

16th International Workshop on Electrodeposited Nanostructures

EDNANO-16

10-12 April 2025

Florence

Organizing Committee

The organization of EDNANO-16 is chaired by Walter Giurlani, Massimo Innocenti and Marco Pagliai together with Claudio Fontanesi, Antonio De Luca, Marco Bonechi, Giulio Pappaianni, Fabio Biffoli, Elena Mariani, Claudia Giovani, Francesco Montanari, Samuele Mistretta and all the other members of the Laboratory of Applied Electrochemistry

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FULL PROGRAM

Room 209 of the teaching centre "Scuola di Studi Umanistici e della Formazione - Università degli Studi di Firenze", Via Laura, 48, 50121 Firenze (FI), Italy.

Thursday April 10th 2025

8:00 – 9:00	Registration
9:00 – 9:30	Opening Ceremony
I Session – Chair Walter Giurlani	
9:30 – 9:50	(Opening Talk) Electroplating in Today's World Luca Magagnin – <i>Politecnico di Milano, Italy</i>
9:50 – 10:05	Propeline, a green electrolyte for precious metals electrometallurgy? Sophie Legeai – <i>University of Lorraine, France</i>
10:05 – 10:20	Thermoelectric nanowire structures as integrated sensors in composite materials Laurent Gravier – <i>University of Applied Sciences and Arts Western Switzerland, Switzerland</i>
Coffee Break & Poster Session	
II Session – Chair Andreas Bund	
10:50 – 11:10	(Opening Talk) Electroplating of special metals: On the way towards 5-component high-entropy alloys László Péter – <i>HUN-REN Wigner Research Centre for Physics, Hungary</i>
11:10 – 11:25	Pulsed reverse electrochemical synthesis of Ag-TiO ₂ composites from deep eutectic solvents: photocatalytic and antibacterial behaviour Sabrina State Rosoiu – <i>University POLITEHNICA of Bucharest & IMT-Bucharest, Romania</i>
11:25 – 11:40	Effect of Fe/Ni Ratio on Electrodeposition of Ni-Fe Alloys and Their Bifunctional Catalytic Performance in Hydrogen and Oxygen Evolution Reactions Safya Elsharkawy – <i>AGH University of Krakow, Poland</i>
11:40 – 11:55	Self-terminated electrodeposition of ultrathin iron/ iron hydroxide films: concentration and pH buffer dependencies Martin Nichterwitz – <i>Chemnitz University of Technology, Germany</i>
11:55 – 12:10	Enhanced anticorrosion properties of silver via metals nano-strike electrodeposition Roberta Emanuele – <i>Valmet Plating s.r.l., Italy</i>

12:10 – 12:25	Scanning Electron Microscope Observation of micro and nanostructured Coatings by Broad Ion Beam Milling for Cross Section preparation Paolo De Natale – <i>Hitachi High-Tech Europe GmbH, Italy</i>
Lunch – Caffè del Verone, P.za della SS. Annunziata, 13	
III Session – Chair Piotr Zabinski	
14:00 – 14:20	(Opening Talk) Zn-TiO ₂ dispersion coatings electrodeposited in the presence of L-cysteine, N-acetyl-L-cysteine and thiourea Adriana Ispas – <i>Technische Universität Ilmenau, Germany</i>
14:20 – 14:35	Improving the electroplating simulation model for producing uniform coating thickness distribution Caterina Zanella – <i>Jönköping University, Sweden</i>
14:35 – 14:50	Solid lubrication for high-load duties: a graphene-based electroplated multilayer coating approach Lorenzo Fabbri – <i>Nanesa S.r.l., Italy</i>
14:50 – 15:05	Fast EQCM-D and Raman Characterization for (Sub-)Nanoscale Insights into Electrochemical Processes in Layered Oxide Materials Christian Leppin – <i>Ruhr University Bochum, Germany</i>
15:05 – 15:20	Effect of growth parameters on the morphology of electrodeposited Ni films Ayesha Mubshrah – <i>University of Bristol, UK</i>
15:20 – 15:35	Electrodeposited Ni-W Films: Exploring the Impact of Engineered Porosity and Tungsten Content on Mechanical and Magnetic Properties Roger de Paz – <i>Universitat Autònoma de Barcelona, Spain</i>
Coffee Break & Poster Session	
IV Session – Chair Wolfgang Hansal & Andreas Richter	
16:05 – 16:45	Schwäbisch Gmünd Prize Winner election and talk
16:45 – 17:00	Preparation of thin film anodes for post-lithium-batteries Böck Reinhard – <i>fem Research Institute, Germany</i>
17:00 – 17:15	Pulse Plating of Nickel-Germanium Alloys as Diffusion Barriers in Thermoelectric Devices Hannah Hilton-Tapp – <i>University of Leicester, UK</i>
17:15 – 18:55	EAST Meeting – for EAST members
20:00 – 23:00	Social Dinner – Il Foyer, Via S. Gallo, 57

Friday April 11th 2025

V Session – Chair Massimo Innocenti	
9:00 – 9:20	(Opening Talk) Electrodeposition of aluminium composite coatings from chloroaluminate based ionic liquids Andreas Bund – <i>Technische Universitaet Ilmenau, Germany</i>
9:20 – 9:35	Electrochemical synthesis of nanostructured MOFs Wouter Maijenburg – <i>Martin-Luther-University Halle-Wittenberg, Germany</i>
9:35 – 9:50	Electrodeposited copper selenide films and their thermoelectric performance Elena Pérez Picazo – <i>IMN-CNM CSIC, Spain</i>
9:50 – 10:05	Electrodeposition of Tin Selenide on gold substrate Axel Tahir – <i>Université de Lorraine, France</i>
10:05 – 10:20	3D-CuNi interconnected nanonetworks obtained by electrodeposition with high thermoelectric figure of merit Cristina Vicente Manzano – <i>IMN-CNM CSIC, Spain</i>
Coffee Break & Poster Session	
VI Session – Chair Luca Magagnin	
10:50 – 11:05	Effect of heat treatment on electrodeposited Sn NWs in Anodic Alumina Oxide Templates Evangelia Pavlatou – <i>National Technical University of Athens, Greece</i>
11:05 – 11:20	Coinage Metal-Glutathione Nanostructured Gels on Nanoparticles and Electrodes Alexander Vaskevich – <i>Weizmann Institute of Science, Israel</i>
11:20 – 11:35	Optimization of electrosynthesized Zn-based materials for sustainable antimicrobial applications Margherita Izzi – <i>Università degli Studi di Bari Aldo Moro, Italy</i>
11:35 – 11:50	Effect of Growth Temperature on the Physico-chemical Properties of Sprayed cadmium oxide thin films Sandeep Desai – <i>KIT's College of Engineering, India</i>
11:50 – 12:05	Electrochemical deposition of Ni-matrix nanocomposite coatings with 2D nanomaterials prepared by a boric-free electrolytic bath Angeliki Nikolaou – <i>Creative Nano PC, Greece</i>
12:05 – 12:20	Comprehensive study of Ni/SiC coatings deposited from a novel, boric acid free bath as candidate for replacement of hard chromium Kata Berkesi – <i>Creative Nano, Greece</i>

Lunch – Il Foyer, Via S. Gallo, 57	
VII Session – Chair László Péter	
14:00 – 14:20	(Opening Talk) The role of Ni and Co thin film properties on Hydrogen Evolution Reaction Piotr Zabinski – <i>AGH University of Krakow, Poland</i>
14:20 – 14:35	Understanding Hydrogen Evolution Reaction Induced Modification on Electrodeposited Au-Pd Nanoparticles Paolo Cignoni – <i>Ruhr University Bochum, Germany</i>
14:35 – 14:50	Stability investigations of Electrodeposited Ni ₃ Se ₂ thin films after Hydrogen Evolution Reaction Dawid Kutyla – <i>AGH University of Krakow, Poland</i>
14:50 – 15:05	Synergistic effects of an electrodeposited CoNi alloy catalyst for sustainable hydrogen production Judit Lloreda – <i>Universitat de Barcelona, Spain</i>
15:05 – 15:20	Electrochemical Preparation and Characterization of Porous Nickel Layers as Catalyst Support Structures for Anion Exchange Membrane Electrolyzers Christian Höß – <i>Technische Universitaet Ilmenau, Germany</i>
15:20 – 15:35	Electrochemical Dealloying of AgAuCuPdPt Thin Film for Improved Hydrogen Evolution Catalysis Dean-Robin Nettler – <i>Ruhr University Bochum, Germany</i>
Coffee Break & Poster Session	
VIII Session – Chair Adriana Ispas	
16:05 – 16:20	Inkjet Assisted Electroforming of Untethered Magnetic Microdevices for Smart Drug Delivery Applications Roberto Bernasconi – <i>Politecnico di Milano, Italy</i>
16:20 – 16:35	Downscaling magnetic field gradients for copper magnetoelectrodeposition on the micrometer-scale Francesca Sgarbi Stabellini – <i>Leibniz Institute for Solid State and Materials Research, Germany</i>
16:35 – 16:50	Exploring magneto-ionic effects in electrodeposited nickel-iron alloys Anna Ullrich – <i>Chemnitz University of Technology, Germany</i>
16:50 – 17:05	Electrodeposited Ni-MoOx coatings as high efficiency catalysts for green hydrogen production in alkaline solution Aleksandar Petričević – <i>University of Belgrade, Serbia</i>
17:05 – 18:00	Final Announcements and Greetings

Saturday April 12th 2025

9:30 – 12:00

Guided tour of Palazzo Vecchio Museum

List of Posters

1. Electrochemical synthesis, characterization and functionalization of nanoporous Au nanostructures - Anitta Jose, Leibniz Institute for Solid State and Materials Research, Germany
2. Enhancing Ni Thin Film Properties via Electrodeposition in Magnetic Fields: A Deep Eutectic Solvent Approach - Safya Elsharkawya, AGH University of Krakow, Poland
3. Electroless deposition of Ru NPs for heterogeneous catalysis application - Judit Lloreda, Universitat de Barcelona, Spain
4. Giant Spectral Shifts of Electrochemically Polarized Plasmonic Nanoparticle on a Mirror - Alexander Vaskevich, Weizmann Institute of Science, Israel
5. Evaluation of adhesion characteristics of electrolytically produced copper thin films of nanostructured characteristics: theory vs. experiment - Ivana O. Mladenović, University of Belgrade, Serbia
6. Influence of duty cycle in the pulsating current regime on morphology and structure of copper coatings - Ivana O. Mladenović, University of Belgrade, Serbia
7. Combined Effect of Boric Acid and Heterogenous Magnetic Field on Cu-Ni Electrodeposition - Zaher Jlailati, Ruhr University Bochum, Deutschland
8. How electrodeposition conditions of palladium affect hydrogen absorption - Andrea Comparini, Valmet Plating s.r.l., Italy
9. Metal oxide nanofibers made via electrospinning for photoelectrochemical water splitting - Wouter Maijenburg, Martin-Luther-University Halle-Wittenberg, Germany
10. Cu₂O photocathodes: From electrochemical synthesis to improved stability with an ALD-based TiO₂ coating - Anne Noubi, Martin-Luther-University Halle-Wittenberg, Germany
11. Role of the local diffusion fields in electrolytic formation of zinc irregular forms from the alkaline electrolyte - Nebojša D. Nikolić, University of Belgrade, Serbia
12. Anodization of Multicomponent Alloys for degradation of environmental pollutants - Katarzyna Skibińska, AGH University of Krakow, Poland
13. Evaluating the substrate effect and durability of electrochromic WO₃ films for smart window applications - Eve Evans Perks, University of Bristol, UK

14. Characterization of Sb–Pd electrocatalyst formed by electrodeposition technique for application in Direct Ethanol Fuel Cells - Jelena D. Lović, University of Belgrade, Serbia
15. A Supramolecular Approach to Single Atom PGM-based Catalysts: from Metal Recovery and Cross-Couplings to the Oxygen Reduction Reaction - Matteo Savastano, University San Raffaele, Italy
16. The influence of starting plant material on Ni@C-type catalysts' characteristics - Kamil Dudek, AGH University of Cracow, Poland
17. OER Properties of Ni-Co-CeO₂/Ni Composite Electrode Prepared by Magnetically Induced Jet Electrodeposition - Wei Jiang, Technische Universität Dresden, Germany
18. Electrodeposition of Tunable Ag-Au Nanoparticles from Reverse Micelles - Thais Schroeder Rossi, Ruhr-Universität Bochum, Germany
19. P.U.L.S.E.: Unified Process on Zamak, Brass, and Aluminum Alloys, Safe and Eco-Friendly - Arianna Meoli, Creazioni Lorenza srl, Italy
20. The effect of surface morphology on electrocatalytic performances of Pt@Ni and Pt@Cr thin film catalysts for the methanol oxidation reaction - Sanja I. Stevanović, University of Belgrade, Republic of Serbia
21. Comparative Study of Platinum Deposition Methods on Ni Support for Enhanced Formic Acid Electrooxidation - Dragana L. Milošević, University of Belgrade, Republic of Serbia
22. Electrodeposited Near-Room-Temperature Micro-Thermoelectric Generators - Farjana J. Sonia, Leibniz Institute for Solid State and Materials Research, Germany
23. Electrodeposition of Sn-Ni Alloy Nanowires Involving Deep Eutectic Solvents - Liana Anicai, National University of Science and Technology POLITEHNICA Bucharest, Romania
24. The Role of Nanostructuring in Pseudocapacitive Manganese Oxide Materials - Oliver Röth, University Bochum, Germany
25. Electrodeposition of Crystalline Thin Films of Co₃O₄ on Glassy Carbon with Octahedral Nanoparticles-like Morphology: Exploring Shape-Selective Growth Mechanisms - Anas Akhtar, Ruhr-Universität Bochum, Germany
26. Pulse electrodeposition of a free-nickel gold-iron alloy for decorative applications - Giammarco Maria Romano, University of Florence, Italy
27. Electrodeposition-Based Synthesis of Hierarchical Nanoporous Au Nanowire Networks and Their Electrochemical Properties - Mohan Li, GSI Helmholtz Centre for Heavy Ion Research, Germany
28. Obtaining Pd-Decorated Carbon Black and Graphene Catalysts from Electroplating Wastewater for Efficient Oxygen Reduction Reaction - Marco Bonechi, University of Florence, Italy
29. Oxygen reduction reaction (ORR) in alkaline medium catalyzed using an atomically precise Pd (II) catalysts, prepared by extraction of Pd(II) from a mixture of metal ions

- using modified multi walled carbon nanotubes (MWCNT) - Francesco Montanari, University of Florence, Italy
30. Electrodeposition of Metals on Silicon for Enhanced Silicon Nanowires (NWs) Fabrication via Metal Assisted Chemical Etching (MACE) - Giulio Pappaiani, University of Florence, Italy
 31. Electroplating in the presence of Microplastics: investigating their influence on Copper deposition – Claudia Giovani, University of Florence, Italy
 32. Specific ion effects on nickel electrodeposition - Elena Mariani, University of Florence, Italy
 33. Novel sustainable acid copper formulations: the L-Cysteine case - Fabio Biffoli, University of Florence, Italy
 34. P.U.L.S.E: Development of an Innovative and Sustainable Cyanide-Free Electroplating Process for Advanced Surface Treatments - Elena Mariani, University of Florence, Italy
 35. FREEGALVAN: Development and optimization of new processes, products and prototypes for life cycle extension of items from faucets, fashion accessories and jewelry - Fabio Biffoli, University of Florence, Italy
 36. P.U.L.S.E: Design and Development of Recycled Brass Articles to be Treated with an Innovative and Sustainable Cyanide-free Electroplating Process - Roberta Balzelli, Prestige s.r.l.

Electroplating in Today's World

Luca Magagnin

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Electroplating is one of those processes that has significantly influenced human life since its discovery centuries ago. It finds extensive applications across various domains, from household items to commercial and industrial products. Virtually everything we use today has, in some way, undergone an electroplating process due to its undeniable advantages in enhancing material properties. The primary objectives of electroplating include enhancing appearance, protecting against corrosion, improving material properties, and extending the lifespan of the coated items. Electroplating is widely utilized today across numerous industries, including automotive, aerospace, electronics, and medical devices, establishing itself as a highly valued technology. Advances in modern electroplating techniques have focused on making the process more environmentally friendly and sustainable, minimizing its ecological impact. The integration of innovative materials and technologies, along with the creation of novel applications and products, is poised to open up new opportunities for electroplating in the years ahead. With the increasing prominence of artificial intelligence (AI), its integration into the electroplating industry, particularly in automated electroplating processes, can open to renew the plating processes to ensure that this age-old technology stays relevant and maintains its modern edge. The talk will critically discuss some of these topics, highlighting new advances of electroplating and electrodeposition of nanostructures in surface finishing and energy storage industry.

References:

- [1] E.C. Gugua et al, Electroplating in the modern era, improvements and challenges: A review, Hybrid Advances 7 (2024) 100286

Propeline, a green electrolyte for precious metals electrometallurgy?

*Sophie Legeai^a, Calogera Bertoloni^a, Benjamin Rotonelli^a, Stéphanie Michel^a, Eric Meux^a,
François Lapique^b, Romain Duwald^c, Angel Fernandez-Blanco^c*

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“Deep eutectic solvents” (DES), of low reactivity and volatility, are often considered as green alternative to conventional electrolytes for electrometallurgy of precious metals (electrowinning, electrorefining, electroplating, electropolishing...). In particular, the DES named Ethaline (choline chloride-ethylene glycol mixture) has been widely used because of its acceptable viscosity and the presence of substantial chloride concentration leading to a high solubility of numerous metallic compounds [1]. However, if choline chloride (ChCl) can be considered as a “green” reactant, ethylene glycol (EG) is known to be harmful to men and animals in case of repeated exposure or inhalation periods. Comparable DES with a lower toxic nature than Ethaline can be obtained by replacing EG by other glycols e.g. propylene glycol (PG) [2], widely used in cosmetics and pharmacology, with costs comparable to those of EG; the resulting DES is named Propeline. We will present here the potential of this less known DES for the electrometallurgy of silver and gold.

The first part of this work deals with the determination of Propeline density, viscosity, conductivity and electrochemical stability, which are properties of interest for electrochemical processes [3]. The speciation of dissolved metals was then determined by use of cross-linked analysis, namely UV-vis, and EXAFS/XANES spectroscopic techniques. Electrochemical systems were then thoroughly studied by electrochemical methods. In particular, diffusion coefficients of the solvated metal species were determined by electrochemical transient and stationary techniques, using a protocol specifically developed for these viscous media [4]. The influence of electrodeposition conditions (deposition mode, current/potential values, direct or pulsed deposition) on deposit morphology was then evaluated. Anodic and cathodic faradic efficiencies were determined after thorough development of analytical procedures dedicated to elemental analysis e.g. ICP-EOS in DES. Finally, to evaluate the viability of the process, the re-usability of the electrolyte was studied by GC-MS analysis after repeated runs of electrolysis. The influence of water content on DES properties and on the stability of the metallic species was also thoroughly investigated.

As an illustration, the applicability of the process to Ag and Au recovery from WEEE (Waste from Electrical and Electronic Equipment), which is currently under study with the french industrial partner Terra Nova Developpement, will be presented with its technological locks/issues and potentialities.

References:

- [1] Abbott, A. P.; Frisch, G.; Gurman, S. J.; Hillman, A. R.; Hartley, J.; Holyoak, F.; Ryder, K. S. *Chem. Commun.* 2011, 47 (36), 10031–10033. <https://doi.org/10.1039/C1CC13616J>
- [2] LaKind, J. S.; McKenna, E. A.; Hubner, R. P.; Tardiff, R. G. *Crit. Rev. Toxicol.* 1999, 29 (4), 331–365. <https://doi.org/10.1080/10408449991349230>
- [3] Calogera Bertoloni, Vitalys Mba Ekomo, Benoît Villemejeanne, Charly Lemoine, Romain Duwald, Emmanuel Billy, Hakima Mendil-Jakani, Sophie Legeai, *Comptes Rendus. Chimie*, 2024, 27 (S4), pp.1-12. <https://doi.org/10.5802/crchim.297>
- [4] Calogera Bertoloni, Sophie Legeai, Stéphanie Michel, Eric Meux, François Lapique, *Environmental Science: Advances*, 2024, 3 (6), pp.875-884. <https://doi.org/10.1039/D4VA00042K>

Thermoelectric nanowire structures as integrated sensors in composite materials

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Composite materials, especially carbon fiber-reinforced polymers, combine lightness and strength and are intended for high-end applications requiring increased performance, such as aeronautics, aerospace or sports competitions. As a limit, these highly anisotropic materials are difficult to model, and new approaches are needed to further lighten them while maintaining acceptable mechanical properties. Current research trends are to integrate sensors into the composite material to monitor its mechanical properties. However, the presence of these sensors can weaken the composite, so new types of sensors must be developed that can preserve the mechanical properties of composite materials.

This work presents the integration of thin-film nanostructured sensors into composite materials, to monitor their mechanical and thermal properties. Sensors are made by electrochemical growth of thermoelectric material in nanoporous thin polymer film, and each can be used in three different ways: (i) temperature sensors, (ii) heat flux sensors and (iii) strain gauges. Their thickness less than 10 microns keeps mechanical properties barely unchanged.

Measurements show precise monitoring of heat conditions during the curing process, and the features as strain gauges were demonstrated through a series of mechanical tests. These results address these nanostructured sensors as effective real-time monitoring system as well as a precious technique to improve numerical modelling of complex composite materials.

Electroplating of special metals: On the way towards 5-component high-entropy alloys

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The study of near-equiatomic multicomponent metals has been an extensively studied field in the last two decades. In these alloys, neither of the components can be classified as either solvent or solute.

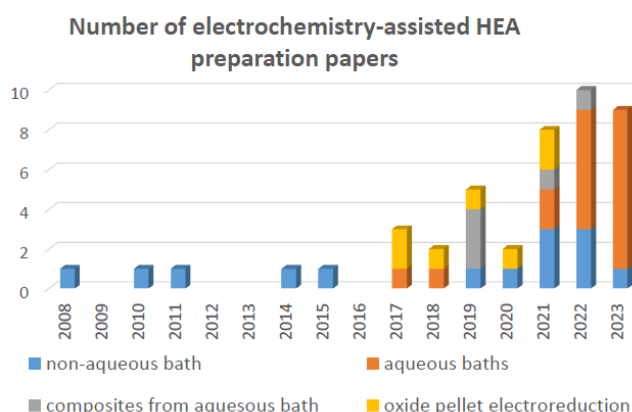


Figure 1: Statistic of the scientific publications on electrochemistry-assisted preparation of HEAs

These materials are called with various names such as multi-principal element alloys (MPEAs) or compositionally complex alloys (CCAs), and the term *high-entropy alloys* (HEAs) is applied for alloys with 5 or more components. The importance of these alloys stems from the very dynamic tunability of the combination of the mechanical properties with the alloy composition. While the reports on HES preparation with classical metallurgical methods range to about 12 000, only a few dozens of works deal with electroplated HEAs (see their statistics in Figure 1).

