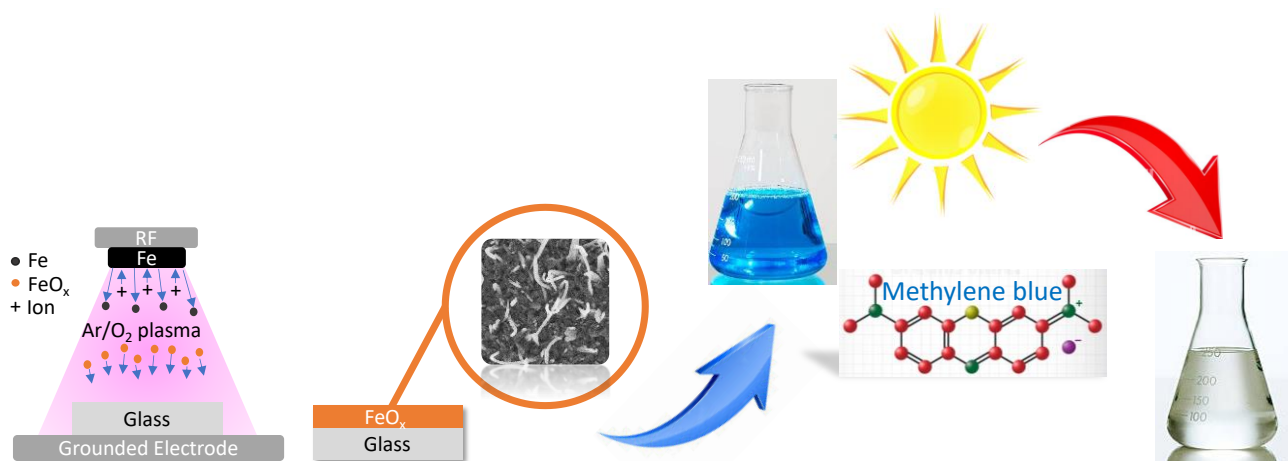


Fig. 1. Schematics for the development of nanostructured iron oxides thin film catalysts for the degradation of methylene blue dye by solar photo-Fenton [1].

Keywords: RF sputtering; iron oxides; solar photo-Fenton; photocatalyst.

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Structure control during in situ printing of functional nanocomposite films for solar cell applications

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Functional nanocomposite-based solar cells receive a growing interest and achieve a substantial progress concerning device efficiency and lifetime during the last years. Moreover, the potential low fabrication costs, fast energy payback times and the use of lightweight materials make them very appealing for real world applications. In terms of champion device efficiency, values above the 18% limit were reported recently. Mainly combinations of novel low bandgap polymers and non-fullerene acceptor materials, forming the functional nanocomposite, have boosted the device efficiencies. Therefore, functional nanocomposite-based solar cells are addressed in many research groups with a very high level of attention. However, basic understanding is still very limited due to the complexity of the systems. Typically, functional nanocomposite-based solar cells have an active layer made out of a mixture of a positive charge carrier conducting polymer and a small molecule electron acceptor material. Light is absorbed in one or both of the components. Excitons are created and split into free charge carriers in case an interface between both components is reached by the exciton within its lifetime. Thus, the morphology of the active layer of a functional nanocomposite-based solar cell has a significant influence on the final device performance. To enable a high interfacial area between the components, so-called bulk heterojunction (BHJ) geometry is realized in a self-assembly process of the materials. This bulk heterojunction geometry is optimized for exciton splitting and charge carrier transport.

However, despite big achievements in the last years, it remains an unresolved challenge to fabricate large-area functional nanocomposite-based solar cells without sacrificing efficiencies. The reason behind is that basic understanding is still very limited due to the complexity of the systems. Moreover, presently a substantial number of researchers use spin-coating for film fabrication, which is not compatible with the needs of a large scale production. Thus, using up-scalable fabrication methods such as printing are of immanent interest.

In the present work, we use multi-modal grazing incidence small- and wide-angle X-ray scattering (GISAXS and GIWAXS) studies in situ during printing of donor:acceptor blends (see figure 1) to gain fundamental understanding about the underlying film formation processes [1-4]. Different examples of polymer donors and small molecule acceptors are presented and the resulting morphologies are correlated with functional nanocomposite-based solar cell device performance data. From these data, models about the morphology evolution are extracted and these models guide the fundamental understanding to increase reproducibility in the solar cell fabrication [1-4]. In particular, more environmental friendly solvents are demonstrated to enable also high efficiency functional nanocomposite-based solar cells [2], if the printing parameters are tuned with the understanding of the film morphology.

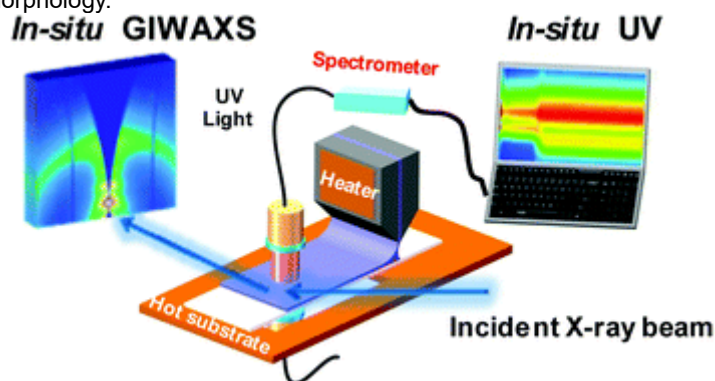


Fig. 1. Schematic of the multi-modal study combining in situ GIWAXS and UV spectroscopy with the printing technique for monitoring the morphology evolution during the film formation of functional nanocomposite films. Image taken from reference 1.

Keywords: functional nanocomposites; solar cell; printing; multi-modal studies; donor:acceptor blends

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Surface-Grafted Atom Transfer Radical Polymerization on Superparamagnetic Iron Oxide Superparticles

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Superparamagnetic iron oxide nanoparticles (SPIONs) are of particular interest for biomedical applications due to their low toxicity and high biocompatibility.[1] However, size- and shape-controlled synthesis of SPIONs is often conducted via thermal decomposition, which results in hydrophobic nanoparticles.[2] To enable applications in biological environments, such nanoparticles require the phase transfer to the aqueous phase and a robust encapsulation with, e.g., a polymer shell to prevent nanoparticle aggregation.[3] Additionally, SPIONs used for magnetic separation of biomolecules should enable short response times to external magnetic fields to increase the separation efficiency. To this end, SPIONs can be assembled to form superparticles.[4]

Herein, we present the synthesis of size- and shape-controlled SPIONs and their self-assembly into superparticles of diameters between 200 and 300 nm via emulsion-based methods.[4, 5] Subsequently, the superparticles are modified using ligand exchange reactions to enable surface-grafted encapsulation.[6] Fourier-transformed infrared (FTIR) spectroscopy confirmed the success of the ligand exchange. The encapsulation of SPION superparticles is conducted in an emulsion via atom transfer radical polymerization (ATRP).[7, 8] Scanning electron microscope images of resulting magnetic composites are depicted in figure 1. These composites show high inorganic loadings, as indicated by electron microscopy and thermogravimetric analysis and, thus short magnetic response times. Furthermore, we found that the polymer shell thickness can be precisely adjusted via the added monomer volume during the ATRP. Vibrating sample magnetometer (VSM) measurements show magnetizations between 8 and 30 emu/g magnetite and the magnetizations can be adjusted by changing both the polymer shell thickness and SPION size. The arrangement of the SPIONs inside the superparticles was characterized via small-angle X-ray scattering (SAXS). SAXS patterns indicate swelling of the superparticles due to the polymer formation but no enhancement of the superparticle crystallinity.

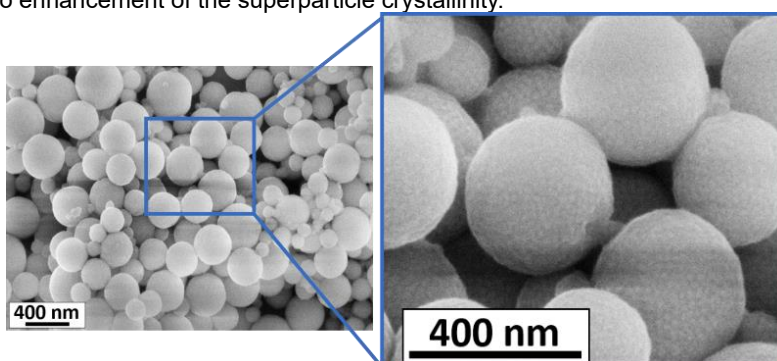


Fig. 1. Scanning electron microscope images of encapsulated superparticles.

For applications as magnetic carriers, functional groups like carboxylic acids (COOH), azides (N₃), and amines (NH₂) are required to enable the binding of biomolecules to the superparticles' surface. To introduce such functionalities, we used functional monomers during the ATRP.[8] The incorporation of COOH, N₃ and NH₂ was confirmed by FTIR spectroscopy and zeta potential measurements. Finally, click chemistry coupling is currently studied to characterize the accessibility of the functional groups to small molecules. The presented composites are promising candidates for applications as magnetic carriers due to their robust encapsulation, the possibility of surface modifications and the short magnetic response times.

Keywords: SPIONs, self-assembly, surface-grafting, atom transfer radical polymerization

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Aerosol assisted atmospheric pressure plasma deposition of nanocomposite coatings for organic water pollutant abatement

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Nanocomposites is a topic of increasing interest in the last decades because of their superior properties when compared to their single components and their wide applications. Metal oxide nanocomposites are largely studied for photocatalytic applications (such as wastewater treatment, photodegradation of organic pollutants or antimicrobial activity). In particular, NPs of TiO_2 , an n-type semiconductor, are often studied alone or together with carbon nanomaterials (CNM) or silver in order to overcome two main limitations typical of the use of such metal oxide as a photocatalyst: first, TiO_2 wide band gap of 3.2 eV leads to a strong absorption in the UV region, thus requiring a high energy irradiation; second, TiO_2 NPs are characterized by a fast electron-hole recombination rate that limits their photocatalytic performance. Nanocomposites combining TiO_2 and CNMs, and in particular with rGO (reduced Graphene Oxide) and C_{60} , can be manufactured, in order to profit of the charge, sink properties of the carbon derivatives that contribute in enhancing the electron-hole recombination time. The reduced size of these nanomaterials can make difficult their recovery and recycle: hence the immobilization onto a solid support can make photocatalysts suitable and technologically viable for environmental applications.

In this work, we will illustrate our recent advancements in the development of Aerosol Assisted Plasma Deposition (AAPD), carried out in atmospheric pressure systems, of TiO_2 -based nanocomposites coatings with the addition of CNM (rGO and C_{60}) in a hybrid siloxane matrix. This is schematized in figure 1.

Furthermore, also results of the effect of the addition of silver nitrate (AgNO_3) to TiO_2 /siloxane nanocomposite will be reported.

The versatility of AAPD has been well illustrated by this research group in the past: it allows to deposit thermodegradable or scarcely volatile species, hence also NPs, in nanocomposite coatings, keeping the activity of the additive, e.g. enzyme, drugs, and so on.

In the present study The coatings are deposited in a dielectric barrier discharge reactor, feeding the plasma with two aerosol generators: one is fed with TiO_2 NPs dispersed in a HMDSO/isopropyl alcohol mixture, and the other with a CNMs suspension or a AgNO_3 solution. The chemical composition and the morphology of the coatings has been characterized by means of FT-IR, EDX, profilometry, SEM and TEM analyses, evidencing the complex nature of the structure of this materials. Finally photocatalytic activity of the coatings has been evaluated in water in terms of discoloration of a model organic pollutant, methylene blue, under UV light irradiation. It has been demonstrated that the TiO_2 hybrid nanocomposite coatings have a good catalytic activity. However such activity can be further increased by addition of CNMs of AgNO_3 .

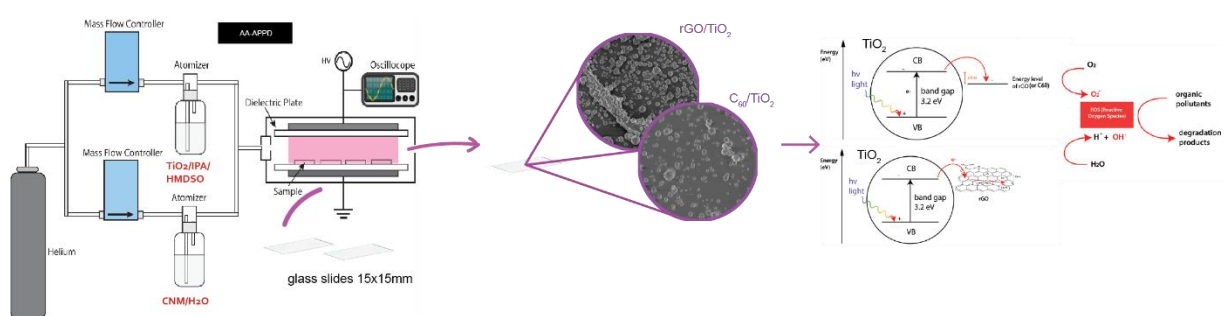


Fig. 1. Figure 1. TiO_2 /CNM nanocomposites are deposited via AA-APPD on a solid support. The so-obtained coatings show an enhanced photocatalytic if compared to TiO_2 alone.

