



# iPlasma Nano-XIII 2024

September  
15-19, 2024  
Hamburg, Germany



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## **Welcome in Hamburg!**

Dear participant of the iPlasmaNanoXIII in Hamburg, it is our pleasure to welcome you at this event. We are looking forward to the time we spend with discussion of the research on plasma and materials.

Your chairs Jan and Ronny

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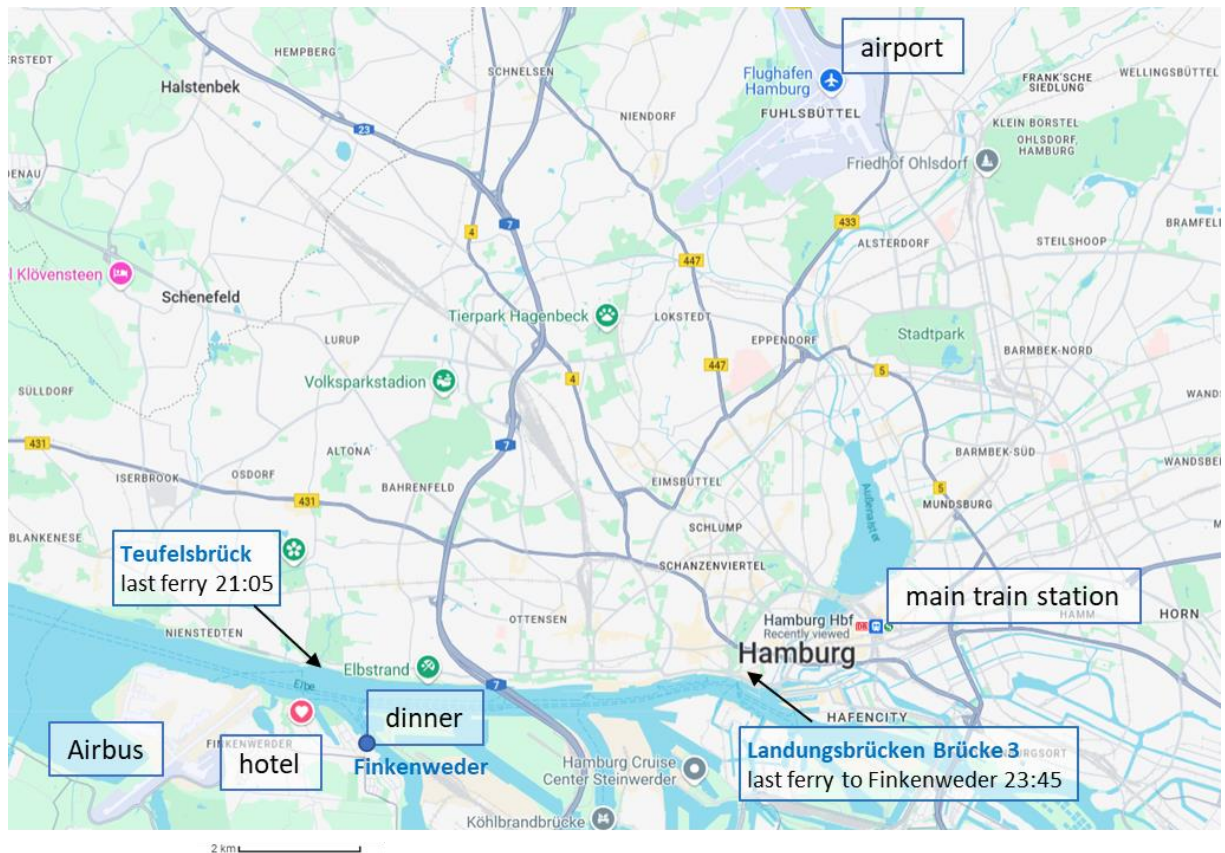
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## Location in Hamburg

We are in the hotel Elaya (formerly Rilano) hotel at Hein-Saß-Weg 40, 21129 Hamburg



## Transportation

*From Airport:*

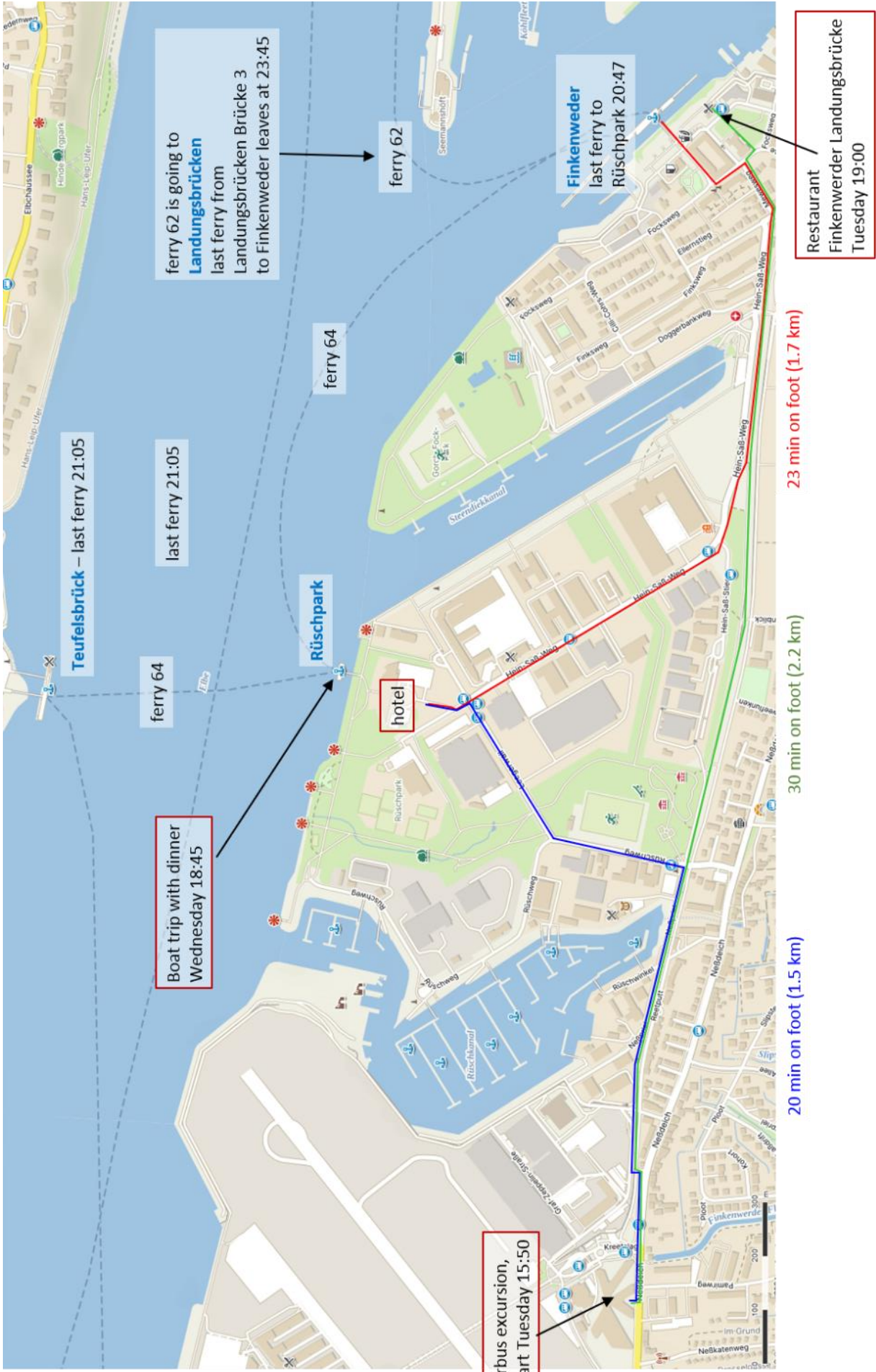
Take the S1 train to “Landungsbrücken” (~ 30 min) and from there from “Brücke 3” the ferry 62 to “Finkenweder” (~30 min), where you quickly change to ferry 64 to “Rüschpark” (~5 min) – it is a very nice trip especially at nice weather.

The single way costs €3.80.

Alternative routes can be found here: <https://www.hvv.de/en>

The ferry is the easiest way to get to the city. Make sure you consider the end of transportation as indicated on the following map.





## Excursion

We will visit Airbus factory in Finkenweder:

<https://werksfuehrung.de/en/aerospace/airbus-factory-tour/airbus-hamburg-1>

We need to be at the visitor center (address: Kreetslag 7, 21129 Hamburg) at 15:50. You can reach it by foot (1.5 km, 20 minutes), but we have minibus (8 persons) and can bring you there in case you prefer it, leaving around 15:30 from the hotel. **Don't forget to take your passport with you!**



The excursion is followed by a dinner at the “Finkenwerder Landungsbrücke” restaurant at Benittstraße 9, 21129 Hamburg. You can walk there within 30 minutes (2 km), but we will offer again a minibus transportation if needed.

## Conference dinner

Conference dinner on Wednesday 18.09. will be on the boat MS HAMBURGER DEERN.



Boarding starts at 18:45!