Our work included the preparation of homogeneous [1] and graded composition [2] Co–Fe–Ni–Zn alloys. Electroplating of sample libraries of multicomponent alloys is a non-trivial task. Unlike for vacuum-based methods, the multiple target approach does not work, but rather a special electrode arrangement and the indirect transport modulation in the electrolyte solution offers an opportunity to produce graded component materials. This method allowed us to scan the Zn content range of 16 to 44 at.%, in which the mechanical properties proved to be nearly constant. This shows that the so-called “cocktail effect” often found for metallurgically processed HEA materials is also valid for the electroplated counterparts.

The deposition of any pair of the components of the Co–Fe–Ni–Zn alloys belongs to the anomalous codeposition type. However, the addition of a fifth component can modify the relative deposition preferences and the deposit composition. While the Co–Fe–Ni–Zn alloys were deposited from a simple chloride-rich bath, the attempts of the electroplating of Sn-containing alloys applied complexing agents in order to tune the deposition potential. The talk will summarize the experience of the deposition of multicomponent Sn–4d metals alloys.

References:

- [1] P. Nagy, L. Péter, Z. Czigány, N. Q. Chinh, J. Gubicza, *Surf. Coatings Technol.* 2023, **467**, 129740. <https://doi.org/10.1016/j.surfcoat.2023.129740>
- [2] P. Nagy, L. Péter, T. Kolonits, A. Nagy, J. Gubicza, *Metals* 2024, **14**, 700. <https://doi.org/10.3390/met14060700>
- [3] Authors, Journal, year, volume, page, doi.

Pulsed reverse electrochemical synthesis of Ag-TiO₂ composites from deep eutectic solvents: photocatalytic and antibacterial behaviour

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Titanium dioxide (TiO₂) has been widely investigated for its potential in photodegrading organic and inorganic pollutants, owing to its affordability and non-toxic nature. However, its practical application in the photodegradation of organic dyes is largely restricted to the ultraviolet (UV) spectrum due to its wide band gap (~3.2 eV), which limits its utilization to about 5% of solar energy, in contrast to the visible light spectrum (~50%) [1]. To enhance the photocatalytic performance of TiO₂ under visible light, Ag doping/deposition has emerged as an effective strategy. Incorporating noble metal nanoparticles (NPs) like Ag into TiO₂ extends its light absorption into the visible range through the localized surface plasmon resonance effect. Consequently, Ag-TiO₂ composites have shown promise in applications such as environmental remediation, antimicrobial treatments, catalytic oxidation, and more.

Numerous approaches have been used to synthesize Ag-TiO₂ composites; however, many of these methods are expensive, multi-step processes that often involve toxic precursors. Electrochemical synthesis offers a simpler, more cost-effective alternative, with the added advantage of allowing precise control over the composite material's properties by adjusting electrodeposition parameters. Among these techniques, pulsed reversed current (PRC) electrodeposition stands out as a more versatile option compared to direct current (DC) electrodeposition, where the applied current is the sole adjustable parameter. Deep eutectic solvents (DESs) have gained significant attention in nanomaterial synthesis as an eco-friendly alternative that supports global sustainability goals. DESs consist of a mixture of a hydrogen bond donor (HBDs) with a hydrogen bond acceptor (HBAs), resulting in a mixture that exhibits a melting point lower than their individual components.

This study explores the synthesis of an Ag-TiO₂ composite using DESs based on a choline chloride eutectic mixture with ethylene glycol by the PRC electrodeposition method. The effects of the PRC parameters on the crystallite size, Ag-loading, morphology, and photocatalytic activity for methyl orange (MO) degradation under UV and visible light irradiation were examined. Additionally, the antimicrobial activity of the optimized Ag-TiO₂ photocatalyst was evaluated against Gram positive (*B. subtilis* var *spizizenii*) and Gram-negative (*E.coli*) bacterial strains.

References:

[1] G. Durango-Giraldo, A. Cardona, J.F. Zapata, J.F. Santa, R. Buitrago-Sierra, Heliyon, 2019,5,e01608. [10.1016/j.heliyon.2019.e01608](https://doi.org/10.1016/j.heliyon.2019.e01608).

Effect of Fe/Ni Ratio on Electrodeposition of Ni-Fe Alloys and Their Bifunctional Catalytic Performance in Hydrogen and Oxygen Evolution Reactions

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Developing advanced electrocatalysts for water splitting is critical due to the energy crisis. Enhancing catalyst electronic structures significantly improves performance. Transition metals, especially nickel (Ni) and nickel-iron (Ni-Fe) alloys, show remarkable properties for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Their surface characteristics, including efficient proton adsorption and gas departure, enhance electrochemical activity. However, quantifying gas bubbles to determine catalytic efficiency remains challenging. In this study, Ni-Fe alloys with varying iron content (0.01–0.1 M Fe; fixed Ni at 0.4 M) were synthesized via electrodeposition from citrate electrolyte at different potentials. The influence of iron content on morphology, composition, wettability, and catalytic performance was investigated. Results revealed higher iron content improved OER, while higher nickel content favored HER. Bubble size decreased with increasing iron content for OER and decreasing iron content for HER. All samples exhibited hydrophilic properties, with contact angles increasing as iron content rose. Advanced characterization techniques, including SEM, XRF, XRD, and EDX, analyzed alloy properties. Findings show iron content impacts morphology, wettability, and electrocatalytic performance, providing insights for optimizing HER and OER.

Self-terminated electrodeposition of ultrathin iron/ iron hydroxide films: concentration and pH buffer dependencies

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Iron and iron oxide nanostructures are of broad interest for numerous applications, such as in the fields of magnetic data storage, spintronics, biosensing or catalysis. In all of these cases, defined deposition on nanometer scale is essential for functionality. For conventional electrodeposition of transition metals, precise thickness control and layer stability at the nanoscale are difficult due to dissolution tendencies in acidic electrolytes after the voltage is switched off. In contrast to previous studies that focused on self-termination of Ni and Ni-based alloys [1], we investigate the thickness control of nanoscale iron oxide/iron layers using self-terminated electrodeposition from sulfate electrolytes. Electrochemical quartz crystal microbalance measurements (EQCM) show that self-terminated thickness can be controlled by various parameters like deposition potential, iron ion concentration or type and concentration of additional pH buffer. Comparison of experimental results with model calculations based on diffusion theory reveal two different growth modes for self-termination. At low iron concentration, self-termination of iron proceeds via the formation of an ultrathin iron hydroxide layer. At larger iron ion concentration, precipitation of bulk $\text{Fe}(\text{OH})_2$ dominates the film growth and self-termination is shifted to more negative potentials.[2] All self-terminated layers exhibit enhanced stability in the electrolyte after the voltage is switched off compared to conventional deposition. Surface analytical and morphological analyses show that the self-terminated layers exhibit a higher iron oxide/iron ratio and are smoother than layers obtained by conventional electrodeposition. The influence of additional pH buffers (citrate and acetate) is also characterized. Self-terminated iron electrodeposition was successfully demonstrated on Au aerogel nanostructures for reversible voltage-controlled magnetoresistance manipulation.[3]

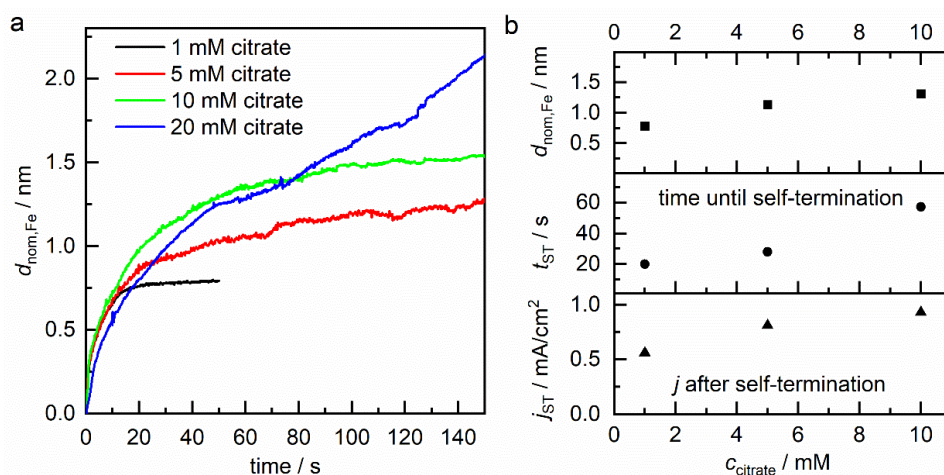


Figure 1: iron deposition with different citrate buffer concentrations: a) nominal iron layer thickness during deposition from EQCM data b) final nominal iron layer thickness, time until self-termination and current density after self-termination in dependence of buffer concentration

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Enhanced anticorrosion properties of silver via metals nano-strike electrodeposition

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Silver substrates are widely used in various industries due to their inherent aesthetic and optoelectronic properties [1]. However, their susceptibility to tarnish and corrosion remains a significant challenge, particularly in fields where long-term aesthetic and functional integrity are crucial. These limitations underscore the importance of improving the tarnish resistance of silver and silver-based alloys to preserve the aesthetic and functional properties [2].

This study aims to enhance the corrosion and tarnish resistance of silver substrates by electrodepositing nanometric layers of various metals. The deposited metals' ability to improve resistance to tarnish and corrosion was evaluated with different techniques. Corrosion resistance was assessed using Open Circuit Potential (OCP) measurements, Linear Sweep Voltammetry (LSV) and Evans diagrams [3]. These techniques provided detailed insights into the electrochemical behaviour, stability, and protective qualities under various conditions. Tarnish resistance was initially evaluated using a 5% sodium sulphide solution, a common tarnishing agent, to simulate real-world exposure. Further testing was conducted with thioacetamide, which offers a more aggressive tarnishing environment, to comprehensively assess the durability and effectiveness of the coatings.

These evaluations aim to identify the most promising nano-strike for enhancing the longevity and performance of silver substrates in various applications. Preliminary results indicate that using different nano-strike can result in huge difference in silver surface corrosion behaviour.

These results will contribute to developing more durable silver coatings, potentially benefiting industries reliant on silver components, such as electronics, jewellery, and medical devices. Further testing and optimization can explore additional metal combinations, aiming to achieve the most effective and practical solutions for enhancing silver and silver's alloy durability.

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Scanning Electron Microscope Observation of micro and nanostructured Coatings by Broad Ion Beam Milling for Cross Section preparation

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The ion milling method, which can process without stress, enables to produce cross section samples eventually with reduced thermal damage by cooling function, and it is effective from understanding whole structure of the coating and to analyzing micro and nanostructure of the coatings different layers through Electron Microscope images and EDX analysis.

Zn-TiO₂ dispersion coatings electrodeposited in the presence of L-cysteine, N-acetyl-L-cysteine and thiourea

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Zinc coatings are widely used to protect steel and iron-based parts against indoor and atmospheric corrosion, due to their capability to perform sacrificial protection. To achieve the required technical layer properties such as brightness, optical appearance, wear and corrosion resistance, or a good throwing power, different additives, levelers and/or surfactants are added in commercial electrolytes, besides the Zn salts [1,2]. The mechanism of how different organic additives act during plating is still not completely understood. Some theories were proposed for individual additives, explaining how they can be specifically adsorbed on the surface and can inhibit further growth of the films or the surface diffusion of the ad-atoms. In this last case, the additives can act as grain refiners [3].

In this contribution we will discuss the electrodeposition of Zn-TiO₂ composite layers from a weakly acidic chloride-based electrolyte in the presence of L-cysteine, N-acetyl-L-cysteine and thiourea. We investigated how the morphologies of the deposits, their structure and their composition (in terms of how many TiO₂ nanoparticles could be incorporated in the Zn matrix) were influenced by the presence of those additives. Besides the ex-situ characterizations, electrochemical methods were used to study the process in-situ. Special attention was given to the electrochemical quartz crystal microbalance, EQCM, technique. Thus, we could monitor the mass-charge balance of deposition process and identify the effect of different additives on the current efficiency of electro co-deposition. The pure Zn electrolyte and the electrolyte containing only TiO₂ particles showed similar features and current densities in the cyclic voltammograms. Addition of L-cysteine inhibited the deposition rate and the dissolution process as proven by the smaller current densities reached in this case when compared to the other electrolytes. Lower cathodic onset potentials of about 60 mV were needed in the presence of thiourea for deposition to set it when compared to pure Zn electrolyte. The N-acetyl-L-cysteine did not seem to have a significant effect on the deposition potential, independent of its concentration. A comparison on the effect produced by the additives on the Zn-TiO₂ deposition will be discussed.

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Improving the electroplating simulation model for producing uniform coating thickness distribution

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Electroplating is a well-known technology widely used in electroforming and manufacturing processes of electronic parts such as semiconductors. Controlling electroplating thickness profile or uniformity is critical to improving product quality and productivity. Many parameters must be controlled for a proper coating distribution, such as current density, electrolyte composition and agitation, anode and cathode distance and configuration. For example, nonuniform current density distribution not only affects the coating thickness but may also affect coating composition, microstructure, and properties. Many experiments are needed to obtain the uniform current distribution for the various shapes of cathodes. Therefore, electroplating simulation can be a promising way to improve the experimental design. Simulation in electroplating has not been broadened as in other fields of science, and in most cases, the focus was on numerical methods. Besides, the industrial application of electroplating simulation is still limited due to the simulation models' complexity and multi-disciplinary nature. In addition, in most studies, electroplating processes were simulated on a simple geometry with 2D model for a short time. In contrast, the results of the simulation are not in good agreement with the experimental results when long plating or complex geometry is used and that has reduced the application of simulation by the plating industry. Therefore, this study aimed to improve the validity of the electroplating simulation model. For this purpose, the effect of practical parameters that exist in all electrochemical systems, such as current efficiency and current density regimes for a geometry with an inner gap, were studied. In addition, the challenges for the simulation of a long plating process were discussed, and the effect of plating duration on the simulation results and their deviation from reality was investigated. The simulation was run in both 2D and 3D models, and the results were compared with the experiments. These considerations are essential to establish a guideline that extends the application of 2D models instead of 3D with good agreement with reality. This paper provides a summary of important aspects that can affect the precision of simulated coating distribution, which are influential in providing a valid model. A valid model is a powerful tool for the electroplating industry to reduce trials and save time and money. Finally, the developed model was used to find a proper current density regime, forming a uniform coating thickness distribution for a geometry with an inner gap.

Solid lubrication for high-load duties: a graphene-based electroplated multilayer coating approach

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Copper plating is extensively employed in industrial applications to enhance bulk material properties, such as electrical and thermal conductivity, and corrosion resistance. However, the utilisation of copper coatings on moving parts is significantly restricted due to copper's relatively low shear and yield strengths, making it highly susceptible to wear and friction-induced degradation under low contact pressures (below 0.1 GPa Hertzian pressure). To address these limitations, the present study explores the development of electrodeposited composite coatings by incorporating a graphene-related material (GRM) into the copper matrix during its electro-crystallization [1,2]. The research aimed to create copper-GRM composite structures and evaluate their mechanical and tribological performance in multilayered coatings. Two multilayered coating systems were developed: a nickel-topped one (ML(Ni)) and a copper-topped one (ML(Cu)). For comparison, a third multilayered system without GRM, called GnP-free ML(Ni), was synthesised. A comprehensive suite of chemical, structural, and mechanical characterisations was conducted to elucidate the coatings' tribological behaviour under varying boundary conditions and the underlying lubrication mechanisms. The results revealed that the hybrid ML(Ni) coatings exhibited remarkable tribological performance, characterized by a low coefficient of friction ($\mu < 0.2$) and a prolonged wear life exceeding 10,000 cycles under engineering load conditions in air. These performance metrics significantly surpassed those of the nickel-free hybrid coating (ML(Cu)) and the GRM-free nickel-based multilayer coating (GnP-free ML(Ni)).

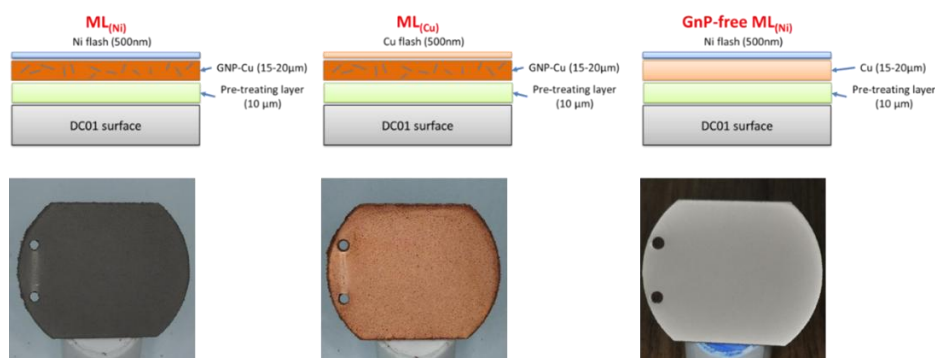


Figure 1 Proposed coating structures and photographs of the ML(Ni), ML(Cu) and GnP-free ML(Ni) coatings produced; the scale bar represents 10 mm.

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Acknowledgements:

All authors would like to thank the EU Graphene Flagship Core 3 (Grant Number 881603) for funding this work.

Fast EQCM-D and Raman Characterization for (Sub-)Nanoscale Insights into Electrochemical Processes in Layered Oxide Materials

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Improving the understanding of electrochemical interfaces in energy storage and conversion processes requires tailored operando experiments capable of resolving dynamic transformations in high-performing layered oxide nanomaterials under aqueous conditions. For insightful combined characterization, it is essential that the time resolution aligns with the electroanalytical technique and provides information on (sub)nanoscale phenomena.[1] Powerful examples are, for instance, Raman spectroscopy and the electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D). The first provides indirect access to the material's potential-dependent structure via lattice vibrations. The latter provides the ability to link electrochemical processes to changes in mass and mechanical properties. The EQCM-D reports shifts in resonance frequency, Δf , often related to the deposited mass (or equivalently film thickness), and half-bandwidth, $\Delta\Gamma$, related to energy dissipation in the system, on several overtones. In addition to mass changes, variations in the Newtonian viscosity of the electrolyte, its viscoelasticity (complex shear modulus – the stress-strain ratio), and the surface roughness can be probed directly by shearing the interface without relying on synchrotron-based diffraction or absorption methods.[2] However, conventional state-of-the-art EQCM-Ds face sensitivity and time resolution limitations during potentiodynamic experiments such as cyclic and pulsed voltammetry. These instruments already require compromises in sensitivity and the number of overtones probed to achieve a rather modest time resolution of ~100 ms. More recently, multifrequency lock-in amplification much improved the sensitivity by a factor of 10 to the subatomic thickness scale ($7 \text{ mHz} \pm 0.12 \text{ ng/cm}^2 \pm 1.2 \text{ pm}$) and the time resolution by a factor of 100 (0.1 - 1 ms).[3,4] Here, we apply the capabilities of fast EQCM-D to layered nanomaterials, namely birnessite-type manganese dioxide, as used in electrochemical energy storage electrodes. The EQCM-D revealed electrodeposited MnO₂ to contain large amounts of water (6 up to 32 water molecules per formula unit MnO₂) situated in the sub-nanometer interlayer space or pores. Furthermore, potential-driven changes in mass and viscoelastic properties due to the uptake/release of (hydrated) cations for pseudocapacitive (dis)charging in aqueous electrolytes are investigated and linked to structural changes inferred from Raman spectroscopy. The study showed the MnO₂ films to be in an expanded, swollen configuration under open circuit conditions. The distorted lattice comprised hydrated cations in the interlayer space to balance negative excess charges. Upon increasing potential, the MnO₂ film releases hydrated cations and becomes mechanically stiffer. During reverse scans, the MnO₂ film swells and becomes more viscous/liquid-like again (loss angle and magnitude of the shear modulus increase). The swelling process corresponds to the uptake of hydrated cations in the interlayer space. Changes in the apparent molar mass-to-charge ratio (M/z) and mechanical properties can be monitored on the millisecond time scale and assigned to chemical species. Furthermore, fast EQCM-D can be combined with polarization techniques beyond cyclic voltammetry, such as potential steps or pulsed voltammetry, to provide insights into the underlying kinetics of the swelling and collapsing processes in layered oxide materials.

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Effect of growth parameters on the morphology of electrodeposited Ni films

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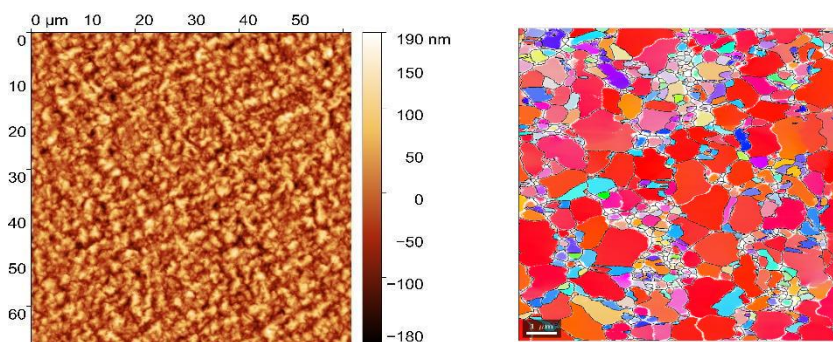
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Electrodeposited nickel layers are extensively used for functional and decorative purposes e.g. the protective coating of spacecraft components [1]. The microstructure and morphology of thin electrodeposited metal films plays a vital role in determining their properties. We prepared a range of electrodeposited polycrystalline Ni films using potentiostatic deposition and investigated the effects of different parameters, such as the deposition rate, electrolyte composition. We characterized the surface morphology using ex-situ atomic force microscopy (AFM) and High-Speed Atomic Force Microscopy (HS-AFM). We used the ex-situ AFM data to perform quantitative surface analysis, including slope and scaling analysis [2] and grain area calculation, as a function of deposition time and chloride addition. Film texture was determined by X-Ray Diffraction (XRD) analysis. For thin films the $\langle 111 \rangle$ orientation was dominant, but for thick films, the dominant crystallographic orientation was $\langle 100 \rangle$.

We also performed electron backscatter diffraction (EBSD) analysis on the electrodeposited Ni thin films, using focused ion beam milling to remove the uneven top surface and obtain clear Kikuchi patterns. EBSD uses diffraction patterns from backscattered electrons to provide information on the crystallographic orientation of the thin films. Misorientation angles of the film's grain structure were also calculated, and twinning was observed in the EBSD data. We also performed HS-AFM and EBSD scans for the same area of an electrodeposited Ni thin to correlate the morphology and microstructural properties. Morphological studies at different growth stages using HS-AFM will provide insights into the growth rates at various points.



a) HS-AFM stitched scan of electrodeposited Ni thin film of 7 μm nominal thickness b) EBSD scan of Ni electrodeposited thin film of 8 μm nominal thickness

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Electrodeposited Ni-W Films: Exploring the Impact of Engineered Porosity and Tungsten Content on Mechanical and Magnetic Properties

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Advanced materials with tailored porosity, mechanical strength and soft-magnetic properties are in growing demand. Electroplated chromium coatings are widely used in industry due to their high hardness, wear, and corrosion resistance, despite the toxicity of Cr(VI) electrolytes and their impact on the environment [1]. Ni-W alloys are among the candidate materials to replace Cr coatings, offering not only the properties commonly associated to Cr but also the potential for tunable magnetic behavior.