Keywords: nanocomposite coatings, plasma deposition, atmospheric pressure plasma, photocatalysis

Inorganic-organic hybrid nanostructures based on biopolymer templating for thermoelectric application

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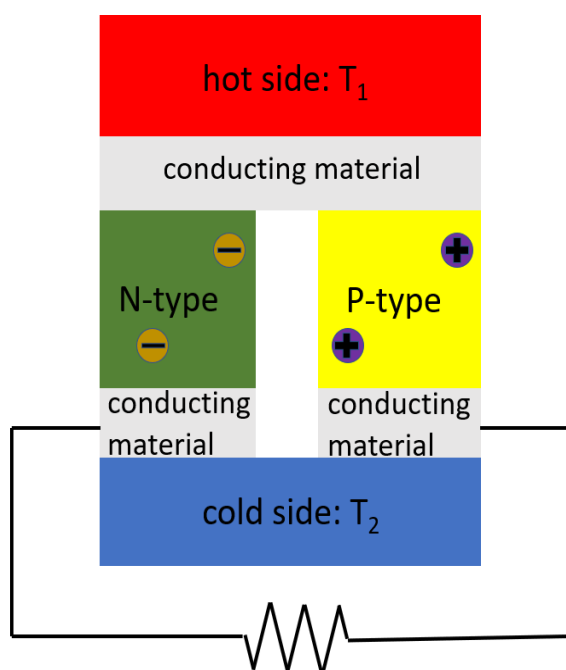
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Thermoelectric power conversion, which enables the direct conversion of waste heat into useful electricity, has garnered significant attention due to its potential for sustainable energy conversion and waste heat recovery applications. Inorganic materials have traditionally dominated the field of thermoelectrics, but recent research efforts have explored the utilization of inorganic-organic hybrid films to enhance thermoelectric performance. [1,2]

Biotemplating is an effective method of nanostructuring hybrid inorganic-organic materials. This approach allows the tuning of material properties like porosity or domain sizes. Therefore, parameters like the electronic conductivity can be adjusted for different applications.

In this work, differently structured titania thin films are investigated for application in thermoelectric generators. The efficiency of materials to produce thermoelectric power is mainly governed by three factors. The Seebeck coefficient (S), the electrical conductivity (σ) and the thermal conductivity (κ). Increasing S and σ while decreasing κ would lead to an increased performance. Nanostructuring can help tune these interdependent parameters independently.

Beta-lactoglobulin is a bovine whey protein, that is known to form different aggregates under different environmental conditions. By changing the pH-value and protein concentration, different morphologies can be achieved. Therefore, beta-lactoglobulin is used to structure titania (TiO_x) using sol-gel synthesis with water as the solvent. Slot-die coating is used to enable industrial mass-production. State of the art thermoelectric materials are rare, toxic and expensive. Biotemplated titania could provide a non-toxic and abundant alternative.



Pure anatase titania thin films have very low electrical conductivity. There are several approaches to improve this property for titania. In this work, we chose to backfill the porous titania structure with carbon black nanoparticles. This approach improved the electrical conductivity by several orders of magnitude. As expected the introduction of carbon black nanoparticles also reduced the seebeck coefficient slightly but the power factor (σS^2) was overall increased. Different carbon black concentrations were tested for their electrical conductivity and their seebeck coefficient.

To investigate the different titania morphologies, in situ GISAXS, GIWAXS and SEM are used. In situ GISAXS printing enables a time resolved investigation of the structure formation, domain sizes and domain distances. UV-Vis and PI are used to analyze differences in the optical properties of the thin films. These structural and optical changes are then correlated with measurements of the seebeck coefficient and the electrical conductivity. Additionally, the long-term stability of these thin films under different humidity conditions was investigated using in operando GISAXS measurements. The morphological changes can be compared to the seebeck coefficient over five hours of operation in relative humidity conditions from zero to 50 %.

Fig. 1. Thermoelectric circuit composed of an n-doped and a p-doped material

Keywords: thin film, biotemplate, hybrid, nanostructure, thermoelectric

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Anti-corrosion polymer gel sheet containing liquid-phase synthesized layered double hydroxide (LDH) nanoparticles

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Naturally occurring layered double hydroxides (LDH), such as hydrotalcite, have anion exchange capacity. Synthetic LDH has long been considered as an anion-releasing material for anion conductors, battery active materials[1], electrocatalyst[2] drug delivery, and other applications. There are various synthetic methods such as coprecipitation and hydrothermal synthesis. We have prepared LDH by liquid-phase deposition from metal fluoride complexes, and have synthesized thin films and nanoparticles with high crystallinity[3][4]. Here, we present an example of synthesis of LDH that releases NO_2^- ions slowly and preparation of a gel sheet containing LDH and showing high anti-corrosion effect on steel [5][6].

In the process of anticorrosion maintenance of metal structures, removal of chlorides from surface pitting corrosion is essential, and the most common method is to apply anticorrosion paint after applying a nitrite electrolyte or other solution that has anticorrosion effects. However, the electrolytic nitrite solution is subject to autolysis due to disproportionation of nitrite ions, and it is difficult to perform stable curing for a long period of time when the electrolyte is applied due to its flow down. We selected the composition and prepared anti-corrosion curing sheets by adding layered double hydroxide (LDH) to sodium polyacrylate-based gel to stabilize nitrite ions. NiAl-based and MgAl-based LDH were used as the LDH to be used. Lithium nitrite and sodium nitrite electrolytes were used as electrolytes to exchange ions with the anions in the LDH.

At first, $\beta\text{-Ni}(\text{OH})_2$ synthesized by adding NaOH solution to $\text{Ni}(\text{NO}_3)_2$ was made into a fluoride complex by adding HF, and the LDHs were synthesized by the liquid phase deposition method using $\text{Al}(\text{NO}_3)_3$ solution as a fluorine consuming agent and Al additive. Ni-Al LDH synthesis by the liquid phase deposition method was performed by depositing Al_2O_3 powder and Ni-Al LDH synthesized by the coprecipitation method on the respective surfaces as substrates, while MgAl LDH was synthesized by adding NH_3 solution to aqueous $\text{Mg}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ solutions. For each sample, a gel sheet was prepared with sodium polyacrylate as the main agent and according to the contents shown in Table 1. For the corrosion test, a 99.99% steel sheet was used, the gel was adhered, platinum was used as the counter electrode and Ag/AgCl electrode as the reference electrode, potential sweep was performed at a sweep rate of 10mV/s, and corrosion current and potential were measured from Tafel plots.

Figure 1 shows SEM image of the prepared Ni-Al LDH deposited on (a) steel plate and (b) fumed alumina by the LPD process. NiAl-based LDH exhibited good ion exchange properties similar to those of conventional MgAl-based LDH.

Figure 2 shows the Tafel plots for the corrosion protection sheets containing each sample. The corrosion current values in each electrolyte were reduced by using LDH, and it was possible to optimize the effect of nitrite ions by including LDH.

We also present in this presentation the properties of LDH, electrochemical evaluation of corrosion phenomena, and corrosion protection effects in demonstration tests. Figure 3 shows Ni-Al LDH sheet for rust-preventive construction and LDH rust-preventive gel sheet applied to a highway bridge steel frame after removal of painting. It was also confirmed that the effect of NO_2^- ions retained in LDH by ion-exchanging was maintained over a long period of time.

Table 1. Typical composition of LDH gel sheet.

Components	Weight /wt%
Tartaric acid	0.3
Sodium polyacrylate	6
Glycerol	20
Ni-Al LDH	2
$\text{Al}(\text{OH})_3$	0.3
LiNO_2 aq	71.4

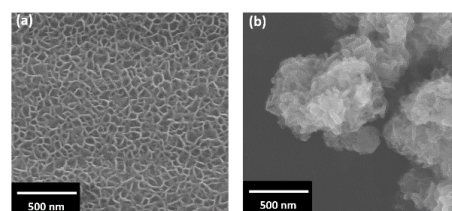


Fig. 1. SEM image of the prepared Ni-Al LDH deposited on (a) steel plate and (b) fumed alumina by the LPD process.

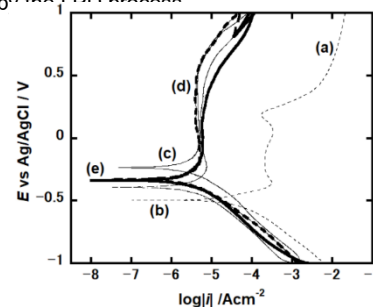


Fig. 2. Tafel plots of anti-corrosion gel composites. Electrolyte: (a) NaNO_2 (b) LiNO_2 (c) $\text{Mg}(\text{NO}_3)_2$ (d) $\text{Ni}(\text{NO}_3)_2$ (e) $\text{Ni}(\text{NO}_3)_2$ + LDH

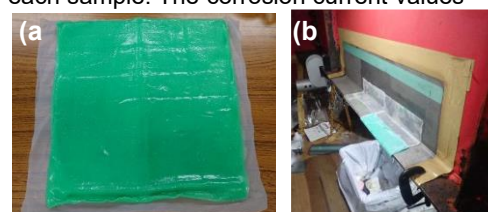


Fig. 3. (a) Ni-Al LDH sheet for rust-preventive construction and (b) LDH rust-preventive gel sheet

Keywords: Liquid phase deposition, Layered double hydroxide nanoparticles, Anticorrosive nitrite inhibitor, core-shell LDH

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Plasma-enabled nanocarbons and nanocomposites for zero-carbon world: recent updates

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Here, we overview and analyze the recent updates in the area of applications of plasma-electrified nanoscale and microscale phenomena described by the plasma nanoscience approaches to synthesize a variety of advanced functional nanomaterials. These materials include nanostructured composites, advanced solid nanocarbon materials, in addition to a range of other products synthesized using plasma-based processes, such as value-added liquid fuels and chemicals, valuable gaseous products such as hydrogen, ammonia, and syngas. These products are achieved through the plasma-assisted conversion of precursors that are rich in carbon.

We highlight the specific plasma-enabled processes that are actively pursued for the advancement of the most promising clean energy and green and sustainable chemistry solutions for industry and society more broadly. These efforts are aimed to ultimately achieve industrial processes that are low or even negative in greenhouse gas emissions and in this way help decarbonize the way we live in. This presentation will utilize the recently introduced analogy with natural enzymes where naming conventions include their function in applications, and also use the articulated “-ase” ending. This concept is referred to as “carbon decarbonase” and implies the fabrication of higher-value carbon-derived products predominantly using precursors in solid, liquid or gaseous forms and that feature rich carbon content. Waste plastic or agricultural waste are salient examples of such carbon-rich precursors. Importantly, the thus derived carbon products have valuable and often unusual functional properties. These properties in turn help address the pursued goals of global decarbonization. Relevant goals have been set by the recent UN sustainability programs and climate-change meetings.

Some examples of the relevant carbon-based functional „decarbonases“ discussed in this presentation are: (i) water desalination and purification membranes, (ii) various high-performance composite structures for energy conversion, (iii) selected electro- and photo-catalytic processes for energy and environment-related applications, (iv) advanced functional composite electrode materials for renewable and clean energy storage materials as well as some other examples. These applications have the potential to help decarbonize the major industries that emit the largest amounts of greenhouse gases. One of the viable and radically new approaches to achieve these challenging goals is based on (including plasma-assisted) electrification of the production of materials, chemicals, and fuels.

This presentation will continue with discussing some case studies where we propose and implement the *re-carbon – de-carbon – up-carbon* sustainable cycle concept in the plasma-enabled production of advanced carbon nanomaterials and nanocomposites which can perform as „decarbonases“. To achieve this goal, the innovative P2X (Power-to-X) approach is utilized, where X means the diverse products to be produced using renewable and clean power P, including the plasma-electrified power. We further analyze a few possibilities to utilize the plasma-power-based approach (plasma-P in the P2X equation) and pay strong attention to the energy/matter-efficient processes based on low-temperature plasmas, especially the continuously advancing low-pressure and atmospheric-pressure plasma discharges. Further applications of low-temperature plasmas for the fabrication of selected health, biomedical, and hygiene products using the above approaches are also discussed.

Support from the Alexander von Humboldt Foundation through the Humboldt Award Program, the Australian Research Council, Centre for Materials Science, Centre for Clean Energy Technologies and Practices, and Centre for Waste-free-World is kindly appreciated.

Highly Porous Activated Carbon Electrodes Prepared from The Bio-Wastes – for High-Performance Supercapacitor Applications

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Supercapacitor is an important component of electrical vehicle(EV) technology, generally coupled to batteries as an auxiliary power source to improve acceleration, offsetting the need for extra battery mass. Primarily, being electrolytic double-layer electrolytic capacitors (EDLCs), electric charge is usually stored at the electrode/electrolyte interface through the electrostatic interaction between the surface of the electrode and the charge carriers (ions) of the electrolyte. The design and performance of the electrode materials in the supercapacitors play a crucial role in improving energy storage. With ongoing growth in this industry, it is very important to achieve sustainable and eco-friendly devices in the long run. With this vision we are trying to develop supercapacitor's electrodes from biowastes like seeds, fruit pulps, plant stems, etc.