## Program

Sunday 15. Sept.		
16:00 - 18:00	Registration	
18:00 - 19:30	Welcome reception	
Monday 16. Sept.		
8:50 - 9:00	Welcome	
9:00 - 9:45	Rebecca Anthony	<i>Nonthermal plasma synthesis of nanomaterials</i>
9:45 - 10:15	Andrey Choukourov	<i>Hybrid Boron/Plasma Polymer Nanoparticles for Green Energy Generation</i>
10:15 - 10:45	Edgar Felizardo	<i>Versatile plasma-based machine for the production of Nanomaterials</i>
10:45 - 11:00	Coffee break	
11:00 - 11:30	Uros Cvelbar	<i>Quo Vadis Plasma Nanoscience and Nanotechnology</i>
11:30 - 12:00	Wei-Hung Chiang	<i>Plasma Engineering of Zero-Dimensional Semiconductor and Metal Nanostructures</i>
12:00 - 12:30	Santosh Marath	<i>Plasma-designed Nanohybrids for Future Energy Storage Applications</i>
12:30 - 14:00	Lunch	
14:00 - 14:30	Franz Faupel	<i>Ways out of the climate and sustainability crisis – what is opinion, what is knowledge, do we have the power to change something?</i>
14:30 - 15:00	Michael Keidar	<i>Adaptive Low-temperature plasmas</i>
15:00 - 15:30	Klaus-Dieter Weltmann	<i>Plasma Medicine – Knowledge and technology transfer FROM THE IDEA TO THE PRODUCT</i>
15:30 - 15:45	Coffee break	
15:45 - 16:15	Mohamed Chaker	<i>Synthesis and characterization of oxide materials</i>
16:15 - 16:45	Martin Košiček	<i>Thermal and plasma-assisted manipulation of copper oxide nanomaterials</i>

Tuesday 17. Sept.		
9:00 - 9:45	Masaharu Shiratani	<i>Application of Gray-Box Approach Using Machine Learning to Plasma Deposition</i>
9:45 - 10:15	Juan Ramon Sanchez-Valencia	<i>Plasma synthesis of advanced multifunctional nanoarchitectures for energy harvesting applications</i>
10:15 - 10:45	David Ruzic	<i>Advanced Techniques for the Growth and Monitoring of Nano-Structured Carbon Materials in Plasma Environments</i>
10:45 - 11:00	Coffee break	
11:00 - 11:30	Angel Barranco	<i>Development and applications of conformal aerogel-like oxide films by plasma deposition</i>
11:30 - 12:00	Tomáš Kozák	<i>Plasma diagnostics and modelling of NbC sputtering and deposition in HiPIMS discharges</i>
12:00 - 12:30	Kristian Amand Reck	<i>Early-Stage Silver Growth on SiO<sub>2</sub> and Polystyrene deposited by DCMS, HiPIMS and Bi-Polar HiPIMS</i>
12:30 - 14:00	Lunch	
14:00 - 14:30	Ali Khatibi	<i>In-flight Synthesis of Individual Atoms Via Atmospheric Pressure Non-Equilibrium Plasma</i>
14:30 - 15:00	Jan Benedikt	<i>Atmospheric plasma helix jet for the generation of functionalised semiconductor and metal nanoparticles</i>
15:00 - 15:15	Coffee break	
15:50 - 18:40	Excursion Airbus	
19:00 -	Dinner	

<b>Wednesday 18. Sept.</b>		
9:00 - 9:45	David Go	<i>Electrifying the Future: Non-Thermal Plasmas for Revolutionizing Goods Production</i>
9:45 - 10:15	Kerstin Sgonina	<i>Plasma-assisted catalysis at atmospheric pressure</i>
10:15 - 10:45	Volker Brüser	<i>Enzyme catalyzed CO<sub>2</sub> conversion supported by nanosecond-pulsed DBD</i>
10:45 - 11:00	Coffee break	
11:00 - 11:30	Robin De Meyer	<i>In-situ Plasma Studies using a Direct Current Microplasma in a Scanning Electron Microscope</i>
11:30 - 12:00	Dilver Fuentes	<i>Operando-DRIFTS investigations on non-thermal plasma induced generation of CO from CO<sub>2</sub>: Experimental Set-up and preliminary results</i>
12:00 - 12:30	Svetlana Radovanov	<i>Microwave discharge modeling in Argon and Hydrogen</i>
12:30 - 14:00	Lunch	
14:00 - 14:30	Holger Kersten	<i>Investigation of the Ionization Region in a Magnetron Plasma of a Gas Aggregation Source for Cluster Formation</i>
14:30 - 15:00	Daniil Nikitin	<i>Gas aggregation for Cu<sub>3</sub>N nanoparticle formation using a cylindrical post-magnetron</i>
15:00 - 15:30	Viktor Schneider	<i>New insights into plasma parameters in a dual-frequency capacitively coupled rf discharge</i>
15:30 - 15:45	Coffee break	
15:45 - 16:15	Jessica Niemann	<i>Optically trapped microparticles in a dual-frequency capacitively coupled rf discharge</i>
16:15 - 16:45	Ronny Brandenburg	<i>Carbon Dioxide Splitting in Dielectric Barrier Discharges: Scaling with the Specific Input Energy</i>
19:00 - 22:00	conference dinner	

<b>Thursday 19. Sept.</b>		
9:00 - 9:45	Thierry Belmonte	<i>How do you select your nanoparticle synthesis process in the plasma-in- liquid aisle of your supermarket?</i>
9:45 - 10:15	Thomas Strunskus	<i>Vapor phase deposited metal-polymer nanocomposite thin films for biomedical applications</i>
10:15 - 10:45	Paula Navascués	<i>Near-plasma Chemistry: a Novel Approach in Plasma Surface Engineering</i>
10:45 - 11:00	Coffee break	
11:00 - 11:30	Peter Mascher	<i>Plasma-assisted Fabrication of Functional Coatings for Photonics Applications</i>
11:30 - 12:00	Alexander Vahl	<i>Plasma-derived nanogranular matter for brain-inspired electronics</i>
12:00 - 12:30	Luka Hansen	<i>Silicon nitride membrane as entrance window for plasma-induced VUV radiation</i>
12:30 - 14:00	Lunch	



# Controlling Nanoparticle Synthesis in Low-Temperature Plasmas

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Advanced manufacturing strategies have immense potential to reduce time and production costs for a range of applications. Meanwhile, the multiple functionalities and small size of nanomaterials can influence the versatility and capabilities of many devices including solar cells and solid-state lighting, energy conversion technologies and batteries, wearable electronics, and coatings. Combining advanced manufacturing with nanotechnology opens the door to exciting applications based on thin films and microstructures, with on-demand tunable functionality. One promising route to achieving advanced nanomanufacturing is to use low-temperature plasmas for synthesis of nanoparticles, together with advanced manufacturing methods which are compatible with roll-to-roll or additive printing methods. I will present my group's recent work on using low-temperature radiofrequency plasmas for synthesis of nanocrystals, and the merger of this synthesis technique with an additive manufacturing approach to deposition for tunable-property nanoparticle layers and patterns. The low-temperature synthesis of otherwise difficult-to-make semiconductor nanoparticles is uniquely paired with direct deposition onto arbitrarily chosen substrates – including temperature-sensitive materials such as polymers – for versatile deposition with on-demand property modulation. I will share our exploration of parameters such as ambient environment, pressure, and supplied radiofrequency power for controlling the properties of the silicon nanoparticles and the layer deposition characteristics, as well as present ongoing research on other low-temperature plasma reactors for nanoparticle synthesis.

## Acknowledgments

This work has been supported by the US National Science Foundation through the CMMI CAREER grant 1651674, and the US Department of Energy through Grant DOE-SC002321. The author gratefully acknowledges the efforts of her prior and current Ph.D. students who contributed to this work: Dr. Alexander Ho, Mr. Sankhadeep Basu, and Mr. Cameron Papson.

## References

“Constriction Requirement for Nanoparticle Crystallization in a Non-Thermal Atmospheric Pressure Plasma” C. Papson, S. Basu, and R. Anthony, *Appl. Phys. Lett.* **125** (5)

“Integrated Plasma Synthesis and Aerosol Jet Printing of Silicon Nanoparticles at Atmospheric Pressure” A. Ho and R. Anthony, in preparation, 2024



# Hybrid Boron/Plasma Polymer Nanoparticles for Green Energy Generation

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Human dependence on non-renewable energy sources has led to a global energy crisis. A possible solution can be found in laser-driven proton-boron (pB) nuclear fusion which relies on the irradiation of materials rich in boron and hydrogen with high-energy laser pulses. Under proper conditions, protons are accelerated to energies sufficient for fusion with B nuclei, producing energetic alpha-particles without creating neutrons, thus without radioactive activation or waste. Alpha particles can then be captured by a magnetic field to produce green electric energy. We developed innovative hybrid nanomaterials based on boron and hydrocarbon plasma polymers (nanoparticles, multilayered coatings) and studied how the structure, porosity, and elemental content in such nanomaterials can be tuned to influence the alpha-particle yield using lasers in different regimes.

## Acknowledgments

Research was supported by the Czech Science Foundation through the grant GACR24-11398S. Purchase of consumables was partially supported by the Grant Agency of Charles University through the student grant GAUK 208123.

# Versatile plasma-based machine for the production of Nanomaterials

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A disruptive plasma technology and a corresponding laboratory prototype of a versatile microwave plasma-based machine for gram-scale fabrication of high-quality graphene and derivatives (N-graphene, Graphene/N-graphene-metal oxides) was developed. The machine enables the conversion of cheap carbon-based precursors (ethanol, CH<sub>4</sub>, CO<sub>2</sub>, biomass slurry, etc.) into high-quality graphene derivatives with tailored properties. Different structures (e.g.: graphene sheets, N-graphene, hybrid nanomaterials) can be fabricated using the same device by applying the corresponding synthesis protocols. Controllable, continuous fabrication of graphene/N-graphene at a gram scale with high-level of single layer selectivity (~50 %), high production rate (~30 mg/min) and repeatability has been achieved using ethanol, methane and acetonitrile as starting materials. The fabricated graphene/N-graphene sheets possess high quality as evidenced by comprehensive physicochemical analyses made (for pure graphene C/O ratio: > 50; sp<sup>2</sup>% ~ 70%; for N-graphene C/O ratio: > 40; sp<sup>2</sup>% >60%).