In this study, dense and pseudo-ordered porous Ni and Ni-W (6 wt.% W) films have been electrodeposited potentiostatically from a Ni-W gluconate bath [2] on unpatterned and patterned metallized Si substrates, respectively. Patterned substrates were created using templates of colloidal polystyrene spheres with diameters of 200 and 20 nm. This templating approach enables the electrodeposition of films with controlled porosity, where the pore size is determined by the diameter of the polymer spheres (Fig. 1a). The morphology and elemental composition of the Ni-W films were analyzed using SEM/EDX and ICP, while the crystal structure was obtained using grazing incidence XRD. The mechanical properties of the films were characterized via nanoindentation. Magnetic hysteresis measurements and first-order reversal curves (FORCs) were performed with VSM to study their magnetic behavior and inter-grain interactions. The dependance of Curie temperature (T_C) on the W content and porosity was also investigated.

As expected, the porous Ni and Ni-W films showed both lower hardness and reduced elastic modulus compared to their dense counterparts. The alloying of Ni with W decreased the saturation magnetization with respect to Ni while preserving its crystal structure. In-plane shape anisotropy was preserved in films with 20 nm pore size (Fig. 1b). More importantly, the addition of W lowered T_C whereas the introduction of porosity had little or no effect.

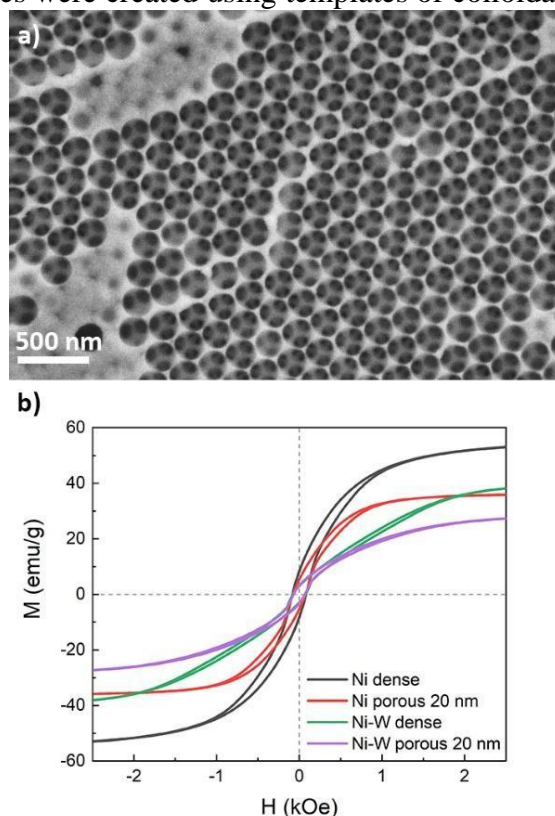


Figure1: a) SEM image of a porous Ni-W film with 200 nm pore size, b) in-plane hysteresis loops of dense and porous (20 nm pore size) Ni and Ni-W films.

Acknowledgement:

This work has received funding from Horizon Europe under grant agreement No 101058076 - NICKEFFECT.

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Preparation of thin film metal anodes for post-lithium-batteries

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The realization of grid-scale electricity storage and the increase in global electromobility require batteries with higher energy and lower costs. The maximum storage capacity of conventional lithium-ion batteries (LIB) has almost been reached. Furthermore, the extraction of battery materials - such as cobalt, graphite and lithium - entails political, ecological and economic risks. For this reason, activities have been started worldwide to develop new alternative battery systems.

Alkali and alkaline earth metals have a high specific capacity compared to common carbon-based anode materials. Metal anodes made of Li, Na, Ca or Mg could significantly increase the overall performance of batteries. Na, Ca and Mg-compounds are abundant in the earth's crust and also often less expensive. This can reduce the production costs of batteries and increase economic sustainability. However, the use of Li, Na, Ca or Mg as metal anodes in post-lithium-ion batteries can bring with it a number of disadvantages that hinder the development of metal-anode-batteries. Li and Na in particular are well known to form dendrites during electrochemical deposition. In addition, the high reactivity of these metals can lead to the decomposition of the organic solvents in the electrolyte. This leads to side reactions that reduce the stability of the electrolyte and can also cause the formation of passivation layers. These undesirable effects make it difficult to develop suitable electrolytes and processes for the electrochemical deposition of compact, homogeneous and adherent Li, Na, Ca or Mg layers. For the production of thin metal anodes, as required in battery technology, electrochemical deposition processes are promising in themselves, since the electro-crystallization (mass, shape, morphology or thickness of the layers) can be controlled by adjusting the parameters current density, metal concentration, hydrodynamics and temperature [1].

In this presentation, different results from current research projects on the production of Li, Na and Ca metal anodes by electrodeposition from non-aqueous electrolytes (with carbonate- or ether-based solvents and hexafluorophosphate- or tetrahydroborate-based metal salts) under inert gas atmosphere conditions are presented. The results show that the organic electrolytes must be specifically adapted for each of these metals. The stability of the electrolytes and the quality of the deposits depends strongly on the properties of the solvent, metal salt and used plating conditions. This leads to increased complexity in the development of suitable electrolytes. Therefore, considerable research efforts are still required to develop stable and functional metal anodes for post-lithium-ion batteries.

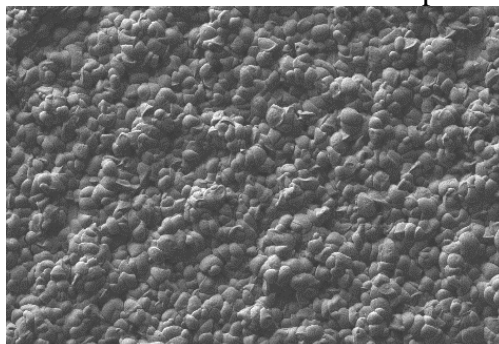


Figure: Ca-deposit on Cu substrate.

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Pulse Plating of Nickel-Germanium Alloys as Diffusion Barriers in Thermoelectric Devices

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For highly reliable thermoelectric (TE) generators to be realised for Radioisotope Power Systems (RPS), robust metallisation coatings are required to prevent interdiffusion between the bulk TE material and the metal ohmic interconnects. Nickel is a well-established metal commonly used as a diffusion barrier layer for bismuth telluride (Bi₂Te₃)-based thermoelectric materials, but it is well known to diffuse and form a Ni-Te intermetallic alloy after sufficient thermal aging at 200 °C and above. This work looks into using pulse plating to produce highly tailored nanocomposite diffusion barriers that could not be otherwise electroplated using traditional methods. Nickel-germanium (NiGe) alloys, produced by thermal evaporation deposition and rapid thermal annealing, have been shown in previous studies by researchers at Sandia National Laboratories to significantly prevent interdiffusion and intermetallic formations preserving the thermoelectric power factor [1]. However, the thickness of these barrier layers was sub-micron and therefore insufficient for practical solder joints. In this work, NiGe alloy coatings, with sufficient thickness, will be produced via pulse plating methods in conjunction with a rapid annealing step. Developing robust metallization alloys with long-term stability at elevated temperatures will complement the extensive half-life of Am-241 RTGs for future long duration space exploration missions.

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Electrodeposition of aluminium composite coatings from chloroaluminate based ionic liquids

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This paper will discuss recent results from the authors' labs on the electrodeposition of aluminium layers containing various nanoparticles. The electrodeposition was performed from Lewis acidic chloroaluminate melts at room temperature [1].

Composite layers of aluminium with embedded nickel particles are termed reactive layers because the application of an activation energy (e. g. an electric spark) releases a decent amount of heat due to the formation of an Al-Ni-intermetallic (Figure 1). Possible applications of reactive layers are joining processes for electronic and electric devices. We will discuss how the preparation conditions affect structure and properties of the reactive layers.

Another system that shall be discussed are composite layers of aluminium with embedded particles of an active material for lithium ion batteries. Such layers are interesting candidates for battery electrodes with high specific power.

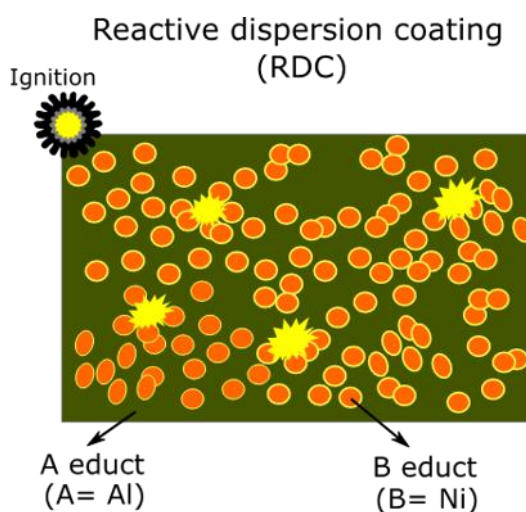


Figure 1: Schematic representation of a reactive layer, consisting of nickel particles embedded in an aluminium matrix.

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Electrochemical synthesis of nanostructured MOFs

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Metal-organic frameworks (MOFs) are a relatively new class of hybrid materials, which consist of metal ions or clusters as the secondary building unit (SBU) and organic linkers connecting these SBUs via coordination bonds of moderate strength, forming a nanoporous crystalline network. Thereby, MOFs combine the robustness and crystallinity of inorganic materials with the flexibility of organic molecules. Thus, MOFs possess a wide range of unique properties, like framework flexibility, uniform pore sizes, easy functionalization, high porosity and chemical stability. However, the development of synthetic techniques that allow the control over the size and shape of MOF particles at the nanoscale regime has a central role in the integration of MOFs within different kind of devices, such as gas sensors, membranes and photoelectrodes [1-3].

One method that is perfectly suited for the directed growth of nanostructured materials is templated electrodeposition, and as I will show here, we managed to apply this method to the directed growth of nanostructured MOFs (also called nano-MOFs). For this, we applied a two-step electrochemical procedure in which we first grew Cu or Cu₂O nano- and microstructures that were subsequently converted into the respective Cu-based MOF (Cu₃(BTC)₂ or Cu(TCCP)) via electrochemical oxidation. During the electrochemical conversion of such Cu or Cu₂O nano- and microstructures, we have several options for fine-tuning our final product, for instance:

1. Converting the complete parent nanostructure inside the template results in nanostructures consisting solely of the prepared MOF (Figure 1, left);
2. Converting part of the parent nanostructure results in core-shell structures (Figure 1, middle);
3. Changing the linker molecules available inside the electrolyte results in the synthesis of different kinds of MOFs (e.g. Cu(TCCP) (Figure 1, right) instead of Cu₃(BTC)₂).

Additional parameters, such as the pore size of the membrane, electrodeposition time, voltage, pulse duration and the use of additives in the electrolyte, play an important role in the final MOF-containing structure obtained. Finally, we found that our Cu₂O@Cu₃(BTC)₂ nanowire networks outperformed bare Cu₂O nanowire networks as photocathodes for photoelectrochemical H₂ evolution.

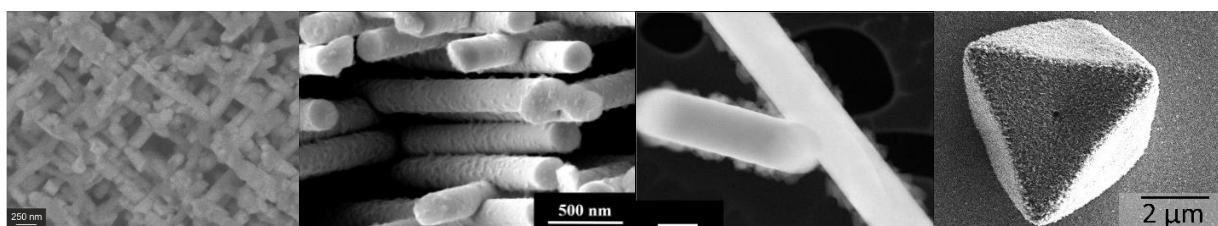


Figure 1, from left to right: Cu₃(BTC)₂ nanowire network [1], core-shell Cu₂O@Cu₃(BTC)₂ nanowire network [2], core-shell Cu₂O@Cu₃(BTC)₂ nanowires (TEM) [2], and core-shell Cu₂O@Cu(TCCP) microstructure [3].

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Electrodeposited Copper Selenide films and their Thermoelectric Performance

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The growing interest in thermoelectric applications has driven a shift towards affordable, sustainable and easily scalable materials that continue to offer high performance, such as copper selenide (Cu_2Se)[1-2]. In this work, copper selenide films with different compositions were grown by electroposition using new optimized solutions. The structural, morphological and compositional characteristics of the films were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray fluorescence (XRF). The thermoelectric properties, such as electrical conductivity (σ), Seebeck coefficient (S) and thermal conductivity (k) of the films were also measured. A maximum power factor ($PF=\sigma \cdot S^2$) of $912 \pm 188 \mu\text{W}/\text{m}\cdot\text{K}^2$ was obtained (figure 1), surpassing all previous records reported in the literature for electrodeposited copper selenide films[3]. These results open new paths for the development of high performance thermoelectric materials, setting a new benchmark for electrodeposited copper selenide films and showing great potential for energy conversion applications.

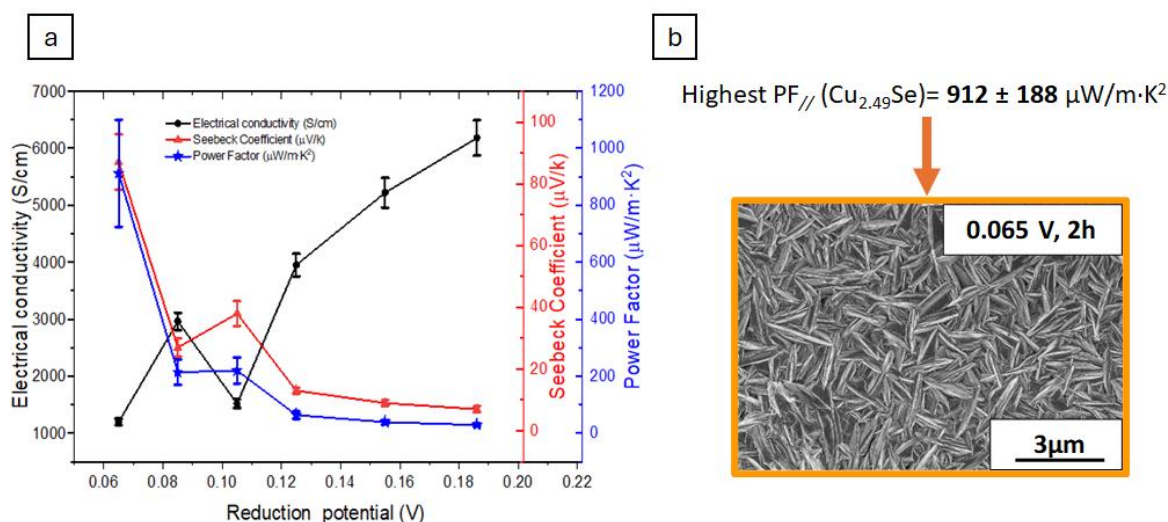


Figure 1. (a) Electrical conductivity, Seebeck coefficient and Power Factor of copper selenides films electrodeposited at different potentials at room temperature. (b) FE-SEM image of the copper selenide film with the maximum power factor of $912 \pm 188 \mu\text{W}/\text{m}\cdot\text{K}^2$ electrodeposited at 0.065 V for 2 hours.

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Electrodeposition of Tin Selenide on gold substrate

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Polycrystalline SnSe have become more and more popular for thermoelectric (TE) applications at high temperature (900 K). One of the main reasons is that SnSe is less toxic, more abundant, and presents itself as a competitive alternative to common compounds such as Bi₂Te₃. Since the controversial work of Zhao et al. [1], which reported a thermal conductivity lower than 1 W.m⁻¹.K⁻¹ and a TE figure of merit ZT of 2.6 at 923 K, various researches have been carried out on this type of systems with improved TE properties. At room temperature, SnSe has poor thermoelectric performances mainly because of reduced electronic conductivity. However, this behavior can be counterbalanced by further diminishing the lattice part of the thermal conductivity. A promising way, demonstrated numerically by Al-Alam et al. [2], is the reduction of the TE layer below 1 μm which may lead to a thermal conductivity lower than 0.5 W.m⁻¹.K⁻¹. In this work, we studied electrodeposited SnSe thin films. The electrodeposition technique, as a wet technique, proves to be cost-effective, easy to process, capable of achieving good crystallinity and exhibits a relative high growth rate. First, we demonstrated the use of gold substrate, instead of Pt [3], limits the issue of side reactions such as the H₂Se reduction. Consequently, we achieve to have better Faradic yield up to 70%. Then, we will present microstructure analysis made with XRD and STEM HAADF images of electrodeposited SnSe thin films by changing the potential, the thickness and by adding a surfactant to diminish the rugosity.

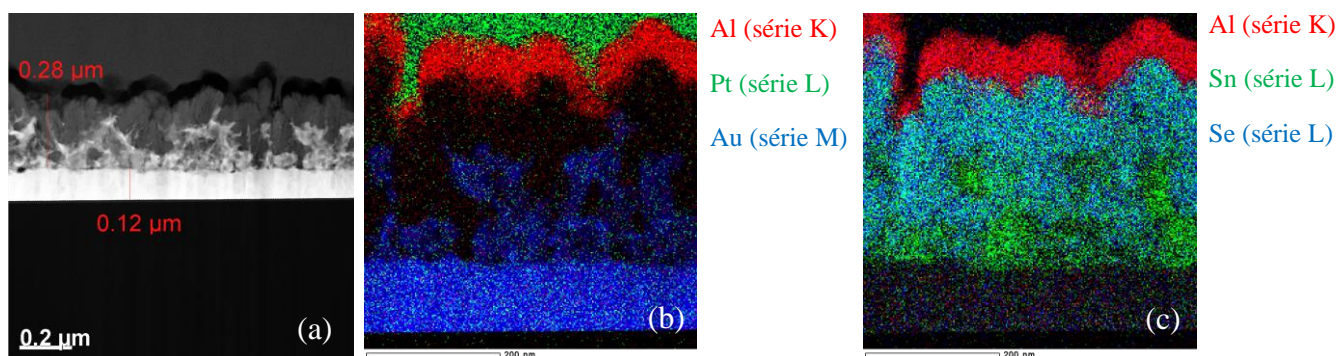


Figure SEQ Figure * ARABIC 1: (a): STEM HAADF image of SnSe deposited at -0.60 V vs Ag/AgCl sat. on gold substrate; (b) and (c): STEM EDS maps of the sample displayed on (a).

Moreover, we will demonstrate that by carefully tuning the growth potential, it is possible to avoid the formation of an interlayer AuSn such as reported by Petersson and Ahlberg [4] and produce (111) oriented texture films of SnSe (Figure 1.).

Finally, we will present the electrical conductivity measurements carried out by IR-Ellipsometry (IRSE) and thermal conductivity measurement studied by Laser Thermoreflectance method.

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3D-CuNi interconnected nanonetworks obtained by electrodeposition with high thermoelectric figure of merit

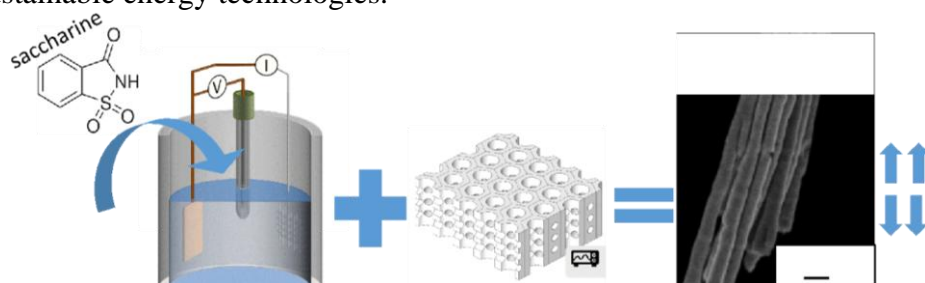
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The pursuit of efficient thermoelectric materials, particularly those composed of low-toxicity and earth-abundant elements, has intensified in recent years. This study introduces an approach to increase the thermoelectric properties of CuNi alloys through the synergistic application of two nanostructuring techniques: the incorporation of saccharine in the electrolyte to achieve a crystallite size reduction to 23-26 nm [1,2], and the utilization of three-dimensional (3D) anodic aluminum oxide (3D-AAO) templates to fabricate nanowires networks. While the electrical conductivity and Seebeck coefficient remained consistent between the nanocrystalline CuNi films and the 3D-nanonetworks, a significant reduction in thermal conductivity was observed, decreasing from 29 W/m·K for the bulk material to 4.9 ± 0.6 W/m·K for free-standing 3D CuNi nanonetworks. This reduction is attributed to enhanced phonon scattering within the 3D architecture together with the nanocrystalline size inside the nanowires. The figure of merit (zT) exhibited an impressive increase of more than four times (4.8) time for free-standing 3D-CuNi nanonetworks, when compared to bulk. Our findings underscore the potential of dual nanostructuring strategies to optimize the thermoelectric performance of environmentally friendly, stable, and abundant materials like CuNi, paving the way for advancements in sustainable energy technologies.



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Effect of heat treatment on electrodeposited Sn NWs in Anodic Alumina Oxide Templates

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Tin nanowires are considered to be very interesting material for several applications, such as gas sensors, anodes in Li-ion batteries, catalysts etc. [1-3]. In all of these applications, the increase of the surface area is one of the most widely used approaches for enhancing their performance [4]. The aim of this study is to develop a simple and cost-effective process to produce vertically aligned tin nanowires attached to a tin film, with high surface area and mechanical stability after the removal of the AAO (anodized aluminium oxide) template. For the synthesis of Sn nanowires template assisted electrodeposition in anodized aluminium oxide porous membranes (AAO) was applied, as it is one of the most effective techniques with significant technical and economic advantages, such as simplicity, low cost, and the ability to operate at low temperature and in different electrolytes media [5]. Anodised aluminium oxide (AAO) membranes were fabricated by one step anodization of aluminium in 0.3M oxalic acid. Two types of AAO templates were fabricated with the same mean pore diameter of ~100nm and pore length ~15µm and ~8µm, subsequently. Tin nanowires were electrolytically deposited from a commercial acidic tin electrolyte. After the filling of the AAO pores with tin nanowires, the electrodeposition continues until the entire surface is coated with a tin film. The tin film works as mechanical support for the nanowires after the removal of the AAO template. As heat treatment is known as an efficient approach for relaxation of stresses caused by electrodeposition, a series of heat treatment experiments in the range of 120 to 210 °C (while nanowires were still embedded in the AAO template) was applied in order to investigate the effect of heating on the mechanical stability of tin nanowires and as a consequence to their surface area. Electrochemical measurements were applied in order to evaluate the surface area moderations between the as deposited and heat-treated tin nanowires. A series of analytical techniques were applied to define the structural and morphological characteristics of tin nanowires (X-ray Diffraction, Field Emission Microscopy and TEM).