India is one of the major producers of mustard, used as a green leafy vegetable. It is an important oilseed crop of India, contributing about one third to total oilseeds production. It gives edible oil, which is used in more than 50% Indian kitchens for cooking. In addition, mustard plants are also used as green vegetables. Some of the leftover seed skin after extracting oils is mixed in the cattle fodder and the rest of it goes as biowaste. We have optimized the chemical process to produce mesoporous activated carbon structure with a high specific surface area of about 570 m²/g. The processing route is quite inexpensive as compared to other carbon processing routes. The device displays an excellent specific capacity (198 F/g, at a current density of 0.25 A/g) retention [1]. The coulombic efficiency of the EDLC cells was found to be in the range of 90% and 100% during the charge-discharge cycles, which is quite reasonable. Overall, the specific capacitance and power density in our case were 16 F/g (at 0.25 A/g) and 7000 W/Kg respectively, which are significantly higher than values reported in other references [1, 35] We observed a low value of equivalent series resistance (~ 4 Ω) and charge transfer resistance (~ 29 Ω), indicating an excellent electrode/electrolyte interface which can reversibly facilitate the electrolyte ion transport across the electrodes.

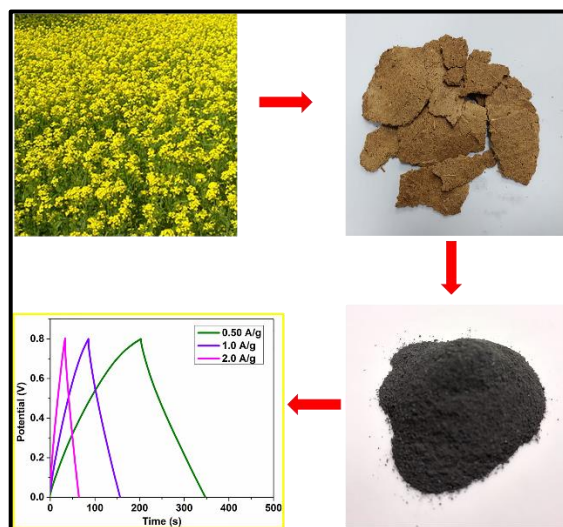


Fig.1. From crop to supercapacitor

Keywords

Activated carbon, Bio-waste, Yellow mustard seed plant, Electrode, Supercapacitor

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Memsensor Devices: An innovative approach to bio-inspired sensing

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The storage and processing units in conventional von Neumann architecture are physically separated but with advancement in neuromorphic engineering and inspired by brain functionalities, there is a need for combined data detection and processing in single-devices. The existing architecture limits the overall performance and results in huge power consumption, which is called von Neumann bottleneck. Neuromorphic computing system in the contrary has shown attractive prospects in highly efficient information processing with less redundant data and low power consumption. Typical behaviours of biological neural system can be mimicked by artificial synaptic devices. Diffusive memristive switching has attracted interest in the implementation of enhanced synaptic functionalities in neuromorphic systems. Memsensor is a typical two-terminal device combining the functionalities of memristive switching and sensor devices together and is highly promising for future electronics [1]. It is also shown via conductive atomic force microscopy (c-AFM) study that the memristive switching can be operated at the border of stability by spontaneous formation and decay of conducting states, resembling the irregular spiking patterns of neurons in biological neuronal systems [2].

In our material systems, we have implemented both planar memristive device and memristive devices based on Ag-based alloy nanoparticles (NPs) embedded into SiO_xN_y matrix. The memristive device displays filamentary switching which exhibits both diffusive and bipolar type of switching. Absence of a serial resistor in a planar memristive device leads to the observation of bipolar switching. To enhance the reliability and robustness of the device, number of stacks of tailored Ag-alloy NPs can be increased. Introduction of wide-bandgap metal oxides (TiO₂, ZnO) as the matrix material will combine the functionality of sensor due to their sensitivity towards UV light into the memristive device. In this study, it is analysed how the switching performance of the memsensor device is modulated under the application of UV light. Such insights will help in understanding and implementing memsensor functionalities with filamentary switching processes in details and are key requirements for future development of biologically motivated, efficient computer architectures.

Keywords: *neuromorphic engineering, cAFM, diffusive memristor, memsensor, resistive switching*

Acknowledgements:

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 434434223 – SFB 1461

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Wet-coated sensors for virus detection

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Plasmonic nanoparticles (NPs) or core-shell NPs are extensively used in various applications [1], in particular, surface-enhanced Raman spectroscopy (SERS), which has been widely used in viral molecular detection due to its high sensitivity, simple operation and rapid detection. Virus Raman detection research is mainly focused on the detection of viral nucleic acid and various bases that make up the nucleic acid, but the detection of viral proteins is rare [2, 3]. In addition, there is limited knowledge about the interaction between virus proteins and the core-shell NPs with different shapes. Therefore, obtaining more detailed information on the relationship between the behaviour of viruses at the surface of core-shell NPs and the enhanced Raman intensity can lead to the development of advanced NPs for the detection of viruses. Here, taken into the consideration of sustainable and scalable demand for industry, spraying water-based cellulose nanofiber (CNF) [4] and core-shell NPs solutions is preferred for the fabricating of sensors. The in-situ small- and wide-angle grazing incidence X-ray scattering (GISAXS/GIWAXS) techniques are used to investigate the self-assembly of CNF and NPs with various shapes in real-time during deposition. After the fabrication of sensors, to have a deep insight into how the different proteins interact with the shaped NPs, some measurements will be taken, such as in-situ Raman, atomic force microscopy (AFM), transmission electron microscopy (TEM), fluorescence microscopy (FM) and X-ray photoelectron spectroscopy (XPS) et al. Furthermore, the relationship between the shape of NPs, sensor performance, and virus behaviour is explored and constructed to lay solid foundations for the fabrication of sensors for virus detection.

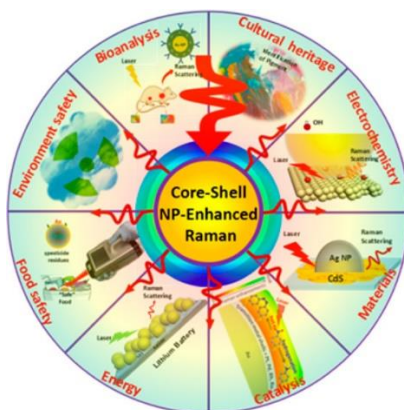


Fig. 1. Applications of core-shell nanoparticles in SERS [1].

Keywords: SERS, Cellulose nanofiber, Core-shell NPs, Virus detection, GISAXS/GIWAXS.

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Polarizonics: Earth-Abundant Nanocomposites for Colored Solar Absorbers that Outshine Black

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The concept of Polarizonics encompasses the remarkable dipolar polarization observed in ultrafine and predominantly non-scattered nanoclusters. This concept has led to the emergence of diverse phenomena, including the development of vivid colored and dynamic coatings, antireflection coatings, omnidirectional colored solar absorbers, polarity detection in matrices, and selective biodetection of exosomes, as highlighted in our recent invited review.

In this work, we emphasize the significance of Polarizonics and present our recent advancements in leveraging its potential by utilizing ultrafine earth-abundant nanoparticles. Despite the absence of plasmonic characteristics, these nanoparticles exhibit extraordinary polarizonic properties, allowing for the creation of sustainable nanocomposites with exceptional functionality. Our primary focus lies in the development of a colored solar absorber that surpasses the performance of traditional black materials. Through strategic engineering of the nanocomposite structure and harnessing the distinct polarizonic color, we achieve enhanced light absorption and tailored optical properties across the visible and near-infrared spectrum.

Our findings exemplify the immense potential of these sustainable materials for groundbreaking applications. The utilization of ultrafine earth-abundant nanoparticles in the formation of nanoclusters opens up new avenues for designing high-performance, environmentally friendly materials with unparalleled functions. Through the exploration of Polarizonics, we are paving the way towards a future of innovative and sustainable materials that transcend conventional limitations."

Keywords: *Polarizonic, sustainable nanocomposites, earth-abundant nanoparticles, colored solar absorber.*

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Boosting effect of Ag-Cu nanoparticle-built surfaces for LSPR detection of pathogens

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The contribution reports the investigation of surfaces for Localized Surface Plasmon Resonance (LSPR) detection of Lyme disease pathogen providing high selectivity and sensitivity. Lyme Disease is caused by spirochetes belonging to the *Borrelia burgdorferi* transmitted by tick vectors. Our research is motivated by the current need for sensors that provide quick and specific point-of-care testing [1]. The approach presented in this study is based on the utilization of nanostructured surfaces exerting the effect of localized surface plasmon resonance (LSPR). LSPR is an optical phenomenon that occurs when light interacts with metal nanoparticles whose size is smaller than the wavelength of the incident light [2].

The concept utilizes of Ag-Cu/C:H:N:O nanocomposite of excellent thermal, chemical, and mechanical stability; for details, see [21, 22]. The nanocomposite is based on C:H:N:O plasma polymer matrix, prepared by rf magnetron sputtering [23] of the cathode made of nylon 6.6, with incorporated Ag and Cu nanoparticles. The Ag, Cu nanoparticles were prepared by a gas aggregation source (GAS) reported elsewhere [24, 25]. The nanoparticles are formed in a gas phase by condensation of Ag or Cu metal vapour, respectively, and deposited onto the substrate, i.e. C:H:N:O matrix. The excellent stability of Ag/C:H:N:O nanocomposite, which can sustain the ultrasonic bath, is achieved by tailoring the deposition process and thermal treatment [22].

The functionalization of Ag-Cu/C:H:N:O was done as a sequence of (i) thin-film plasma polymer deposition for the introduction of -NH₂ groups that (ii) enable subsequent immobilization on the surface with specific antibodies for (iii) final binding of the target agents. *Borrelia* proteins-specific polyclonal antibody, *Borrelia* lysate, and live *Borrelia* (*Borrelia afzelii* strain CB43) were employed as testing target agents. The presence of *Borrelia*s immobilized onto the functionalized surface resulted in a measurable red-shift of the LSPR absorption spectra for both Ag and Cu nanoparticles; a so-called double-LSPR peak absorption. Detailed investigation indicates both a high selectivity for the target agents and high sensitivity with a practical detection limit in the range of tens of *Borrelia*s causing LSPR response with a shift of the LSPR absorption peak in range of nanometre units. The LSPR activity (pronounced by the modulation and the shift) of both LSPR absorption peaks was studied in detail. The more pronounced response of Ag LSPR absorption was observed if compared with Cu. However, the boosting and significant enhancement of LSPR response was observed for the nanocomposite of plasmonic Ag-Cu whose explanation is supported by the simulation of electric field propagation.

Keywords: localised surface plasmon resonance, nanoparticles, nanocomposites, plasma deposition, pathogen detection

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CdS/ZnS core/shell nanostructures based broadband Photodetector

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The growth of wide bandgap semiconductor nanostructures (NSs) like ZnS on the surface of relatively narrower bandgap semiconductor NSs like CdS leads to the appreciable passivation that results in enhancement of the various properties of the material. Because of the improved properties, core/shell nanoparticles are widely used in different applications such as biomedical, catalysis, electronics, photonics etc. [1-4]. Herein, CdS/ZnS core/shell nanorods (NRs) were successfully synthesized via three-step synthesis method-(a) solvothermal synthesis of CdS NRs, (b) surface functionalization of CdS NRs by using citric acid and (c) growth of subsequent ZnS NRs shell with varying concentration of the precursor used for the shell and the reaction time (0.5h, 1h and 2h) during growth process. The as-prepared CdS NRs and CdS/ZnS core/shell nanostructures were used to study the morphology, structural and optical properties by using TEM, XRD, PL and UV-Vis spectroscopy. The XRD confirms the crystal structure of CdS/ZnS NRs having peaks corresponds to the hexagonal and cubic structures of CdS and ZnS nanostructures respectively. UV-Vis absorption spectra having broad peak at ~ 505 nm corresponds to the CdS in visible region and a small hump of ZnS at ~ 349 nm confirms the formation of ZnS shell over the core CdS. The PL spectra of CdS/ZnS core/shell NRs exhibits emission peaks centered at ~ 530 nm, 485 nm, 422 nm and 407 nm assigned to the sulfur vacancies, band edge emission of CdS, CdS/ZnS interface and sulfur vacancies in ZnS. Further, the photosensing study has been done with the illumination of light of varying wavelength from UV to NIR region. The enhancement of photocurrent was observed upon the illumination of sample with different wavelengths. The maximum sensitivity is observed to be ~ 2491 for CdS/2ZnS_{1h} upon illumination of light under UV region (310 nm) while all the fabricated devices shows overall spectral Responsivity in the entire UV-Visible region as shown in Fig. 1. (b-c). Thus, the highly performed broadband photodetector with simple architecture and cost effective approach is presented here.

