13th International Workshop on Electrodeposited Nanostructures

30th August – 1st September, Bristol U.K.

Abstract booklet

Oral contributions

Electrodeposited core-shell nanowire arrays as photocathode model systems for solar hydrogen production

Florent Yang[1], Nada Fahmi[1,2], C. Schroeck[1], Dimitri Korjakin[1], Maria Eugenia Toimil-Molares[1]
[1]GSI Helmholtz Centre for Heavy Ion Research, Department of Materials Research, Planckstraße 1, 64291 Darmstadt, Germany
[2]Chemistry Department, Faculty of Science South Valley University, Egypt
E-mail: m.e.toimilmolares@gsi.de

In the past decades, research on the synthesis and characterization of semiconductor nanowires has considerably increased, especially for applications in the field of energy conversion, such as for instance solar cells and photoelectrochemical water splitting for hydrogen production. The use of nanowire architectures is being discussed since they offer various advantages. First, they offer large surface areas which can be adjusted as a function of nanowire dimensions and wire density. Second, thanks to their elongated geometry, their diameter and length can be adjusted to match the minority carrier diffusion length (~ hundred nm) and the light absorption depth (~ few µm), respectively. However, in this configuration, the majority carriers still have to transported along the whole semiconductor wire towards the back electrical contact.

We present the fabrication and characterization of core-shell nanowire arrays consisting of a metallic core acting as nanostructured electrical contact, and a well-defined semiconductor shell responsible for light absorption and charge carrier generation and transport. The metallic Au core wires are first fabricated by electrodeposition in etched ion-track membranes. Diameter, length, and number density of the nanowires is adjusted by the fabrication parameters. Subsequently, the polymer foil is selectively dissolved, and a semiconductor layer is electrodeposited on the Au nanowire arrays. The thickness of the semiconductor layer is controlled by the deposition time. Finally, to increase their chemical stability in aqueous electrolyte the photoelectrodes are conformally coated with a thin TiO_2 film by atomic layer deposition. Two semiconductor materials have been electrodeposited as shells, Cu_2O and ZnO. The photoelectrochemical performance of these core-shell nanowire-based electrodes will be also discussed.

Fast anodic hematite nanotubes for photoelectrochemical cells

Paula Quitério[1], Arlete Apolinário[1], Célia Sousa[1], Adélio Mendes[2] and João Pedro Araújo[1]*

1: IFIMUP and IN-Institute of Nanoscience and Nanotechnology and Dep. Física e Astronomia, Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal

2: LEPABE, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, Portugal

** Corresponding author. E-mail: jearaujo@fc.up.pt*

Hydrogen is considered an energy vector critical for the decarbonization of the energy sector. It can be easily produced directly from renewable resources such as sunlight and water using photoelectrochemical cells (PEC) [1,2]. Hematite (α-Fe_2O_3) photoanodes for photoelectrochemical solar water splitting has attracted considerable attention due to its high chemical stability [3], availability, nontoxicity and narrow band gap (2.2 eV), which allows reaching solar-to-hydrogen conversion efficiencies of 16.8 % [2]. However, it displays poor electron mobility, resulting in short charge carrier diffusion lengths [2]. To overcome such limitations the nanostructuring, in particular the nanotubular architecture, has emerged as one of the best tools to allow an efficient electron transport and charge separation [4]. One simple and low cost route for obtaining hematite nanotubes (NTs) is by the electrochemical anodization of a Fe foil.

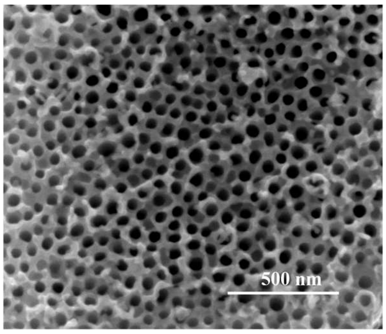

Figure 1. Hematite nanotubes obtained by electrochemical anodization

In this work, we obtained hematite NTs by a fast anodization process (Figure 1). The current density (*j*) history during the anodization process allows to understand the inherent mechanisms of the NTs formation and growth. Several anodization parameters (potential, temperature, time, pH, etc.) influence the NTs structure and dimensions. In addition, the effect of anodization potential (20-100 V) on the NTs morphology at controlled temperature and anodization time was studied. A thermal annealing treatment was performed to convert the amorphous anodic oxide NTs into hematite crystalline phase. The photoelectrochemical characterization was performed based on photocurrent-voltage (*J-V*) curves and obtained the photocurrent density. The obtained results revealed to be very promising for the use of hematite photoelectrodes on photoelectrochemical hydrogen production.

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Preparation and characterization of platinized TiO_2/rGO nanocomposite for synergistic photo-electrocatalytic methanol oxidation

J.Georgieva,[1] N.Dimitrova[1], S.Sotiropoulos[2], Tz. Boiadjieva-Scherzer,[3]
[1]Rostislaw Kaischew Institute of Physical Chemistry, Bulgarian Academy of Sciences,
Sofia 1113, Bulgaria
[2]Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece
[3]CEST Kompetenzzentrum für elektrochemische Oberflächentechnologie GmbH, Wiener Neustadt, Austria

Platinized TiO_2/rGO nanocomposite was prepared in order to combine the photocatalytic activity of TiO_2 with the electrocatalytic activity of Pt towards methanol oxidation reaction. TiO_2 was modified with reduced graphene oxide (rGO) in order to increase its conductivity and photosensitivity. Pt was depositied on the surface of mixed TiO_2/rGO powder support by UV photodeposition from chloroplatinate solution. The composition, surface morphology and crystal structure of the samples were characterized by energy-dispersive spectrometry (EDS), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The electrochemical and photoelectrochemical behavior of the Pt/TiO_2/rGO composite was evaluated by cyclic voltammetry (CV) and chronoamperometry (CA) experiments in the dark and under UV light illumination. The electrocatalytic activity of the Pt/TiO_2/rGO catalyst towards methanol oxidation was evaluated and compared to a plain TiO_2 and TiO_2/rGO composite. The Pt/TiO2/rGO electrode showed higher catalytic activity for methanol oxidation, which can be associated with effective dispersion and utilization of Pt, enhanced electron-hole separation efficiency and synergistic effect between Pt and semiconductor oxide.