Acknowledgment: The authors acknowledge the financial support of EU funded COST Action MP1407 “*Electrochemical processing methodologies and corrosion protection for device and systems miniaturization*”- EMINDS.

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Coinage Metal-Glutathione Nanostructured Gels on Nanoparticles and Electrodes

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Functionalized materials with nanostructured organic interfaces are a promising approach to developing biocompatible nanomaterials with controllable properties. Glutathione, a γ -ECG tripeptide, is the most important nonprotein thiol in the cell. It readily forms self-assembled monolayers (SAMs) and clusters with coinage metals which are actively studied due to GSH intrinsic biocompatibility.

Recent studies using 2DIR spectroscopy have shown that when glutathione (GSH) self-assembles on the surface of Ag NPs, an overlayer with a β -sheet-like structure is formed [1] Further studies have shown that the formation of ordered hydrogel-like GSH shells on Ag and Au nanoparticles is aided by the creation of coinage-metal thiolates [2].

The shell thickness can be controlled via the concentration of either the metal ions (Cu(I), Ag(I), Au(I)) or peptides. The growth of nanogel shell on Au NPs was monitored by LSPR spectroscopy which showed saturation of the shift of the plasmon band corresponding to a shell thickness of ca. 5 nm. Evaluation of the thickness of the GSH shell on Ag NPs using XPS yielded a value of 6.5 nm, which is in qualitative agreement with the result obtained using LSPR spectroscopy [3].

We continued our experiments by investigating the formation of Au-GSH and Ag-GSH hydrogels and comparing their properties to GSH SAMs. We found that coinage metals hydrogel readily forms on the macroscopic Au electrodes. The electrochemical stability of GSH-Au gel to reductive desorption increases compared to GSH SAM as expected from an ordered structure.

Particularly interesting behavior was observed for GSH-Ag gel on Au electrode. The antialgal reduction of silver ions accompanies the formation of the GSH-Ag gel. It was observed not only in the formation of GSH-Ag hydrogel but also in the interaction of Ag-ions with the GSH SAM on the gold electrode. Antialgal reduction modifies the Au_{el}-GSH-Ag gel interface to an Au-Ag_{el}-GSH-Ag configuration, significantly enhancing the stability of the hydrogel to reductive desorption.

We expect GSH-based hydrogel shells will be useful additions to the nanomaterial toolbox.

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Optimization of electrosynthesized Zn-based materials for sustainable antimicrobial applications

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The rapid and widespread proliferation of infectious diseases has driven the development of advanced materials aimed at mitigating microbial transmission and counteracting harmful pathogens. In this context, Zn-based materials, such as zinc oxide and zinc phosphate, have emerged as promising candidates for bioactive coatings [1], offering intrinsic antimicrobial properties, biocompatibility, and the potential for eco-friendly applications. However, in alignment with the atom economy and safety criteria outlined by the Green Chemistry Principles, it is crucial to ensure the use of the minimal effective dose of antimicrobial agents. Chemometric tools have proven invaluable for designing and refining experimental protocols, enabling the reduction of potential toxic effects while optimizing antimicrobial efficacy.

In recent years, our research has focused on developing green electrochemical approaches [2-4] for the synthesis of nano- and microstructures, highlighting their simplicity, high yield, and effectiveness in controlling the size and quality of the resulting materials. In particular, sacrificial anode electrolysis in alkaline media has been employed to prepare Zn-based materials in various shapes and sizes by incorporating suitable stabilizers and applying low current densities. More recently, chemometric tools have been applied to this synthetic process to maximize yield and optimize the development of well-defined materials.

The chemometric approach has facilitated the production of materials with reproducible and tuneable properties, achieving synthetic yields exceeding 85%. Comprehensive analytical characterization- including electron microscopy and spectroscopic techniques- has been conducted to establish correlations between synthesis conditions, material properties, and potential applications.

These findings underscore the potential of these bioactive materials for industrial-scale production, addressing critical challenges related to antimicrobial resistance and fostering sustainable material development.

M.I. acknowledges the financial support from the ERC SEEDS UNIBA programme, project H93C23000660001, "REAL - More for less: REthinking Antimicrobial materials".

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Effect of Growth Temperature on the Physico-chemical Properties of Sprayed cadmium oxide thin films

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Transparent conducting cadmium oxide (CdO) thin films have been deposited onto the soda-lime glass (SLG) substrates using facile and cost-effective spray pyrolysis (SPT) technique. The films have been deposited at various substrate temperatures ranging from 250 to 400°C in steps of 50°C. The influence of substrate temperature on structural, morphological and electro-optical properties of CdO thin films has been investigated. Thermo-gravimetric analysis (TGA) study indicates the formation of CdO by decomposition of cadmium acetate after 250°C. The X-ray diffraction study reveals that all samples are polycrystalline with major reflex along (111) and (200) plane, manifested with the homogeneous distribution of roughly spherical clusters all over the substrate of varying grain size. The optical study shows band gap ranging between 2.3 - 2.5 eV. The Hall effect measurement indicates that the resistivity decreases from 2.43×10^{-3} to $0.99 \times 10^{-3} \Omega\text{cm}$ while carrier concentration increases from 2.61×10^{20} – $5 \times 10^{20} / \text{cm}^3$ and mobility lies in the range of 8.26 – 12.55 cm^2/Vs

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Electrochemical deposition of Ni-matrix nanocomposite coatings with 2D nanomaterials prepared by a boric-free electrolytic bath

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Electrodeposition stands as one of the most widely used methods for preparing composite nanostructured coatings, which offers high control to the operating parameters of the process, in conjunction with low manufacturing cost [1]. The most common commercial type of electrodeposition process is the functional “Hard Chromium” deposition, which utilizes hexavalent chromium (Cr^{6+}) compounds. However, these have been classified as carcinogens and mutagens and are therefore restricted under REACH, since 2019 [2]. The present work focuses on the fabrication of Ni-matrix nanocomposite coatings, using 2D nanomaterials as reinforcing agents, under both direct current (DC) and pulse current (PC) plating methods. 2D nanomaterials display remarkable physical, chemical and electronic properties [3]. The soft van der Waals forces account for their outstanding tribological properties and self-lubrication performance superior to that of other nanomaterials [4]. A boric acid-free bath was developed, using a carboxylic acid as a replacement for boric acid. Dynamic Light Scattering has been used to examine the agglomeration behaviour of the nanoparticles. The surface morphology, composition and structure of nanocomposite coatings have been studied by SEM coupled with EDS and XRD, respectively. Vickers's microhardness and Contact Angle were applied to analyse the possible changes in microhardness and hydrophobicity of the samples. Finally, the tribological behaviour of the coatings was studied, to determine the coefficient of friction.



This research work has received funding from the European Union's Horizon research and innovation program under GA No 101058450 (MOZART) [5].

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Comprehensive study of Ni/SiC coatings deposited from a novel, boric acid free bath as candidate for replacement of hard chromium

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In the last decades, chromium-coated components have been predominantly used in industries such as aerospace, automotive, and machinery manufacturing, where excellent wear resistance, high durability and exceptional corrosion properties are required. However, over recent years, hard chromium plating baths have been recognized as toxic, carcinogenic and mutagenic due to the presence of hexavalent chromium (Cr⁶⁺).

On February 15th, REACH Committee imposed stricter regulations for the use of Cr⁶⁺ [1,2] and strongly advocates its replacement with alternative coatings that offer comparable or superior mechanical properties. The development of an innovative bath composition to replace chromium coatings has become a critical priority, aligning with the Safe and Sustainable by Design Guidelines to mitigate risks to human health and reduce environmental impact.

Within the framework of MOZART project, Creative Nano has developed a boric acid-free Ni/SiC nanocomposite bath as a viable alternative to hard chromium, offering comparable mechanical, morphological, and structural properties. Coatings using this innovative bath were produced through both Direct Current (DC) and Pulse Current (PC) plating techniques.

The morphological, structural and mechanical properties of the coatings have been characterized via SEM, EDS, XRD and Vickers hardness meter, respectively.

More focus has been placed on comprehensive corrosion resistance testing, including Tafel polarization and Electrochemical Impedance Spectroscopy analyses.

The findings from the above studies have been systematically compared with data obtained from coatings deposited using a Ni-Watts/SiC electrolytic bath and with literature data on Hard Chromium, providing valuable insights into the performance and efficacy of the developed coatings.



The MOZART project (HORIZON-CL4-2021- RESILIENCE-01) has been funded by the European Union under GA number 101058450 [3].

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The role of Ni and Co thin film properties on Hydrogen Evolution Reaction

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Electrolyte composition, superimposed magnetic fields and post processing of coatings influences the deposition process and its current efficiency. They have a remarkable influence on thin films' surface morphology, physiochemical properties and catalytic activity. Here, we study the correlation between the electrolyte composition, magnetic flux density and the current density on the deposition process in the presence of a magnetic field with different intensities in different directions: the parallel and perpendicular to the electrode surface. The paper also shows how the magnetic field direction impacts the surface roughness. Furthermore, we also analyze the impact of these synthesized films properties on the hydrogen evolution reaction (HER) when using them as electrocatalysts and how the application of a magnetic field in two dissimilar orientations influences the surface roughness and wettability. The synthesized films are characterized using a scanning electron microscope (SEM), X-ray diffraction (XRD), and atomic force microscopy (AFM).

Understanding Hydrogen Evolution Reaction Induced Modification on Electrodeposited Au-Pd Nanoparticles

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Due to their unique properties and the presence of synergistic effects, bimetallic nanoparticles are widely applied as electrocatalysts. In an effort to maximize undercoordinated sites and their activity, particles are often synthesized targeting specific compositions and complex morphologies. However, this search for more active nano-catalysts has left an important question unanswered: Will their properties remain unaltered under reaction conditions?

In this work we showcase how catalyst preparation by electrodeposition can help us to answer this question. We focus our investigation on Au-Pd nanoparticles, a promising catalyst for different electrochemical reaction. [1-2] The deactivation of this system was extensively studied in oxidative conditions, in which Pd dissolution was identified. [3] However, in cathodic conditions, at which the hydrogen evolution reaction occurs, the behavior of this bimetallic system is not completely clarified, yet. We utilize different electrodeposition protocols to synthesize strongly bound Au-Pd nanoparticles directly at glassy electrodes and carbon nanoelectrodes, thus allowing us to limit the effect of catalyst loss due to bubble formation. This strategy allows us to perform extended hydrogen evolution reaction kinetic experiments and evaluate the time dependent activity of the electrodeposited catalysts. By complementing the electrochemical experiments with extensive material characterization (Figure 1), we identify Pd segregation and smoothening of the catalyst surface as the main deactivation processes for the Au-Pd system under hydrogen evolution reaction conditions.

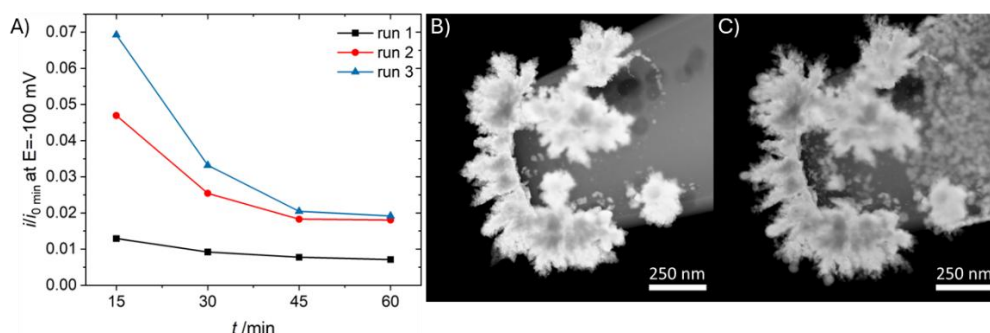


Figure 1: Exemplary plots of the normalized hydrogen evolution reaction current i/i_{0min} at different treatment time (A) and darkfield scanning transmission electron microscopy of Au-Pd nanoparticles electrodeposited before (B) and after (C) the electrochemical treatment.

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Stability investigations of Electrodeposited Ni₃Se₂ thin films after Hydrogen Evolution Reaction

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Abstract: Electrodeposited nickel selenide (Ni₃Se₂) layers demonstrate significant potential as electrocatalysts in water-splitting applications, particularly for the hydrogen evolution reaction (HER). This study investigates the stability of Ni₃Se₂ coatings under cathodic polarization in alkaline media, focusing on their compositional and morphological resilience. Ni₃Se₂ films were synthesized via electrodeposition from a sulfate-based electrolyte under controlled pH and potential conditions[1]. The obtained deposits exhibited excellent adherence to the copper substrate and a uniform greenish appearance, corresponding to the targeted stoichiometry[2].

The stability of the Ni₃Se₂ phase was evaluated through immersion in 1 M NaOH and HER tests under a cathodic current density of -10 mA cm⁻². Depth-profiling analyses, using secondary neutral and ion mass spectrometry (SNMS and SIMS) methods revealed no significant selenium leaching or phase degradation during extended immersion or electrochemical tests. The Ni₃Se₂ phase maintained its compositional integrity, demonstrating robust resistance to deselenation predicted by Pourbaix diagrams[3].

This research highlights the intrinsic stability of Ni₃Se₂ in alkaline conditions, providing a foundation for its application in energy-efficient hydrogen production. Further characterization using X-ray photoelectron spectroscopy (XPS) and low-angle X-ray diffraction (XRD) is underway to elucidate the surface chemistry and crystalline structure of the Ni₃Se₂ films, contributing to the optimization of Ni-Se materials for HER applications.

Keywords: Nickel selenide, Ni₃Se₂, hydrogen evolution reaction, electrodeposition, phase stability, dealloying

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Synergistic effects of an electrodeposited CoNi alloy catalyst for sustainable hydrogen production

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Hydrogen is key for the decarbonisation of energy, and obtaining it from the revalorization of biogas opens a promising although complicated path [1]. Nickel-based catalysts stand out as the affordable best-performing materials for methane dry reforming (DRM) reactions [2]. However, carbon deposition on the catalyst surface stands as the main challenge, which combined with its elevated temperature requirements limits its industrial application. Recent studies focus the efforts on the development of synergies to enhance its properties, where cobalt stands out for avoiding carbon formation during DRM [3], thereby extending the catalyst useful life.

Bimetallic heterogeneous catalysts based on these metals can be prepared by electrochemical means, which favours a subsequent scaling up of the catalyst synthesis process to an industrial level. Hence a CoNi alloy was prepared by electrodeposition. Attending the anomalous behaviour of nickel-cobalt, the electrochemical bath was designed and studied on a glassy carbon substrate. Deposits were prepared and characterized to assess the electrodeposition conditions to achieve an equal proportion of each metal in the alloy. Finally, CoNi catalyst was prepared on a steel substrate, released and subjected to mechanically assisted sonodisgregation to reduce the particle size.

Catalytic tests for DRM were performed using a synthetic mixture of CH₄ and CO₂ in a furnace heated reactor. Analytic results of CoNi show promising conversions at 800 °C with a stable production of hydrogen for 6 h while avoiding catalyst coking. To assess further synergies, composites between the electrochemical CoNi and a commercial nickel alloy material (Ni_{com}) were prepared. The composite exhibits an improvement in H₂ production at all temperatures, specially at 600 °C respect CoNi, while showing a similar trend to the one for Ni_{com}. Those results reflect the benefits of synergies between Ni and Co, as well as the viability of this reaction at lower temperatures when in combination with additional affordable materials.

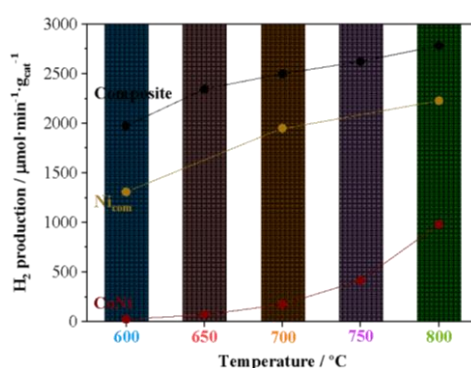


Fig. 1: H₂ production at different temperatures, for CoNi, Ni_{com} and its composite (m_{cat} = 0.7 g).

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Acknowledgments:

With the support of the Industrial Doctorates Program of the Department of Research and Universities of the Generalitat de Catalunya (project 2022 DI 035). The authors would like to thanks the Nanoengineering of Materials Applied to Energy (NEMEN-UPC) research group and Dr. Jordi Llorca, and the CCiT-UB for the use of their equipment.

Electrochemical Preparation and Characterization of Porous Nickel Layers as Catalyst Support Structures for Anion Exchange Membrane Electrolyzers

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With the ongoing decarbonization of many industrial sectors, integrating renewable energy sources and developing sustainable storage systems are crucial to achieve a clean energy supply. Hydrogen may play a key role in this transition as an effective energy carrier. Additionally, hydrogen can serve as a reducing agent in steel production [1]. Currently, hydrogen is mainly produced via steam reforming of natural gas, which generates large amounts of CO₂. However, when produced via electrolysis using renewable energy sources, hydrogen can be produced with a very low carbon footprint. In addition to established techniques like alkaline and proton exchange membrane (PEM) electrolysis, anion exchange membrane (AEM) electrolysis is emerging as a promising electrolyzer concept. AEM electrolysis has the advantages of PEM electrolysis (good long-term stability, high power densities, high current density, high gas purity and high efficiency) while avoiding the use of expensive and rare platinum group metals [2]. This leads to reduced production costs [2].

This contribution will present recent results from the author's lab on the fabrication of catalyst support structures produced via a dynamic hydrogen-bubble templating (DHBT) electrodeposition process for nickel. The thus obtained structures have a high availability of catalyst at the interface to the membrane. The influence of plating conditions, such as bath composition, current density and deposition time on the surface morphology and overall structure (e.g. thickness, size and distribution of pores) will be discussed. Additionally, electrochemical measurements, including the electrochemical surface area (ECSA) through Cyclovoltammetry (CV) and electrochemical impedance spectroscopy (EIS), polarization curves, long-term stability tests will be presented. The resulting data will then be analyzed to assess the suitability for AEM electrolysis applications and to identify further applications and potential improvements.

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Electrochemical Dealloying of AgAuCuPdPt Thin Film for Improved Hydrogen Evolution Catalysis

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Electrochemical dealloying is a promising method for producing nanoporous materials with high specific surface area and unique catalytic properties. [1-4] In this study, electrochemical dealloying was applied to Ag₃₁Au₁₄Cu₂₁Pd₁₈Pt₁₇ compositionally complex solid solutions (CCSS), commonly referred to as high-entropy alloys, which are known to be a special class of electrocatalysts to optimise their structure and catalytic activity for the hydrogen evolution reaction (HER). [5] The CCSS were synthesised by combinatorial magnetron co-sputtering and modified by electrochemical dealloying in an acidic electrolyte solution. The initially granular structure changes after dealloying to a more compact structure, which exhibited an enhancement in catalytic activity for HER in absolute and normalised currents compared to the non-dealloyed alloys. This improvement is attributed to the increase of specific surface area, and optimised composition for HER of the remaining alloying elements (Ag₁₅Au₂₆Cu₆Pd₂₅Pt₂₉). EC-dealloying leads to a decrease of Ag and Cu, while the overall composition of Au and Pt was increasing. The results of this study demonstrate that electrochemical dealloying is an effective strategy for producing highly active catalysts and highlight the potential as a versatile system for electrochemical modification on CCSS.

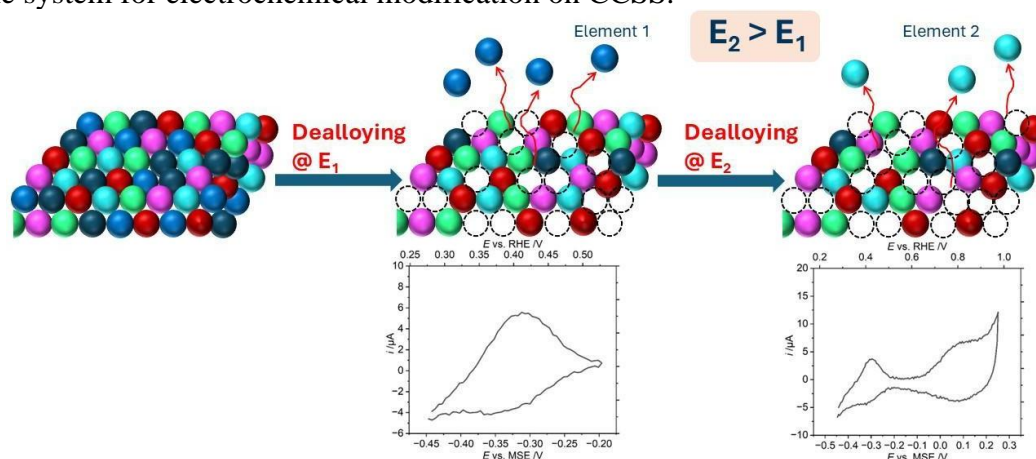


Figure 1: Schematic concept of electrochemical dealloying of a quinary alloy.

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Inkjet Assisted Electroforming of Untethered Magnetic Microdevices for Smart Drug Delivery Applications

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Inkjet Printing (IJP) is a material deposition technique based on the controlled jetting of fluid droplets and well known for its highly attractive features. Its flexibility and ease of operation make it competitive with many already affirmed materials deposition methods. The high precision typical of the technique makes it highly adapt to advanced patterning tasks, even at the microscale. Finally, its capability of optimizing material usage is potentially beneficial to address the needs for sustainable manufacturing highlighted in the Sustainable Development Goals (SDGs) delivered by the United Nations.

One of the most interesting applicative fields where IJP may find application, still largely unexplored, is the realization of untethered magnetic microrobots. These devices, remotely propelled by controlled magnetic fields, have great potential to address a wealth of applications at the microscale [1]. Typical examples are micromanipulation, localized surgery, cargo or cells delivery and targeted drug administration. The high throughput of IJP, in particular, is potentially disruptive for the realization of large swarms of microrobots, where the properties of the single device are enhanced by the cooperative action of many hundreds of single entities.

The present work describes the use of IJP as a supporting technique, in combination with electroforming, for the realization of remotely guided magnetic microdevices. The resulting hybrid approach, identifiable as Inkjet Assisted Lithography (IAL), is highly attractive for the realization of large quantities of identical micrometric devices. In continuity with the existing literature [2], complex shaped microrobots are reproducibly manufactured exploiting the potential of IJP when applied to precision patterning tasks. From the applicative point of view, the microdevices produced are surface functionalized in order to introduce a drug loading capability exploitable in smart delivery applications [3].