The main advantage of the technology arises from the ability to achievement very high and extremely controllable energy densities in the reactor, which allows effective control over the energy and material fluxes towards growing nanostructures at the atomic scale via proper reactor design and tailoring of the plasma environment. The synthesis-by-design feature represents a significant leap from the state-of-the-art methods that rely on cumbersome batch procedures involving harsh chemistry and energy intensive processes. The free-standing sheets are assembled through a single-step process in readily dispersive form, without the need for any kind of postprocessing, including cleaning. The end-result is a high-quality product, obtained in a reproducible manner, with the desired morphological, structural, and functional properties.

## Acknowledgments

This work was performed under de framework of the PEGASUS (Plasma Enabled and Graphene Allowed Synthesis of Unique nano-Structures) project, funded by the European Union's Horizon research and innovation program under grant agreement No 766894, and partially funded by the Portuguese FCT-Fundação para a Ciência e a Tecnologia, under projects UIDB/50010/2020, UIDP/50010/2020 and EAGER (PTDC/NAN-MAT/30565/2017).

# ***Quo Vadis Plasma Nanoscience and Nanotechnology***

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Plasma nanoscience and nanotechnology offer unparalleled precision in manipulating and fabricating nanostructures. This talk critically examines the state-of-the-art in plasma-assisted nanofabrication techniques, focusing on their scientific underpinnings, current applications, and potential future directions. Particular emphasis is placed on the integration of artificial intelligence (AI) in plasma processes to enhance control and materials discovery, with an eye toward supporting green transition initiatives such as the EU Green Deal.

Plasma-based techniques, including plasma-enhanced chemical vapor deposition (PECVD), plasma etching, and plasma surface functionalization, have become indispensable tools in nanoscience and nanotechnology. These methods leverage the unique properties of plasmas, offering indispensable tools for the green processing of materials or devices, thereby enabling the customization of nanomaterials with desired electrical, optical, and mechanical properties. The integration of AI into plasma nanoscience and nanotechnology represents a significant leap forward, addressing the complexity and multidimensionality of plasma processes. Machine learning (ML) models, particularly those employing deep neural networks and reinforcement learning algorithms, have demonstrated their capacity to predict and optimize plasma behaviour in real time. These models can process large datasets from experimental observations and simulations, uncovering non-linear correlations between plasma parameters and material outcomes that would be intractable using traditional methods. This predictive capability is crucial for accelerating the discovery of new nanomaterials and optimizing fabrication processes. However, for discoveries, models like random forests are more applicable.

In the context of sustainability and the EU Green Deal, plasma nanotechnology and AI offer transformative potential. A particularly promising application is in the development of high-value-added materials that don't rely on critical raw materials, for example, high-entropy alloys, which can improve existing catalysts for green hydrogen production, steel manufacturing, or aircraft engines. Furthermore, plasma treatment of surfaces can contribute to the development of advanced materials for energy storage and conversion, such as supercapacitors and fuel cells, which are essential for renewable energy technologies. The future trajectory of plasma nanoscience and nanotechnology is expected to be heavily influenced by its integration with AI. This synergy will not only refine existing processes but also unlock new avenues for research and application, particularly in the realm of sustainable technologies. As the EU Green Deal seeks to transition to a climate-neutral economy, the advancements in plasma nanoscience and nanotechnology, underpinned by AI, will play a pivotal role in enabling this transition. Thus, the intersection of these fields is poised to drive significant scientific and technological progress, contributing to a more sustainable and resilient future.

## **Acknowledgments**

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# Plasma Engineering of Zero-Dimensional Semiconductor and Metal Nanostructures

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Nanomaterials with tunable properties are the forefront of materials research owing to their significance in numerous application fields, including biomedical, optoelectronics, nanocatalysis and energy conversion and storage. However, achieving this in a catalyst-free, low-temperature, rapid, and environmentally friendly manner is challenging. Here we utilize non-equilibrium and low-temperature microplasmas to synthesize zero-dimensional (0D) structure-controlled semiconductor and metal quantum dots (QDs) at ambient conditions without any additional toxic chemicals, expensive catalysts, and sophisticated vacuum technologies. The reactive species generated by the plasma enable not only rapid disassembly of precursors into small moieties, but also simultaneous reconstruction of crystalline cluster domains and nucleation into QDs. Among various QDs, polyethylene terephthalate-derived GQDs (PET-GQDs) exhibit stable white emission under 365 nm UV irradiation with a Commission Internationale de l'Eclairage 1931 of (0.29, 0.35). The colloidal PET-GQDs can be applied for heavy metal ions detection with a low limit of detection of 8.4 nM, while the composite film state can be utilized as a sensitive temperature tag from 10 – 80 °C and a high-brightness white LED panel. This work provides new insights into the effective mechanisms for QD growth in a renewable electricity-driven, scalable, and environmentally sustainable way.



# Plasma-designed Nanohybrids for Future Energy Storage Applications

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The rising demand for sufficient energy supply for the global market requires advancement in the existing lithium battery-based energy storage devices. This scenario increases the research interest in alternative metal ion battery systems and supercapacitors with high energy-power densities and long-term stabilities. Considering that energy-power densities and stability of an energy system are directly influenced by the electrode material and electrolyte combination used in the device, the major research is focused on developing advanced materials with high capacity and long-standing stability. Tailoring material at the nanoscale is one of the promising techniques for improving its intrinsic and extrinsic properties for various applications. Nanostructures with different morphologies, orientations and hybrid compositions will allow intercalation, conversion or alloy-type electrochemical reactions to boost the energy storage performance. Therefore, several efforts have been employed to design advanced nanohybrids as energy materials, which still need to meet the criteria of low cost and environmental cleanliness. From this perspective, plasma offers a fast and safe approach to designing and processing nanohybrids with better controllability. This paper discusses the advantages of plasma as an efficient technique for developing advanced nanohybrids with high structural quality and controllability. Different cases have been discussed in detail, including the single-step atmospheric plasma-produced graphene-metal oxide derivatives for supercapacitors<sup>1</sup>, advancing Li and Na-ion battery performance with plasma-designed vertical carbon/metal sulfide-nanostructures<sup>1,2</sup> and carbon-nickel sulfide nanohybrids high-performing redox supercapacitors<sup>3</sup>. In addition, the potential of plasma-tailored vertical carbon nanohybrids for high-frequency supercapacitors has also been illustrated<sup>4</sup>. All the cases demonstrate the advancement of energy storage performances by using plasma-designed nanohybrids, suggesting the potential of plasma-enabled techniques to be used as alternative techniques to design high-performing energy materials for next-generation electrochemical energy storage devices.

## Acknowledgments

This research is supported by Slovenian Research Agency (ARIS) funded research grants J2-50074, and Z2-4467 (post-doctoral grant), EU Graphene Flagship FLAG-ERA III JTC 2021 project VEGA (PR-11938) and M-ERA.NET 3 project ANGSTROM (The project is funded by Ministrstvo za visoko solstvo, znanost in inovacije – MVZI, Slovenia).

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# Ways out of the climate and sustainability crisis – what is opinion, what is knowledge, do we have the power to change something?

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The climate and sustainability crisis is currently the biggest problem for the survival of humanity. It cannot be solved by technological progress alone but requires a change of thinking at all levels. As scientists, we have a special responsibility and should take a leading role in communicating the need for urgent action to the public and decision makers.

The first part of this talk will highlight the alarming signals, which are meanwhile also clearly visible in Europe. Our climate exhibits the typical features of a strongly interconnected complex system, such as strong nonlinearities, positive feedback, and tipping points, which are characterized by massive irreversible changes and cascade effects. Due to the well-known exponential growth effects in complex systems, there is not much time left before the first tipping points are reached.

The second part of the talk addresses the question of what are the barriers towards change despite the striking evidence and what can be done. Based on examples from Kiel and our very active network *North European Network Nanotechnology* (NINa e.V., <https://www.nina-sh.de>) it will be shown that nanotechnology and new materials are key technologies to overcome the climate crisis. Emphasis, however, will be put on a more general view, ranging from the role of universities and the scientific community to our lifestyle. A sustainable lifestyle and a focus on what is important in life would not only improve our quality of life but also solve many other problems. This has particularly been demonstrated over the last years by Finland, which is the leading nation in terms of sustainability [1] and continues to have the happiest people worldwide [2].

As for the scientific community, we, a group of concerned researchers, recently founded the *International Alliance of Societies for a Sustainable Future* (<https://sfs-alliance.org>). Our vision is to establish an international scientific network as a tool to alert the general public worldwide to the sustainability crisis and to recommend measures for a socio-ecological transformation [3]. The alliance is not restricted to natural sciences and technology but aims to go through all disciplines across borders and cultures.

## References

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# Adaptive Low-temperature plasmas

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The uniqueness of low-temperature plasma is in its ability to change composition in situ. Plasma self-organization could lead to formation of coherent plasma structures. These coherent structures tend to modulate plasma chemistry and composition, including reactive species, the electric field and charged particles. Formation of coherent plasma structures allows the plasma to adapt to external boundary conditions, such as different cell types and their contextual tissues [1]. In this talk we will explore possibilities and opportunities that the adaptive plasma therapeutic system might offer. We shall define such an adaptive system as a plasma device that is able to adjust the plasma composition to obtain optimal desirable outcomes through its interaction with cells and tissues.

Various approaches for plasma therapy based on plasma adaptation to target conditions will be reviewed. These approaches are based on the ability of measuring the cellular response to plasma immediately after treatment and modifying the composition and power of plasma via a feedback mechanism. Plasma self-adaptation might be feasible due to self-organization and pattern formation when plasma interacts with targets. In this talk we present an optimal feedback control scheme to adjust treatment conditions responsive to the biological response as well as approaches based of artificial neural network [2,3]. In addition, we will discuss various modalities associated with cold atmospheric plasmas.