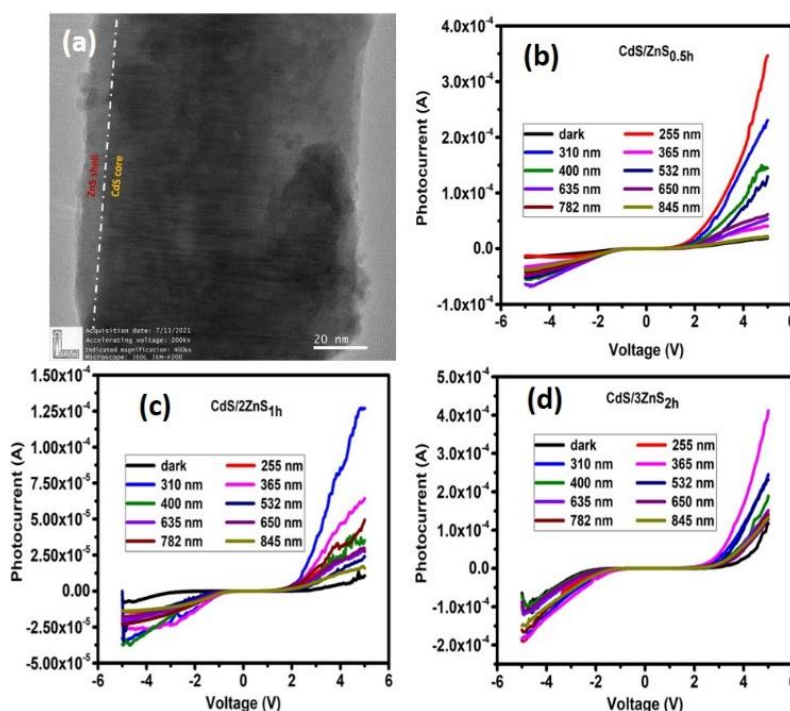


Fig. 1. (a) TEM image of CdS/ZnS core/shell, (b-d) I-V curve of CdS/ZnS_{0.5h}, CdS/2ZnS_{1h} and CdS/3ZnS_{2h} respectively.

Keywords: Nanstructured core/shell; interface; Nanorods and Photodetectors

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Broadband Solar Absorbers Based on Plasmonic Metal-Dielectric Nanocomposites

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The pursuit of a sustainable future necessitates the utilization of green and renewable energy sources, with enhanced solar energy exploitation being a key focus achieved via solar absorbers. Plasmonic nanostructures, well-known for their exceptional absorption and scattering properties, have been extensively investigated as effective broadband solar absorbers. These absorbers demonstrate remarkable efficiency in absorbing a wide range of wavelengths, spanning from 250 nm to 1600 nm, thereby facilitating the efficient conversion of solar energy into heat. In our recent work, we directed our efforts towards fabricating broadband solar selective absorbers using plasmonic metal-dielectric nanocomposites, employing two distinct design concepts. Firstly, a tri-layer thin film stack was employed, consisting of an optically thick metallic mirror, a dielectric spacer, and a nanocomposite layer. Within the nanocomposite layer, plasmonic Cu-NPs were embedded in Al₂O₃ dielectric matrix, facilitating efficient light absorption (~89%) across a broad wavelength range of 250 to 1600 nm at an incidence angle of 45°. Secondly, structured metal thin films have been employed as back reflectors for the plasmonic nanocomposites. The scattering was precisely controlled via 2-step deposition of the metal film atop Ag islands containing substrates. These bi-layer absorbers showed higher absorption (~95%) and higher temperature under 1 sun radiation compared to the absorber fabricated solely with a flat metal film devoid of islands. Furthermore, all films presented in this study were deposited using magnetron sputtering, a simple, cost-effective, scalable, and industrially established method.

Keywords: Magnetron sputtering, solar absorber, plasmonic particles, metal islands

Acknowledgements:

This work has been funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) - project number 413974664 i.e., projects RO 3640/12-1 and FA 234/32-1.

Electron Transport in Discontinuous Thin Metal Films

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Electrical conduction in ultrathin discontinuous metal films has been studied for over 70 years [1,2], and by the mid-1970s there was a general consensus that the transport mechanism was by electrostatically activated electron tunnelling between discrete nanoscale (1-10nm) metal islands separated by nanoscale (2-5nm) gaps [3]. The basic premise was that the number of charged islands was related to the total number by the Maxwell-Boltzmann (M-B) distribution [4] with the electrostatic activation energy, δE , being the energy required to charge an initially neutral island, and conductance, σ , of the form $\sigma = \sigma_0 \exp - \delta E/kT$. The theory was basically validated by linear Arrhenius plots [5] and a non-ohmic behaviour (similar to the Schottky effect) [6,7] predicted by the theoretical field variation of δE [3,8] and by similar agreement of the tunnelling resistance variation with strain [9]. Despite these agreements, many experimental results are incompatible with this simple model, including (i) measured conductance orders of magnitude greater than any tunnelling calculation can explain, (ii) the absence of the expected "gate" bias modulation of the conductance, (iii) the so-called "diode effect" which can be correlated with asymmetrical structures at the electrodes, (iv) the observation of larger fields at the positive electrode than at the negative in the absence of any structural differences, (v) Bode plots that give capacitance values that are inconsistent with δE for simple R-C models, (vi) the development of pseudo-inductive effects for extremely asymmetrical contact structures, (vii) the observation of $R_1C_1-R_2C_2$ equivalent circuits in Cole-Cole (Nyquist) plots, and (viii) the observation of switching (including asymmetrical switching.) These issues and the original references are covered in [10]. Effects (i) and (ii) indicate that the premise of a M-B distribution of charged islands is flawed and that the density of charged islands is much greater, while (iii) to (viii) all point to some form of contact effect, as originally proposed in [11,12].

An alternative model has been developed [13,14] based on contact injection charging of neutral islands and contact discharging of charged islands by electron tunnelling at both electrodes. The traditional charge separation and recombination events in the "bulk" of the film are retained but have negligible effect. Most of the charge transport is by tunnelling charge transfer from charged to neutral islands in the "bulk," analogous to electron and hole drift in semiconductors. The activation energy comes from the charge injection at the contacts. Simulations based on this revised model and an idealized asymmetrical structure (100x100 3nm islands with 3nm gaps except for a single row of 1nm islands with a 5nm gap at one of the contacts) explain all of the observed anomalous effects [10,13,14]. (i) The initial conductance is consistent with the M-B model (with a few random charged "seed" islands) but rises many orders of magnitude to the final steady-state value. (ii) The absence of expected "gate" bias effects is because the steady-state charge density is much larger than the M-B prediction. (iii) & (iv) The "diode effect" is due to different space charges at the positive and negative electrodes which correlate with non-linear fields along the film. (v) The measured film capacitances are consistent with the parallel capacitances between the contacts and the adjacent islands, an estimate that can be made without the simulations. (vi) The pseudo-inductance comes from the time-dependent build-up of injected charge carriers (see (i)) and (vii) the equivalent circuit is due to asymmetrical contacts and charge carrier "drift" in the "bulk" of the film. (viii) The simulations show a collapse of the contact space charge and a more uniform field and charge distribution along the film following high-to-low resistance switching. It is hypothesized that this happens when the field at a contact is sufficiently large to remove the barrier to injection, but this needs a different focus to the simulations to confirm.

There is considerable opportunity to move this field forward, e.g., by switching simulations and simulations of increasingly realistic film structures, e.g., bimodal island distributions due to secondary nucleation, randomly distributed island locations, etc., but the real challenge lies in experimentation. The early work [1-14] was almost all done on unstable, irreproducible vacuum deposited ultrathin films with "bulk" structures, characterized by bimodal size distributions, coalescence, and drift. Also, the physical problems with the preparation of transmission electron microscopy samples meant that almost none were taken near the contacts where it mattered. With more advanced film fabrication techniques and equipment, modern characterization by atomic force microscopy, etc., the experimental results described above, many of which have never been verified by other research groups, can be confirmed and explored systematically in more detail. There are other more recent techniques which could produce regular, stable, reproducible films, and these are briefly reviewed in [10]. The conclusion there was that the deposition of self-assembled monolayers of appropriately polymer-coated metal nanoparticles [15] offers the best path forward. Monomolecular polymer coatings provide constant tunnelling gap widths and vendors offer narrow known nanoparticle size distributions. Multilayer depositions offer the opportunity to vary nanoparticle sizes along a vertical conduction path and it is possible that polymer coatings with tailored diffusivities could provide selective gas detection. Research possibilities abound!

Keywords: discontinuous thin metal films, electrostatic activation, electron tunnelling, contact injection, conduction model.

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Self-organized Nanoparticle Network Retains Brain-like Critical Dynamics after Covering with an Insulating Matrix

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Self-organised memristive networks have recently attracted high interest for applications in neuromorphic computing. One class of these networks are the nanoparticle networks at the percolation threshold (NPN). These NPN shows complex brain-like dynamics like criticality, long-range temporal correlation (LRTC), scale-free network properties and leaky-integrate-fire mechanism (LIF) on the atomic scale, which are similar to bio-neural networks [1]. Under a voltage bias, the memristive tunnel gaps distributed across the NPN causes the electric field to be distributed in such a manner that conductance response shows these complex brain-like dynamics. However, for practical applications, the question remains whether these NPNs can retain their brain-like dynamics after incorporation into a matrix. To answer this question, we studied the self-organised critical dynamics of Ag NPN fabricated at an electrical percolation threshold, with and without an oxynitride matrix (SiO_xN_y). At this percolation threshold, the electro-chemical metallization mechanism dominates. We show that the network exhibits critical brain-like dynamics which is preserved after incorporation into the dielectric matrix [1]. To gain a deeper understanding of the physical mechanism that gives rise to the brain-like complex dynamics, we conduct an investigation of the current path within the memristive network. A percolating NPN comprising of silver core, CHO_x shell and a top layer of silver NPs is fabricated. After investigating the critical dynamics, the current path is visualized using the electron beam absorbed current imaging (EBAC) method. Imaging of the current path gives an experimental approach towards understanding the complex resistive switching of self-organised neuromorphic networks. Also, the retention of the critical dynamics after covering with an oxynitride matrix is an important contribution towards the practical implementation of such self-organised memristive NPNs.

Acknowledgements: Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 434434223 – SFB 1461.

Keywords: nanoparticle networks, percolation threshold, switching, criticality

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A Stretchable and Flexible Neuromorphic Device for in-Materia Adaptive Computing

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Artificial neuromorphic systems aim at the reproduction of the brain performances in terms of classification and pattern recognition, typically using components obtained by top-down lithographic technologies regularly employed by digital computers. [1] Unconventional in-materia computing has been proposed as an alternative strategy, exploiting the complexity and collective phenomena originating from various classes of physical substrates. [2,3]

The employment of materials composed by a large number of non-linear nanoscale junctions, random assembled according to a non-deterministic strategy on a substrate, are of particular interest for the implementation of in-materia computing systems. [4,5] In particular, the employment of random-assembled memristive materials is a strategic solution for the development of energy efficient and neuromorphic computing devices, well beyond the von Neuman bottleneck. [6]

In this contest, films obtained by the assembling of metallic nanoparticles and, in particular, Au cluster-assembled films have shown interesting non-linear electrical properties and complex resistive switching phenomena. [7-9] This has been exploited for the fabrication of devices (Receptrons) able to perform binary classification of boolean functions. [10]

However, in loco processing of analog data and the need of computing units integrated with sensor devices in the same compact hardware system exceed the Boolean algebra and the information coding based on binary inputs. Furthermore, hardware computing solutions able to perceive and to adapt to external stimuli are strategic for the implementation of embodied intelligent system.

Here we demonstrate the development of a memristive switching device based on nanostructured gold able to integrate and process voltage pulse trains autonomously. In particular, the device performs durable, controlled and reversible resistive switching events between two main resistance levels, separated by four orders of magnitude, holding after hundreds of cycles. The reversible change in resistance is related to the intensity and the temporal features of the voltage pulses. Interestingly, the two resistance levels correspond to different conduction mechanisms, from ohmic to a non-linear one. Furthermore, we prove the integration of such a type of memristive device into a polymer matrix of polydimethylsiloxane (PDMS), which is one of the most common flexible and stretchable silicon elastomers, widely used for stretchable electronics and biomedical applications, microfluidic devices, prostheses, as also as food additive. The composite Au/PDMS device preserves the electrical conductivity even in stress conditions and adapts it in response to the different mechanical stimuli the system receives in a non-trivial manner. Even more interestingly, the memristive flexible and stretchable composite device processes and integrates differently specific train pulses according to the external mechanical stimuli applied to the device.

We here propose the integration of a resistive switching nanostructured metallic film into a flexible and stretchable medium, as polydimethylsiloxane (PDMS). The computation capability and the integration of voltage pulse trains is here reported for the memristive composite device, as the controlled and reversible adaptation of the computational capability of the system according to the external mechanical stimuli received. The employment of such a neuromorphic device is proposed as a representative key solution for the development of embodied intelligent system.

Keywords: resistive switching, soft memristor, neuromorphic device, nanocomposite, embedded computing

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The matrix matters: field-driven phenomena in Ag-based nanofluids prepared by cluster-beam deposition

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The demand of modern society in processing and storing big data with high speed and energy efficiency forces people to search for novel advanced computational techniques. The biological brain has outstanding computing capabilities, which performs very complex tasks, such as image or speech recognition, extremely fast and with low power consumption. The unique attributes of neural networks, such as robustness, adaptivity, self-organized ordering, and 3D connectivity, ensure their performance. Nowadays, researchers worldwide are trying to implement these principles in neuromorphic devices. Memristors mimic the behavior of synapses – the connections between individual neurons. Memristive devices change their conductivity in response to the external electric field. Plenty of solid-state nanostructures have been proposed for memristive devices, including those based on nanoparticles (NPs). For example, percolating networks of nanoparticles produced by the bottom-up technique of cluster-beam deposition demonstrate collective spiking behavior in conductivity typical for neuronal burst firing. The individual spikes correspond to switching events in the tunnel gaps between the NP agglomerates.