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Downscaling magnetic field gradients for copper magnetoelectrodeposition on the micrometer scale

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Copper deposition techniques are highly valued in the electronics industry due to their diverse application fields [1]. Magnetochemistry combines electrochemical, hydrodynamic, and magnetic phenomena, with key forces acting on the electrolyte, i.e. the Lorentz force and magnetic gradient force [2]. By employing pulse-reverse plating (PRP), effects of magnetic field gradients on electrodeposition of paramagnetic species have been demonstrated. Firstly, micrometer-scale 3D copper structures in millimeter-size magnetic field gradients ($(\vec{B} \cdot \vec{\nabla})\vec{B}$) were obtained [3].

This raises an important question: how far can those effects be downscaled?

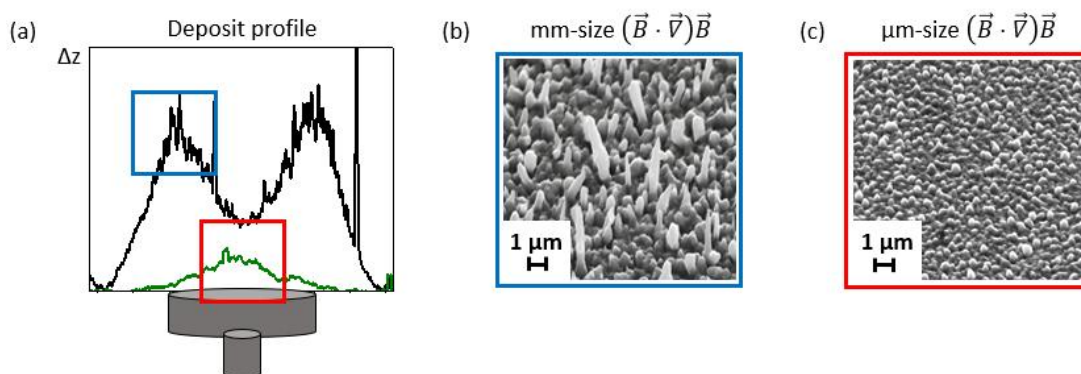


Figure 1. (a) Profilometries of Cu deposits, SEM images of Cu deposited in high magnetic field gradient areas for (b) mm-size, and (c) μm -size $(\vec{B} \cdot \vec{\nabla})\vec{B}$ at -1.30 V vs. MSE.

Our new study addresses PRP of copper in combination with successively downscaled magnetic field gradient templates, i.e. iron wires with diameters of 1 mm to 125 μm . Structuring effects of Cu deposits are demonstrated for all templates. The deposit structures closely resemble the calculated profile of the magnetic field gradient term. Significant differences in surface roughness were detected revealing the influence of the magnetic field gradient scale on the deposit morphology. Applying more negative deposition potentials leads to improved structuring. Based on current transient analyses, this effect is explained by the action of the curl of the magnetic field gradient force [4]. Future work will focus on Co/Pt templates in multidomain states, employing in-situ Kerr microscopy and cyclic voltammetry to investigate the effects of nanometer-scale magnetic field gradients. Funding was provided by the IFW Excellence Program 2020.

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Exploring magneto-ionic effects in electrodeposited nickel-iron alloys

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Magneto-ionic effects offer a promising way to achieve low-voltage, non-volatile manipulation of magnetic materials, which is critical for the next-generation of energy-efficient devices. To date, research has primarily focused on magneto-ionic control of iron- and cobalt-based thin films and nanostructures [1], using voltage-induced interfacial oxidation and reduction reactions and ion migration to reversibly tune magnetic properties. We have previously demonstrated ON-OFF switching of coercivity and magnetoresistance in 5-10 nm thick FeO_x/Fe nanostructures via oxidation/reduction in alkaline solution. [2,3] While Ni-Fe alloys, known for their soft magnetic properties, are highly relevant for various magnetic devices, their magneto-ionic behavior has not yet been systematically investigated. [4,5] In addition, the exploration of ferromagnetic alloy films beyond a few nanometers in thickness holds the potential for magnetic sensing and actuation applications.

This work systematically explores the magneto-ionic behavior of electrodeposited Ni_xFe_{1-x} films, with thicknesses of (155 ± 25) nm, as a promising platform for enhanced magneto-ionic functionality. The alloy films were synthesized by electrochemical deposition at -1.1 V vs. SCE on Si/SiO₂/Cr/Au substrates, using the content of nickel and iron salts in the electrolyte to adjust the alloy composition. In accordance with the literature [6], the coercivity of the films ranges from (0.4 ± 0.1) mT in Ni₈₀Fe₂₀ (permalloy) to (44.6 ± 0.6) mT in pure Fe with a weak or no uniaxial anisotropy in the film plane, as determined by magneto-optical Kerr effect magnetometry. Electrochemical modification of the films is achieved by electrolytic gating in aqueous 1 M KOH solution using a three-electrode electrochemical cell in combination with Kerr microscopy. So far, highest magneto-ionic effects are achieved in Ni₄₆Fe₅₄ by a relative coercivity reduction of 90 % with respect to the pristine state at -1.24 V versus Ag/AgCl (3 M KCl). We interpret the observed modifications to be caused by a reduction of surface oxides as a mechanism responsible for modifying domain wall pinning. [3] These results highlight the potential of Ni_xFe_{1-x} alloys, particularly in comparatively thick films, and extend the scope of research into magneto-ionic materials.

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Electrodeposited Ni-MoOx coatings as high efficiency catalysts for green hydrogen production in alkaline solution

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Ni-MoOx catalysts were electrodeposited on Ni mesh 40 under severe hydrodynamic conditions from the electrolyte containing 2.0 M NH₄Cl + 0.2 M NiCl₂ and MoOx powder of different concentrations. XRD analysis of as-prepared MoOx powder, obtained by modified rheological procedure [1], confirmed that sample contains following compounds: MoO_{2.8}, H₂MoO₄, MoO₃, MoO₂ and (NH₄)₂Mo₂O₇. XPS analysis confirmed the following coating composition: Mo₆₊ and Ni₂₊ species being placed on top of the surface, while Mo₄₊, Mo₅₊ and Ni₀ were detected deeper in the coating (fig. 1).

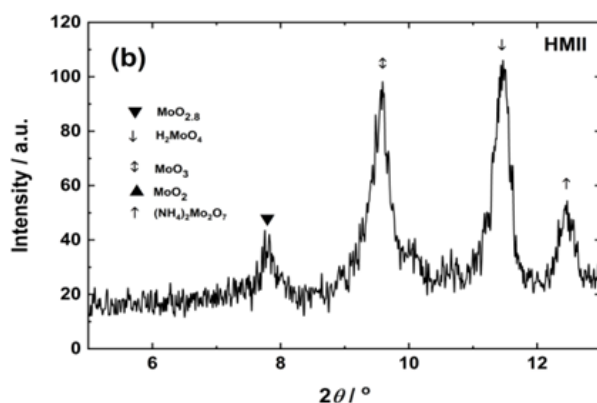


Fig. 1. XRD analysis of as-prepared Mo oxide based powders at room temperature

SEM-EDS surface and cross-section analysis of samples showed that coatings with higher amount of Mo had higher roughness. The amorphous structure of the Ni-MoOx coatings was confirmed by SAED analysis. The HER was investigated in 30 wt. % KOH at 70 °C. The lowest overpotential at $j = -500 \text{ mA cm}^{-2}$ was only -88 mV for the best activity Ni-MoOx sample. A new approach to electrochemical impedance spectroscopy analysis [2], from Nyquist plots enabled determination of the exchange current densities for the charge transfer reaction, intermediate adsorption reaction and total HER. It was clearly indicated that any of the partial reactions could be rate determining ones. Advantages and disadvantages of these novel catalysts in comparison to state of the art were discussed, as well.

Acknowledgements: This work was supported by the Federal Ministry of Education and Research–Germany, through the WBC2019 call–project NOVATRODES 01DS21010, and by the Ministry of Science, Technological Development, and Innovation of the Republic of Serbia (Contract No. 451-03-65/2024-03/200135 and 451-03-66/2024-03/200053).

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Electrochemical synthesis, characterization and functionalization of nanoporous Au nanostructures

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Nanoporous Au (NPG) nanomaterials are emerging novel materials that exhibit outstanding functional and structural properties, e.g. enhanced surface area, high conductivity, and tunable physical, chemical, and optoelectronic properties. NPGs have a wide range of applications such as electroanalytical chemistry, SERS, catalysis and drug delivery [1]. Electrodeposition (ED) is a powerful techniques to synthesize Au alloys as nanomaterials. Electrochemical dealloying is used for producing nanoporous bicontinuous structures. It can be carried out in less corrosive media by dissolving the least noble element out of a metal alloy [2].

This work mainly focuses on the synthesis of NPG nanowires (in AAO templates with-85nm pore diameter) and NPG dendritic structures (on Au sputtered Si wafer). Potentiostatic ED of AuCu alloy (25 at% Au, 75 at% Cu) nanowires (-0.15 V) and dendrites (-0.60 V) was performed in a three-electrode cell (CE: Pt, RE: SCE) in a mixture of 0.02 M Cu²⁺/0.006 M Au³⁺ electrolyte. NPG nanowires (at 0.70 V, Fig. 1a) and dendritic structures (at 0.87 V, Fig. 1b) were obtained by potentiostatic dealloying in 0.1 M H₂SO₄ via dissolution of Cu. Suitable deposition and dealloying parameters have been identified by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The obtained nanoporous structures were analyzed by SEM, EDX, TEM, and XRD.

Electrochemical active surface area (ECSA) analysis [3] of those NPG dendritic structures showed a more than 40 times increased surface area compared to a flat Au film (Fig. 1c). This makes those structures particularly interesting as highly sensitive sensor materials. Preliminary SERS measurements on Rhodamine 6G and melamine molecules confirm the impact of NPG structures on signal amplification and sensitivity enhancement, up to single molecule detection.

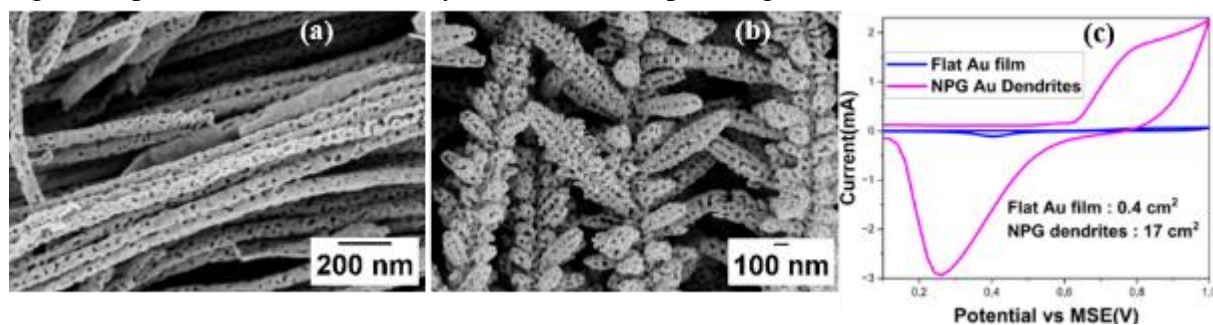


Figure 1: SEM images of (a) NPG nanowires and (b) NPG dendrites (c) ECSA measurements in 0.05 M H₂SO₄ vs. MSE

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Enhancing Ni Thin Film Properties via Electrodeposition in Magnetic Fields: A Deep Eutectic Solvent Approach

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This study investigates the electrodeposition of nickel (Ni) thin films on copper (Cu) substrates from a deep eutectic solvent (DES), *ethaline*, consisting of choline chloride and ethylene glycol in a 1:2 molar ratio, at 45°C. The deposition process was conducted in the absence and presence of an external magnetic field to evaluate its influence on the structural, morphological, and catalytic properties of the deposited films. The effect of magnetic field direction on the deposition process was also examined. Characterization techniques, including scanning electron microscopy (SEM), X-ray diffraction (XRD), and atomic force microscopy (AFM), revealed significant modifications in film morphology, crystalline structure, and surface roughness under the influence of the magnetic field. Electrochemical studies demonstrated enhanced catalytic performance of the Ni thin films deposited in the presence of the magnetic field, showing superior activity for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). These findings underscore the potential of DESs and magnetic field-assisted deposition for tailoring catalytic properties of Ni-based thin films.

Electroless deposition of Ru NPs for heterogeneous catalysis application

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Ruthenium is well-known for its outstanding performance as a catalyst in heterogeneous catalytic processes, including methanation and reforming reactions. This highly active metal facilitates not only good conversions, but also high selectivity towards specific products. At the nano-scale, ruthenium provides enhanced surface areas, thereby boosting its catalytic activity. The electroless deposition technique, in addition to its capacity to deposit metal on a broad array of substrates, enables the control of particle composition and morphology through the modulation of plating bath [1]. The balance achieved among metal precursors, reducing agents and additives is pivotal for the effective autocatalytic reaction of the metastable solution. However, the use of phosphates or boranes as reducing agents causes heteroatom codeposition. Even though the presence of P or B may be beneficial for some applications, it can hinder the desired catalytic effect. To address this challenge, hydrazine was selected as a reducing agent due to its complete oxidation, which results in its decomposition into H₂ and N₂ without leaving any heteroatoms on the metal deposit.

In this study, ruthenium particles were electrolessly deposited over fluorine-doped tin oxide coated glass (FTO) substrates, using a Ru plating bath containing hydrazine [2]. The entire process, encompassing Ru dissolution in acidic pH, bath basification and the electroless deposition itself, was meticulously monitored using UV-vis spectrophotometry. A series of samples were prepared at varying deposition times and subjected to morphological and compositional characterization via scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS). Furthermore, the stability of the bath was studied over an extended period, to assess the performance of the ruthenium solution and its plating capacity. The results obtained from this study will be further applied to prepare ruthenium-based catalysts over different supports, such as carbon-based materials, to check electroless deposition suitability as preparation method for heterogeneous catalysts.

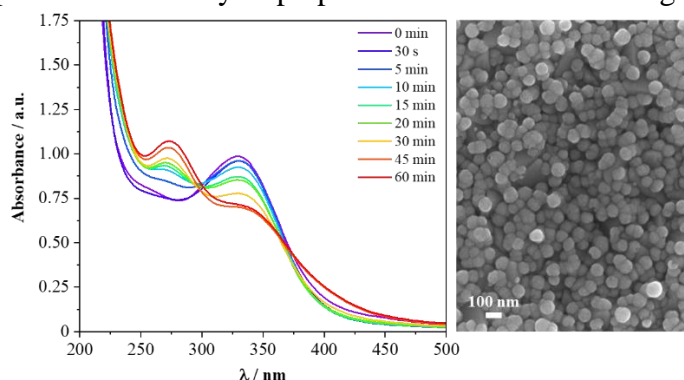


Fig. 1: Time dependent UV-vis spectra of the electroless deposition of Ru (left) and SEM micrograph of Ru particles (right).

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Acknowledgments:

With the support of the Industrial Doctorates Program of the Department of Research and Universities of the Generalitat de Catalunya (project 2022 DI 035). The authors would like to thanks the CCiT-UB for the use of their equipment.

Giant Spectral Shifts of Electrochemically Polarized Plasmonic Nanoparticle on a Mirror

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Metal nanoparticles (NPs) interact strongly with light, which leads to the creation of localized surface-plasmon resonances (LSPR) that depend on the metal type, particle size geometry, and the environment. A particularly intriguing configuration allowing electrochemical control involves a nanoparticle-on-mirror (NPOM), where an NP is positioned over a metallic surface (mirror) with a gap typically filled with a dielectric material. Modulation of the properties of coupled NPOMs under electrochemical conditions is important in plasmonic catalysis and analytical applications including SERS.

We studied systematically single NPOM scattering for Au NPs and Ag NPs separated from Au electrode by a short (less than 1 nm) self-assembled monolayer (SAM) of aminoethane thiol (AET), ethylene dithiol (EDT) or polyallylamine hydrochloride (PAH) under electrochemical control.

We found a giant reversible spectral shift of the coupled plasmon during electrode polarization in an alkaline solution (Figure 1A, B), reaching in some cases 100 nm. A blue shift of the surface plasmon resonance was observed during negatively going potential steps and found for both Au NPs and Ag NPs. Surprisingly, this massive spectral shift occurred over a narrow range of potentials, typically between 0.4 and 0.2 V. The observed spectral shifts were reversible and could be tuned back and forth several times by changing the electrochemical potential. In acid solution, we observed only moderate linear change of the coupled plasmon with potential (Figure 1B, C), which resembled the charging of NPs immobilized on a conductive transparent electrode.

Numerical modeling of the NPOM showed that a simple model of NP and electrode charging cannot reproduce experimental results observed in an alkaline solution. The observed effect likely stems from changes in the conductivity of the gap between the NP and the electrode.

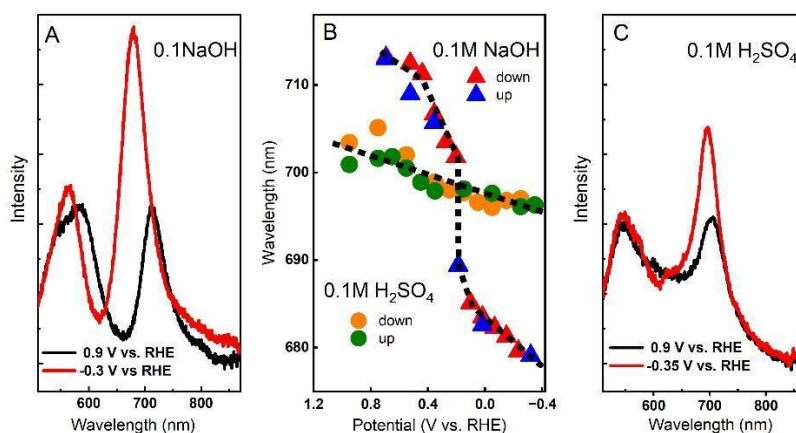


Figure 1. Electrochemically controlled spectroscopy of AuNP/AET/Au NPOM. (A) and (C) – spectra of NP at most positive and negative potentials. Intensity normalized to coupled plasmon band at the most positive potential. (B) Variation of the coupled plasmon resonance during negatively and positively going potential sweeps in acid and alkaline solutions

Evaluation of adhesion characteristics of electrolytically produced copper thin films of nanostructured characteristics: theory vs. experiment

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In this study, adhesion of thin copper films of nano structural characteristics produced via electrochemical deposition method on Cu and stainless-steel 316L cathodes has been estimated theoretically and experimentally verified. The thin Cu films were electrodeposited galvanostatically at room temperature from various types of electrolytes applying the magnetic stirring of the electrolyte. The electrolyte without addition of any additive (the basic sulphate electrolyte), as well as those with an addition of chloride ions, chloride ions and polyethylene glycol (PEG), and a combination of chloride ions, PEG and MPSA (3-Mercapto-1-propanesulfonic acid) were analysed. Morphology and structure of Cu films electrodeposited on the Cu electrodes were examined by application of scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) techniques, respectively. The Cu films obtained from additive-free electrolyte and the electrolyte with chloride ions were fine-grained, the Cu film obtained from the electrolyte with the addition of chloride ions and PEG was coarser than them, while the combination of all three additives gave to the film mirror-bright appearance. The roughness of the Cu films increased with an addition of chloride ions, chloride ions and PEG relative to the pure Cu film, giving considerably lower roughness of mirror bright Cu film obtained from the electrolyte with all three added additives. The theoretical estimation of adhesion of the Cu films electrodeposited on the Cu cathodes was performed by application of Chen-Gao (C-H) composite hardness model [1-2]. For an estimation of adhesion of the Cu films according to this model, the knowledge of a hardness of film was necessary, and since Cu films electrodeposited on Cu cathode belong to "hard film on soft substrate" composite hardness type, Korsunsky (K) model [3] was selected to do it. It was shown that adhesion of the Cu film increased with an addition of the additives, that was experimentally verified by use of bidirectional bending and tape tests. Using well known fact that the Cu films electrodeposited on stainless-steel cathodes shows relatively weak adhesion, the additional both theoretical and experimental verification of adhesion characteristics of the Cu films was performed by comparison of the Cu films obtained from the basic sulphate electrolyte and the electrolyte with all three added additives on the Cu cathodes with those obtained on the stainless-steel cathodes.

Acknowledgements: This research was funded by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia funded the research (Contracts No. 451-03-66/2024-03/200026, 451-03-66/2024-03/200162, and 451-03-47/2024-01/200135), and by the bilateral research project between the Ministry of Science, Technological Development and Innovation of the Republic of Serbia and German Academic Exchange Service (DAAD).

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Influence of duty cycle in the pulsating current regime on morphology and structure of copper coatings

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In this investigation, the copper coatings were electrodeposited from the basic acid sulphate bath on Si(111) wafer using pulsating current (PC) regime. An adhesion/nucleation layer of chromium and gold was sputtered on silicon wafer samples before electrochemical deposition process. Copper coatings obtained with variations of duty cycle (θ) in the range (15–50 %), i.e. with varying average current densities between 15 and 70 mA·cm⁻², and keeping the current density amplitude constant (100 mA·cm⁻²). The thickness of the copper coatings was 40 µm. The aim of investigation was to calculate grain size of deposits and to investigate the impact of square waves PC regime and duty cycle to obtain uniform compact coatings suitable for potential application in MEMS devices. Copper coatings obtained in the range of the duty cycles between 15 and 50 % were characterized by scanning electron microscope (SEM), atomic force microscope (AFM) and X-ray diffraction (XRD). The XRD analysis of the obtained Cu coatings confirmed their nano-structural grain size. The average grain size was in the 29.95-38.58 nm range according to Debye-Scherrer analysis method applied to XRD patterns. The average roughness parameter of Cu coatings obtained after AFM analysis was in the 100-150 nm range. As the duty cycle increased from 15 % to 50 %, the regularity and size of the Cu grains decreased. With a 50 % duty cycle, the fine-grained structures are created. The crystal structure of electrodeposited Cu coatings modified from the strong (220) to the strong (111) preferred orientation, and the coatings' shape changed from large-grained to fine-grained as the average current density increased. The best structural and morphology characteristics were observed for the Cu coating with fine-grained and nano-size grains synthesized with a 50 % of duty cycle, pause duration of 5 ms, and at an average current density of 50 mA·cm⁻².

Acknowledgements: This research was funded by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia funded the research (Contracts No. 451-03-66/2024-03/200026, 451-03-66/2024-03/200162), and by the bilateral research project between the Ministry of Science, Technological Development and Innovation of the Republic of Serbia and German Academic Exchange Service (DAAD).