Acknowledgments:

Financial support of CEST, Austria in the frame of the COMET program is gratefully acknowledged.

Nanoporous gold transformations using underpotential deposition of Pb

Vinicius Cruz San Martin[a], Niel Fox[a], Andrei Sarua[b], Natasa Vasiljevic[a]

[a]Bristol Centre for Functional Nanomaterials, H. H. Wills Physics Laboratory, Tyndall Avenue, University of Bristol, BS8 1TL, UK
[b]School of Physics, H. H. Wills Physics Laboratory, Tyndall Avenue, University of Bristol, BS8 1TL, UK

Abstract:

Development of new plasmonic materials has been actively pursued due to their broad application potential in biosensing[1], photovoltaics[2], and catalysis[3]. One of the materials of interest is nanoporous gold (NPG) that exhibit unique plasmonic properties. NPG is a bi-continuous interconnected structure of Au ligaments and pores obtained by dealloying of the less noble metal from an alloy, usually Ag from Au_xAg_{1-x} alloys. Manipulation and changes of the NPG porosity size result in the modifications on the plasmonic properties. The method commonly used to change the porosity length scale is thermal annealing[4], but more recent studies showed the interest in using surface-sensitive electrochemical methods[5].

Here in this work, we will present the Pb underpotential deposition (UPD) induced changes of the porosity, i.e. coarsening of the NPG structures. First, AgAu alloys of different compositions were electrodeposited from thiosulfate-based solutions with varying ratios of Au and Ag ions. Ag was then selectively dissolved from the alloys, and the NPG samples of different size of porosity were obtained. Pb UPD on Au was used as an alternative to Brunauer–Emmett–Teller (*BET*) method for obtaining the initial surface area measurement[6]. Following that, multiple potential cycles (~ 100-200) within the Pb UPD region were done and changes on the NPG structure were characterised. Surface area decreased with number of potential cycles as a result of porous structure coarsening. The structural transformations of NPG at different stages were also characterised by SEM. Porosity changes showed dependence on scan rate, number of cycles and the initial size of NPG ligaments.

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Microstructure of Cu deposits fabricated from water-containing deep eutectic solvents

Priscila Valverde[a], Antonio Mulone[b], Uta Klement[b], Sudipta Roy[a], Todd Green[a]
[a]*Department of Chemical and Process Engineering, Strathclyde University*
James Weir building, 75 Montrose Street, 4th Floor, Scotland-United Kingdom, G1 1XJ
[b]*Department of Industrial and Materials Science, Chalmers University of Technology*
SE-412 96 Goteborg, Sweden
priscila.valverde-armas@strath.ac.uk, mulone@chalmers.se, uta.klement@chalmers.se
sudipta.roy@strath.ac.uk, todd.green@strath.ac.uk

Deep eutectic solvents (DESs) are a promising type of Ionic Liquids (ILs) for metal electrodeposition due to their tolerance to water and stability under ambient conditions. Although DESs are hygroscopic chemicals, most of the studies have been carried out either from dry DES systems or neglecting their intrinsic water content. Since water cannot be avoided in a real electrodeposition process, it is likely that metal electrodeposition proceeds from a hydrated electrolyte. Thereby, the effect of water on the metal electrodeposition requires thorough investigation. Until now, our group has studied the electrodeposition of Cu from water-containing 'ethaline' which is a DES prepared by mixing choline chloride and ethylene glycol. It has been established that 'ethaline' can adsorb up to 15 wt% of H_2O over a month period. Also, water reduced the viscosity of the liquid which promotes the diffusivity of Cu^{2+} ions. As a result, the limiting currents of the process increased, which was indicative of the enhanced mass transport of the electroactive species. However, the plated films became less uniform and differences in morphology were found. In this line, to further characterise the microstructure of the deposits, Electron Backscattered Diffraction (EBSD) was carried out. Cu samples were sectioned to expose their cross-sectional areas and thereafter metallographically prepared. Fig. 1 shows the EBSD maps and inverse pole figures of the deposits (at 1 and 10 wt% H_2O) that revealed grain shape, size and texture.

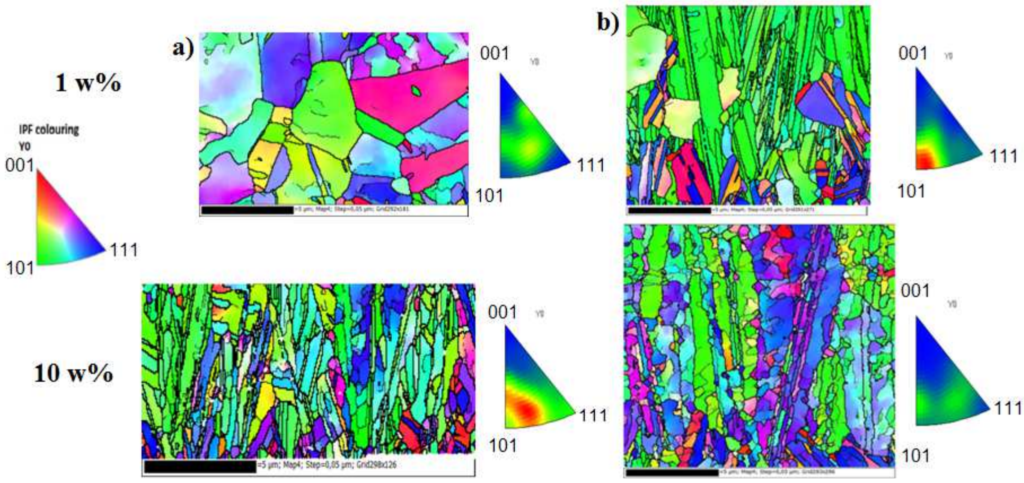

Figure 1. EBSD maps and IPF of Cu deposits at the a) centre and b) edge fabricated from electrolytes containing 1 and 10 wt% of H_2O.