## References

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- [2] Li Lin and Michael Keidar, Artificial intelligence without digital computers: Programming matter at molecular scale, *Advanced Intelligent Systems*, 2200157 (2022).
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# Plasma Medicine – Knowledge and technology transfer FROM THE IDEA TO THE PRODUCT

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For more than two decades, plasma medicine has been developing worldwide into a new field of medical research at the interface between plasma physics and biosciences. Plasma medicine is the application of physical plasma for medical purposes. Plasma medicine represents an exciting and pioneering area of medical research and application. It uses physical plasma, an ionized gas produced by high energy input, to achieve therapeutic effects. This technology offers a wide range of potential applications, particularly in wound healing, fighting infections and cancer therapy.

The path from idea to market-ready product is characterized by numerous challenges. These include choosing the right legal form, raising capital, obtaining certification in accordance with the German Medical Devices Act (MPG), training employees and complying with strict quality management requirements (ISO 13485). The characterization and development of reliable plasma sources that are suitable for therapeutic applications is particularly challenging.

An essential element for the technological breakthrough in plasma medicine is the complete characterization of plasma sources. This includes the operating parameters, plasma physics, plasma effects and plasma diagnostics.

The lecture will present various areas of application for medical plasma, including wound healing, fighting infections and cancer therapy. Clinical studies demonstrate the effectiveness of cold atmospheric plasma in the treatment of chronic wounds, with a healing rate of 96.7%. The role of plasma in the inactivation of multi-resistant germs and in cancer therapy is also discussed.

Finally, the perspectives and future challenges of plasma medicine will be discussed. Future research work will focus on the continuous further development of plasma sources, the expansion of clinical trials and the development of new areas of application. The aim is to establish plasma medicine as an integral part of modern medical practice and thus make a significant contribution to improving patient care.

This presentation provides a comprehensive overview of current developments, challenges and successes in the field of plasma medicine and shows the path from scientific idea to successful, marketable product.

## Acknowledgments

Special Thanks to the University Medicine Greifswald for their support and collaboration. Special thanks to all researchers and partners involved in the plasma medicine projects.

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# Synthesis and Characterization of Oxide Materials

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Innovation in materials science and engineering resides in our ability to control the structure of materials at the nanoscale in order to design advanced materials with outstanding functional properties (electrical, optical, magnetic, photocatalytic, etc.). One of the most powerful means to arrange matter at the nanoscale is to use laser produced plasmas due to their exceptional ability to provide simultaneously ions and neutral atoms with various energies in a non-equilibrium environment. Moreover, the possibility to perform growth in a reactive environment such as oxygen or to operate in a double-beam configuration offers an additional flexibility to control the stoichiometry of oxide materials, the dopant content and the surface quality. In this presentation, we will focus on the use of pulsed laser deposition for the growth of various oxide materials in the form of thin films, including undoped and doped vanadium dioxide and titanium oxide. They are exploited for the development of the next generation of photonic devices or for advanced environmental applications such as water treatment.

# Thermal and plasma-assisted manipulation of copper oxide nanomaterials

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Copper based semiconductors represent a class of materials gaining attention for their potential applications in electronics and renewable energy technologies. Their unique electronic properties, such as tunable conductivity and bandgaps make them promising candidates for various applications, including solar cells, gas sensors, and other electronic devices. Furthermore, due to copper abundance, they represent cost effective alternative to expensive noble metal based materials in water splitting applications. Copper chalcogenide nanomaterials, particularly copper oxides and sulfides are ideal candidates for these applications. However, particularly for synthesis of copper sulfides, the control over material phase and morphology can be challenging. For that purpose, ion exchange transformations in ionic materials have proven as advanced methods for synthesis and manipulation of nanomaterials, enabling formation of metastable phases and morphologies and enhancing their properties for different applications. Numerous factors, ranging from experimental conditions to properties of initial material can influence the reaction mechanism and in this way alter the outcome of the transformation. Utilization of plasma for such transformation represents a new approach towards conducting ion exchange. In this research, CuO nanostructures were synthesized by thermal and plasma-assisted oxidation. Their growth was studied in detail and conditions for their growth were determined. Among CuO nanostructures, CuO nanowires were selected as a model material for exploring thermal and plasma-assisted exchange of oxygen ions with sulfur. Differences between the mechanisms observed in thermal and plasma-assisted transformation, were explored.

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# Application of Gray-Box Approach Using Machine Learning to Plasma Deposition

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Optimization and control of various processes using machine learning, quantum annealing, and other techniques are spreading. The main purposes of these techniques are to quickly understand and control the state of a process based on data, to discover problems, and to discover new possibilities. Machine learning and quantum annealing are black box approaches that do not provide information about the internal physical and chemical processes. Modelling, simulation, and analysis based on a set of differential equations describing conventional physical and chemical processes are white box approaches. Both approaches have their advantages and disadvantages. Here, we recommend the use of the gray-box approach, which is a mixture of the two approaches. Modelling, simulation, and measurement are performed in parallel with the application of machine learning to achieve the gray-box approach. Although the gray-box approach is more expensive than the black-box approach, but it is powerful not only for optimizing current equipment operation, but also for developing the next generation equipment, understanding similarities and differences among many equipment and processes, and realizing more advanced processes. For instance, we developed a hybrid machine learning technique by combining appropriate classification and regression models to address challenges in plasma deposition films, such as crystalline ITO (c-ITO), amorphous ITO (a-ITO), SiO<sub>2</sub>, DLC. The model predicted the boundary conditions of crystallinity and experimental conditions with high mobility for a-ITO films. Based on this model, we identified the boundary conditions between amorphous and crystalline crystallinity and thin film deposition conditions that resulted in a-ITO films with 30% higher mobility near the boundary than previous studies.<sup>1-3)</sup> The model identified key parameters and optimal sputtering conditions necessary for producing high-mobility a-ITO films. In my presentation, I will also show some other examples of the gray-box approach.

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# Plasma synthesis of advanced multifunctional nanoarchitectures for energy harvesting applications

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Emerging single- and multi-source environmental energy harvesters and nanogenerators are poised to revolutionise the landscape of Industry 4.0 and Smart Cities. However, further progress focuses on refining the design of functional nanomaterials and optimising their intricate synthesis and processing protocols. In this presentation, we will demonstrate the application of vacuum and plasma-assisted deposition techniques to process surfaces and thin films and 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 implementation of these nanomaterials as supported or in-device applications will be presented together with our latest accomplishments in the field of solar cells,<sup>[1-4]</sup> piezoelectric and triboelectric nanogenerators<sup>[5-7]</sup> and self-powered sensors.

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# Advanced Techniques for the Growth and Monitoring of Nano-Structured Carbon Materials in Plasma Environments

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The synthesis of nano-structured carbon materials, such as graphene, using plasma reactors is of growing interest due to the unique properties and potential applications of these materials. In this talk, we explore the growth of graphene in an atmospheric pressure microwave Ar/N<sub>2</sub> plasma with methane as a precursor gas, where carbon radicals are decomposed and rearranged into flowing sheets. Copper TEM grids are strategically placed along the plasma column to collect and analyze the material grown under varying methane flow rates and microwave power levels. Scanning Electron Microscopy (SEM) analysis reveals how particle diameter and density are influenced by proximity to the plasma source, with closer positions yielding smaller primary particles and higher particle counts, likely due to gas-phase merging as the particles cool. Adjustments in methane flow rate and microwave power are shown to significantly affect the length of the bulk plasma and, consequently, the primary particle size.

In parallel, we address a critical challenge in plasma-based synthesis—the need for precise gas temperature control, which is essential for optimizing the growth of carbon materials in the gas phase. Traditional methods for estimating gas temperature based on rotational transitions are often limiting, requiring spectrometric analysis that can be time-consuming and cumbersome. To overcome these limitations, we present the design and testing of a stand-alone 2-D optical sensor capable of real-time, in-operando gas temperature measurements. This sensor utilizes the emission intensity of specific rovibronic transitions of the C<sub>2</sub> Swan system, split into three color channels and analyzed through photodiodes/CCD sensors. By comparing the relative intensity of light in each channel to simulations based on Boltzmann statistics, we infer the rotational and vibrational temperatures with high precision. Together, these studies provide valuable insights into the growth mechanisms of graphene and other nano-structured carbon materials in plasma environments, while also introducing innovative tools for the real-time monitoring of critical process parameters, paving the way for more controlled and efficient synthesis processes.

# Development and applications of conformal aerogel-like oxide films by plasma deposition

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Developing new fabrication methods for nanostructural control is crucial to synthesizing rationally designed materials with enhanced properties.[1] In such a context, plasma-activated deposition methods have evolved during the last decade from a focus on compact thin films towards the controlled deposition of nanoscale materials, including nanoporous layers, low dimensional carbon materials, and complex one-dimensional nanostructures.[2,3] Advantages of these vacuum-plasma methods mainly rely in their straightforward scalability, low deposition temperatures, compatibility with an ample variety of substrates, and high accuracy in the composition (including doping) of the deposited materials as well as the control of their morphological characteristic as microstructure, texture or alignment.[2,3] However, a critical bottleneck for applying such procedures for depositing nanoscale materials is the limited availability of volatile metalorganic and metal halide precursors. On the other hand, although many examples of the synthesis of porous oxides by plasma CVD,[4-5] the fabrication of ultraporous layers as aerogels has been mainly limited to wet-chemistry deposition methods.

The present work establishes the bases for a vacuum and plasma-supported methodology for fabricating metal-oxide nanostructured layers with controlled microstructure using solid metal precursors, phthalocyanines, and porphyrins.[6-8] Combining remote plasma synthesis and plasma processing of the growing films at low or room temperature,[9] we have deposited conformal aerogel-like functional films of an ample variety of oxides. These films have direct applications in optics, photonics, and optoelectronics. The most advanced features of this method rely on its ample general character from the point of view of the material composition, crystallinity and microstructure, mild deposition and processing temperature and energy constrictions, and, finally, its straightforward compatibility with the direct deposition on processable substrates and device architectures. Examples of the fabrication of antireflection films, omniphobic surfaces, perovskite solar cell photoelectrodes, and thermochromic coating will be presented using this novel plasma-based approach that is directly scalable for industrial fabrication.