Most memristive devices are solid-state; however, in biological neural networks, all processes occur in a liquid state. Moreover, the realization of a memristor in the fluidic medium could improve its versatility, approaching the achievement of real 3D conductivity in neuromorphic systems. At Charles University, cluster-beam deposition has been applied for the vacuum-based linker-free fabrication of metal nanofluids, demonstrating resistive switching. Silver NPs produced by a gas aggregation cluster source (GAS) were loaded to vacuum-compatible dielectric liquids (PEG, silicon oil, and paraffin). The mean diameter of NPs used in these experiments was ~ 50 nm. The NP mass concentration of 500 $\mu\text{g/ml}$ was recalculated to obtain the volume fraction of 5×10^{-4} . It was revealed that the behavior of NPs in all three liquids is substantially different. The stability of nanofluids improves in a sequence of paraffin \rightarrow PEG \rightarrow Si oil, as confirmed by optical microscopy and by the change of the color of the nanofluids. This dependence is associated with the difference in the ζ -potential of NPs in all base liquids, which was measured by electrophoretic light scattering.

The electrical properties of the nanofluids are also substantially different. They were characterized by recording the I-V characteristics, which were complementary with the optical microscopy observations. It should be noted that the dielectric constant of PEG is much higher (14.1) compared to Si oil and paraffin (2.5 and 2.2, respectively). When the electric field was applied to Ag-PEG nanofluid, the nanoparticles self-organized in a fractal-like conductive path between the electrodes. This effect was accompanied by the transition of the system from a high resistive state (HRS) to a low resistive state (LRS) according to the growth of current by 2 orders of magnitude. The SET voltage was always in the range of several volts. Ag NPs moved toward a positively biased electrode, confirming the results of ζ -potential measurements. The switching back from HRS to LRS occurred in a random manner, independent of the polarity of the biased electrode. It should be emphasized that the Ag-PEG system tends to switch back to the LRS almost immediately after RESET.

In the Si oil, the NPs behave similarly and move towards the positively biased electrode. However, they do not form a conductive path. Seemingly, the NPs are stabilized by the Si oil shell with a thickness of more than 10 nm, as revealed by near-ambient pressure XPS. The shell prevents the NPs from sticking to each other, limiting the electrical conductivity. Furthermore, the low dielectric constant of Si oil, combined with the thickness of the shell, hinders electron tunnelling.

Finally, dendrite-like NP-based wires grow in the vicinity of both positive- and negative-biased electrodes in paraffin. This can be explained by the dielectrophoretic nature of the movement of NPs when each particle becomes a dipole. Surprisingly, no electric conductivity was detected in this case, even though the electrodes were seemingly connected by NPs, as observed by optical microscopy.

Acknowledgments: The work was supported via the grant GACR 23-06925S from the Czech Science Foundation and via the Czech-German Mobility grant number 8J23DE016 from the Ministry of Education, Youth and Sports. A.V., B.A., J.L. and F.F. would like to acknowledge funding by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 434434223 – SFB 1461. A.V. and B.A. would like to acknowledge funding by the Deutscher Akademischer Austauschdienst (DAAD, German Academic Exchange Service) Project-ID 57654440.

Keywords: nanofluid, gas aggregation cluster source, zeta-potential, resistive switching

Relationship between structure, mechanical properties and function in locust cuticle, a functional nanocomposite

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Insect cuticle is a multifunctional nanocomposite. One of its striking characteristics is the wide range of its mechanical properties. The elastic modulus of insect cuticle, for example, covers a range of more than eight orders of magnitude [1]. Why do cuticle properties vary so dramatically? With the aim to address this question, researchers have used a set of different testing methods to measure properties of cuticle specimens, which were selected from various body parts, across a variety of insect species and often preserved/prepared in different ways [2-5]. However, almost all these factors can influence obtained data. Hence, the literature data cannot be simply compared with each other, and no solid conclusion can be drawn regarding the mechanisms that underlie the property variations in the cuticle. To fill this gap in the literature, our studies are focused on two key questions. First, how do the mechanical properties of insect cuticle differ in a single species, when all testing conditions are kept constant? Second, what are the mechanisms behind the wide range of cuticle properties? Using a combination of scanning electron microscopy (SEM), micro-computed tomography (micro-CT), confocal laser scanning microscopy (CLSM) and nanoindentation, we performed one of the most comprehensive studies to date, where we simultaneously investigated the microstructure, sclerotization and the elastic modulus of locust cuticle. We have shown that, in the desert locust *Schistocerca gregaria*, the elastic moduli of tibiae, femora and compound eyes range from 0.5 GPa to 8 GPa [6-8]. This property change can be explained almost fully by the differences in the microstructure and sclerotization of the investigated specimens. Our results suggest that, in most of the cases, sclerotization determines the difference between the elastic moduli of different body parts, whereas anisotropic properties of each body part are controlled by their microstructure, in particular by fiber orientation. However, it is still possible that a cuticle specimen that is not as sclerotized as others shows a stiffness as high as more sclerotized specimens. This is in contradiction to the common understanding and is particularly observed in the hind femur, which consists of a cuticle that is less sclerotized than those of the fore and mid femora but can still reach a stiffness higher than others in certain directions. This, therefore, suggests that the interaction between the microstructure and sclerotization may not be as simple as previously thought. We expect that our results help to better understand the complex structure-material function relationship in insect cuticle.

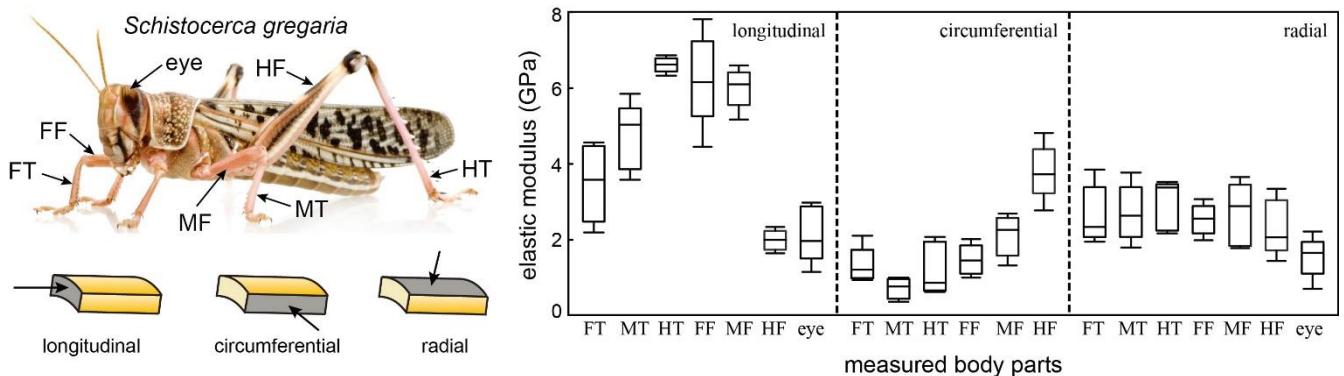


Fig. 1. Mechanical properties of locust cuticle in different body parts.

Keywords: Insect cuticle, Mechanical properties, Sclerotization, Anisotropic properties, Fiber orientation.

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Controls of Visible-Light Driven Reduction Reaction at Plasmonic Cathode Electrode

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The establishment of the high-efficient visible light energy conversion system is an important challenge for the sustainable society. For the achievement of it, the wide-band gap semiconductor electrodes can often be the promising candidates. However, on the conventional chemically stable wide-band gap semiconductor, the available wavelength for the energy conversion is often limited to the ultraviolet region because of their wide band gap energy. Recently, as the breakthrough for it, the introduction of the plasmonic nanostructures onto the semiconductor electrode surfaces has been received much attention. In that system, the excited electrons or holes within metal nanostructures are injected into the semiconductor while remained holes or electrons trigger the chemical reactions at metal-semiconductor interfaces. Up to date, various anodic systems which are the combination of plasmonic nanostructures with n-type semiconductor electrodes have been proposed. For example, the water oxidation reaction under the near-infrared light illuminations has been demonstrated [1]. In our previous study, we have successfully determined the absolute electrochemical potential of excited holes through the oxidative polymerization of conductive polymer materials [2]. Recently, in addition to the plasmonic anode system, the cathodic reaction systems have also proposed by combining the p-type semiconductor with the nanostructures. We have also proposed the plasmonic cathodic system which consists of p-type GaP and Ag nanostructures to control the visible light driven hydrogen evolution reactions [3]. In that report, the unique pH dependence on the reaction efficiency was observed, indicating unique molecular selectivity of plasmon-driven photoenergy process. Although we have clarified unique reaction characteristics, the detail information about the charge transfer process or the electrochemical potential of excited electron on the system was still under discussion.

In this study, we have investigated detailed charge transfer process and electrochemical potential of excited electrons through various photoelectrochemical measurements. At the present system, the chemically synthesized Au nanorod (AuNR) structures were supported on various types of p-type semiconductors to achieve the multi-colour response photoconversions. Figure shows the photocurrent responses under visible light illuminations ($\lambda > 610$ nm) obtained on the AuNR supported p-GaP (AuNR / p-GaP) and bare p-GaP. It is clear that only the case for AuNR / p-GaP achieved the visible light response cathodic reactions. We have also examined the incident photon conversion efficiency (IPCE). From the IPCE spectrum, we have observed the good correlations of photocurrent response with the absorption property of AuNR. From this point, the occurrence of plasmon-driven cathodic reactions has been confirmed. In addition, by the photodeposition of metal under visible light illuminations, it was capable of determining the electrochemical potential of excited electrons. In addition, we have used various types of p-types semiconductor and confirmed the occurrence of the cathodic reduction. From various photoelectrochemical measurements, we have proved that the absolute electrochemical potential of excited electrons was dependent on not only the incident wavelength but also the flat band potential of substrates. As the conclusions, our current research would provide the novel insight for the accurate design of the high efficient light conversion device.

Keywords: localized surface plasmon, plasmonic photoconversion, visible light driven chemical reactions

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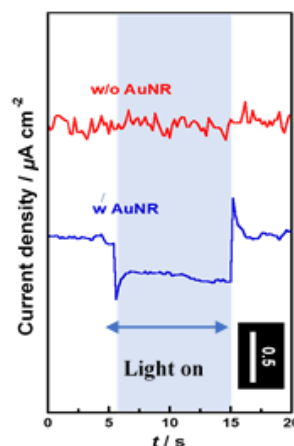


Fig. Photocurrent obtained from (blue) AuNR / p-GaP and (red) bare p-GaP under visible-light irradiation ($\lambda > 610$ nm). The electrode potential was kept at -0.3V vs. Ag/AgCl.

Cellulose-based smart hybrid materials

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Biomaterials as sustainable resources are excellent candidates for replacing synthetic materials. In view of this, cellulose nanofibrils (CNFs) are prominent starting points for novel templates in functional nanocomposites. In addition to being light-weight, CNFs show high mechanical strength, their dimensions and surface properties can be tailored. One big advantage is their easy processability in water-based solutions. By blending CNFs with conjugated polymers, such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), and using scalable spray coating technology, functional, conductive thin films are facilitated [1]. This hybrid material shows stable and reversible conductivity responses under cyclic humidity changes. This behaviour is directly correlated to nanoscale rearrangement of the CNF network and the PEDOT:PSS domains in this hybrid material. The reason lies in the nanoscale structure of thin, sprayed CNF films. They are ultrasmooth, and show a hierarchical and porous, interconnected nanoscale morphology, being stable under humidity changes [2]. Especially the use of X-ray and neutron scattering methods proved vital to correlate the nanostructural changes in these functional materials with their macroscopic functionality in response to external fields.

As a first application in devices, a scalable supercapacitor is presented [3]. Spray coating is applied as scalable and industrially relevant technology to apply a high-quality PEDOT:PSS/CNF electrode with optimized electrode thickness as part of an all-printed supercapacitor, in combination with a flexible solar cells. The superior quality of the electrode compared to traditionally-used drop casting was correlated to its smaller agglomerations, resulting in a more homogeneous film deposition. Such cellulose-based electronics is very interesting for smart, flexible, environmentally-friendly wearable electronics.

Increasing the complexity of the CNF-based hybrid materials, a novel biomimetic actuator is presented [4]. Here polyvinyl alcohol (PVA) and polystyrene sulfonate (PSS) are used to fill the porous structure of the CNF template. Again, PVA and PSS are water-processable, which is very advantageous in view of sustainable processing. The resulting PSS/PVA/CNF film shows a double network structure, physically crosslinked through electrostatic interactions and hydrogen bonds. Due to a simple drop casting process, internal stresses are created in the PSS/PVA/CNF film, which yield reversible and anisotropic mechanical deformations in response to humidity gradients. The hydrogen bond network in addition yields superior mechanical properties and self-healing ability during moisture expose, see Fig. 1. This approach has tremendous potential for robust smart robotics, biosensors and smart packaging.