The author wants to acknowledge the Department of Industrial and Materials Science of Chalmers University of Technology for the EBSD analysis and COST Action MP1407 for funding them under the STSM scheme.

Electrodeposition of Ni-Rh alloys from chloride solutions.

Dawid Kutyła, Karolina Kołczyk, Anna Kwiecińska, Remigiusz Kowalik and Piotr Żabiński

Department of Physical Chemistry and Metallurgy of Non-Ferrous Metals

AGH University of Science and Technology in Kraków

Al. A. Mickiewicza 30, 30-059 Kraków - Poland

e-mail: kutyla@agh.edu.pl

Nickel alloys are used in fuel and electrolytic cells for industrial production of hydrogen and oxygen. Literature indicates that the addition of Co, W, Mo and platinoids into nickel electrodes can decrease the overpotential of hydrogen evolution process and also increase corrosion resistance in sodium hydroxide solutions which are widely used in the industrial process.

Properties of plated cobalt or nickel – platinoids alloys are similar to the pure platinum-group elements, but their cost is significantly lower. The work comprises the results of the electrochemical synthesis of nickel-rhodium alloys from chloride solutions.

Electrochemical investigations were performed by CV-measurements onto polycrystalline golden and GC electrode. Obtained results show the mechanism of co-deposition of nickel-rhodium alloys. Moreover, alloys with varied composition were deposited on copper substrates under potentiostatic conditions. Nickel and rhodium concentration in alloys were estimated by the XRF analysis. Structural changes of obtained materials were discussed according to X-ray diffraction measurements and SEM observations.

Electrochemical characterisation of coatings was examined in 1M NaOH solutions. The catalytic activity for hydrogen evolution reaction was also investigated.

Acknowledgements: This work was supported by the Polish National Center of Science under the grant UMO-2016/21/N/ST8/00222.

Silver Nanoplatelet Films for Flow- and Electrocatalysis

Falk Muench,[1,2]* Mehtap Oezaslan,[3] Ronit Popovitz-Biro,[1] Yishay Feldman,[1] Tatyana Bendikov,[1] Israel Rubinstein,[1] Alexander Vaskevich[1]

1: Weizmann Institute of Science, Department of Materials and Interfaces,
Herzl Street 234, 7610001 Rehovot, Israel

2: Technische Universität Darmstadt, Department of Materials and Earth Sciences,
Alarich-Weiss-Straße 2, 64287 Darmstadt, Germany

3: Carl von Ossietzky Universität Oldenburg, Institute of Chemistry, Carl-von-Ossietzky-Straße 9-11,
26129 Oldenburg, Germany

Corresponding author. E-mail: muench@ma.tu-darmstadt.de

Electroless plating represents a compelling synthetic option for fabricating metal nanomaterials: It can homogeneously metallize complex shaped substrates by simply immersing them in aqueous plating baths. Recently, we have shown that the method is capable of directly depositing high aspect ratio Ag nanoplates (Fig. 1A), without the need for shape-guiding templates.[1]

These nanoplates are characterized by a rugged outline, exposing numerous edges, at which stacking faults surface in high density (Fig. 1B). The particularly reactive nature of these edges can be showcased by applying consecutive solution deposition reactions, which result in site-selective nucleation (Fig. 1C,D).

In this contribution, we want to demonstrate the catalytic potential provided by both the flexibility of the deposition method and the specific architecture of the obtained nanoplate films, based on three examples: The utilization in the CO_2 reduction reaction (Fig. 1E), and the realization of miniaturized flow reactor designs for heterogeneous (Fig. 1F) and electrocatalysis.