## Acknowledgments

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# Plasma diagnostics and modelling of NbC sputtering and deposition in HiPIMS discharges

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Non-reactive high-power impulse magnetron sputtering (HiPIMS) of NbC films from a single compound target is an attractive deposition method because of its simplicity and scalability. The film composition (C/Nb ratio), microstructure and, consequently, mechanical properties can be controlled by varying the power density in the pulse [1] which changes the degree of ionization of sputtered atoms in the discharge.

This work develops the general objective of understanding the complex relations between process parameters, discharge parameters and film properties in HiPIMS depositions. It focuses on explaining the observed change in the composition of NbC films ranging from C-rich to stoichiometric, corresponding to an increase in the pulse-averaged power density. The Nb and C atoms sputtered from the target are under the influence of multiple processes that together affect their transport towards the substrate (sputtering, scattering off the process gas atoms, ionization in the high-density plasma and return of ions onto the target or loss of ions to chamber walls). Plasma diagnostics (mass spectroscopy and optical emission spectroscopy) and plasma modelling are used to evaluate the ratios of Nb and C neutral and ionic species near the target and at the substrate position [2]. Moreover, a newly developed particle-based Monte Carlo simulation is used to analyse in detail the transport of Ar, Nb and C species in the HiPIMS discharge.

It is found that C<sup>+</sup> is almost negligible in the deposition flux while Nb<sup>+</sup> and Nb<sup>2+</sup> ions contribute significantly. Moreover, a high density of Nb species in the discharge plasma contributes to the scattering of sputtered C atoms which is one of key factors explaining the observed change in film composition.

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# Early-Stage Silver Growth on SiO<sub>2</sub> and Polystyrene deposited by DCMS, HiPIMS and Bi-Polar HiPIMS

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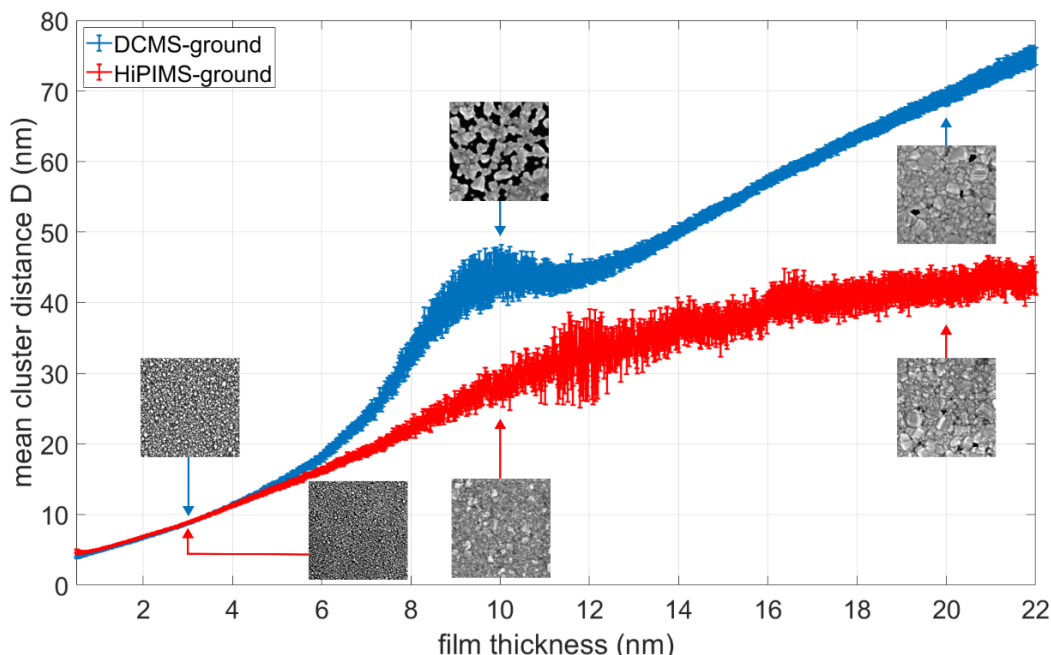
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Silver thin films integration in optoelectronic devices is gaining interest due to their excellent conductivity, high optical transparency and compatibility with flexible substrates. High-power impulse magnetron sputtering (HiPIMS) with/without further ion acceleration is explored to overcome limitations of conventional direct current magnetron sputtering (DCMS) due to the formation of islands during early stages of film growth. SEM and 2-point probe measurements analyze layer morphology and electrical properties of the silver thin films on SiO<sub>2</sub> and polystyrene substrates [1]. Additionally, in-situ grazing-incidence small-angle X-ray scattering (GISAXS) is utilized to track growth evolution [2]. The results show different growth regimes for DCMS and HiPIMS, where HiPIMS results in a higher surface coverage, lower percolation threshold and lower surface resistance, further enhanced by ion acceleration [1]. This study highlights HiPIMS potential for fabricating ultrathin conductive layers on organic and oxide substrates without the need of extra fabrication steps [3].



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# In-flight Synthesis of Individual Atoms Via Atmospheric Pressure Non-Equilibrium Plasma

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The introduction of low-dimensional materials, such as 2D materials[1,2] and Quantum Dots[3], has revolutionized materials science, enabling the development of materials with highly desirable properties. However, reducing dimensionality to gas-phase synthesize atomic-scale materials is extremely challenging, particularly at atmospheric pressure[4-6]. In this study, we developed a gas-phase non-equilibrium plasma method at atmospheric pressure to synthesize individual atoms. High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM), and Energy Dispersive Spectroscopy (EDS), confirmed the deposition of individual bismuth (Bi) atoms on graphene oxide layers. Using Optical Emission Spectroscopy (OES), we demonstrated that the interaction between plasma-generated species and metal wire can lead to the formation of individual atoms and clusters. These results suggest that atmospheric pressure plasma can be a novel and effective method for in-flight synthesis of individual atoms in atmospheric pressure, with exciting applications in single atom catalysis and magnetism.

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# Atmospheric plasma helix jet for the generation of functionalised semiconductor and metal nanoparticles

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Generation of nanoparticles with the help of non-thermal atmospheric plasma jet has been studied in radio frequency HelixJet [1]. This plasma source with electric field in both perpendicular and parallel direction relative to the gas flow can generate non-equilibrium plasma with relatively large volume, reducing the negative effect connected to deposition of material on the jet walls and increasing the material throughput. We have applied this jet to generate semiconductor silicon nanoparticles (NPs) from silane precursor [2] and metal NPs from wire precursor in the form of additional grounded electrode on the jet axis [3]. NP generation under atmospheric pressure conditions allows the use of particle sizers for fast determination of NP size distribution and the convection-dominated transport enables modular combination of several plasma sources for NP surface treatment or implementation of an annealing stage for thermal treatment leading for example to reproducible formation of Janus NPs [4]. This contribution will report on these processes and on the latest results obtained with the HelixJet.

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# Electrifying the Future: Non-Thermal Plasmas for Revolutionizing Goods Production

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Plasmas, also called gas discharges, are one of the unsung heroes of modern science and engineering. In addition to being used for important scientific discoveries throughout history – such as the discovery of argon – one class of plasmas, called non-equilibrium or non-thermal plasmas, have also formed the backbone of many technologies that sustain the modern world, from microelectronics to lighting. Recently, a number of advances have shown that the non-equilibrium environment in the plasma is well-suited to overcoming challenges across a wide variety of domains, leading to a number of emerging areas where plasma engineering is well-posed to make important contributions over the next several decades. One area where non-thermal plasmas can be impactful is in replacing thermal processes in industrial goods production, from chemical production to manufacturing. Replacing thermal processes that rely on fossil fuel-based heating sources with non-thermal plasmas that can be generated from renewable electricity is one step to de-carbonizing industrial practices. Two areas will be overviewed in this talk: using non-thermal plasmas for chemical production, either via liquid-phase plasma electrochemistry or gas-phase plasma catalysis, and integrating non-thermal plasmas into emerging additive manufacturing technologies, such as aerosol jet printing. Recent results from our research group will be overviewed that highlight advances in both areas as well as needed research and development to move the field toward practical technologies.

# Plasma-assisted catalysis at atmospheric pressure

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Today, energy-efficient and decentralized performance of catalytic reactions, such as the production of ammonia, has become even more important. Plasma-assisted catalysis can help achieve these goals as it is available on demand and operates without the need for enormous external heating, such as is required for ammonia synthesis. Therefore, non-equilibrium plasmas at atmospheric pressure are used to dissociate gaseous molecules, which can then react at the surface of the catalyst to form the desired products [1]. Atmospheric pressure plasma-assisted catalytic reactors are often realized by packed bed reactors, in which the catalyst is packed into or deposited on millimeter-sized spheres [1-3]. However, these millimeter-sized spheres are not feasible for all types of possible catalysts.

Therefore, plasma reactors for plasma-assisted catalysis have been constructed and tested with and without different catalysts for in-plasma catalysis, where the catalyst is in direct contact with the plasma, and for post-plasma catalysis, where only reactive species from the plasma reach the catalyst. Different types of possible catalysts are being tested, such as MOFs or cobalt-based inorganic catalysts. Dielectric barrier discharges operated at kHz frequencies are used for ammonia synthesis using N<sub>2</sub> and H<sub>2</sub> as working gases and for methane formation experiments using CO<sub>2</sub> and H<sub>2</sub>. Mass spectrometry is used to identify the products formed. Depending on the reactor type and working gas, the gas temperature during plasma operation ranges from room temperature up to 200 °C. In order to compare the results of plasma-assisted catalysis with those of purely thermal catalysis, an externally heated setup has been developed. It can be shown that the products observed during plasma-assisted catalysis do not originate from thermal catalysis.