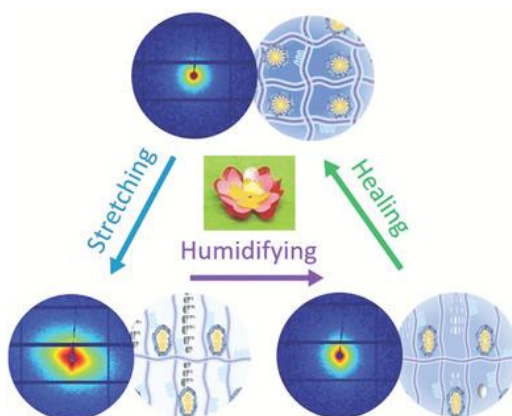


Fig. 1. Using a cellulose nanofibril-synthetic polymer hybrid material, a programmable and healable actuator is designed. The fabrication process is entirely water-based, and the nanoscale origin of humidity-response and healing is elucidated by X-ray scattering.

Keywords: abstract, Arial. (max. 5 keywords) Biomaterial, functional nanocomposites, bio-inspired, cellulose nanofibril, scattering

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Facile Scalable Single Step Multi-Level Structure Engineering Makes TNO₄/Carbon Nanohybrids a New Promising Lithium-Ion Battery Anode

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Titanium/niobium oxide-based lithium-ion battery anodes are characterized by their excellent safety, superior rate capability and high theoretical capacity.[1-2] However, the intrinsic poor electron conductivity of the metal oxides significantly limits the anode performance.[3-4] In this work, Ti_{0.667}Nb_{1.333}O₄ (TNO₄) has been synthesized and utilized as the lithium-ion battery anode for the first time. Displayed in Fig. 1. (inset), a facile scalable single step multi-level structure engineering in terms of electronic, morphology, and surface structures is applied to TNO₄, leading to an effective performance improvement. Compared to TiO₂ and NbO₂, the electronic structure, in regard to the band gap and lithium-ion diffusion energy barrier, is well tuned by a stoichiometric atomic substitution of titanium by niobium. The reduced band gap of TNO₄--0.38 eV (vs. TiO₂--3.10 eV, NbO₂--0.81 eV) and increased energy barrier of TNO₄ along the c-axis--0.13 eV (vs. TiO₂--0.04 eV, NbO₂--0.04 eV) accelerate the electrochemical kinetics and increase the actual capacities. In combination with particle size reduction and surface carbon composition, the electrochemical performance of TNO₄/carbon nanohybrids is further improved as shown in Fig. 1. The lithiation/delithiation mechanism of the TNO₄ anode is investigated by in situ X-ray diffraction (XRD) and density functional theory (DFT) computations. In situ transmission electron microscopy (TEM) is applied to reveal the structure changes upon lithiation and delithiation, where a limited volume change around 6.66 % is observed. Differential electrochemical mass spectrometry (DEMS) also shows a slight gassing process of TNO₄/carbon nanohybrids.

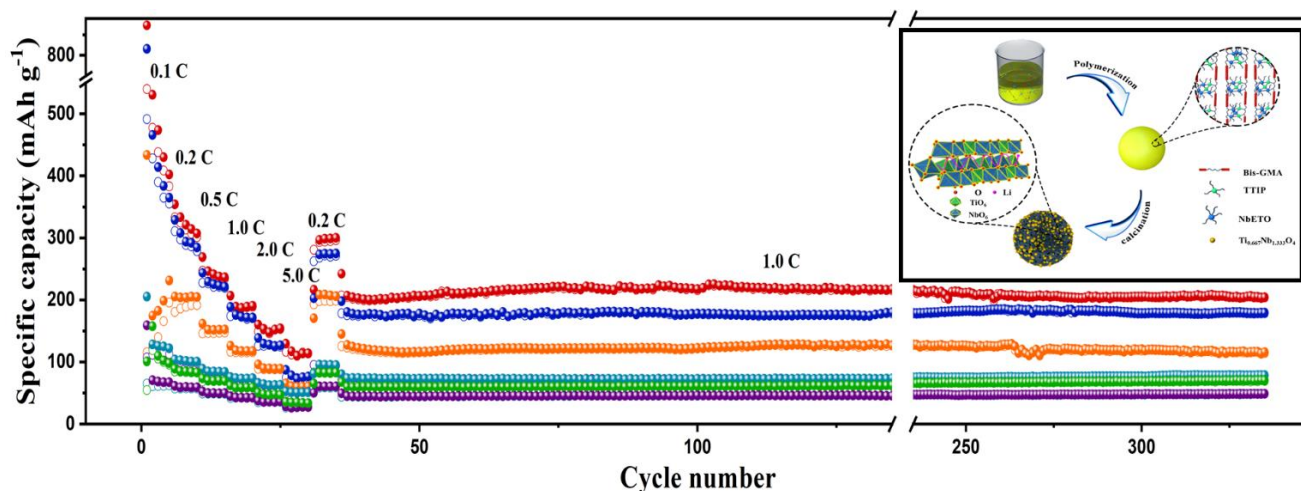


Fig. 1. Rate capability test from 0.1 C to 5 C, followed by a return to 0.2 C and a subsequent long-term cycling performance at 1 C with 300 cycles of TiO₂ (purple), NbO₂ (green), TNO₄ (cyan), TiO₂/carbon (orange), NbO₂/carbon (blue), and TNO₄/carbon (red). (inset) Schematic diagram for the synthesis and structure of the TNO₄/carbon solid solution.

Keywords: nanohybrids; solid solution; in situ XRD & TEM; band gap engineering; density functional theory (DFT).

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In-situ GISAXS/GIWAXS investigation of dcMS and HiPIMS deposited gold onto polymers

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Gold deposition via high power impulse magnetron sputtering (HiPIMS) allows to coat thin metal layers on heat sensitive materials such as polymers allowing for increased adhesion and density [1-3]. HiPIMS allows deposition at a lower total deposited thermal energy in comparison to conventional magnetron sputtering, but this energy is delivered in a very short pulse exhibiting very high power and ionization. The consequences for the nucleation and growth processes during HiPIMS deposition are not sufficiently known. Therefore, we investigate the morphology evolution of thin gold layers on three polymer templates, namely polystyrene (PS), polystyrenesulfonicacid (PSS) and poly-4-vinylpyridin (P4VP). These polymers show different functional moieties and thus are expected to influence the growth of the gold layer. Results of the in-situ investigations combining grazing incidence small angle X-ray scattering (GISAXS) and grazing incidence wide angle X-ray scattering (GIWAXS) will be presented.

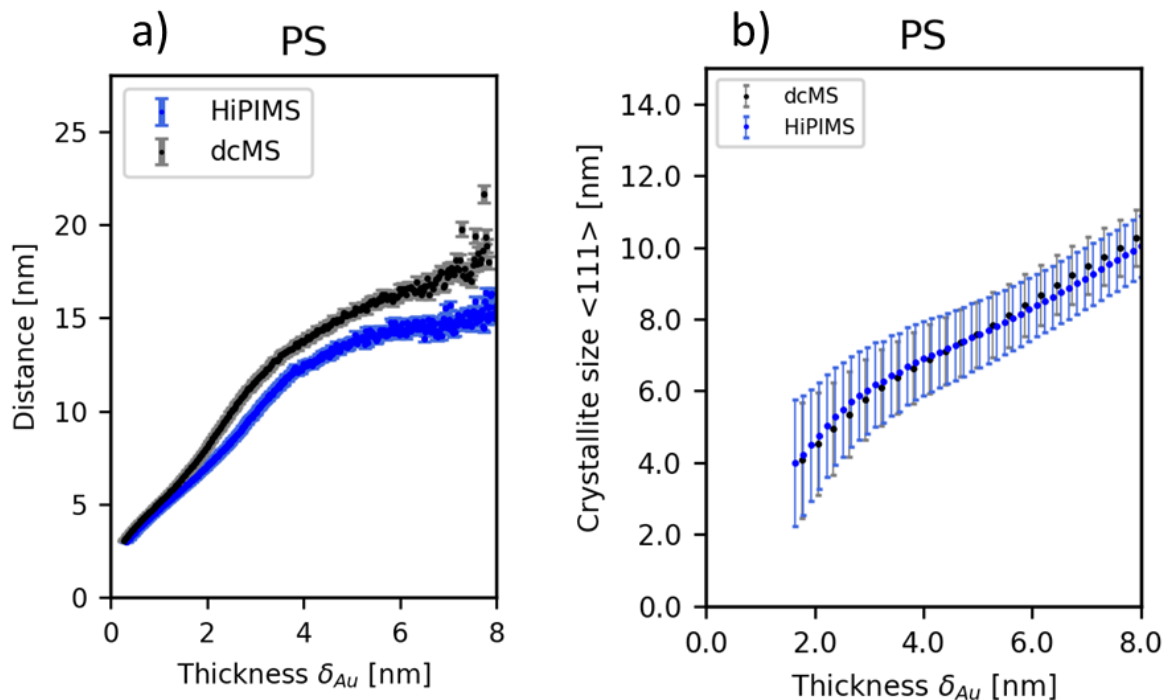


Fig. 1. a) In-situ GISAXS evolution of the distances of HiPIMS and dcMS gold deposition on polystyrene and b) in-situ GIWAXS evolution of gold of the the HiPIMS and dcMS <111> crystallite size during gold sputter deposition.

Keywords: GISAXS, GIWAXS, growth kinetics, polymer-metal interface, metal cluster percolation (max. 5 keywords)

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Morphology changes at the organic-metal interface: effects on the structure, electronic and thermoelectric performance

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Flexible organic electronics are one of the most sought-after devices in the field of photovoltaics [1], sensors [2], or smart wearables [3]. In addition to conducting organic materials, i.e., the conducting polymer blends like PEDOT: PSS, metal-organic materials gathered increasing influence for optical [4], electronic [5] and energy harvesting applications [6]. In case of flexible photovoltaics and thermoelectrics, poly(3-hexylthiophen-2,5-diyl) (P3HT) is one of the most prominent semiconducting, conjugated polymers due to its favorable energy band gap, general availability, and potential up-scalability [1]. For a solar cell stack, the polymer-gold interface of the active layer is of utmost importance for a competitive efficiency compared to traditional silicon-based solar cells [2].

The aim of this study was to link the structural and morphological differences with the thermoelectric properties of these thin polymer films depending on their fabrication technique. We choose both spin-casted and spray-deposited thin films since they both are industrially relevant, and spray-coating offers excellent scalability in future industrial applications. From our previous studies, the fabrication routes influence the surface morphology and penetration of Au into a subsurface layer. Grazing incidence small-angle X-ray scattering (GISAXS) allowed for the determination of the structural properties, e.g., size, morphology, and distance distribution, of the formed gold clusters on the surfaces and the interface region as well as the respective polymer domains. These results were cross-checked with optical and atomic force microscopy of the film surfaces. Here, mixed-scale dense convolutional neural networks [7, 8] were applied for image analysis on both scattering and microscopy data to track the dopant surface coverage and layer growth. Using both neutron (NR) and X-ray reflectivity (XRR), this dopant distribution throughout the films was tracked and correlated with crystallinity changes observed by grazing incidence wide-angle X-ray scattering (GIWAXS). This information will be crucial for improving the thermoelectric properties of thin films using less dopant material and providing a scalable approach for future industrial manufacturing.

Keywords: thermoelectrics, X-rays, neutrons, machine learning, doping

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POSTER ABSTRACT

Gas Sensing Behavior of Different Two Dimensional Nanostructured Materials for Hydrogen Gas: A Comparative Study

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Due to their physical porous structure, high surface area and chemically reactive surface properties the two dimensional (2D) nanostructured materials are promising material for gas sensing application. In this present work, we have synthesized different 2D materials like Graphene oxide (GO), Reduced Graphene oxide (rGO), MXene (Ti_3C_2) and Graphitic carbon nitride (GCN) nanosheets. Further these 2D materials functionalized with transient metal oxide and characterized the physicochemical properties using XRD, SEM, TEM, and Raman spectroscopy. The structural effect on the gas sensing properties of functionalized 2D material was analyzed for hydrogen (H_2) gas by preparing chemiresistor type gas sensors. The XRD, SEM, TEM, and Raman measurements clearly show that the properties like crystallite, conductivity, stability, and morphology of 2D material have been affected and improved after functionalization. The sensor performance at room temperatures was tested by monitoring the variation in resistance of the chemiresistor after hydrogen gas exposure. The capacitive study shows that the sensing behavior of sensing thin film is affected by surface morphology and physical structure offered by different 2D materials.

Keywords: Chemiresistor gas sensors; Graphene oxide (GO), Reduced Graphene oxide (rGO), MXene (Ti_3C_2) and Hydrogen gas sensing

Synthesis and Self-Assembly of Titania Nanoplatelets and Their Subsequent Encapsulation in a Polystyrene Shell *via* Surface-Grafted Controlled Radical Polymerization

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Natural composite materials such as nacre have gained significant scientific interest due to their exceptional mechanical properties including high hardness, strength, and toughness. These materials consist of a strong inorganic phase and a softer organic material and are structured on multiple hierarchical levels [1]. Very promising bio-inspired materials are inorganic nanoplatelets stabilized by a soft layer of organic ligands. Such nanoplatelets can self-assemble into hierarchically ordered superlattice structures, resembling the architecture of tough biocomposites. Here, we explore the synthesis and surface modification of titania nanoplatelets (TNPs) and their self-assembly into supraparticles *via* emulsion-based methods. Firstly, we present new findings regarding the synthesis of shape-controlled TNPs *via* an adapted seeded-growth approach [2]. These TNPs can be seen in figure 1A. The focus is on the tunability of the edge length (15 to 35 nm) and thickness (6 to 11 nm) as well as the optimization of the synthesis parameters to obtain monodisperse TNPs. The influence of different parameters is studied using different characterization methods including transmission electron microscopy (TEM), x-ray diffraction, thermogravimetric analysis, and dynamic light scattering (DLS).