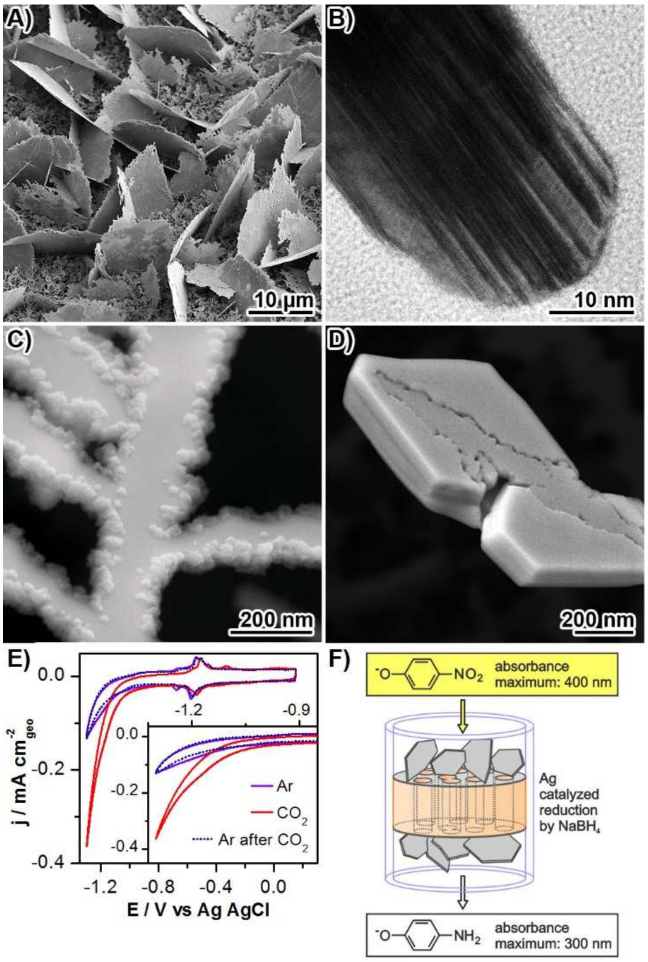

Figure 1. A) SEM image of nanoplates deposited on glass. **B)** TEM image of a Ag nanoplate edge in side view, revealing the high density of stacking faults. **C, D)** SEM images of dendritic Ag nanoplates, showing the selective nucleation of Cu_2O nanoparticles (C) and epitaxial Ag deposits (D) at their edges. **E)** CVs of a Ag nanoplate film in $NaHCO_3$ solution, during alternate bubbling with Ar (pH 8.5) and CO_2 (pH 7.5); note that the influence of the pH change is marginal (ca. 0.06 V). Scan rate: 20 mV s^{-1}. **F)** Scheme of our flow microreactor design, in which a Ag nanoplate film – supported by a porous polymer membrane – is employed for catalyzing the reduction of 4-nitrophenol.

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Electrochemical control of magnetism in FeO_x/Fe films and nanoislands

Karin Leistner [a,b], Kenny Duschek [a], Mingze Yang [c], Karen L. Kavanagh[c], Kornelius Nielsch [a,b]

[a] IFW Dresden, P.O. Box: 270116, D-01171 Dresden, Germany

[b] TU Dresden, Faculty of Mechanical Engineering, Institute of Material Science, D-01062 Dresden, Germany

[c] Simon Fraser University, Department of Physics, 8888 University Drive, Burnaby, British Columbia, V5A 1S6, Canada

The control of interfacial properties offers genuine routes to tailor magnetism at the nanoscale. Epitaxial growth on suitable substrates is one approach to define the shape and orientation of nanobjects. We investigated the electrodeposition of iron nanoparticles on GaAs(001) to achieve epitaxial growth. For electrochemical conditions with dominating hydrogen evolution, the deposited nanoparticles exhibit a faceted shape, crystallographic alignment and notable magnetic in-plane anisotropy. The beneficial role of the hydrogen evolution on the epitaxy is found to be related to the effect of hydrogen adsorption during the Fe/GaAs interface formation [1]. In optimized conditions, we achieved the formation of epitaxial nanocuboids that are aligned throughout the substrate [2]. Surface {100} facets predominate with a thin crystalline oxide shell that protects the nanoparticles during prolonged storage in air. The single crystallinity of the iron in combination with structural alignment leads to an in-plane magnetic anisotropy. These immobilized, oriented, and stable nanoparticles are promising for applications in nanoelectronic, sensor, and data storage technologies, as well as for the detailed analysis of the effect of shape and size on magnetism at the nanoscale.

While in the previous case, electrochemistry at the interface is exploited to irreversibly define the shape, structure and magnetism of the iron nanoparticles, a reversible manipulation of solid/liquid electrolyte interfaces can be achieved by magneto-ionic reactions. The magneto-ionic effect relies on voltage-triggered charge transfer reactions in solid or liquid electrolyte-gated architectures [3,4]. For instance, a repeatable electrochemical transformation between metal and oxide can be exploited to manipulate magnetic metals at room temperature and via the application of only a few volts. Up to now, magneto-ionic reactions have mainly been investigated for thin films. We utilized electrodeposited iron/iron oxide nanoislands as magneto-ionic starting material and achieve almost complete voltage-controlled ON/OFF switching of magnetism. This represents a highly promising path for the development of tunable and energy-efficient magnetic nanodevices.

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Influence of magnetic field on 3D prints metallization

Karolina Kołczyk, Katarzyna Skibińska, Dawid Kutyła, Anna Kwiecińska, Remigiusz Kowalik, Piotr Żabiński

The 3D printing is one of the newest method of precise elements production. One of advantages of this technique is possibility of production elements with any geometry, very often impossible to obtain in traditional techniques, very good tolerance of dimensions, low costs and good scalability. Often in this technology plastics are used, but depending on the purpose, the prints can be improved by additional properties through applying metallic coatings.

As a result, there is a possibility to obtain elements with combination of properties of plastics and metal. To obtain such special properties the prints should be coated by metallic layers. This operation gives the plastic elements new functionalization like electric and thermal conductivity or magnetism. As a results of this, elements with mix of plastic and metallic properties are obtained. It allows to increase the number of application of these elements. Depending on the material, the plastics covered by metallic coatings can find application in many field of technology like medicine, automotive, metallurgy or energy industry.

In this work it will be presented process of metallization of 3D prints from light-hardened resins. The metallization is a few steps process demanding precise parameters. The prints are coated by copper or nickel coatings or bimetal coatings containing of these metals.

In results of this work the optimum parameters of metallization processes are obtained. Variation of many parameters like duration time of every steps of process, composition of electrolytes were analyzed. Additionally, the influence of magnetic field on the coatings was investigated. The magnetic field can significantly change the morphology of obtained surfaces.

The financial support from Faculty of Non-Ferrous Metal under grant number 15.11.180.968/2018 is gratefully acknowledged.