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# Enzyme catalyzed CO<sub>2</sub> conversion supported by nanosecond-pulsed DBD

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The rising concentration of carbon dioxide (CO<sub>2</sub>) in the atmosphere, primarily caused by the combustion of fossil fuels and global industrialization, necessitates the development of innovative technologies for effective CO<sub>2</sub> reduction and utilization. Non-thermal plasma (NTP) has been reported as a promising approach for the conversion of CO<sub>2</sub> at atmospheric pressure and room temperature [1, 2].

In this work, a NTP assisted enzyme catalytic approach was used for CO<sub>2</sub> conversion to CO and formic acid. Despite a vast number of examples for the use of enzyme-catalyzed reaction and plasma-mediated syntheses of substances a combination of both processes, despite their respective high potential gain, is rarely investigated and thereby of high risk [20, 21]. It was observed that direct exposure of enzymes to plasma treatment might lead to reduced enzyme activity, potentially due to factors such as enzyme inactivation, substrate limitation, or degradation of the product by short-lived plasma species.

In our own experiments the plasma process and enzymatic reaction occurs directly and in the same volume within the process. The reduction of CO<sub>2</sub> with H<sub>2</sub> for the synthesis of formate ions using the enzyme formate dehydrogenase from *Candida boidinii* was supported by a Dielectric Barrier Discharge (DBD) reactor. The enzyme was immobilized on a porous solid support (beads) either by adsorption or covalent bonding. Our findings indicate that the covalent immobilization is more efficient, allowing the enzymes to remain active over long exposures with/in plasmas. The experiments were conducted using different ratios of H<sub>2</sub> and CO<sub>2</sub>, namely 1:1 and 1:3, both with and without the presence of 20% Argon and in presence of deionized water within a coaxial DBD reactor which was operated with positive nanosecond high-voltage pulses of 500 ns duration and 20 kV amplitude at a repetition rate of 1 kHz. The reactor volume was filled with a mixture of immobilized formate dehydrogenase as enzyme preparation and (non-reactive) beads. The inclusion of immobilized enzymes led to a substantial increase from 0.07 to 0.73 mg/L in formate formation in the liquid. This enhancement was observed compared to samples containing only beads and deionized water, without any immobilized enzymes in the reactor. Additionally, obtained results indicated that the rise in the concentration of enzyme in the solution from 90 mg to 360 mg led to an increase in the formation of formate by the factor of approximately 3 that showcases the possibility for further up-scaling. Noteworthy, in this particular application, even the addition of the rather costly cofactor NADH was not necessary as an electron donor for the underlying enzyme reaction. The findings contribute to the development of efficient plasma-based CO<sub>2</sub> reduction processes.

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# In-situ Plasma Studies using a Direct Current Microplasma in a Scanning Electron Microscope

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A scanning electron microscope (SEM) enables structural and chemical investigations of materials from the mm- down to the nm-scale. In this work, we incorporated a DC microplasma inside an SEM [1]. For the first time to our knowledge, we were able to perform microscopic electron-based imaging while treating the sample with a plasma at the same time. In our setup, a metal tube with a small orifice at the end is introduced in the vacuum chamber of the SEM. This tube is connected to the outside of the microscope where it is connected to a gas cylinder. At the same time, the metal tube is powered by a DC power supply and placed close (ca. 100  $\mu\text{m}$ ) to the grounded sample. By applying a sufficiently high voltage, a stable DC glow plasma was formed. Furthermore, we were able to acquire true in-situ SEM images of the sample being treated by the plasma, where we could obtain a real-time view of the sputtering characteristics of the plasma [2]. Moreover, energy dispersive X-ray (EDX) spectroscopy enabled the visualisation of the elemental composition of the sample, which was acquired quasi in-situ, between plasma treatments. These analyses illustrated the oxidative properties of a CO<sub>2</sub> plasma affecting a Cu surface. Finally, the polarity of the powered electrode was reversed. Hereby, the positive ions accelerated toward the nozzle, sputtering the steel orifice and depositing some of that material on the sample. At the same time, the sputtering of the sample was eliminated and the oxidation by CO<sub>2</sub> plasma was observed for a broad area.

This work reports the technical details and requirements for achieving true in-situ SEM analyses. The characteristics of the plasma are studied, and the properties of the setup are analysed. This work serves as a stepping stone toward more advanced plasma diagnostic techniques, as well as potential novel applications. A number of paths forward are envisioned, for example the addition of an optical fibre for spectroscopic analyses, EDX analyses of the plasma discharge, analysis of the downstream gas composition, incorporating different types of plasma (e.g., dielectric barrier discharge), and more.

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# Operando-DRIFTS investigations on non-thermal plasma induced generation of CO from CO<sub>2</sub>: Experimental Set-up and preliminary results

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The conversion of the greenhouse gas CO<sub>2</sub> to value-added chemicals and fuels (e.g., CO, CH<sub>4</sub> and MeOH) by non-thermal plasmas (NTPs) is a promising route to reduce CO<sub>2</sub> emissions and contributes to sustainability and carbon neutrality. The combination of plasma with heterogeneous catalysts (plasma-catalysis) can contribute to a significant enhancement of both CO<sub>2</sub> conversion and energy efficiency<sup>[1,2]</sup>, but the fundamentals of interactions occurring are not yet fully understood. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is a highly sensitive method for the detection of intermediates adsorbed on solid catalyst surfaces and can be used for the *in situ* analysis of adsorbates on the catalyst surface. Herein, we present the development of a customized NTP-DRIFTS cell based on the established Harrick reaction cell, which integrates a miniaturized dielectric barrier discharge (DBD), implemented in a Bruker Invenio S FTIR spectrometer. The stable operation of AC-driven (10 kHz), filamentary, asymmetric DBDs in binary gas mixtures of argon and CO<sub>2</sub> is monitored by means of electrical measurements, which also allow the determination of discharge power. The impact of applied discharge voltage under the variation of the gas composition, gas flow, catalyst pretreatment procedure and the distance between electrode and catalyst bed have been studied. First results with ceria as a promoter for plasma-induced CO<sub>2</sub>-splitting show that oxidative and reductive pretreatment only affects the population of adsorbates with a slight effect on products formation. The variation of CO<sub>2</sub> concentration has no influence on adsorbates formation whereas low flow rates lead to higher concentration of formate adsorbates. The distance between the electrode and the catalyst bed has an impact on the composition of adsorbates and CO<sub>2</sub>-conversion.

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# Microwave discharge modeling in Argon and Hydrogen

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Microwave confined atmospheric plasma is an increasingly prevalent plasma source for both industrial and scientific applications due to its attractive features such as electrodeless operation capability, high energy efficiency, and adaptability to diverse operational conditions. However, designing efficient and controllable systems for research presents significant challenges. To address these challenges, this study employs a time-dependent modeling approach. The data derived from this methodology are then utilized to perform illustrative fluid simulations of Argon and Hydrogen microwave plasmas. The computational findings in both two-dimensional and three-dimensional domains provide a comprehensive understanding of microwave plasma using an electromagnetic model coupled with a heat transfer model within a laminar flow regime. These simulations elucidate the well-established electric field behaviour in the presence of plasma and offer valuable insights for the design and optimization of microwave plasma-based systems.

## Acknowledgments

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# Investigation of the Ionization Region in a Magnetron Plasma of a Gas Aggregation Source for Cluster Formation

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A global (volume averaged) model is developed for the ionization region of a gas aggregation source (GAS) plasma [1,2]. The case of using argon gas and a copper target is considered. The proposed model describes the densities of thermal and hot electrons, argon and copper ions, copper atoms and argon atoms in different excited states, the temperature of thermal electrons, the kinetic energies of the bombarding ions to the target, the sheath width near the target cathode and the energy fluxes by different plasma species to a planar probe (substrate) in the ionization region. Also, the fraction of input power is estimated which is dissipated to energize the thermal electrons in the region investigated.

The gas discharge properties are analysed for different gas pressures and discharge currents under conditions corresponding to experimental conditions [3]. The calculated dependences on pressure and current for the GAS properties are used to explain the measured dependences for the deposition rate and the energy flux. It has been found that the deposition rate increases with increasing discharge current because of the increasing fluxes of copper atoms and ions. With increasing pressure, the deposition rate decreases due to drop of the densities of copper atoms and ions which is a result of the decreasing kinetic energy of the ions with which they bombard the copper target.

The model indicates that in the relevant pressure regime, typical for GAS, the energy flux by the ions dominates in comparison with the energy fluxes of the other plasma species.

## Acknowledgments

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# Gas aggregation for Cu<sub>3</sub>N nanoparticle formation using a cylindrical post-magnetron

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Copper nitride (Cu<sub>3</sub>N) attracts great scientific attention due to a relatively narrow bandgap in the range of 1.2 eV – 2 eV, which is helpful for visible light absorption. The efficient formation of electron-hole pairs in Cu<sub>3</sub>N has also been successfully demonstrated. This makes the material attractive in different applications, including optics and photocatalysis. Nanoparticles (NPs) of Cu<sub>3</sub>N are of particular interest in applications requiring a high specific area. Nevertheless, the methods of synthesis of Cu<sub>3</sub>N NPs are now limited to chemical approaches, which barely meet the demands of sustainability and require additional purification and filtration steps.