The synthesized oleyl amine stabilized nanoplatelets are assembled into supraparticles *via* emulsion induced self-assembly [3]. This process yields supraparticles with sizes of approximately 200 – 400 nm, which are shown in figure 1B. Subsequent encapsulation in a polymer shell is expected to enhance the mechanical properties of these supraparticles. A proof of concept study demonstrates that the encapsulation with a polystyrene shell is possible *via* free radical polymerization and surface-grafted atom transfer radical polymerization (ATRP) [4]. For the latter, a phosphonic acid ligand is used to enable surface-grafted controlled radical polymerization. The encapsulated supraparticles are characterized with TEM, DLS and Fourier transform infrared spectroscopy. In addition, it is possible to tune the polymer shell thickness by varying the amount of monomer (styrene and divinylbenzene). A supraparticle encapsulated in a polystyrene shell can be seen in figure 1C. Additionally, we are currently transferring these assembly and encapsulation concepts to titania nanorod and nanodot systems.

Further experiments targeting at the encapsulation of the supraparticles focus on the implementation of TNPs in photoinitiated polymerizations. To this end, we plan to exploit the inherent photocatalytic activity of titania nanoparticles. The titania nanoparticles enable the photocatalytic surface-initiated free radical polymerization resulting in the controlled encapsulation of the three-dimensional supraparticles in a polymer shell. The double bond of the oleyl amine ligands located at the nanoparticle surface ensures surface-grafting of the polymer. We expect that the encapsulated supraparticles and their higher-level assemblies will provide new insights into the mechanical properties of hierarchically ordered artificial nanocomposites.

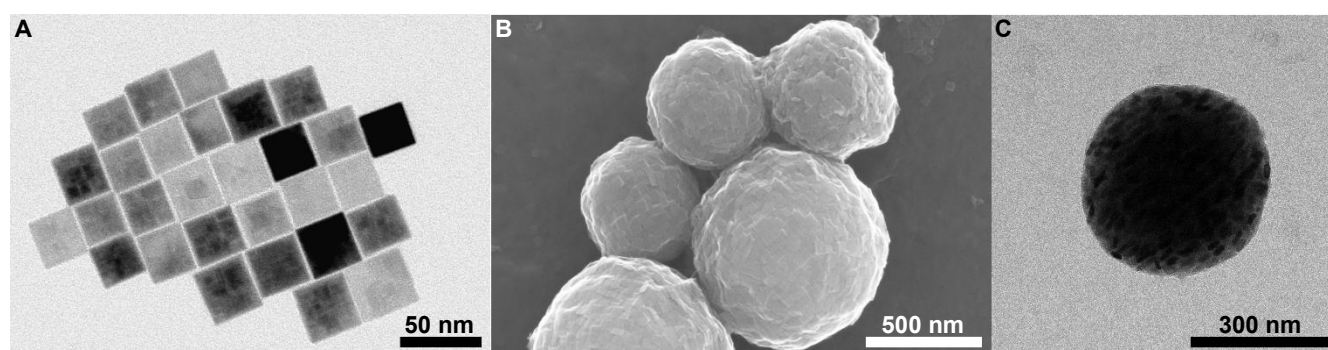


Fig. 1. A) TEM image of synthesized titania nanoplatelets, B) scanning electron microscopy image of self-assembled supraparticles, C) TEM image of an encapsulated supraparticle.

Keywords: titanium dioxide nanoplatelets, shape-controlled synthesis, self-assembly, encapsulation, bioinspiration

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Nanoparticles of plasma polymerized hexane as targets for laser-driven proton-boron fusion

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In the last years, the laser-driven proton boron (pB) nuclear reaction ($p+^{11}\text{B}\rightarrow^3\text{He} + 8.7\text{ MeV}$) has become a very interesting and attractive topic for the scientific community. In this method, laser pulses of high intensity irradiate hydrogen- and boron-rich materials to trigger the pB fusion with the generation of three energetic alpha particles. These can be useful in different applications, including the medical treatment of cancer [1] development of new power plants without nuclear waste [2] and also in space travel fuel [3]. Recently, thin films of hydrocarbon plasma polymers have been used as sources of hydrogen to enhance the alpha particle yield when they conveniently match the laser parameters [4], [5]. In this work, we present plasma polymerized hexane nanoparticles (ppC:H NPs) produced in a gas aggregation cluster source (GAS) as more advanced targets for laser-driven pB fusion. Hexane and argon were mixed at a constant total pressure of 50 Pa, keeping the partial pressure ratio of Ar/hexane = 5.5. An r.f. power supply with an automatic matching unit was used to ignite and maintain plasma at different powers to tune the mean size of NPs between 600 nm (at 30 W) and 120 nm (at 100 W). SEM images of submonolayers of these NPs are shown in Fig.1 a-b, whereas thick deposits are shown in Fig.1 c-d. Because nanostructured materials are envisioned to enhance the volumetric absorption of the laser energy as compared to thin films, we investigated the porosity of the NP deposits by measuring Brunauer-Emmett-Teller (BET) isotherms. In addition, we investigated the retention of hydrogen using a combined method of Rutherford Back Scattering and Elastic Recoil Detection Analysis (RBS/ERDA). Furthermore, we prepared hybrid nanostructures by r.f. magnetron sputtering of 100-nm boron thin films over the multilayers of 120 and 600-nm ppC:H NPs. The penetration of boron into the voids between the NPs was characterized by Nuclear Depth Profiling. Together, the results allow us to predict that ppC:H NPs combined with B-rich materials can be extremely useful as targets for laser-driven pB fusion.

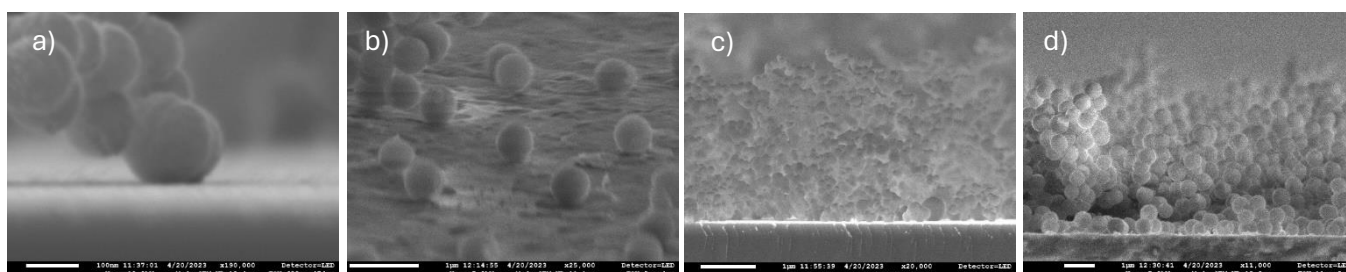


Fig. 1. SEM images of ppC:H NPs prepared at different power: a) 100 W (submonolayer, the mean size is 120 nm); b) 30 W (submonolayer, the mean size is 600 nm); c) 100 W (3 μm thick multilayer, the mean size is 120 nm); 30 W (3 μm thick multilayers, the mean size is 600 nm).

Acknowledgments: MT thanks the support of Charles University through the student GAUK: 110-10/252390 2023

Keywords: Plasma polymer nanoparticles, Laser-driven proton boron fusion.

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Biopolymer-Templated Deposition of Hierarchical 3D-Structured Graphene Oxide/Gold Nanoparticle Hybrids for Ultrasensitive Surface-Enhanced Raman Scattering

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Nowadays, sustainability of resources and energy has become among the biggest problems on Earth, the exploration of renewable biomass resources for developing functional materials is of great value and has attracted considerable attention [1]. Cellulose, a well-known natural biopolymer, possesses numerous advantages such as cost-effectiveness, renewability, ease of processing, and biodegradability [2]. Due to these inherent merits, cellulose has emerged as a promising bio-based substrate capable of synergistically combining with conductive materials (e.g., metals or carbon-based materials) for diverse applications including sensors, smart windows, and bioelectronics [3]. Typically, Surface Enhanced Raman Scattering (SERS), an advantageous analytical technique, allows for the rapid detection and structural analysis of biological/chemical compounds through their spectral patterns in nanotechnology [4]. Crucial for SERS is fabricating the substrates with strong and reproducible enhancements of the Raman signal over large areas and with a low fabrication cost. Herein, we present a straightforward approach utilizing the layer-by-layer (LBL) spray coating method to fabricate cellulose nanofibrils (CNF) films loaded with gold nanoparticles (AuNPs) and Graphene Oxide (GO) to serve as SERS substrates. Compared to conventional SERS substrates, the hybrid three-dimensional (3D) structures comprising GO/AuNPs significantly enhance the SERS sensitivity due to their synergistic effect. In addition, the incorporation of 3D CNF substrates, which serve as templates for the morphology of GO/AuNPs, contributes to a more uniform distribution. To gain comprehensive insights into the nanostructuring evolution, advanced X-ray scattering techniques, including grazing incidence small-angle X-ray scattering (GISAXS) and grazing incidence wide-angle X-ray scattering (GIWAXS), were employed to investigate the fundamental mechanisms. Thereby, our approach provides a reference for facile and scalable production of universally adaptable SERS substrates with exceptional sensitivity. This research opens up new avenues for achieving high-performance electronic materials in a more sustainable manner.

Keywords: cellulose, gold nanoparticles, graphene oxide, SERS

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One-step synthesis of hybrid ZrN/Ag nanoparticles with tunable optical properties

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Nowadays, scientific and industrial communities are increasingly focusing their attention on new and promising materials. The IV group of transition-metal nitrides is garnering a lot of interest as alternative refractory materials that exhibit unique properties. For example, zirconium nitride (ZrN) demonstrates a high melting point, high hardness, and good stability, which are essential for several applications. ZrN also shows a plasmon response in the red/near-IR region, which can be further modified by combining ZrN with other plasmonic materials. Silver (Ag), as one of the noble metals, is very popular because of its optical properties showing the plasmon response in the blue region. Using such a difference between ZrN and Ag, one can obtain materials with tunable optoelectronic properties for exciting applications. Thin films of ZrN with embedded Ag have already been reported [reference]. In this study, we investigate the synthesis of hybrid ZrN/Ag nanoparticles using a unique sputter-based setup, which allows for a single-step preparation of ZrN NPs and their in-flight decoration with Ag. ZrN was prepared by reactive dc magnetron sputtering of Zr in the Ar/N₂ mixture in a gas aggregation cluster source (GAS). An additional chamber with differential pumping was introduced behind the exit orifice of the GAS in which an Ag magnetron was installed transversely to the beam of ZrN NPs. The decorated NPs were then collected on substrates in the third vacuum chamber.

Computational Fluid Dynamics simulations were used to model the gas flow and velocity of NPs inside the decoration chamber. The results allowed us to estimate the residence time of the NPs in the vicinity of the Ag magnetron and to calculate the required Ag sputtering rate. The system was also found to provide the size separation of the NPs depending on whether the differential pumping was turned on or off. SEM and TEM showed the formation of cubic ZrN NPs of a mean size of 20 and 50-nm. The additional sputtering of Ag resulted in the formation of hybrid NPs consisting of a cubic ZrN core and spherical Ag satellites attached at the periphery. It should be mentioned that single-metal Ag NPs have also been produced under given conditions. The addition of silver affected the optical transmittance of the NP deposits, which showed two plasmonic bands corresponding to Ag and ZrN.

In summary, the decoration of ZrN NPs with Ag opens up opportunities for the utilization of such hybrid nanomaterials in various applications, including plasmonic devices, catalysis, energy storage, and biomedicine. Further investigation is required to explore the full potential of these decorated nanoparticles and optimize the coating process for specific applications.

Acknowledgments: The work was supported via the grant GACR 21-12828S from the Czech Science Foundation and the Charles University Grant Agency under Contract 372322.

Keywords: gas-aggregated nanoparticles, zirconium nitrides, silver, in-flight decoration, magnetron sputtering.

Memristive planar devices based on a tunable nanostructured Au/ZrOx composite film

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A major research area is the development of electronic devices that transcend the increasing limitations of classical electronics based on Von Neumann's architecture. A fundamental concern in seeking unconventional computation systems is the search for novel materials with which to construct new basic elements for computation. Memristive technology, a unique non-volatile memory technology whose memory effect is based on resistance changes caused by voltage application [1], is one of the most promising candidates for this goal. Gold cluster-assembled films show electrical switching and spiking capabilities [2], representing an interesting solution mainly because of their self-assembled structure. To explore new conductive features typical of insulating materials usually exploited in memristive devices, for instance ion migration, we characterized multilayer ZrOx-Au films [3]. These films show hysteretic current-voltage curves and potentiation and depression behaviours. As complex interfaces are involved in such planar layered devices and very high resistances are reached as the device is activated, we developed a two-source Supersonic Cluster Beam Deposition (SCBD) approach capable of manufacturing two materials composite cluster-assembled films. We used this technology to first study the percolation characteristic of this new composite cluster-assembled film from a fundamental point of view with the purpose of finding the right recipe to fine-tune the gold and zirconia-related conduction characteristics by varying the relative concentrations of the two materials.