The role of Cu length on the magnetic behaviour of Fe/Cu multi-segmented nanowires

Suellen Moraes1, David Navas1, Fanny Beron2, Mariana P. Proenca1,3, Kleber R. Pirota2, Célia T. Sousa1,* and João P. Araújo1

1 IFIMUP and IN-Institute of Nanoscience and Nanotechnology and Dep. Física e Astronomia, Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal;

2 Instituto de Física Gleb Wataghin (IFGW), Universidade Estadual de Campinas (UNICAMP), Campinas, SP 13083-859, Brazil;

3 Instituto de Sistemas Optoelectrónicos y Microtecnología, Universidad Politécnica de Madrid, Avda. Complutense 30, E-28040 Madrid, Spain;

Abstract: Ferromagnetic nanostructures with complex and controlled magnetic behavior have been extensively studied during the last years. The need for low energy technologies and the recent advances in chemical and self-assembly synthesis techniques have boosted the growth of three-dimensional nano-objects [1]. This capacity to control size and shape, not only in the plane but also along the vertical direction, leads to the appearance of new effects in spin configurations. A set of multi-segmented Fe/Cu nanowires were synthesized by a two-step anodization process of aluminum substrates and a pulsed electrodeposition technique using a single bath. While both Fe segment length and diameter were kept constant to (30 ± 7) and (45 ± 5) nm, respectively, the Cu length was varied between (15 ± 5) and (120 ± 10) nm. The influence of the non-magnetic layer thickness variation on the nanowires' magnetic properties was investigated through first-order reversal curve (FORC) measurements and micromagnetic simulations. Our analysis confirms that in the multi-segmented Fe/Cu nanowires with shorter Cu segments, the dipolar coupling between Fe segments controls the magnetic behavior of the nanowires and its performance is like a homogenous Fe nanowire array of similar dimensions. On the other hand, multi-segmented Fe/Cu nanowires with larger Cu segments act like a collection of non-interacting magnetic entities and their global behavior is mainly controlled by the neighbor-to-neighbor nanodiscs' dipolar interactions [2].

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Magnetic control over compositionally graded Fe-Mn oxide based catalytic micromotors prepared by electrodeposition.

Mónica Fernández-Barcia[1], Bumjin Jang[2], Carlos Alcántara[2], Margitta Uhlemann[1], Ulrike Wolff[3], Annett Gebert[1], Jordi Sort[4,5], Eva Pellicer[4], Salvador Pané[2]

[1]Institute of Complex Materials, IFW Dresden, Helmholtzstraße 20, 01069 Dresden, Germany

[2]Institute of Robotics and Intelligent Systems, Swiss Federal Institute of Technology (ETH) Zurich, ETH-Zentrum, Tannenstraße 3, 8092 Zurich, Switzerland

[3]Institute of Metallic Materials, IFW Dresden, Helmholtzstraße 20, 01069 Dresden, Germany

[4]Departament de Física, Universitat Autònoma de Barcelona (UAB), 08193 Bellaterra (Cerdanyola del Vallès), Spain

[5]Institució Catalana de Recerca I Estudis Avançats (ICREA), Passeig Lluís Companys 23, 08010 Barcelona, Spain

Chemically powered micromotors have attracted a great deal of attention in the last few years for biomedical and environmental applications. The majority of these devices are typically driven by the decomposition of hydrogen peroxide occurring at the surface of these machines [1-2]. Due to its outstanding catalytic activity toward hydrogen peroxide decomposition, platinum (Pt) has been the most widely used material to build these micromotors. However, Pt is a costly metal and thus, it is highly desirable to find alternative materials, which can show the same activity as Pt but are economically viable [3]. Recently, Mn-based micromotors have been proposed as an alternative to precious metals [2]. The present work shows Fe-Mn oxide based micromotors with a hollow mushroom-like shape can be manufactured by a facile one-step template-assisted cathodic electrodeposition. Owing to their compositionally graded nature and their specific geometry, the resulting micromotors can swim by bubble propulsion, and can be steered using external magnetic fields. A sustainable water-based bath, free of hazardous and toxic compounds, was implemented to synthesize the Fe-Mn oxide based micromotors. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX) were applied to investigate the morphology, shape and chemical composition of the electrodeposited micromotors. X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) imaging were used for structural characterization. Magnetic measurements were performed with a vibrating sample magnetometer (VSM). The speeds of the electrodeposited Fe-Mn oxide based micromotors were comparable to those of Pt-based micromotors. Furthermore, the use of magnetic fields allowed for controlling the trajectories of the microdevices.

Funding of this work by the European Commission within the H2020-MSCA-ITN-2014 SELECTA, grant agreement no. 642642 is gratefully acknowledge.

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Dynamic studies of electrodeposition of Ni and Fe systems performed via in-situ transmission electron microscopy

K. Zuzek Rozman[1,2], U. Wolff[3], B. Ambrozic[1],[2] M. Koblar[1,2], S. Trafela[1,2], K. Nielsch[3], B. Likozar[4], M. Ceh[1,2], S. Sturm[1,2]

[1] Jozef Stefan Institute, Ljubljana, Slovenia

[2] Jozef Stefan Postgraduate school, Ljubljana, Slovenia

[3] Leibniz Institute for Solid State and Materials Research, Dresden, Germany

[4] National Institute of Chemistry, Ljubljana, Slovenia

In-situ transmission electron microscopy (TEM) combined with the specialized liquid electrochemical cell offers, unprecedented experimental and characterization tools for a direct study of the electrodeposits nucleation and growth. Ni and Fe were studied with an intention to study the growth kinetics of both systems. The experiments were performed on a JEM-2100 (JEOL Ltd., Tokyo, Japan) microscope operated at 200 kV which is equipped with an energy dispersive X-ray spectrometer (EDXS). A Poseidon 510 TEM (Protochips Inc., Raleigh, NC, USA) holder was used with a Gamry Reference 600 potentiostat (Gamry Instruments, Warminster, PA, USA) for conducting the electrochemical experiments. A study of the deposition parameters was made via cyclic voltammetry in Ni (II) solutions in a concentration range between 0.01 and 1 M at pH = 2.5 to 5.5. The reduction peak which corresponds to Ni reduction was observed at concentrations c (Ni (II)) = 1M at E= -0.8 V, after which the liquid TEM experiments were performed using the same conditions. For Fe deposition, Fe sulphate containing solution with pH = 2 was used as electrolyte for Fe deposition, that was deposited potentiostatically at -1.2 V. In the first stages of the deposition Fe is amorphous and subsequently transforms to crystalline Fe and FeO_x, respectively. In order to minimize artifacts such as the beam-induced radiolysis of water or secondary radical chemistry which will be discussed in this study, the electron beam was blocked during the electrodeposition.