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Combined Effect of Boric Acid and Heterogenous Magnetic Field on Cu-Ni Electrodeposition

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The growing demand for new materials with superior properties that meet advancements in various aspects of modern life drives materials science to explore innovative materials derived from individual metals. Nanomaterials and bimetallic systems have emerged as promising candidates to provide novel properties that are absent in their individual components. Cu-Ni bimetallic systems are widely recognized for their exceptional corrosion resistance, thermal stability, and mechanical strength, making them vital in marine, energy, and electronic applications.^[1] In addition, Cu-Ni systems constitute a promising alternative to noble metals as electrocatalysts, e.g., for hydrogen evolution reaction (HER), owing to their low cost, high corrosion resistance and environmental friendly properties.^[2] However, controlling their microstructure and composition during fabrication remains a challenge. Magnetic field-assisted electrodeposition has emerged as a promising tool to address these challenges by leveraging magnetic forces to enhance mass transport, control particle movement, and influence deposition patterns.^[3,4]

In this study, we examine how a gradient magnetic field affects the electrodeposition of Cu-Ni, with an emphasis on the structural and compositional characteristics of the deposits. We also investigate the role of boric acid as an additive, both with and without the magnetic field. Optical and scanning electron microscopy reveal that the established gradient magnetic field significantly influences compositional patterning and morphology of the deposits, leading to the formation of flower-like pillars with branching increasing steadily with boric acid concentration. X-ray diffraction confirms the crystalline nature of the deposits, while energy dispersive X-ray spectroscopy provide compositional insights, demonstrating an increase in copper content when a gradient magnetic field is applied and/ or boric acid is added in the electroplating bath. Cyclic voltammetry measurements show a negative shift of the electrodeposition potential of nickel with and without copper by increasing boric acid concentration. Consequently, electrochemical quartz crystal microbalance experiments show accordingly a decrease in the total amount of deposits as well as the current efficiency by increasing boric acid concentration. These results highlight the critical interplay between a gradient magnetic field and chemical additives, specifically boric acid, in tailoring the properties of bimetallic systems.

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How electrodeposition conditions of palladium affect hydrogen absorption

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Palladium is a critical material used both as final coating as well as intermediate layer to enhance corrosion resistance and to act as a diffusion barrier, especially within the fashion industry. However, a common issue with Pd and PdFe alloy electroplating baths is the formation of microcracks in the deposits due to hydrogen evolution during the electrochemical deposition [1 - 2].

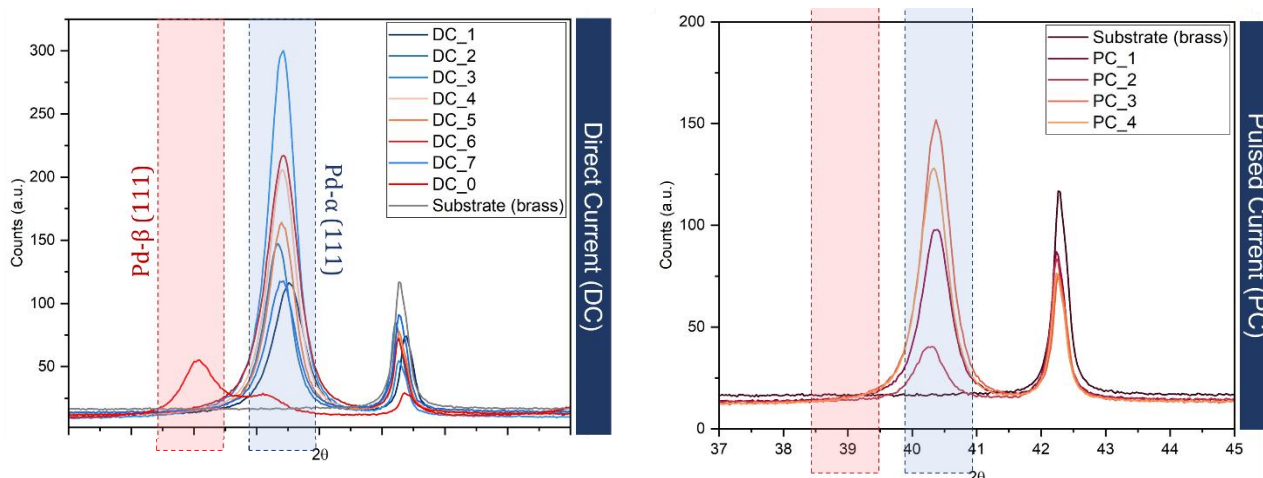
This study explores the impact of electrodeposition conditions on the hydrogen absorption properties of palladium using the innovative pure palladium galvanic bath, “PalmetEco”.

The present study sheds lights on PalmetEco, which seems to predominantly deposit the thermodynamically stable α -phase of Pd hydride, which does not result in microfractures over time, as opposed to the β -phase, which is usually predominant under typical deposition conditions from common Pd-based electroplating baths.

X-ray diffraction (XRD) was employed to differentiate between the α and β hydride phases, using characteristic peaks at 39° and 40°, respectively.

Various operational parameters, including temperature, deposition time, and brighteners content, were varied in direct current samples, while different waveforms were used in pulsed current samples. The results showed that the β -phase peak was mostly absent. Nevertheless, the PalmetEco bath seems to effectively deposit primarily the α -phase of Pd hydride, thereby reducing the likelihood of microfracture formation. Starting from our findings, further investigations may improve the conditions for consistent α -phase deposition across different conditions.

The authors acknowledge Regione Toscana PR FESR 2021/2027, Azione 1.1.4, Bando 1 “Progetti strategici di ricerca e sviluppo” which made possible the project “FREE GALVAN” (CUP-ST: 27716.29122023.042000059).



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Metal oxide nanofibers made via electrospinning for photoelectrochemical water splitting

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The unique physical and chemical properties of quasi one-dimensional nanostructures that arise by their high surface-to-volume ratio make these nanostructures very promising for many applications, including solar water splitting. Furthermore, the physical properties of most semiconductors also demand the use of such elongated nanostructures for photo(electro)chemical applications. For instance, the diffusion length of minority charge carriers (i.e. electrons for a p-type semiconductor or holes for an n-type semiconductor) in Cu₂O is only 20-100 nm, while the absorption depth near the bandgap is approximately 10 μ m. This means, that with the use of one-dimensional nanostructures, a maximum of solar light can be absorbed over the nanowire length, while the nanowire diameter is small enough for efficient electron and hole diffusion, and therefore high efficiency.

Besides templated electrodeposition, electrospinning is also a highly efficient, scalable and cost-effective synthesis technique for the preparation of elongated nanostructures. The electrospinning process can be easily combined with sol-gel-chemistry, which is a well-known low-cost solution-processing method for the preparation of different kinds of metal oxides, including photoactive materials. An interesting advantage of electrospinning, is that there are a lot of parameters that can be varied for optimum water splitting efficiency, e.g. solution properties, processing parameters and the setup design.

Here, the electrospinning process will be explained, together with several examples of electrospun nanofibers consisting of different materials (Figure 1). Additionally, the photoelectrochemical performance of our CuBi₂O₄ and BiVO₄ nanofibers will be presented, and intensity-modulated photocurrent spectroscopy (IMPS) and electrochemical impedance spectroscopy will be introduced as advanced electrochemical methods for the in-depth understanding of such photoelectrodes.

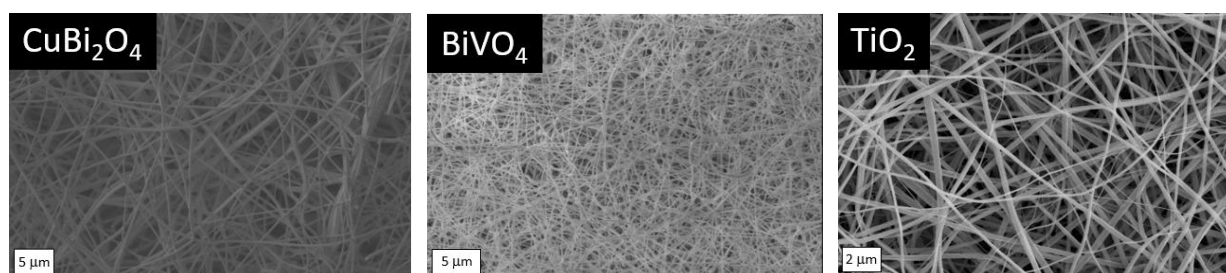


Figure 1: SEM images of different kinds of electrospun nanofibers.

Cu₂O photocathodes: From electrochemical synthesis to improved stability with an ALD-based TiO₂ coating

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Photoelectrochemical reactions with semiconductor electrodes offer the possibility to produce chemicals and fuels from widely available starting materials in a climate-neutral way, e.g. hydrogen from water. A common photocathode material is p-type copper(I) oxide. Its band structure allows the hydrogen formation reaction with a high solar-to-hydrogen efficiency ($\eta(\text{max}) = 18\%$). The major limitation of the material is that it is not stable under application conditions, but is reduced to metallic copper [1].

Here, we describe an electrochemical process for the preparation of copper(I) oxide layers and show how nanostructured copper(I) oxide rods with high aspect ratios (Figure 1) can be prepared in a multi-stage process by depositing them in polymer templates [2,3]. To increase the temporal stability, the samples were coated with titanium dioxide by atomic layer deposition.

Scanning electron microscopy shows that octahedral copper(I) oxide particles are formed at the beginning of the deposition process, which then transform into cube-shaped crystallites. Using X-ray diffraction, we show that the materials are crystalline and preferentially orientated along (111) for the compact layer and along (200) for the nanostructured sample.

We present cyclovoltametric data to show how the titanium oxide layers suppress the anodic and cathodic corrosion reactions of the semiconductor electrodes. The performance and temporal stability under operational conditions are discussed using chronoamperometric measurements for dark and illuminated photocathodes.

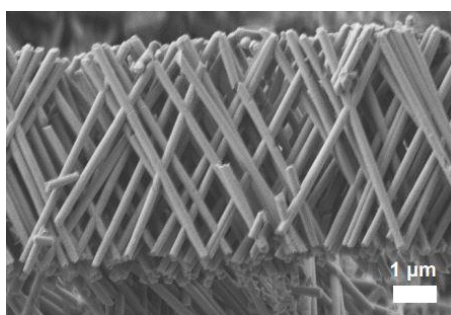


Figure 1: SEM image of highly crystalline Cu₂O nanowires.

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Role of the local diffusion fields in electrolytic formation of zinc irregular forms from the alkaline electrolyte

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The alkaline electrolytes are a component of Zn-air secondary batteries, representing promising candidate for energy storage with numerous advantages relative to the other battery types, such as Li-air, Al-air, and Mg-air [1]. One of the largest challenge in a development of this battery type is a formation of irregular forms of nanostructured characteristics during the charging process, such as dendrites, irregular and regular crystal grains of various shape including those having hexagonal shapes. The formation and growth of all these forms occur in conditions of the diffusion control of the electrodeposition process, and while a mechanism of formation and growth of dendrites is relatively well investigated [2], it is not case with a mechanism of a growth of crystal grains, especially those with a hexagonal shape. For that reason, this study aims to investigate it.

The growth of the hexagonal grains formed in the moment of nucleation inside the diffusion layer of the macroelectrode depends on their orientation towards bulk of the electrolyte. These grains can be oriented towards the bulk of electrolyte by either the tip (Figure 1a) or lateral side (Figure 1b), and the local diffusion fields, such as the spherical and cylindrical ones, formed around their tips or the lateral sides are responsible for their final shape. The spherical diffusion layer is formed around the tip of hexagonal crystal grain oriented by the tip towards the bulk of the electrolyte and Zn crystals of elongated shape are formed in the growth process (Figure 1c). The cylindrical diffusion layer is formed around the lateral side of hexagonal Zn crystal oriented by the lateral side towards the bulk of electrolyte, and this orientation of Zn grain survives the growth process (Figure 1d). Mathematical model has been developed to show that the rate of growth in the conditions of the spherical diffusion is larger than that in the conditions of the cylindrical diffusion, that is confirmed by morphological analysis of Zn crystal grains obtained with various times of the electrodeposition (Figure 1).

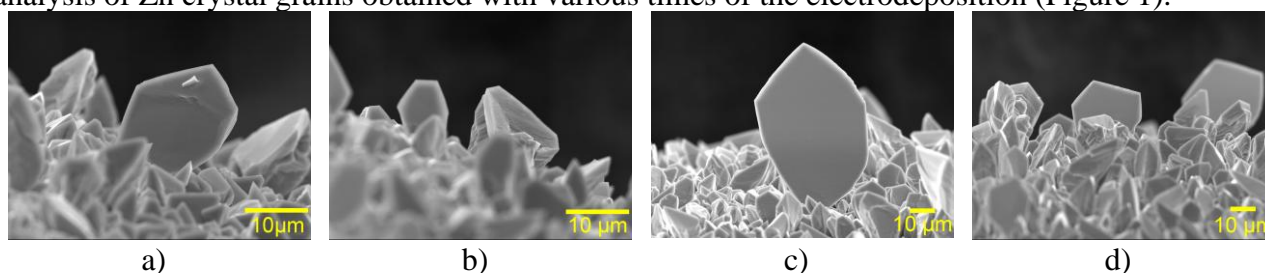


Figure 1. Morphology of Zn crystal grains electrodeposited from 0.35 M ZnO in 6.0 M KOH at an overpotential of 160 mV with the electrodeposition time of: a) and b) 450 s, and c) and d) 800 s.

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Anodization of Multicomponent Alloys for degradation of environmental pollutants

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Improvement of the air quality is an important goal of The European Green Deal. Indoor air pollution is a major environmental health concern as it can lead to serious health effects, including respiratory diseases, heart disease, and cancer. It is essential because this is where we spend most of our time. One of the proposed methods to reduce the potential risks associated with air pollutants and their impact on the environment and human health is photocatalysis [1]. TiO₂ photocatalyst, due to its high purification performance, environmental impact and economic benefits, is an attractive alternative solution to conventional air purification methods. Therefore, photocatalysts in the form of multicomponent alloy could be potentially utilized for the degradation of diverse pollutants in the air. In this work, multicomponent alloys containing metals which oxides show photocatalytic properties (e.g. Ti, Zr, or V) were anodized under various parameters. Anodization is an example of a surface treatment process used for the fabrication of nanostructured metal oxides [2]. The chemical and structural properties of the alloys after the anodic oxidation process were analyzed using XRD, SEM, and EDX and compared with those of untreated materials. In the future, the developed materials could be promising candidates as photocatalysts for the degradation of air pollutants.

Research project supported by program „Excellence initiative – research university” for the AGH University of Krakow, Grant No. 9705.

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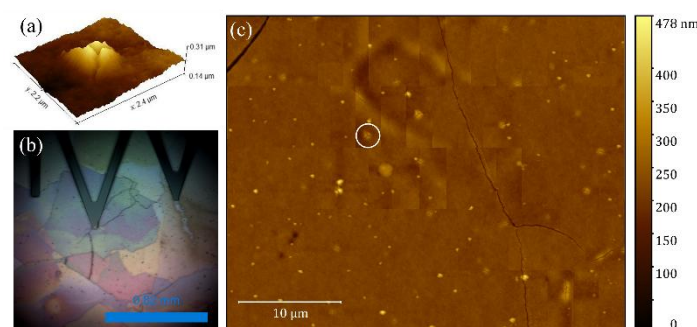
Evaluating the substrate effect and durability of electrochromic WO₃ films for smart window applications.

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In the face of climate change and growing concern for energy security, minimising global energy consumption is increasingly important. Smart windows are a promising energy-saving technology with widespread applications, offering an alternative to the use of air-conditioning and artificial lighting, alongside additional benefits including increased privacy and dynamic displays. Current smart window materials are limited by deterioration of electrochromic films by cracking and delamination after repeated cycling, resulting from compressive and tensile stresses induced by ionic transfer into the film structure [1-3]. An improved understanding of the mechanism of these processes and impact of substrate could enable the deterioration process to be suppressed and present a breakthrough for this technology.

This work investigates the deterioration of 410-510nm thickness WO₃ films electrodeposited on FTO and Au substrates and repeatedly cycled in the presence of Na⁺ ions. Simultaneous in-situ High-Speed Atomic Force Microscopy (HS-AFM) and chronoamperometric measurements were applied to analyse surface changes between individual cycles and identify features which correlated with crack initiation and loss of electrochromic performance. The fast imaging speed and in-situ capabilities of HS-AFM allowed real-time observation of the structural evolution of the film surface and resolved many of the challenges associated with conventional AFM. The formation of triple-point blister-like features, illustrated in the figure, was correlated with regions of cracking, delamination and loss of colouration response. Blisters initially formed during deposition but grew during cycling, eventually cracking and propagating through weaker sections of the film. The accelerated degradation of Au substrate films was partially attributed to increased ion trapping due to the more densely packed structure. FTO substrate films had better durability due to the higher roughness, producing films with larger grains which better accommodated the stresses of ion intercalation. Rougher films additionally demonstrated superior adhesion to the substrate.



(a) 3D render, (b) optical microscope image, and (c) HS-AFM raster image of 510nm thickness WO₃-Au sample after cycling demonstrating fragmentation, delamination and blistering.

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Characterization of Sb–Pd electrocatalyst formed by electrodeposition technique for application in Direct Ethanol Fuel Cells

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Electrochemistry in alkaline solution is substantial for the examination on electrooxidation of liquid fuels [1]. Ethanol is attractive as an eco-friendly fuel which could be efficiently produced with biomass sugar-containing raw materials, giving energy density of 6100 Wh L⁻¹ [2]. Some metals may have a promoting effect on a variety of electrocatalytic reactions and well-studied examples comprise p-group metals as promoters of Pd for the oxidation of small organic molecules. Within this context, the galvanostatical preparation of Pd and bimetallic Sb–Pd catalyst from surfactant free electrolytes was applied. The bimetallic catalyst was obtained in two-step electrochemical route with electrodeposition of Sb followed by Pd electrodeposition. Combining the characterization techniques it was signified for the bimetallic catalyst that Sb is successfully covered by Pd particles and the presence of Sb morphology with the octahedron-shaped grains and Pd nanospheres was revealed. The influence of Sb in the structure of Sb–Pd catalyst on the electrocatalytic performance to ethanol oxidation reaction (EOR) was investigated. Another aspect that was examined is the contribution of the selected alkali metal cations on the electrocatalytic activity of Pd and Sb–Pd electrocatalysts in EOR. The capability of Pd and Sb–Pd catalysts toward EOR was examined utilizing the electrochemical methods showing a more negative onset potential and higher peak current of Sb–Pd (–0.65 V; 21.3 mA cm⁻²) than Pd catalyst (–0.55 V; 15.2 mA cm⁻²) in LiOH solution while in 1 M NaOH the onset potential was shifted to positive direction on both investigated electrodes. Likewise, the peak current of EOR at Pd and Sb–Pd catalysts in the solution with Li⁺ cations is 2.5 times higher compared to the values obtained in the solution with Na⁺ cations. Improved activity and tolerance of Sb–Pd catalyst against poisoning during EOR with respect to Pd, is a result of the electronic modification induced by the interaction of Sb with Pd. The contribution of the alkali metal hydroxide on electrocatalyst activity toward EOR was established and explained through the influence of OH⁻ – cation clusters. It was concluded that the electrodeposition approach for the synthesis of Pd-based catalysts can open a suitable pathway for research in the field of electrocatalysis, while the choice of alkali metal hydroxide regulates the catalyst's capability toward EOR.

Acknowledgment

This research has been financially supported by the Ministry of Science, Technological Development and Innovation of Republic of Serbia (Contract No: 451-03-66/2024-03/200026).

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A Supramolecular Approach to Single Atom PGM-based Catalysts: from Metal Recovery and Cross-Couplings to the Oxygen Reduction Reaction

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Ten years ago we began our journey in the supramolecular decoration of graphitic-type surfaces (AC, CNTs, Graphene, etc.) with ligands for ionic species. Potential for these systems in recovery of metal cations (or their complex anions), was already appreciated [1]. Later on, we explored application of the resulting carbon-ligand-metal materials in catalysis, both as such, i.e. exploiting well-defined single ion catalytic sites at the surface, and as a way to produce small (2-5 nm) nanoparticles in a controlled fashion: Pd-catalyzed cross-couplings were the first contact point of this line of research with redox processes [2]. A turning point was the leap towards electrocatalysis. This was necessitated by global driving forces, such as necessity of green energetic solutions, the need to spare critical materials, and the blooming of hydrogen-based technologies. So, a fruitful partnership with the Laboratory of Applied Electrochemistry at the University of Florence began. The design ideas accumulated over time started to find significant implementations, and the single-ion design of the catalysts allowed us to surpass important technological target (US DOE mass activity) [3]. Still, our systems are far from perfect: we keep improving our understanding, implementing newly found design criteria to verify if they really work in practice, in order to achieve nano- and single-ion well-defined surface sites to be exploited in the realm of electrocatalysis [4].

Herein we detail the methodology so far used (**Figure 1**), some of its main possibilities and results, and share the design direction we will be following in the immediate future.

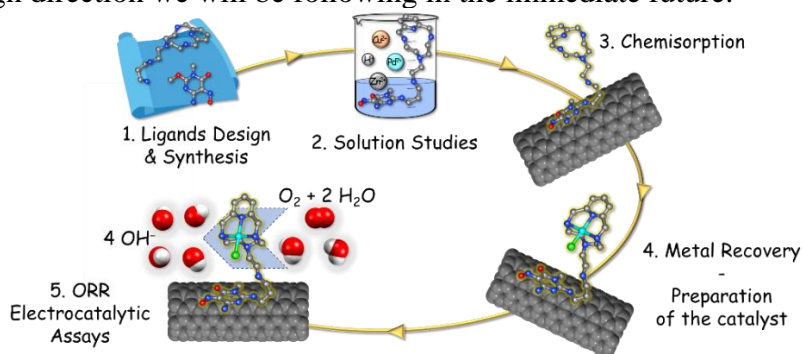


Figure 1. A general scheme of our approach to Carbon-Ligand-Metal single-ion catalysts.

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- Contribution of the research fund of the San Raffaele Roma University is gratefully acknowledged.

The influence of starting plant material on Ni@C-type catalysts' characteristics

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In our study, we developed and characterized a set of materials based on activated carbon (AC). We made pills of willow, knotweed and maple dried biomass and pyrolyzed them to obtain different ACs. Ni nanoparticles on our materials were formed according to the bottom-up strategy – we impregnated carbons with nickel nitrate solution.

To characterize the surface and structure of these materials, we applied SEM, MP-AES and DSC-TGA techniques. To determine mineral ingredients input in carbons, we checked their ash content. From DSC-TGA results we can see good thermal stability for each of our carbons even at the temperature of 800°C. We performed BET study as well and the isotherms revealed a well-developed surface for most of our specimens.

High efficiency of the impregnation process was proved by MP-AES results – 167 mg of Ni was deposited on 1 g of carbon derived from willow's stems. Adsorbed Ni was well distributed across carbons' surfaces, which is shown in microphotographs taken with SEM-EDS apparatus. We also conducted catalytic tests in order to assess the catalytic performance of each material in the CO₂ methanation process. IR spectroscopy and gas chromatography techniques allowed us to check concentrations of methane in post-reaction mixtures. We also made a comparison of our systems to similar materials from other works.