Magnetron sputtering is a well-known technique used to fabricate Cu<sub>3</sub>N in the form of thin films. In the current work, this method, for the first time, was combined with the gas-phase aggregation to fabricate Cu<sub>3</sub>N NPs. Gas aggregation sources are convenient devices for the clean, environmentally friendly, and controlled preparation of NPs. Usually, planar magnetrons were used; however, in our case, we employed a custom-made tubular post magnetron with a rotating magnetic circuit. First, we used the tubular magnetron installed co-axially to the gas flow for the deposition of mono-metallic Cu NPs and bi-metallic CuAg NPs. It turned out, however, that the perpendicular arrangement is preferential as it gives a narrower size distribution than in the co-axial case. Different mixtures of Ar and N<sub>2</sub> have been used to vary the chemical composition of resulting NPs. It has been found that the deposition in pure N<sub>2</sub> results in cubic-shaped and stoichiometric Cu<sub>3</sub>N nanoparticles. They are thermally stable until 200 °C under the ambient atmosphere, transforming to CuO at higher temperatures. The photocurrent measurements irradiating NPs deposits with a solar simulator confirmed the semi-conducting nature of these nanoparticles. Further perspectives of gas-aggregated Cu<sub>3</sub>N NPs are outlined.

# New insights into plasma parameters in a dual-frequency capacitively coupled rf discharge

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The standard (industrial) frequency for common rf plasmas used in technology and its applications is 13.56 MHz. The gas pressure and, due to the geometrical asymmetry of the device, the dc self-bias mainly determines the plasma sheath extent as well as the potential and, thus, the ion current density and the ion energy towards the electrode or substrate surface. An independent control of these important properties - especially in industrial applications, e.g. etching, coating etc. - is desirable but usually not possible. By adding a second frequency (2nd harmonic, 27.12 MHz), a so-called electrical asymmetry effect (EAE) is created, which enables the control of the bias voltage and, thus, the ion energy almost independent of the ion flux by varying the phase angle between the two harmonics, while other discharge parameters, e.g. gas pressure, stay constant [1,2]. An extended characterization of this dual-frequency (2f) plasma is crucial for its optimization and improvement of its applications.

In this work, we focus on the diagnostic of a dual-frequency capacitively coupled discharge at 1 Pa and 3 Pa argon gas pressure using a passively compensated Langmuir probe (LP) [3-5]. Two plasma chambers with different degrees of geometric asymmetry are subject of investigation. Floating potential, plasma potential, electron temperature and electron density are measured for various phase angles between 0°– 180° in these two reactors to conduct a cross-chamber validation of parameter trends.

Similar to the dc self-bias, the plasma parameters show a pronounced dependence on the phase. Their general behavior can be explained by phase-dependent sheath expansion dynamics as shown by PIC/MCC simulations, where beams of electrons are generated by the respective expanding sheath and accelerated into the plasma bulk, leading to phase-dependent electron temperature and density [6,7]. However, the measured profiles of the density and temperature as a function of phase in both experimental setups are not symmetric around  $\theta = 90^\circ$ , unlike the dc self-bias. This observation is confirmed by PIC/MCC simulations, which reveal asymmetrical electron excitation/ionization dynamics at the corresponding phases [8]. This implies that the observed trends are a property of the 2f discharge in combination with a geometric asymmetry of the device. These new insights into the behavior of important plasma parameters in a dual-frequency discharge contribute to the controllability of plasma processes, such as surface treatment or fabrication of coatings.

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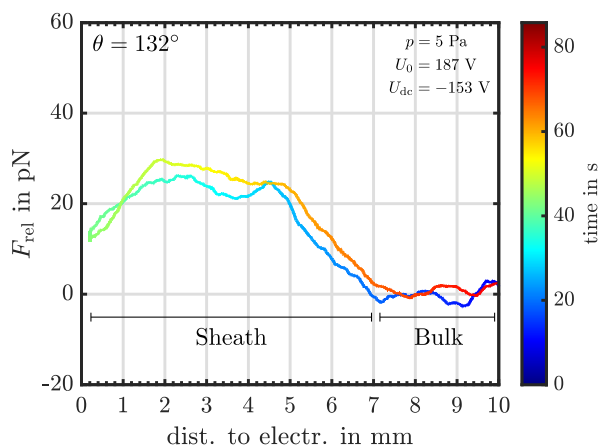
# Optically trapped microparticles in a dual-frequency capacitively coupled rf discharge

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Many different diagnostics can be used to measure the spatial distribution and temporal evolution of plasma parameters. Over the past decade, the concept of utilizing externally injected microparticles as non-invasive probes, influenced by various forces and energy fluxes in plasmas, has been implemented. Information about local electric fields [1], energy fluxes towards the particles [2], and momentum transfer by ions to the particles [3] can be obtained based on their behavior in the surrounding plasma. Especially, the manipulation of microparticles by an optical tweezer is of great interest, as it enables the microprobe to be positioned in areas of the plasma that are typically inaccessible by conventional diagnostic methods, such as the plasma sheath.



**Figure 1:** The graph shows the measured relative force profile obtained by the use of an optically trapped microparticle for a certain pressure  $p$  and a specific dc self-bias  $U_{dc}$  and phase angle  $\theta$  in a dual-frequency discharge. The electrode surface is positioned at 0 mm. The color gradient illustrates the time required for the measurement.

phase angle between the two harmonics, the extent of the sheath, as well as the particle charge evolution within the sheath are obtained.

In this study, optically trapped microparticles in an optical tweezer are used to investigate the sheath of a dual-frequency CCRF discharge. This type of discharge is known, in particular, for its ability to control the ion flux and the ion energy almost separately based on the utilization of electrical asymmetries in the plasma [4,5]. It is generated by a superposition of two consecutive harmonics with variable phase angle between them.

The crucial parameter to measure when employing optical tweezers is the external force acting on the microprobe. This force is determined by observing the displacement of the particle within the optical trap. The confined microprobe is moved through the plasma and the sheath, thereby moving relative to the discharge [6].

On the basis of the determined force profiles (Fig. 1), the strength of the electric field force in the sheath as a function of gas pressure and

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# Carbon Dioxide Splitting in Dielectric Barrier Discharges: Scaling with the Specific Input Energy

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The conversion of carbon dioxide (CO<sub>2</sub>) to carbon monoxide (CO), oxygen and ozone in planar volume dielectric barrier discharges (DBDs) is studied. In particular, the energy yield (EY) of CO formation is evaluated. The influence of the type of the electrode, the barrier material, the barrier thickness, the discharge gap, the presence of a CeO<sub>x</sub> coating on the dielectric, the flow rate, the high voltage frequency and amplitude as well as the electrode area have been varied systematically. However, the EY results in similar values of about 25 g/kWh in pure CO<sub>2</sub> within the specific input energy (SIE) range 20 – 2,000 J/L, independent on the above mentioned parameters [1]. SIE higher than 3,000 J/L yield a slightly lower EY of about 22 g/kWh. Based on the EY a comparison with various other DBD-reactors is done and the role of SIE as a scaling parameter is discussed. According to Hegemann [2], the SIE is a microscopically and macroscopically defined parameter governing the energy transfer by the electric field to the molecules via inelastic collisions. Similar as in [3], the CO formation also scales with the total number of charges being transferred through the discharge during the residence time of the gas.

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# How do you select your nanoparticle synthesis process in the plasma-in-liquid aisle of your supermarket?

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In our consumer-driven society, the variety of plasma methods for synthesizing nanoparticles rivals the array of yogurt brands in a supermarket's chilled section. Specifically focusing on plasmas in liquids, numerous solutions exist, each with distinct features and limitations. These methods generally fall into two categories: "solution plasma" and "glow-discharge electrolysis," although there's often overlap in terminology [1]. The primary difference lies in the applied voltages, typically below or above ~1 kV, corresponding to interelectrode gap distances below or above ~1 cm. This division arises from the use of different DC power supplies, providing either high pulsed voltages or low continuous voltages.

The predominant method for nanoparticle synthesis is "solution plasma," albeit known by various names. This approach involves generating a discharge between metallic electrodes submerged in an electrolyte, possibly containing chemicals. Electrode erosion and electrolyte reduction can be employed individually or in tandem to produce nanoobjects and hierarchical structures.

The discharge process can also induce defects and activate the surface of existing nanoobjects in the liquid medium. Originating from proposals by Takai [2] and Saito [3], this method involves two wire electrodes, partially insulated, immersed in a conductive electrolyte and subjected to pulsed DC high voltage (usually around 1 kV), with frequencies typically in the kHz range and pulse widths of about one microsecond. If the electrodes are hollow or surrounded by pipes, gas (such as N<sub>2</sub> or Ar) can be blown through, creating a bubble connection. The solution is typically stirred at a few hundred revolutions per minute and parameters like pH, electrical conductivity, and temperature can be controlled, influencing nanoparticle characteristics, which heavily depend on applied current densities. The alternative technique, termed "glow-discharge electrolysis," requires voltages exceeding those for typical electrochemical processes, typically in the tens of volts range. Electrodes are spaced several centimetres apart, and liquid conductivity must be sufficient to conduct charges. As voltage rises, so does current in the solution, forming a gaseous envelope around the electrodes due to reaction evolution. When this insulating envelope becomes continuous, current flow ceases, leading to breakdown and discharge appearance. At this transition, the current initially drops, then gradually increases, albeit slower than before, with increasing applied voltage [4].

With these various processes, it becomes feasible to generate nanoparticles with diverse characteristics. We will delineate which solution is best suited for producing a range of nanostructures, including nanoparticles with narrow size distribution, nanowires, nanosheets, non-equilibrium alloys, multi-component alloys such as high entropy alloys, etc. Furthermore, we will illustrate how artificial intelligence can significantly advance the creation of nanoparticles with desired properties, akin to the strategy one might employ in selecting yogurt in the future.

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## Vapor phase deposited metal-polymer nanocomposite thin films for biomedical applications

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Functional metal-polymer nanocomposites are required for highly tailored surface properties. However, past approaches like cosputtering, physical evaporation or plasma polymerization could not retain the functionality of the polymer matrix or produce tailored nanoparticles. In this study we present a new kind of single step codeposition of nanocomposite polymer thin films via the combination of a gas aggregation cluster source (GAS) and initiated chemical vapor deposition (iCVD) without breaking the vacuum. iCVD of polymers delivers ultraprecise and defect-free thin films on the nanoscale while a GAS creates nanoparticles that form in the gas phase and are thus surface independent. In this study a PTFE polymer thin film that includes silver nanoparticles is deposited in an automatized self-built vacuum reactor setup. The first of its kind deposited material proved applicable in antibacterial, antiviral and anticancer applications. This new kind of codeposition allows the fabrication of functional nanocomposite thin films combining the advantages based on the growing iCVD monomer palette as well as functional nanoparticles by GAS.