Anomalous small angle x-ray scattering as a composition sensitive method for investigation of nanostructures

D.Tatchev, J.Georgieva, E. Valova, S.Armyanov
Rostislaw Kaischew Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

Small-angle scattering offers measurement on a relatively large sample volume while probing only the nanoscale structures it contains. The chemical composition of the scattering objects can be assessed by using of variable X-ray energy near an X-ray absorption edge of a chemical element in the sample. Thus, the anomalous small-angle scattering (ASAXS) represent unique possibility to probe both size and composition of nanoscale inhomogeneities in a bulk sample regardless of bigger structures it may contain.

ASAXS is applied to chemically obtained powder supported Pt(Ni) catalysts. The supports were TiO2 and mixed TiO2–C nano-meter sized powders. The catalysts were prepared by electroless deposition of Ni followed by partial galvanic replacement with Pt. ASAXS measurement and analysis were performed on both Ni/support precursor and the final Pt(Ni)/support catalyst. The results show no alloying between Ni and Pt in the catalyst, but Ni is mainly in oxidized form in the precursor. The results comply with estimation of the chemical state by XPS.

The average catalysts size as determined by SAXS and observed by TEM is around 2 nm. The ASAX findings, coupled with XPS results allowed to ascribe the improved activity of the catalysts to a synergistic effect of TiO_2 on facile CO poison removal from Pt sites.

Additive manufacturing through galvanoforming of 3D nanocrystalline nickel microarchitectures: Simulation assisted synthesis

Patrik Schürch[1], Laszlo Pethö[1], Jakob Schwiederzik[1], Johann Michler[1] and Laetitia Philippe[1]

1 *EMPA (Swiss Federal Laboratories for Materials Testing and Research), 3602 Thun, Switzerland*

Electrodeposition in combination with templates created by two-photon lithography is used to fabricate dense metallic 3D microcomponents. We present nanocrystalline nickel microcomponents deposited from nickel sulfamate electrolyte in 3D templates. Using 3D electrodeposition simulation, different template designs for a bridge-like microcomponents were investigated. The influence of the template design on current density is described. Electrodeposition conditions and pulse parameters were optimized with the simulation to achieve a high filling ratio within the template. Unlike previous work done in the field, the template were made from negative tone photoresist which was removed subsequent to the electrodeposition with plasma etching process. This allows for free-form galvanoforming of freestanding nanocrystalline nickel microcomponents. Focused ion beam cross sections were made to investigate the microstructure within the specimen. The grains within the specimen show elongation along growth direction. Furthermore, the grain size distribution within the specimen shows correlation to the local current density values supplied by the simulation.

Electrodeposited Nanowire Composites Structures: some applications and perspectives

Laurent GRAVIER, Damien PIDOUX.

University of Applied Sciences and Arts – Western Switzerland, Institute of Micro and Nanotechniques,
HEIG-VD/MNT, Avenue des Sports 20, CH-1401 Yverdon-les-Bains, Switzerland
** Corresponding author. E-mail: laurent.gravier@heig-vd.ch*

Composite structures made by electrochemical deposition in nanoporous polymer template foils draw interest from both academic and industrial worlds, (i) for their unique ability to tailor physical properties of materials into very tiny volumes, i.e. at very high integration levels, and (ii) for its scalability in terms of mass production.

Exploring for long the advantages of this nanotechnology in our lab, we will present in this talk our research program in nanowire composite structures. This program is twofold:
Process engineering: in a scheme of technology transfer, the fabrication steps of nanowire composite structures have to converge at most on existing industry processes. We specifically develop proprietary techniques to this purpose, taking advantage of the wide range of engineering skills of our university's institutes.
Materials research: metal and semiconductor alloys and other composites in nanowire shapes are needed mainly for sensor and actuator applications. This research need the collaborations with the academic world.

We will review our recent applied research works in various applications domains, e. g. energy harvesting, sensors, flexible PCBs, Bio and Medtech and the more recent Industry 4.0.

We will finally propose a glance at metamaterials, a promising emerging trend for nanocomposite materials.

Electrocatalytic oxidation of formaldehyde in alkaline media on KOH-modified Ni nanowires based electrode

Špela Trafela[1,2], Sašo Šturm[1,2] and **Kristina Žužek Rožman**[1,2]
[1] *Department for Nanostructured Materials, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*
[2] *Jožef Stefan International Postgraduate School, Jamova 39, SI-1000 Ljubljana, Slovenia*
spela.trafela@ijs.si

Modified Ni nanowires were investigated for the electro-oxidation of formaldehyde (HCHO), which are promising to be used as effective electrochemical receptor element. A Ni nanowire arrays (200 nm diameter, retaining the size ~2.3µm) for formaldehyde detection were generated by electrodeposition of Ni into AAO template. The Ni nanowires array electrode was generated using the potentiostatic electrodeposition method by applying the constant potential -1.0 V/1200 s vs. Ag/AgCl. Electrodeposited Ni nanowires were investigated using SEM and EDX analysis that revealed the presence of the nickel in completely filled pores of the nanochannel alumina template. After the electro-deposition of the nanowires, the template was removed in 10 M solution of NaOH in order to get free standing wires.

Ni nanowires based electrode was further treated with KOH to prepare Ni-NiO(OH)/Ni$(OH)_2$ electrode using cyclic voltammetry and the potential scan rate of 200 mV s^{-1} [1, 2]. The fast scan rate was chosen in order to form monolayer of Ni$(OH)_2$/NiO(OH) on the surface of Ni nanowires. Such electrode (Ni-NiO(OH)/Ni$(OH)_2$) was further used as a catalyst for HCHO electro-oxidation.