OER Properties of Ni-Co-CeO₂/Ni Composite Electrode Prepared by Magnetically Induced Jet Electrodeposition

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Abstract: Hydrogen production from water electrolysis with catalysts is a simple, effective, and environmentally friendly way. While the high cost of noble metal catalysts limits their engineering applications. Therefore, there is an urgent need to develop an economical and abundant catalyst with efficient OER performance to replace noble metal catalysts to reduce costs. In this work, Ni-Co-CeO₂/Ni composite electrodes were prepared by magnetically induced jet electrodeposition and compared with jet electrodeposition, it was found that the addition of nano-mixed particles resulted in the formation of a unique micro-nano structure of Ni-Co-CeO₂/Ni composite electrode in magnetically induced jet electrodeposition. It was found that the Ni-Co-CeO₂/Ni composite electrode deposited by magnetically induced electrodeposition exhibited a lower overpotential of 301 mV@10 mA/cm² when the nano-mixed particle concentration was 2 g/L, and the corresponding Tafel slope was as low as 43.72 mV/dec. The key parameters of overpotential and Tafel slope were even better than those of some industrial noble metal catalytic electrodes, indicating that the Ni-Co-CeO₂/Ni composite electrode prepared by magnetically induced jet electrodeposition has better OER catalytic performance, and it can be used as a new preparation method of catalytic electrodes.

Keywords: Jet electrodeposition; Magnetic field; Catalytic electrode; Oxygen evolution reaction

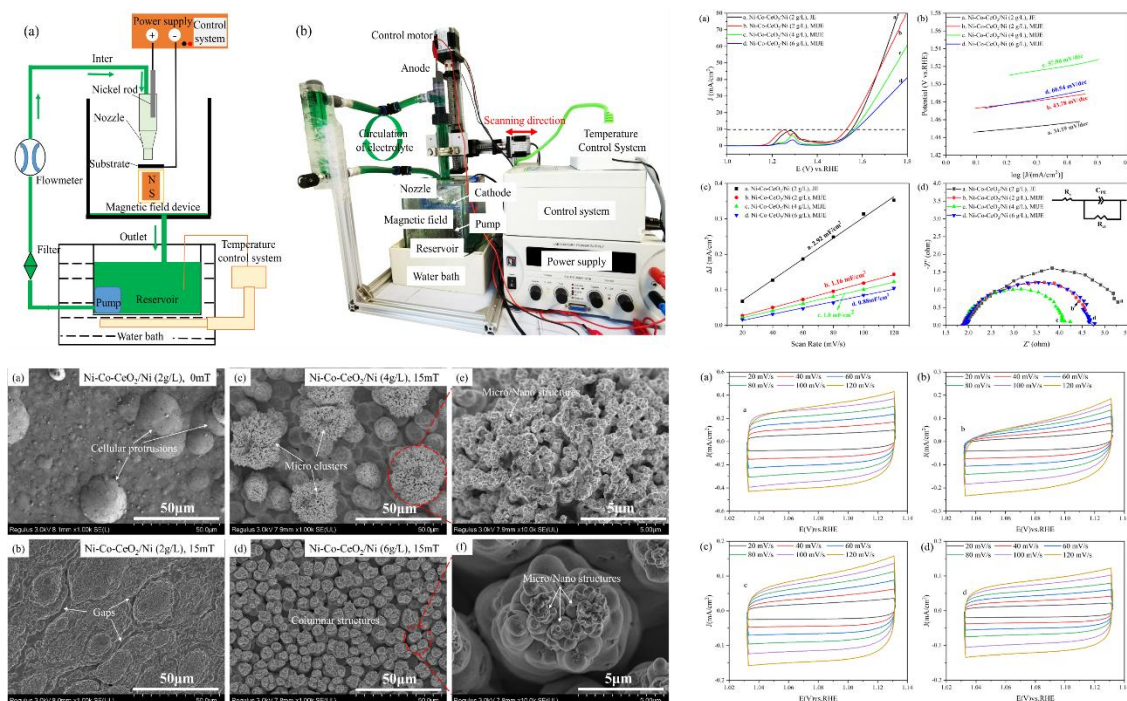


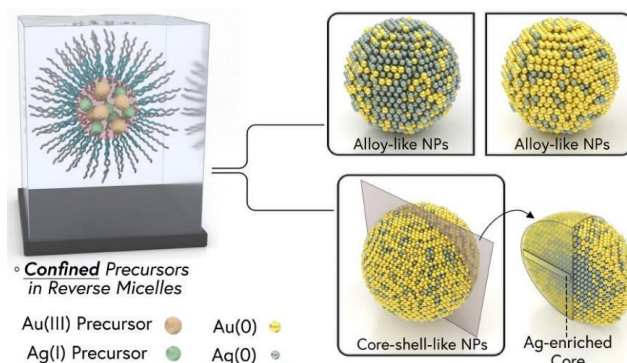
Fig. 1. Graphical abstract

Electrodeposition of Tunable Ag-Au Nanoparticles from Reverse Micelles

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Despite the numerous and diverse applications of nanoparticles (NPs)[1,2] as well as their captivating properties[3], gaps persist in understanding how to properly tune NPs characteristics to the desired application. We introduce a versatile approach to form bimetallic Ag-Au NPs of different sizes, compositions and element configurations (alloy and core-shell) in a single step by employing reverse micelles as nanoreactors at the polarized electrolyte/electrode interface. The noble metal precursors were encapsulated in the nanocavities of polystyrene-*b*-poly(2-vinylpyridine) (PS-P2VP) reverse micelles, therefore allowing control of the NPs size without the need for additional chemicals. The effect of the applied potential and the electrolyte identity (organic electrolyte vs ionic liquid) on the final NP properties was analysed. By adjusting the aforementioned parameters, bimetallic Ag-Au NPs with sizes ranging from below 10 nm to 140 nm were synthesized with tunable element configuration and composition. At a more negative polarized electrode, smaller Ag-rich and Au-rich alloy NPs were formed in organic electrolyte and ionic liquid, respectively. These NPs were synthesized from single reverse micelles, as evidenced by single-entity electrochemistry measurements. At less negative applied potentials, larger NPs were formed from the precursors encapsulated inside more than one reverse micelle, forming Au-rich alloy NPs in ionic liquid. In organic electrolyte, however, the same process resulted in Ag-rich core-shell-like NPs with tunable core and shell compositions. Finally, the electrocatalytic activity of the prepared NPs was evaluated towards hydrogen evolution reaction, where the core-shell-like NPs showed the best performance. Starting with both precursors in solution and forming core-shell-like NPs with Ag-rich core in a single step is a strong highlight of this work, and it could be achieved by tuning synthesis conditions when the precursors are encapsulated inside PS-P2VP reverse micelles. The influence of nanoconfinement on the NP formation was further explored by performing the synthesis from unconfined precursors, i.e., free in the same electrolytes, which resulted in entirely different coverages. Notably, such a synthetic pathway led to micrometre sized agglomerates of individual Ag NPs and Au NPs with no alloy or core shell characteristics.



Scheme 1. Ag-Au NPs formed from precursors-loaded reverse micelles under different synthesis conditions.

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P.U.L.S.E.: Unified Process on Zamak, Brass, and Aluminum Alloys, Safe and Eco-Friendly

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In a global context that demands the development of sustainable models, the electroplating industry, including its metal coating electroplating methods, has to deal with a necessary transition to innovative technologies. Indeed, upgrades oriented for sustainability and resource efficiency are needed.

The Unified Process on zamak, brass and aluminum alloys, Safe and Eco-Friendly (P.U.L.S.E.) project focuses on eliminating the use of cyanides in electroplating baths and develop new technologies that can ensure metal coatings with improved quality, uniformity and performance.

While in the traditional galvanic process, direct current (DC) achieves the deposition of a metal deposit, several studies have shown the possibility of applying pulsed current (PC) and reverse pulsed current (PRC) [1]. The main purpose of the project is to adopt pulse plating, a technology that justifies its practical application, mainly through its ability to influence the electrocrystallization mechanisms, which affect the mechanical and physical properties of the metal coating. These techniques make it possible to deposit precious and non-precious metals, resulting in products with superior aesthetic and functional characteristics [2-3].

Pulsed and reverse pulsed current electrodeposition techniques prove particularly effective for copper. With these technologies, copper layers with a more homogeneous surface grain and complete reduction of the Cu(II) ion in each pulse can be obtained [4-5].

Copper plating has a widespread use and is characterized by the presence of cyanides in solution. [6] Therefore, the project is involved in studying the effects of pulsed and reverse pulsed current on copper electrodeposition using a (CN)-free bath.

Through collaboration between universities and the electroplating industry, the (CN)-free copper bath will be tested on different substrates as brass alloys, aluminum and zamak.

Surface analysis such as X-ray fluorescence (XRF), scanning electron microscopy (SEM) will be carried out to investigate deposit properties such as thickness and morphology. The investigation will also focus on the uniformity of coatings in order to contribute to significant progress in the sustainability and performance of electroplating processes.

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The effect of surface morphology on electrocatalytic performances of Pt@Ni and Pt@Cr thin film catalysts for the methanol oxidation reaction

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Direct methanol fuel cells (DMFCs) are attractive alternative energy sources due to their non-toxic nature, reduced hazardous pollutants, and high energy density. They can be used in a wide range of applications, among which the most significant include transportation and stationery and portable power sources. The main challenges for their widespread commercialization include the high cost of noble metal-based catalysts (mainly platinum), the poisoning of Pt catalysts by intermediates during methanol electrooxidation, issues with fuel crossover and long-term catalyst durability. Strategies to overcome these difficulties are directed towards alloying Pt with inexpensive and widely available metals through various deposition techniques and using innovative supports to improve Pt utilization. Surface morphology plays one of the key roles in improving the performance of electrocatalysts. Therefore, by precisely modifying surface structures at the atomic scale, the efficiency of catalysts can be significantly improved. Heat treatment is also efficient for promoting surface atom rearrangement, hence modifying the catalyst's characteristics. This study investigated the influence of thermal annealing on the morphology and surface reconstruction of platinum electrodeposited Ni and Cr supports.

The electrodeposition of Pt on Ni or Cr substrates was conducted under potentiostatic conditions in an H₂PtCl₆ solution. After the deposition, the as-prepared Pt@Ni and Pt@Cr electrodes were annealed in a reductive atmosphere (95% Ar + 5% H₂) at 300 °C. The activity of the catalysts was tested for the methanol oxidation reaction.

The influence of thermal treatment on the surface morphology was monitored using atomic force microscopy (AFM) focusing on surface morphology, roughness, and nanoscale structure. AFM revealed distinct surface features related to the Pt deposition process and thermal treatment, providing valuable insights into how these modifications influence catalytic behavior. It was found that even a modest annealing temperature of 300°C was enough to induce diffusion across the surface and grain boundary migrations that resulted in coalescence and particle growth. In addition to AFM, cyclic voltammetry and CO stripping techniques were used to evaluate the electrochemical activity. The annealed catalyst shows a notable improvement in methanol oxidation reaction performance, approximately 2.5 times greater than the as-prepared sample. Pt@Ni catalyst showed the best activity (considering the amount of precious metal consumed) reaching, at E~0.905 V, a mass-specific current density that is larger by one order of magnitude than that obtained on Pt@Cr catalysts. The observed behavior is attributed to the significant contribution of smaller Pt particles, the greater specific surface area, and the lack of agglomerates at the Pt@Ni electrode. Based on the obtained results it was pointed important role of surface characterization in understanding and optimizing the functional properties of catalysts for green energy.

Keywords: thin-film catalysts; AFM surface investigations; thermal treatment; methanol electro-oxidation;

Acknowledgment: This work was financially supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (contract no. 451-03-66/2024-03/200026) and the Science Fund of the Republic of Serbia under grant no. 7739802.

Comparative Study of Platinum Deposition Methods on Ni Support for Enhanced Formic Acid Electrooxidation

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Reducing dependency on fossil fuels and developing efficient renewable energy sources are still important issues for sustainable development. Fuel cells powered by small organic molecules, such as formic acid, have attracted significant interest due to their potential for clean energy production. Platinum (Pt) is recognized as a highly effective catalyst for formic acid electrooxidation (FAO), but its high cost, scarcity, and susceptibility to CO poisoning prevent widespread use.

To address these issues, we have investigated two different methods for depositing Pt onto nickel (Ni) substrate: electrochemical deposition and galvanic displacement, and compared their effects on FAO activity. The first method involved the electrochemical deposition of thin Pt film onto Ni (Pt@Ni) followed by controlled thermal treatment. The second method involved spontaneous galvanic displacement, in which a drop of hexachloroplatinic acid was applied to a Ni substrate, resulting in an ultra thin Pt@Ni film. As in the first method, a similar annealing treatment optimized the catalyst's surface morphology and stability, achieving better activity with minimal Pt usage.

Catalysts were characterized using cyclic voltammetry, CO monolayer oxidation, and atomic force microscopy (AFM) to evaluate the effects of the deposition method and annealing conditions.

The activity of the Pt@Ni catalyst obtained by the electrochemical deposition method is highest at 500 °C compared to the as prepared and catalyst annealed to 300 °C. In the case of electrochemical deposition, the annealing process induces surface reconstruction and Ni migration to the surface, thus enabling the bifunctional effect and improving catalytic performance by reducing CO poisoning at low potentials. In the case of the spontaneous galvanic displacement method, the activity of the Pt@Ni catalysts annealed to 300 °C is the highest due to the excessive amount of Ni present at the surface of the catalyst annealed to 500 °C. This result was confirmed by the CO stripping experiment. The results demonstrated that the choice of deposition method and thermal treatment substantially impacts catalytic performance. The electrochemical deposition approach showed advantages in surface reconstruction, while the galvanic displacement method achieved higher Pt utilization efficiency. This comparative study emphasizes the important role of synthesis processes, substrate characteristics and thermal treatment in developing cost-effective, high-performance FAO catalysts.

Keywords: Pt thin films; electrochemical deposition; galvanic displacement; nickel; thermal treatment; electrooxidation; formic acid

Acknowledgment: This work was financially supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (contract no. 451-03-66/2024-03/200026) and the Science Fund of the Republic of Serbia under grant no. 7739802.

Electrodeposited Near-Room-Temperature Micro-Thermoelectric Generators

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Due to the proficiency in converting thermal energy to electricity with high power density and high output voltage, micro-thermoelectric generators (μ -TEGs) stand out as promising solution for energizing the next-generation portable electronics, including Internet of Things (IoT) and wearable electronic devices.[1] However, compared to macro TEGs, commercialization of μ -TEGs has been hindered because of the intrinsic connection between material growth and device fabrication, involving intricate processes such as lithographic patterning and etching. This obstructs the optimization of the material's deposition parameters for different units of the devices. Consequently, only a limited selection of p/n-type materials and growth methodologies is currently available for μ -TEGs, resulting in generally inferior TE properties to their bulk counterparts.[1] This highlights an urgent need for cross-disciplinary research spanning materials science, nanofabrication and electrical engineering to achieve a high figure of merit and quest for a peerless synthesis technique to maintain the obtained properties of TE materials during μ -TEG fabrication.

Electrochemical deposition (ECD) emerges as a powerful choice for fabricating various TE materials. Widely utilized in industrial systems, including microelectronics, ECD stands out for its cost-effectiveness, ultra-precise batch production of microdevices, and facile stoichiometry/doping/morphology engineering. Additionally, this room-temperature technique is advantageous, especially for temperature-sensitive materials. Notably, ECD provides the unique advantage of depositing the top metal contact immediately after the deposition of TE material in μ -TEGs, significantly reducing the contact resistance.[2] Consequently, ECD is one of the preferred methods for fabricating μ -TEGs. Hence, we choose ECD for fabricating various p/n type materials (e.g., Ag_2Se , Zn_4Sb_3 , CuBiTe).

Preliminary investigations have demonstrated the effectiveness of ECD, revealing uniform deposition of the TE films. An atomic ratio of 1:3.8:9.9 for Cu:Bi:Te in CuBiTe films was determined by energy-dispersive X-ray spectroscopy and the Seebeck coefficient of $\sim -30 \mu\text{V/K}$ was measured with potential-Seebeck microprobe. Ongoing efforts focus on modulating the TE properties of these materials through stoichiometric optimization, doping with foreign elements and morphology alterations. Ultimately, p/n-couples with optimized TE properties will be utilized to design high-performance μ -TEGs.

Acknowledgments:

This work is funded by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG), grant number RE3973/1-1.

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Electrodeposition of Sn-Ni Alloy Nanowires Involving Deep Eutectic Solvents

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Electrodeposition represents a faster and cheaper route suitable to synthesize a large range of nanostructured materials, including 1-D structures (i.e. nanowires, nanotubes, nanorods), widely involved to build applications related to nano-electronics, opto-electronics, renewable energy, coatings and sensors. In addition, the use of electrolytes based on ionic liquids (ILs) and deep eutectic solvents (DESS) allows obtaining of a quite constant alloys composition which mainly depends on the metallic cations ratio, with no need for supplementary addition of surfactants, grain refiners and brighteners or oxidation inhibitors, as compared to classical water based electrolytes. This issue represents a significant advantage, especially when binary and ternary alloys are intended to be electrodeposited, thus providing an easier bath control. Therefore, the paper presents some experimental results regarding the electrodeposition of Sn-Ni alloy nanowires from choline chloride-ethylene glycol (denoted ILEG) eutectic mixtures, using template-assisted method. Commercial polycarbonate membranes (Whatman, 47 mm disk diameter) (denoted PC) with pores diameter of 400 nm were used as template for the electrochemical synthesis. Usually, homogeneously distributed ensembles of Sn-Ni (≈ 73 wt.% Sn and 27 wt.% Ni) nanowires have been prepared, having lengths in the range 3-11 μm , depending on the electrodeposition duration (see Fig.1). The influence of the main applied operation parameters (i.e. the current density, electrolyte temperature, the electrodeposition duration) on the prepared Sn-Ni alloy nanowires morphology and composition is discussed.

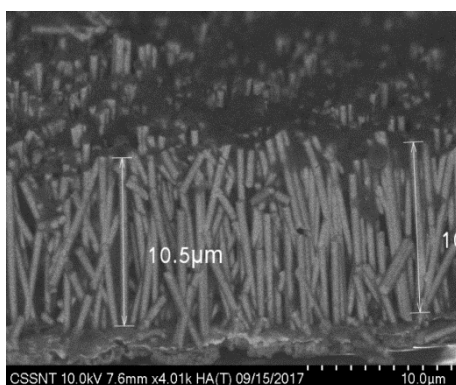


Fig.1 - SEM micrograph of Sn-Ni alloy nanowires electrodeposited from 0.5M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ -0.5M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in ILEG ($i=-7.6 \text{ mA/cm}^2$, 55°C , 15min)

Acknowledgements: Part of this work was supported by Romanian Ministry of Education/ Executive Agency for Higher Education, Research, Development and Innovation Funding, under NOVTINALBEST project 38/2016, M Era Net Program.

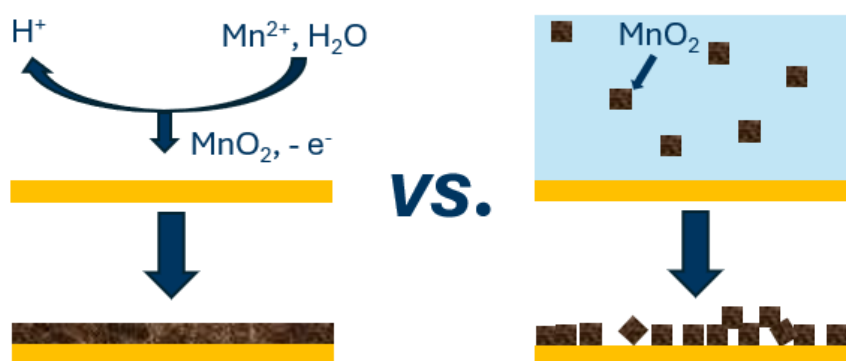
The Role of Nanostructuring in Pseudocapacitive Manganese Oxide Materials

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Manganese dioxide materials are being studied intensively for their ability to store energy[1, 2]. In particular, layered manganese dioxide (birnessite) has attracted considerable interest because the insertion of cations into the interlayer space is accompanied by a pseudocapacitive current response of the material[3]. In this study, we compare the electrochemical capacitive properties of electrodeposited films and nanoparticle electrodes prepared by drop casting. For in-depth characterisation, we used the CV_{CaRe} software tool[4], which allows the analysis of distorted capacitive cyclic voltammograms in terms of capacitance and resistance.

Literature reporting that nanomaterials such as nanoparticles, nanosheets, or nanowires are beneficial for the stability and rate capability of MnO₂ electrodes, attribute this to increased accessibility of electrochemically active sites, shorter conduction paths within the solid electrode, and improved diffusion of ions[1,5]. Here, however, a series of experiments with electrodes of different MnO₂ loadings and scan rates indicated that the electrolyte resistance within the porous electrode films was critical to reduced electrochemical energy storage performance.



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Electrodeposition of Crystalline Thin Films of Co₃O₄ on Glassy Carbon with Octahedral Nanoparticles-like Morphology: Exploring Shape-Selective Growth Mechanisms

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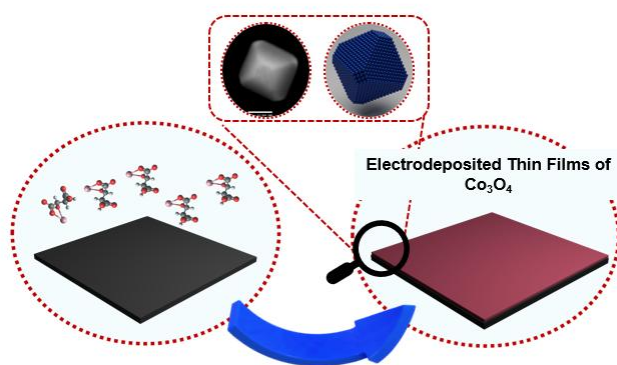
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The electrodeposition of cobalt oxide (Co₃O₄) spinel thin films has raised significant attention for their application in catalysis, optoelectronics, and energy storage/conversion [1-2]. This study demonstrates the successful synthesis of spinel-type Co₃O₄ on glassy carbon electrodes at elevated temperatures, yielding thin films of octahedral nanoparticles. While previous studies predominantly focused on epitaxial growth on crystalline substrates like Au(111) [3], this work explores the deposition on an amorphous substrate, revealing that shape-selective growth is achievable without substrate crystallinity. Detailed structural and morphological characterizations by grazing incident X-ray diffraction, atomic force microscopy and electron microscopy suggest that the observed crystal structure and morphology depend strongly on the deposition potential, temperature and composition of Co-precursor. Octahedral morphology is observed for spinel-type Co₃O₄ due to its cubic crystal lattice, which can only be obtained at elevated deposition temperature, small overpotential, and in the presence of tartrate as complexing agent. Other deposition conditions yield amorphous or CoOOH-type deposits with a more spheroid-like morphology. These findings expand the understanding of cobalt oxide nucleation and growth, offering a pathway for cost-effective synthesis of nanostructured catalysts on amorphous substrates.