# Near-plasma Chemistry: a Novel Approach in Plasma Surface Engineering

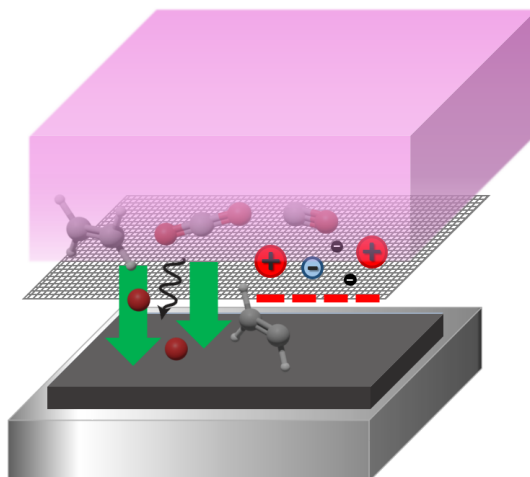
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Avoiding ion bombardment during plasma surface engineering, while simultaneously benefiting from the contribution of reactive plasma species, is a targeted objective for materials processing. In this regard, experimental configurations such as afterglows or remote plasmas have been designed [1]. However, when samples are located with increasing distance from the plasma in these configurations, the number of all interacting plasma species is reduced, not just the high-energy plasma components. In this context, we have recently developed a new experimental strategy called near-plasma chemical (NPC) surface engineering [2]. By introducing a polymeric mesh between the substrate and the plasma, close to the plasma-sheath boundary, charged particles are attracted to the mesh. As a result, unlike direct plasma exposure, high-energy deposition at the sample surface is avoided without modifying the plasma properties. The beneficial impacts of NPC have been demonstrated for plasma activation of polymers to enhance wettability and durability, as well as for the plasma polymerization of siloxanes to obtain nanoporous SiO<sub>x</sub> coatings [2]. Furthermore, NPC can prevent dust deposition onto the samples, even in highly dusty plasmas, resulting in smooth surfaces at the nanoscale [3]. NPC surface engineering thus offers highly defined plasma chemical modifications at the surface, promising precise tuning of surface properties at room temperature.



Scheme of the Near-Plasma Chemistry approach: a polymeric mesh introduced between the substrate and the plasma extracts ions, while all other plasma species can reach the substrate.

## Acknowledgments

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# Plasma-assisted Fabrication of Functional Coatings for Photonics Applications

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Silicon nitride (SiN<sub>x</sub>) based films have been recognized as essential dielectric films in the microelectronics and optoelectronics industry due to their desirable properties, such as high electrical insulation, excellent thermal stability, and compatibility with integrated circuit fabrication processes. They serve as effective host materials for rare-earth dopants [1] and are also a potential candidate for fabricating wavelength-selective reflective coatings and surface passivation layers in building-integrated photovoltaics (BIPV) technologies. SiN<sub>x</sub>-based films are one of the popular choices for anti-reflective coatings in photovoltaics as well. Recently, SiN<sub>x</sub> and oxynitride (SiO<sub>y</sub>N<sub>x</sub>) based thin film optical filters have been explored to provide distinct color rendering to solar-charged EVs [2], replacing the anti-reflective coating in standard solar cells with a custom-designed notch filter, which ensures high transmission across the solar spectrum and creates a distinct color rendering effect in the visible range, making the cells more visually appealing.

Notch filters can be designed using a rugate filter structure consisting of continuously modulated refractive indices or a repetitive two-material stack of alternating high and low refractive index materials with precise thickness, known as the standard two-material technology (S2MT). We used OptiLayer to simulate our S2MT designs. The gradual evolution optimization technique was used to obtain the structures. We explored three color ranges represented by reference wavelengths of 400 nm, 550 nm, and 632 nm. Detailed analysis of various design parameters and their physical limitations will be presented.

Our designs were realized using electron cyclotron resonance plasma-enhanced chemical vapor deposition (ECR-PECVD) and Radical Assisted Sputtering (RAS) with three material pairs - Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> (index ratio 1.71), SiN<sub>x</sub>/SiO<sub>x</sub>N<sub>y</sub> (index ratio 1.38), and Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> (index ratio 1.21). The structures were characterized using variable angle spectroscopic ellipsometry and Cary spectroscopy. A detailed comparison of our simulation and fabrication results will be presented.

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This work was funded by the NSERC CREATE TOP-SET program (NSERC Award Number 497981) and an NSERC Discovery Grant (Grant No. RGPIN-2019-06023). The authors thank Iridian Spectral Technologies Ltd, an IDEX Corporation, for access to the RAS fabrication process.

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# Plasma-derived nanogranular matter for brain-inspired electronics

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Brain-inspired electronics aims to replicate functionalities of biological neural systems, such as highly parallel processing, pattern recognition and pattern separation, distributed sensing and in-memory data processing. To accomplish bio-inspired functionalities in a robust and efficient way, there is a high demand to explore novel hardware approaches.

One particularly promising approach to obtain brain-inspired electronics with neuromorphic properties is to employ nanoobjects as building units for self-ordered networks. This contribution will highlight gas phase synthesis of nanoparticles with tailored morphologies and showcase their organization towards percolated nanogranular networks. The contribution points out different pathways to fabricate metal, metal-oxide and composite nanoparticles and elucidates the applicability of segmented targets in a magnetron-based gas aggregation source. In the context, a custom-developed magnetron source with concentrically reconfigurable erosion zone is discussed. [1]

A particular focus is put on the resistive switching properties in nanoparticle assemblies and their brain-inspired functionalities. Reconfigurable current paths, both in electrophoretically arranged nanoparticle assemblies in liquid media [2] and in solid-state, two-dimensional nanoparticle networks are investigated. For the latter, a scanning electron microscopy approach featuring complementary information from resistive contrast imaging and passive voltage contrast is presented, opening up new pathways to understand current path reconfiguration in nanogranular networks. [3]

## Acknowledgments

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# Silicon nitride membrane as entrance window for plasma-induced VUV radiation

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Vacuum-ultraviolet (VUV) radiation is crucial for several applications including the biomedical field [1], lithographic processes [2], material modifications [3], and photocatalysis [4]. A fundamental problem, especially outside of vacuum environments, is the transfer of the VUV radiation from its origin to the to be treated sample. Furthermore, the diagnostic of VUV radiation sources operated at atmospheric pressure, like microplasmas or plasma jets, is heavily aggravated by the necessity to transfer the photons into a vacuum environment. Typical window materials like LiF or MgF<sub>2</sub> are not suited for this transfer due to their cut off wavelength at 115 nm [5].

Different approaches have been pursued in the past involving pneumatic valves [6], differential pumping [7], or an aerodynamic window [8]. All these approaches are coming with different challenges and drawbacks. A new solution to overcome this transfer problem is presented by utilizing thin Si<sub>3</sub>N<sub>4</sub> membranes originating from transmission electron microscopy (TEM). These membranes are stable enough to withstand the pressure gradient between one atmosphere and a vacuum environment, while being thin enough to transmit VUV photons. Further, Si<sub>3</sub>N<sub>4</sub> membranes have been shown to be resistant to plasma and plasma-generated species [9,10], and therefore should be well suited for use as either an entrance or exit window for plasma-induced VUV radiation.

For precise diagnostics and applications knowledge about the transmission of the Si<sub>3</sub>N<sub>4</sub> membrane is necessary. Further, the interaction of the Si<sub>3</sub>N<sub>4</sub> membrane with VUV photons and plasma-generated species is key, as all induced changes to the Si<sub>3</sub>N<sub>4</sub> membrane will directly influence the transmission and stability [11].

First results reveal not only interesting self-absorption effects of noble gases influencing previously reported VUV spectroscopy measurements, but also modifications of the Si<sub>3</sub>N<sub>4</sub> membrane that may open pathways to the production of thin oxide films from nitrides.

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## Notes

## Notes

iPlasmaNanoXIII 2024, Hamburg

	Sunday 15. Sept.	Monday 16. Sept.	Tuesday 17. Sept.	Wednesday 18. Sept.	Thursday 19. Sept.
8:50		Welcome			
9:00		1	2	3	4
9:15		Anthony	Shiratani	Go	Belmonte
9:30					
9:45		1	11	18	28
10:00		Shukurov	Sanchez-Valencia	Sgonina	Strunskus
10:15		2	12	19	29
10:30		Felizardo	Ruzic	Brüser	Navascués
10:45		Coffee break	Coffee break	Coffee break	Coffee break
11:00		3	13	20	30
11:15		Cvelbar	Barranco	De Meyer	Mascher
11:30		4	14	21	31
11:45		Chiang	Kozák	Fuentes	Vahl
12:00		5	15	22	32
12:15		Marath	Reck	Radovanov	Hansen
12:30		Lunch	Lunch	Lunch	Lunch
12:45					
13:00					
13:15					
13:30					
13:45					
14:00		6	16	23	
14:15		Faupel	Khatibi	Kersten	
14:30		7	17	24	
14:45		Keidar	Benedikt	Nikitin	
15:00		8	Coffee break	25	
15:15		Weltmann		Schneider	
15:30		Coffee break		Coffee break	
15:45		9	Excursion Airbus	26	
16:00		Chaker		Niemann	
16:15		10		27	
16:30		Košiček		Brandenburg	
16:45	Registration				
17:00					
17:15					
17:30					
17:45					
18:00	Welcome reception				
18:15					
18:30					
18:45					
19:00				Dinner	Conf. dinner