Keywords: nanostructured films, clusters, composite, memristor, neuromorphic system.

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Observation of early stages of HiPIMS film formation on polymers with GISAXS

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High-power impulse magnetron sputtering (HiPIMS) is a widely used coating process that offers enhanced and specialized coating properties, e.g., better adhesion or higher hardness, in comparison to regular DC magnetron sputtering (DCMS) [1]. The main factors responsible for these benefits are the higher degree of ionization and increased kinetic energy of the target material.

Our objective is to explore the relationship between the distinctive characteristics of the HiPIMS process and the formation of thin films during the initial stages of metal deposition on polymers. The primary diagnostic technique deployed for this purpose is grazing incidence small-angle X-ray scattering (GISAXS), conducted at P03, PETRA III, DESY. This method allows for real-time monitoring of nanostructures, even at sub-monolayer levels, with excellent temporal resolution and reliable statistical data owing to the extensive surface area probed. The size, shape, and density of clusters on the substrate surface can be tracked throughout the deposition process until a fully covered layer is formed. Additionally, the acquisition of in-situ UV-Vis data facilitates the correlation of optical properties, such as absorption resulting from surface plasmon resonance or band gap energy. Previous experiments conducted with metals on different polymers using DCMS, e.g., Au on polystyrene, have been performed [2,3], establishing a solid foundation for modelling and comparing the obtained data.

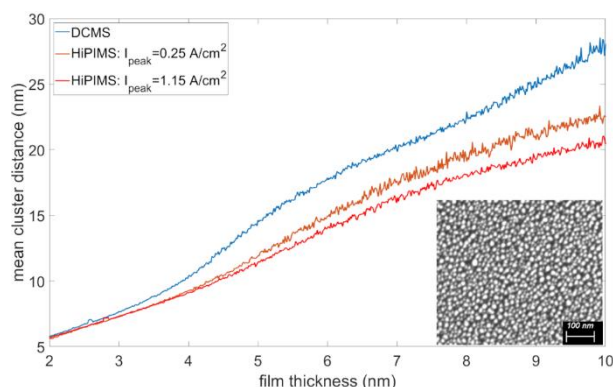


Figure 2: Mean cluster distance vs. film thickness of Ag deposited by DCMS and two different HiPIMS parameters on PV4D4. Inset shows SEM image of 2 nm Ag deposited on PV4D4 with DCMS.

In-situ measurements are conducted on model polymers like spin coated polystyrene (PS) and Poly(methyl methacrylate) (PMMA) as well as polymers deposited by initiated chemical vapor deposition (iCVD), e.g., Poly(tetra vinyl-tetramethylcyclotetrasiloxane) (PV4D4) and Poly(tetrafluoroethylene) (PTFE) as hydrophobic and superhydrophobic specimens. The distinct functional groups of these polymers influence the growth in different ways. The iCVD coatings are chosen because of their potential use as dielectric film or electret and because of their conformity and flatness due to the iCVD process being beneficial for GISAXS[4,5]. Sputter materials used are Au, Ag and TiO₂ (reactively sputtered). The results show a pronounced influence of the sputter technique used on the early nucleation stage. For HiPIMS, the number of clusters is increased, i.e., the cluster size is reduced, compared to DCMS. Increasing the peak current further amplifies this tendency. This observation is probably linked to the creation of defects on the polymer surface due to ion bombardment as additional starting points for nucleation. These results are complemented with UV-Vis and SEM measurements to link the observed length scales with optical features.

Keywords: cluster growth, HiPIMS, GISAXS, metal-polymer interface, iCVD

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Forming process and electrical-structural properties of 2D and 3D nanostructured Au resistive switching networks

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Networks of random-assembled gold clusters produced in the gas phase exhibit resistive switching (RS) activity at ambient temperature and they are suitable for the fabrication of devices for neuromorphic data processing and classification. Continuous cluster-assembled nanostructured Au films have a granular structure rich of crystallographic flaws, grain boundaries, and interfaces. Here we report a systematic characterization of the electroforming process of the cluster-assembled films demonstrating the interplay between the nano- and mesoscale film structure and the neuromorphic characteristics of the resistive switching activity. The understanding and the control of the influence of the forming process on the organization of specific structures at different scales of the cluster-assembled films, provides the possibility to engineer neuromorphic architectures for data processing task. The attention is focused on bi-dimensional networks realized on rigid silicon-based substrates and on three-dimensional networks implanting Au nanoclusters on soft, transparent and bio-compatible Polydimethylsiloxane substrates in order to realize mechanoresponsive electric neuromorphic devices.

Keywords: *Cluster-assembled gold, memristive switching, neuromorphic behaviour, temporal correlation, network electrical connectivity.*

Exploring the potential of magnetic, reactant-free nickel nanofluids: a preliminary study

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Nickel (Ni) is one of a few ferromagnetic metals that is widely used in industry as a doping for stainless steel, in magnetic alloys, and in magnetic sensors. Furthermore, Ni nanoparticles (NPs) show prospects for use in medicine for drug delivery, medical imaging techniques, and hyperthermia treatment.

This study presents preliminary results on the production of Ni nanofluids using a reactant-free method developed by our group in 2021¹. The synthesis of NPs is based on magnetron sputtering of a Ni target inside a gas aggregation cluster source (GAS). The NPs formed in the GAS are then loaded directly into the volume of a host liquid. The effect of argon flow, magnetron current, and aggregation length on the size of Ni NPs was investigated. The variation of these three parameters facilitates the synthesis of NPs with tailored properties. In-situ and ex-situ X-ray Photoelectron Spectroscopy (XPS) analysis showed the formation of an oxide shell on the surface of the NPs after contact with air. In the current investigation, Ni NPs of different sizes were loaded onto tetramethyl tetraphenyl trisiloxane (DC704), a vacuum-compatible high-temperature silicone fluid. Ni/DC704 nanofluids show a brownish-grey color, the intensity of which is determined by the NP size and concentration. NPs with a diameter of 10 nm show greater stability compared to 30 nm particles. Indirect and direct magnetic measurements were carried out. It has been observed that when a magnetic field is applied to NPs in a liquid, they do not sediment but instead adhere to a wall as a result of magnetic attraction. The Physical Property Measurement System (PPMS) was used to confirm the ferromagnetic properties of Ni nanofluids. Further investigation into the properties of Ni nanofluids will enable us to broaden their potential applications.

Acknowledgments. This work was supported via the grant GACR 21-12828S from the Czech Science Foundation and the Charles University Grant Agency under Contract 298722.

Keywords: *gas aggregation cluster source, magnetron sputtering, nanoparticles, magnetic nanofluids, tetramethyl tetraphenyl trisiloxane (DC704).*

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Tailored polymer thin films enabled by initiated chemical vapor deposition (iCVD)

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Functional polymer films are applied in a vast number of applications. Device miniaturization and the consequent need for new thin films on the nanoscale require precise thickness control and defect free films especially for advanced electronic devices in research as well as industrial production lines. Solvent-free, single-step initiated chemical vapor deposition (iCVD) circumvents de-wetting and surface tension effects encountered in classical wet-chemical polymer thin film fabrication. The process enables in this way the fabrication of tailored polymer thin films on the nanoscale on complex geometries and large-area substrates due to its CVD-typical growth characteristics. The application field of these thin films ranges from advanced electronic devices to biomedical applications. It turns out that also the combination of iCVD with a gas aggregation cluster source (GAS) indicates the fabrication of functional nanocomposites for even more advanced application pathways.

Keywords: *initiated chemical vapor deposition, polymer thin films, organic electronics, electrets*

AUTHOR INDEX

Abdelaziz, Moheb	26,29	Harder, Constantin	25,44
Adejube, Blessing Oluwasayo	31,33	Hartig, Torge	29,50
Adel Assad, Mhd	26,29	Hassanien, Abdou	24
Adelung, Rainer	24	Hecker, Dominic	11
Aktas, Oral Cenk	3	Hosseinaei, Omid	6
Ali-Ogly, Suren	9,12,33,45	Huang, Tzu-Yen	39
Álvarez, Covadonga	2	Huber, Linus	20
Asnaz, Oguz Han	10,31	Huttel, Yves	2
Azari, Amirhossein	26	Jauquet, Valentine	13
Bajtosova, Lucia	14,33	Kaftan, David	15
Benedetti, Danilo	16,19,31	Kalsi, Tania	28
Benedikt, Jan	10	Kamon, Kota	21
Bengtsson, Andreas	6	Kampferbeck, Michael	18
Bengtsson, Jenny	6	Kaps, Sören	24
Betker, Marie	38,39	Kaur, Amarjeet	23
Biederman, Hynek	9	Kersten, Holger	10
Biliak, Kateryna	12,32,43,45,49	Kienle, Lorenz	31
Bittinger, Sophia Caroline	42	Klauke, Lea Regina	18
Bol, France-Emmanuelle	13	Klinkenberg, Sigrun	11
Borghi, Francesca	32,46,48	Kolská, Zdeňka	43
Borras, Ana	5	Konstantinidis, Stephanos	13
Brown, Simon Anthony	31	Kosutova, Tereza	9,12,48
Bulut, Yusuf	38,39,44,47	Kousal, Jaroslav	7
Cannavò, Antonino	43	Kozák, Tomáš	15
Carstens, Niko	24,31	Kumar, Pragati	28
Ceccio, Giovanni	43	Kumar, Sanjay	15,27
Černochová, Zulfiya	33	Kumawat, Arjun	41
Charan, Sheetal	41	Kuzminova, Anna	14,27
Chavez, Tanny	38	Kykal, Carsten	39
Chen, Shouzheng	44	Kylian, Ondrej	32
Cheng, Yajun	37	Laarmann, Tim	39
Choukourov, Andrei	9,12,33,43,45,47	Le Brun, Anton	39
Cieslar, Miroslav	12,45	Lemke, Jonathan	32
Cornil, David	12	Li, Chuchu	34
Cornil, Jérôme	12	Liang, Suzhe	38
Cosmai, Savino	16,19	Liu, Jiliang	6
Čurda, Pavel	15,27	Lo Porto, Chiara	19
de Andrés, Alicia	2	Ludwig, Nicola	48
Del Sole, Regina	16,19	Lupan, Oleg	50
Drewes, Jonas	10,29,31,47	Macková, Anna	43
Elbahri, Mady	26,29	Madurawala, Roshani	24
Erbes, Elisabeth	44	Maki, Hideshi	21
Falqui, Andrea	46	Mares, Pavel	9
Faupel, Franz	3,10,14,24,29,33,47,50	Margarone, Daniele	43
Fracassi, Francesco	16,19	Martínez, Lidia	2
Franzen, Laura Ronja	42	Maskova, Hana	27
Fröhlich, Eleonore	11	Mayoral, Álvaro	2
García-Martín, José Miguel	2	Meyer, Andreas	18
Giuffrida, Lorenzo	43	Mikšová, Romana	43
Gloess, Daniel	11	Milani, Paolo	46,48
Gorb, Stanislav	34	Milella, Antonella	16,19
Greiner, Franko	10	Minamimoto, Hiro	35
Gronenberg, Ole	31	Mizuhata, Minoru	21,35
Guan, Tianfu	38	Morris, James Eliot	30
Guo, Yingjian	25,44	Müller-Buschbaum, Peter	17,20,25,37,39,44,47
Gupta, Rohit	24	Nadalini, Giacomo	48
Hanuš, Jan	9,12	Nikitin, Daniil	9,12,33,43,45,49
Hao, Guanhua	39	Nizard, Harry	11

Odent, Jeremy	13	Shondo, Josiah	3
Oechsle, Anna Lena	38	Skorvankova, Katerina	13,14
Ostrikov, Kostya {Ken}	22	Sochor, Benedikt	44
Palumbo, Fabio	16,19	Solar, Pavel	14
Paulsen, Joschka	50	Spadaro, Maria Chiara	4
Perdana, Nanda	29	Srivastava, Subodh	41
Piehl, Julia	50	Sterba, Jan	27
Pleskunov, Pavel	9,12,27,33,43,45,49	Straňák, Vítězslav	15,27
Polonskyi, Oleksandr	10	Struck, Jana	42
Profumo, Filippo	46	Strunskus, Thomas	10,24,29,31,47,50
Prokleška, Jan	49	Tajiri, Yuto	35
Protsak, Mariia	12,32,43,45,49	Terasa, Maik-Ivo	24
Rajabi, Hamed	34	Tjardts, Tim	3,14
Reck, Kristian Amand	47	Tosca, Marco	12,32,43,45,49
Rego, Ryan	27	Ulmefors, Hanna	6
Rehders, Stefan	10	Umek, Polona	13
Roberts, Eric	38	Vahl, Alexander	10,14,24,29,31,47,50
Rockstuhl, Carsten	29	Veziroğlu, Salih	3
Rogall, Kevin	29	Vossmeier, Tobias	18,42
Roth, Stephan Volkher	25,36,39,44,47	Vyskocil, Jiri	9
Saini, Sachin	41	Xia, Yonggao	37
Schraad, Simon	38	Xu, Zhuijun	37
Schröder, Stefan	47,50	Yang, Yun	21
Schürmann, Ulrich	31	Yu, Shun	6
Sergievskaia, Anastasiya	12,13	Zhang, Peng	25
Sezemský, Petr	15	Zhou, Jungui	26
Sharma, Nutan	41	Ziegler, Florian	31