The electro-catalytic properties of KOH-modified Ni nanowires electrode enables detection of HCHO. Before this studies, an electrochemical active surface area (A_{ecsa}) of Ni nanowires were determined by an accurate and precise method, known as an oxalate method [1, 2]. This valuable result was expanded and used in the electrochemical studies of HCHO oxidation, because all the current values obtained in further studies were normalized on the calculated surface area, 4.2 cm^2.

The investigation of the electrochemical behavior of HCHO electro-oxidation in 0.1 mol L^{-1} NaOH solution at the surface of Ni-NiO(OH)/Ni$(OH)_2$) were carried out by cyclic voltammetry and chronoamperometry. The sensors responded to HCHO in a concentration range from 0.8 µM to 0.2 mM. Obtained results from cyclic voltammograms showed that formaldehyde oxidation peak current density increase drastically with increasing formaldehyde concentrations, but the onset potential shifted to more positive as a result of IR drop. Amperometric measurements confirmed two broad linearity ranges (from 10 µmol L^{-1} – 2 mmol L^{-1} and 2 mmol L^{-1} – 20 mmol L^{-1}) and fast response (3s). Taking into account the determined A_{ecsa} value we have been able to calculate the sensitivities: 0.3419 mA L cm^{-2} $mmol^{-1}$ and 0.0458 mA L cm^{-2} $mmol^{-1}$ and the sensing element has a detection capabitility of 0.8 µmol L^{-1} (experimentally determined and calculated according to the IUPAC 3δ recommendation).

This study reflects the ability to process the Ni-based receptor elements via a cost effective electrodeposition method. This approach enables an easy fabrication of a novel and efficient non-enzymatic sensor for the electro-oxidation of HCHO with good sensitivity and low detection limit 0.8 µmol L^{-1} which is comparable and even surpassing those achieved for nanostructured noble metals and other reported Ni – based electrodes.

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Ultra-Small Nanopore Architectures in Anodic Aluminum Oxide

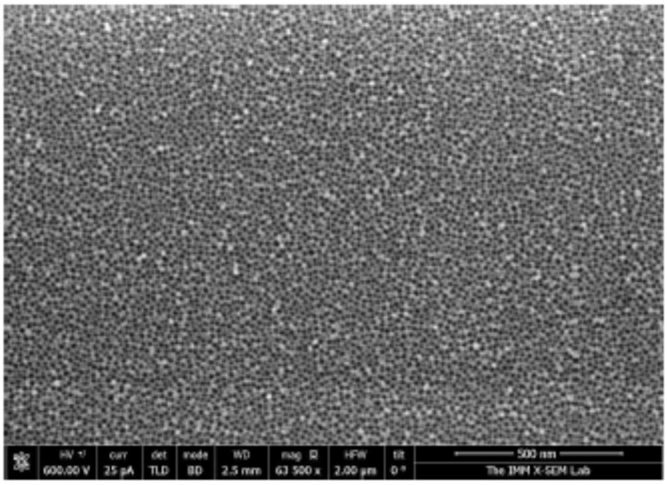
Pedro M. Resende[1], Marisol Mártin-González[1,*]

[1] Instituto de Micro y Nanotecnología (IMN-CSIC), calle Isaac Newton 8, PTM, 28760, Spain

* Corresponding Author - E-mail: marisol@imm.cnm.csic.es

Abstract

The versatility of Anodic Aluminum Oxide has led to the development of a variety of templates with ranging sizes, periodic modulations and network-like architectures. These templates allow for the nanostructuration and study of new meta-materials, with interesting and important properties enhanced through size-reduction effects. In this work, we further extend the utility of these templates through the use of current anodization in concentrated sulfuric acid under low current density values, obtaining small pore architectures with sub-10 nm features. These reduced size features allow for their application in the search for new properties in low dimension materials, by the use of this sub-10 nm pores as templates, or to be used as filters.



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Direct and indirect syntheses of oxidic 1D nanoobjects by (electro)chemical methods

Markus Antoni*, Wolfgang Ensinger

Department of Materials and Earth Sciences, Technische Universität Darmstadt,
Alarich-Weiss-Straße 2, DE-64287 Darmstadt

** Corresponding author. E-mail: antoni@ma.tu-darmstadt.de*

Metallic nanostructures are well known for their extraordinary catalytic properties and, hence, attract a lot of attention in contemporary research. In the recent past, oxidic nanoobjects have become of interest due to their enhanced properties not only in catalysis. Since oxides are already oxidised, they are less prone to phenomena such as corrosion in comparison to metals. Oxides tend to be semiconductors or isolators. Especially the semiconducting properties offer an utilisation as photocatalyst, solar cells, and gas sensors.[1] Nanoobjects stand out due to their enormous surface-to-volume ratio which qualifies them particularly for catalytic and sensor applications. The advantage of one-dimensional nanoobjetcs consists in their extended stability, less tendency of agglomeration and the associated loss of active surface area which is why they are suited for support of other active structures, too.[2]

Therefore, we investigated a spectrum of possible syntheses for this class of materials. Template synthesis is a suitable tool for the manufacturing of one-dimensional nanoobjects. A forming template is filled or lined by the desired material in order to obtain either nanowires or nanotubes, respectively.[3] Electrodeposition and electroless plating in ion-track etched polymer foils stand by as handy tools. For the synthesis of one-dimensional oxidic nanostructures, direct and indirect syntheses can be deployed. The term *"indirect"* refers to fabrication routes which require at least a two-step process for the manufacturing of oxidic nanoobjects. Here, an electrodeposition or electroless plating of a metal is conducted and followed by an oxidation treatment. The oxidation treatment can occur in terms of plasma or heat treatment.[4] The term *"direct"* refers to a synthesis which immediately results in the desired oxide nanoobject. Electroless plating of oxide nanotubes, cathodic and anodic electrodeposition of oxide nanowires are exploited to result in the final structure without any delay.[2] The direct methods bear the advantage of reducing the stress by heat or plasma treatment on the structures, which can influence the nanoobjects in a strong manner.