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Pulse electrodeposition of a free-nickel gold-iron alloy for decorative applications

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Electroplating is an essential technique used in various industries, including automotive, electronics, and decorative sectors. This process allows for the enhancement of substrate materials by imparting new properties, such as improved corrosion resistance, increased hardness, and enhanced aesthetic appeal [1]. Gold finishing is widely used across numerous industries, thanks to its exceptional electrical conductivity, resistance to corrosion, good mechanical properties and biocompatibility. In addition to these functional advantages, gold and its alloys are also highly valued for its aesthetic qualities [2]. The use of pulsed current (PC) is widely acknowledged as an effective research technique for exploring the mechanisms behind metal electrodeposition. It also plays a significant role in improving the properties and overall appearance of the deposits [3]. Among the most commonly used gold alloys, those containing nickel are frequently employed in the fashion industry to create the characteristic white gold colour. However, it is important to note that approximately one in eight individuals experiences an allergic reaction to nickel-containing alloys. Due to these potential adverse reactions, most jewellery manufacturers opt to avoid the use of nickel in white gold, as alloys that are free from nickel tend to be less allergenic and safer for consumers with sensitivities [4]. In light of this, our study focuses on the development of a nickel-free gold-iron bath intended for use in the decorative industry. This bath is specifically designed to serve as a final coating in the electroplating process, offering an alternative to traditional nickel-based solutions. The primary emphasis of this research is on achieving a light, aesthetically pleasing colour for the deposited layers, ensuring that the final product meets both functional and aesthetic requirements while mitigating the risk of allergic reactions associated with nickel exposure. The use of PC has shown the potential to moderately modulate both the iron content of the deposit and its appearance characteristics, as well as to influence colour properties over time. Additionally, further results regarding the corrosion behaviour of the deposited material will be presented providing a comprehensive understanding of its long-term stability and durability.

Authors acknowledge Regione Toscana for financial support of the MetalRec Project (CUP B97G23000210009) within the program "Progetti di alta formazione attraverso l'attivazione di assegni di ricerca nell'ambito della transizione verde".

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Electrodeposition-Based Synthesis of Hierarchical Nanoporous Au Nanowire Networks and Their Electrochemical Properties

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Nanostructured materials offer promising prospects across various fields such as electronic devices, catalysts, and biomedicine.[1,2] Here, we report on the synthesis and investigation of stable three-dimensional (3D) porous structures with optimized specific surface area and electrochemically activity towards methanol oxidation.

By combining ion-track nanotechnology and electrochemical deposition, self-supporting 3D nanowire networks of $\text{Au}_{1-x}\text{Ag}_x$ alloys are synthesized. The dimensions and interconnectivity of the nanowires are tailored by varying the fabrication parameters. Subsequently, the Ag atoms are chemically dealloyed to fabricate nanoporous nanowires with various pore sizes.[3] By employing the dealloying method we attain a significant decrease of the weight of the synthesized material, accompanied by a corresponding increase of the surface area. This design approach enables the creation of innovative 3D nanostructures with robust structural stability, adjustable geometry, and exceptional surface roughness,[4,5] yielding nanostructures with precisely tailored characteristics at the nanoscale and with two levels of roughness. Notably, the surface roughness of the nanostructured samples can be significantly higher (up to ~400 times) than that of a flat electrode.[6,7] In this poster, we will present the synthesis process of $\text{Au}_{1-x}\text{Ag}_x$ nanowire networks with tailored compositions and dimensions, and how these parameters influence the dealloying process, detailed structure analysis, as well as the initial electrochemical evaluation of nanoporous nanowires compare to the solid ones.

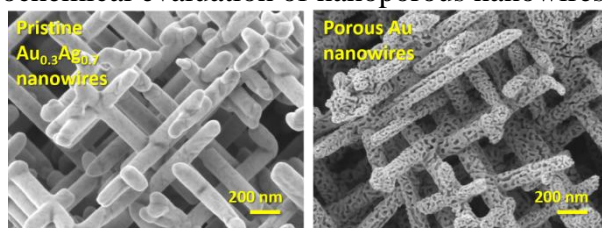


Figure 1: Scanning electron microscopy images of pristine $\text{Au}_{0.3}\text{Ag}_{0.7}$ nanowire network before (left) and after (right) dealloying.

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Obtaining Pd-Decorated Carbon Black and Graphene Catalysts from Electroplating Wastewater for Efficient Oxygen Reduction Reaction

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The progressive depletion of fossil reserves and the increase in energy demand have led to a rise in fuel and electricity prices. This major problem is closely related to the increasing demand for critical raw materials (CRM). These materials are crucial for the implementation of many industrial processes and for a climate-neutral economy, eventually contributing to the digitalization and well-being of society. CRM are often essential for developing key sectors such as renewable energies and electric mobility [1,2]. For these reasons, nowadays more and more attention is paid to the recovery of precious metals and the promotion of a circular economy. This work proposes a new strategy for obtaining low-content PGMs carbon-based electrocatalysts for the Oxygen Reduction Reaction (ORR). This approach aims to achieve catalysts by recovering precious metals from industrial wastewater and promoting the development of a circular economy, specifically from the electroplating industry. Indeed, electroplating wastewater from precious plating procedures not only contains palladium but it must be properly processed with expensive procedures to be reused in the production cycle. Carbon black (CB) and graphene-type materials were tested obtaining a possible recovery 97% of palladium from industrial waters. The two materials were also functionalized with a pyrimidine tren derivative capable of complexing Pd(II) and results show that functionalization dramatically increases the recovery rate.

With the proposed methodology we obtained novel Pd functionalized carbon materials that are promising candidates for use as catalysts for the ORR in alkaline fuel cells. Rotating ring electrode measurements (RRDE) were performed to investigate the ORR catalytic pathway and determine the number of electrons exchanged per oxygen molecule [3]. The results confirm that the tested materials support the four-electron reaction pathway and reduce the formation of hydrogen peroxide. Moreover, the functionalization with the TREN derivative significantly increased the Pd recovery during wastewater treatment and increased catalytic properties in terms of onset potential and number of electrons exchanged. These approaches promote the development of a circular economy and provide a basis for further development to improve the efficiency of future low-cost catalysts for alkaline fuel cells.

Authors thank Project 2022NW4P2T CUP B53D23013890006 “From metal nanoparticles to molecular complexes in electrocatalysis for green hydrogen evolution and simultaneous fine chemicals production (FUTURO)” PRIN2022 Progetti di Ricerca di Rilevante Interesse Nazionale funded by the Italian Ministry of University and Research and NextGenerationEU.

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Oxygen reduction reaction (ORR) in alkaline medium catalyzed using an atomically precise Pd (II) catalyst, prepared by extraction of Pd(II) from a mixture of metal ions using modified multi walled carbon nanotubes (MWCNT)

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Following the new European policies, such as the European Green Deal, the usage of renewable energy sources and their use in clean energy production has become a core object[1]. In these circumstances, metal waste management and its upcycling as electrocatalysts in the hydrogen field plays a key role in the circular economy[2]. The oxygen reduction reaction (ORR) plays a pivotal role in governing the efficiency of fuel cells, allowing the conversion chemical energy into electrical energy without producing no waste residual beyond water. Nonetheless, the sluggish kinetics of ORR necessitate highly efficient electrocatalysts to improve fuel cell performance[3]. It is well known that the best available catalysts, in terms of raw bulk elements, belong to the platinum group metals (PGMs). Since PGMs are finite and expensive resources, reducing their content in ORR catalysts and recovering them from wastewater are among the primary research focuses[4].

We report the preparation of an atomically precise heterogeneous catalyst containing Pd(II) ions anchored on multi-walled carbon nanotubes (MWCNTs) and the results of its application in accelerating the oxygen reduction reaction (ORR). The catalyst was prepared by selectively and quantitatively extracting Pd(II) from a mixture of metal ions typically found alongside Pd(II) in wastewater from the processing of this metal[5], leading to an in situ conversion of Pd(II) waste into a high-value ORR catalyst. This was made possible by the appropriate choice of the ligand used to functionalize the surface of the MWCNTs and the whole process to assemble the catalyst (MWCNT-LPd) is carried out under environmentally friendly conditions, occurs spontaneously in water, at room temperature, does not need a protected atmosphere and requires only minimal energy consumption. The newly developed catalyst was treated with a Nafion polymeric dispersion to conduct rotating ring-disk electrode (RRDE) experiments, aimed at exploring the ORR catalytic mechanism and determining the number of electrons transferred per oxygen molecule. Additionally, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) were performed to analyze the catalyst's morphology and composition. X-ray photoelectron spectroscopy (XPS) was essential for characterizing the metallic state of the coordinated metal. The authors acknowledge the support offered by Project 2022NW4P2T CUP B53D23013890006 "From metal nanoparticles to molecular complexes in electrocatalysis for green hydrogen evolution and simultaneous fine chemicals production" PRIN2022 Progetti di Ricerca di Rilevante Interesse Nazionale funded by Italian Ministry of University and Research and NextGenerationEU.

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Electrodeposition of Metals on Silicon for Enhanced Silicon Nanowires (NWs) Fabrication via Metal Assisted Chemical Etching (MACE)

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The electrodeposition of nanostructured metals onto silicon substrates represents an opportunity to combine the advantageous characteristics of metals with the exceptional electronic properties of silicon. This synergy can provide significant benefits in electrodes for water-splitting devices, supercapacitors, fuel cells, sensors, and photovoltaic cells [1]. This deposition technique was chosen for its affordability, scalability, and fast synthesis potential. It operates under room temperature and atmospheric pressure conditions, utilizing aqueous solutions with customizable properties. The advantages listed are relevant compared to other routes used at the state of the art, such as physical vapor deposition (PVD) techniques [2]. In this study, we examined the feasibility of Metal Assisted Chemical Etching (MACE) of doped silicon starting from the electrodeposition of the metal. The initial metal selection for electroplating was based on the articles present in the literature. Voltammetric analyses were conducted using solutions containing Au and Ag. Optimal electrochemical deposition conditions were sought. The best etching conditions were then identified to obtain silicon nanowires (NWs) of the desired morphology and size. The resulting deposits and NWs were morphologically and compositionally characterized using Scanning Electron Microscope (SEM) techniques, complemented by Energy-Dispersive X-ray Spectroscopy analysis (EDS). This procedure could create new opportunities for small-size and better-performing sensors and high specific surface area electrodes, particularly when the NWs are decorated with metals or other chemical species [3]. The authors acknowledge the support offered by Fondazione CR Firenze, Fondazione per la Ricerca e l’Innovazione of the University of Florence and Confindustria Florence within the FABER4 project. The following projects are also acknowledged: FREEGALVAN, CUPST 27716.29122023.042000059, LINEA 1 - PRFESR 2021-2027 OP1 OS1 Azione 1.1.4 Bando n.1; and P.U.L.S.E, CUPST 27717.29122023.043000271, LINEA 2 - PRFESR 2021-2027 OP1 OS1 Azione 1.1.4 Bando n.1.

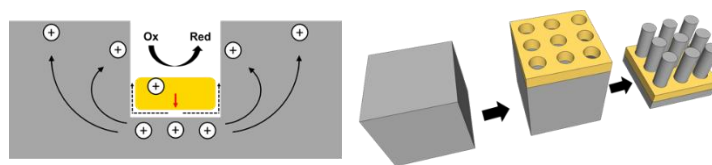


Figure 1 Metal Assisted Chemical Etching (MACE) mechanism and operational steps.

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Electroplating in the presence of Microplastics: investigating their influence on Copper deposition

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Microplastics (MPs) have garnered significant attention in recent years due to their ubiquitous presence and accumulation in various systems and ecosystems [1]. Currently, there is a growing trend towards polymer metallization, a novel additive manufacturing technique that addresses the limitations of polymers by coating them with a metallic layer that acts as a functional outer skin [2]. In the electroplating industry, the increasing use of plastic substrates further underscores the importance of understanding the interactions between MPs and heavy metal ions. Contaminated plating baths can lead to surface defects, poor adhesion, corrosion, and inconsistent deposit thicknesses, resulting in material waste and inefficiencies in production lines, compromising the quality of electroplated products and increasing the toxicity of industrial waste [3]. Despite these concerns, the interactions between pollutant MPs and heavy metal ions in electroplating environments remain largely unexplored. This study addresses a critical and emerging challenge in the electroplating sector: the impact of MPs on electrodeposition processes, specifically in acidic copper plating baths. We investigate the behavior of self-produced "Nylon PA" MPs [4] dispersed in acidic copper baths and their interactions with copper ions in solution. The characterization of the coated samples was performed using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) to analyze the surface morphology, revealing various surface defects in copper deposits induced by MPs in the bath. Furthermore, electrochemical analyses conducted on contaminated baths, including cyclic voltammetry (CVS) and chronoamperometry (CA), indicate significant changes in nucleation and growth mechanisms, with MPs exhibiting effects like suppressors in copper deposition. These findings shed light on the impact of MPs on copper electrodeposition, emphasizing the urgent need for further research and mitigation strategies to address this emerging issue in the electroplating industry. The authors acknowledge the support offered by Project 2022NW4P2T CUP B53D23013890006 "From metal nanoparticles to molecular complexes in electrocatalysis for green hydrogen evolution and simultaneous fine chemicals production" PRIN2022 Progetti di Ricerca di Rilevante Interesse Nazionale funded by Italian Ministry of University and Research and NextGenerationEU.

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Specific ion effects on nickel electrodeposition

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Electroplating is a widely used industrial technique for both technical and decorative applications [1,2]. Although electrodeposition has been used for a long time, the development of new processes and formulations is still a primary need to reduce the use of precious metals and organic additives in order to provide green alternatives to the electroplating industry.

In this study the effect of different anions (Cl^- , Br^- , I^- , SO_4^{2-} , NO_3^- , ClO_4^- , $\text{C}_6\text{H}_5\text{O}_7^-$, CH_3CO_2^-) in solution on nickel electrodeposition was investigated [3,4].

In order to highlight the different effect due to the action of the supporting electrolytes, the electroplating solution was formulated by using only the nickel precursor, the background electrolyte and the conjugated acid, in concentrations compatible with those of a common electroplating bath, without the addition of any further organic additive and surfactants.

A preliminary electrochemical study was carried out through cyclic voltammetry and chronoamperometry. We evaluated the nucleation and growth mechanism, performed morphological characterization by scanning electron microscopy and deposition efficiency by measuring film thickness by X-ray fluorescence.

This study aims at opening new perspectives in the field of electrodeposition, both from a scientific and applicative point of view, and particularly with the perspective of providing ecological alternatives to the galvanic industry.

Significant differences in the growth mechanism and morphology of the electrodeposited films were observed as a function of the background electrolyte.

The authors acknowledge for the support offered by Fondazione CR Firenze, Fondazione per la Ricerca e l'Innovazione dell'Università degli Studi di Firenze and Confindustria Firenze within the FABER4 project.

Authors also acknowledge Regione Toscana PR FESR 2021/2027, Azione 1.1.4.1, Bando 2 “Progetti di ricerca e sviluppo per le MPMI e Midcap” which made possible the project “Processo Unificato su Leghe di zinco, ottone e alluminio, Sicuro e Ecofriendly” (P.U.L.S.E) CUP-ST 27717.29122023.043000271.

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Novel sustainable acid copper formulations: the L-Cysteine case

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Acid copper electroplating is among the most fundamental industrial procedures for many industries such as electronic and decorative. The capability of obtaining coating with desired mechanical and aesthetic features is due to the interaction of organic and inorganic molecules with the deposition process. Those species are usually called additives and, despite acid copper formulation are known since the early years of 1940, they are stuck to the classical trifecta of brightener, leveler and suppressor. To delve into the advances in copper electroplating, reducing the additives and promoting eco-sustainable alternatives, multidisciplinary approaches mixing experimental and theoretical analyses seem perfectly suited for understanding the mechanism of action of additives [1]. The presented work aims to test and exploit L-Cysteine (L-Cys) as an additive for new acid copper formulations. L-Cys, as well as being a green molecule, being in its N-protonated form at bath pH (< 1) and having a carboxylic group could be suited to act as a suppressor without the need of sodium chloride to enhance the migration to the cathode [2]. But, more important, the thiol group is promising for a brightener effect and its levelling power was already tested in a formulation associated with other classical additives [3]. Copper was electrodeposited with different L-Cys concentrations (from 0.25 mM to 5 mM) by adding it to standard virgin make-up solution. The morphology and the grain refinement effect were evaluated by scanning electron microscopy (SEM) evidencing how the addition of L-Cys is associated with a diminishing of grain size and homogenization in size distribution, which at a macroscopic level is reflected by a shiny and compact deposit. Atomic force microscopy (AFM) served to evidence more morphological details, like the formation of grain aggregates until 1.50 mM and to evaluate by roughness (Sq) analysis if L-Cys was capable to level the brass substrate. Then, X-ray diffractometry (XRD) was employed to study the influence on the preferential growth direction of the deposit and X-ray photoelectron spectroscopy (XPS) served to characterize the surface composition. Finally, electrochemical experiments and molecular dynamics (MD) were used to rationalize the roles of L-Cys and inorganic ions within the electrodeposition process while the reactivity and selectivity of L-Cys functional group was studied thanks to Fukui condensed indices, calculating the population density (CM5) from calculations at B3LYP(D3BJ)/6-31++G(d,p) level.

The authors acknowledge for the support offered by Fondazione CR Firenze, Fondazione per la Ricerca e l'Innovazione dell'Università degli Studi di Firenze and Confindustria Firenze within the FABER4 project. The authors acknowledge Regione Toscana PR FESR 2021/2027, Azione 1.1.4.1, Bando 1 “Progetti strategici di ricerca e sviluppo” which made possible the project “Sviluppo e ottimizzazione di nuovi processi, prodotti e prototipi per il prolungamento del ciclo di vita di articoli di rubinetteria, accessori moda e gioielli” (FREEGALVAN) CUP-ST 27716.29122023.042000059.

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P.U.L.S.E: Development of an Innovative and Sustainable Cyanide-Free Electroplating Process for Advanced Surface Treatments

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P.U.L.S.E project aims to introduce an innovative and sustainable electrochemical deposition process through pulse current technology, with a focus on developing a cyanide-free (CN-Free) copper plating process for brass and aluminum alloys. This study seeks to create an advanced multicomposite galvanic coating process that improves the quality and sustainability of treated products while minimizing the environmental impact. Traditional cyanide-based copper plating baths will be replaced with eco-friendly alternatives, ensuring safer working conditions and reducing chemical waste.

The initial phase involved extensive electrochemical studies to define the optimal deposition parameters. These parameters were then validated through a laboratory-scale prototype, enabling precise control over layer morphology and reducing surface defects. The project will then scale up to a semi-industrial prototype capable of operating under real-world conditions.

This approach will improve adhesion and coating uniformity while reducing the amount of precious metals used, resulting in more cost-effective and sustainable production. In addition to technical advances, the project aims to promote a cultural change toward sustainability within the fashion and furniture industry.

By combining technological innovation with environmental protection, this project sets the foundation for a new standard in electroplating processes for the fashion industry. This initiative will enhance product aesthetics, increase durability, and allow for the treatment of more complex geometries.

Authors acknowledge Regione Toscana PR FESR 2021/2027, Azione 1.1.4.1, Bando 2 “Progetti di ricerca e sviluppo per le MPMI e Midcap” which made possible the project “Processo Unificato su Leghe di zama, ottone e alluminio, Sicuro e Ecofriendly” (P.U.L.S.E) CUP-ST 27717.29122023.043000271.

FREEGALVAN: Development and optimization of new processes, products and prototypes for life cycle extension of items from faucets, fashion accessories and jewelry

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The FREEGALVAN Project was born from the union of the needs and the spirit of innovation of Valmet Plating Srl, Materia Firenze Lab Srl, Jessica Spa and Rubinetterie Treemme and aims to introduce sustainable innovation (SOI - Sustainability Oriented Innovation) in its deepest sense within the fashion, jewelry and faucets sectors. The partnership has as its cornerstone the specialization in surface finishing and metal ennobling. The decorative electroplating sector remains a defining industry of the Tuscan fabric, capable of being a world leader and should be considered by the constituent industries as a boast and an asset to be maintained and expanded. Materia Firenze Lab, specialized in the electroplating of fashion accessories, is in charge of testing and optimizing new electroplating formulations made with sustainability in mind. FREEGALVAN aims to propose highly eco- and socio-sustainable and innovative processes and solutions capable of depositing new materials with performance at least comparable, if not superior, to current standards, which are no longer sustainable. In the industry's current state of the art, chrome plating is still predominantly made with Cr(VI)-based electrolytes (a known carcinogen), and nickel-free lines, although they lead to hypoallergenic materials, are characterized by the high use of cyanides, which are found in abundance as “free” species (about 60 g/L) in the white bronze baths, the pivotal barrier layer of the entire process. Not only that, baths containing such anions very often operate at high temperatures, which requires the continuous addition of cyanide salts, at a rate of up to 1 g/L per day. In perfect eco- and socio-environmental sustainability, the partnership therefore aims to realize specific alternative solutions, such as barrier layers free of free cyanides and nickel, and a Cr(III)-based electrolyte free of Cr(VI), capable of producing a material with comparable corrosion resistance and aesthetic appearance characteristics. Barrier layers performances are going to be tested towards corrosion, skin compatibility [1] and intermetallic diffusion [2,3] to ensure performance at least equal to standard non-sustainable solutions.

The authors acknowledge Regione Toscana PR FESR 2021/2027, Azione 1.1.4.1, Bando 1 “Progetti strategici di ricerca e sviluppo” which made possible the project “Sviluppo e ottimizzazione di nuovi processi, prodotti e prototipi per il prolungamento del ciclo di vita di articoli di rubinetteria, accessori moda e gioielli” (FREEGALVAN) CUP-ST 27716.29122023.042000059.

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P.U.L.S.E: Design and Development of Recycled Brass Articles to be Treated with an Innovative and Sustainable Cyanide-free Electroplating Process

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The P.U.L.S.E. project is an innovative and environmentally friendly project of electrochemical deposition through the use of pulsed current. This plating process will be used on brass and aluminium alloys, using cyanide-free copper (CN-Free).

The research related to our design part is to design and create products, using recycled brass alloys, which treated with this innovative galvanic process are qualitatively better and ecological.

First of all, our studies for the design of brass elements to be tested are based on simpler developments, checking in detail all the phases preceding the melting and finishing of the product, which will then be ready for the last phase, the galvanic.

Subsequently we will move on to the creation of more complex prototypes.

This phase will require in-depth study and design in order to create prototypes that can validate as many cases as possible (spherical, convex, cuspid, pre-embedded surfaces, etc.) in order to establish for each element, after checking all the processing phases by our galvanic collaborator, the adhesion and uniformity of the galvanic coating as well as the use of a smaller quantity of precious metals with the aim of improving the final object in terms of quality, ecology and cost.

This Project will result in improving the quality of the product, the galvanic resistance even on more complex surfaces and is the first step towards creating an innovative galvanic Standard for the Fashion sector.

Authors acknowledge Regione Toscana PR FESR 2021/2027, Azione 1.1.4.1, Bando 2 “Progetti di ricerca e sviluppo per le MPMI e Midcap” which made possible the project “Processo Unificato su Leghe di zama, ottone e alluminio, Sicuro e Ecofriendly” (P.U.L.S.E) CUP-ST 27717.29122023.043000271.