We want to illuminate the differences, advantages and drawbacks of the various methods for producing oxidic nanostructures based on Ce, Co, Mn, Ni, Sn, Ti, and Zn. Additionally, we highlight the benefit of the synthesised structures by portraying examples of application fields, which reach from fuel cell catalysis via electrochemical sensing towards gas sensing.

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Structure and thermal stability of electrodeposited $Ni_{1-x}Mo_x$ alloys (x<0.06)

László Péter[1*], Garima Kapoor[2], Éva Fekete[2], Jenő Gubicza[2]

1: Wigner Research Centre for Physics, Hungarian Academy of Sciences,
P.O.B. 49, Budapest, H-1525, Hungary
2: Department of Materials Physics, Eötvös Loránd University,
P.O.B. 32, Budapest, H-1518, Hungary
*Corresponding author. E-mail address: peter.laszlo@wigner.mta.hu

Alloying Ni with another highly corrosion-resistant component is a field of interest in plating industry. Alloying Ni with oxoanion-forming metals such as Mo, W and Re is possible from citrate-type baths with the so-called induced codepositon mechanism. Several earlier works in this field applied alkaline baths with high ammonia content, which is very cumbersome and difficult to treat. At the same time, the optimal pH of the Ni-Mo codepositon baths is debated.

In this work, electrodepositon was performed from a solution of small citrate content with no volatile component. The concentration of the major components was as follows: $c(NiSO_4)$ = 0.52 mol/liter, $c(Na_3Cit)$ = 0.26 mol/liter, and the Na_2MoO_4 concentration was varied. The initial optimization procedure showed that the highest deposition efficiency at room temperature can be obtained at pH = 6.1, regardless of the current density applied. Further optimization involved the measurement of the composition of samples obtained at various current densities and molibdate concentrations. Both the increase in the molibdate concentration and the decrease in current density resulted in the increase of the Mo mol fraction in the deposit. It was found that the application of saccharine as a stress reliever is beneficial for the deposition of crack-free samples.

X-ray diffraction line profile analysis was carried out to study the microstructural parameters such as the crystallite size, the dislocation density and the stacking fault probability. It was found that the increase in the Mo content led to one order of magnitude enhancement of the dislocation density while the crystallite size reduction was less significant. In addition, the twin boundary formation activity during deposition increased with increasing Mo concentration. The results obtained were compared with bulk nanocrystalline Ni-Mo materials with similar compositions but processed by severe plastic deformation. It was found that the microstructure in electrodeposited Ni layers is more sensitive to the Mo concentration than bulk ultrafine-grained Ni-Mo materials processed by severe plastic deformation.

The influence of the addition of Mo on the thermal stability of the nanostructures in electrodeposited Ni layers was also studied. For this purpose, differential scanning calorimetry (DSC) experiments were performed on the Ni films deposited with and without Mo. It was revealed that the increase of the Mo mole fraction in the deposit significantly improved the thermal stability of the nanocrystalline microstructure in Ni layers, despite the much higher defect density and smaller grain size which act as thermodynamic driving force for recovery and recrystallization. The better thermal stability can be attributed to the pinning effect of Mo solute atoms on the lattice defects (e.g., dislocations and grain boundaries) during annealing.

Pulse electrodeposition of anticorrosive Zn-Mn coatings: relations between deposition parameters and microstructure.

Florian Claudel[a,c], Nicolas Hajczak[a], Albert Tidu[a], Nathalie Allain[a], Nicolas Stein[b], Damien Close[c]

[a] *Université de Lorraine, CNRS, Arts et Métiers ParisTech, LEM3, F-57000 Metz, France*
[b] *Université de Lorraine, CNRS, IJL, F-57000 Metz, France*
[c] *Daimler AG, 70327 Stuttgart, Germany*

Zn-based coatings are extensively used in the automotive industry for the sacrificial corrosion protection of steel components. A particular interest was found in Zn-Ni, Zn-Co and Zn-Mn alloy coatings due to their enhanced anticorrosive properties. Amongst them, Zn-Mn alloys have gained an interest due to the preferential dissolution of the Mn leading to the direct formation of a compact zinc hydroxychloride (ZHC) layer [1]. As a result, numerous studies have been focused on the anticorrosive properties of Zn-Mn deposits. It appears that the corrosion behavior is not only affected by the chemical composition but also by the microstructure of the deposits. However, very few studies were conducted on the synthesis and microstructure of the Zn-Mn coatings.

The cathodic mechanism leading to the synthesis of Zn-Mn is a normal codeposition which means that high Mn contents are obtained at high current densities resulting in various drawbacks: low current efficiencies and poor appearance of the deposits. One way to overcome these drawbacks consists in using additives in order to enhance Mn deposition and to improve the microstructure of the deposits [2]. However, the presence of additives reduces the stability of the electrolyte and may induce the incorporation of unwanted elements affecting the properties of the deposits. Another approach consists in the use of pulse plating instead of continuous mode. This process provides numerous advantages for a precise control of the microstructure [4]. Because of the short duration of the cathodic pulses, the phenomenon of grain growth is inhibited and the nucleation rate is enhanced permitting the formation of smaller grains.

In this study, the influence of deposition modes and parameters on composition, morphology, texture and crystallinity of the deposits will be discussed based on a comprehensive characterization study. A strong influence of the deposition modes and applied parameters was observed on the texture and microstructure of the hexagonal closed packed structure of the ε_2-ZnMn phase. Use of continuous current leads to the formation of basal texture, while the use of pulse plating leads to various fiber orientations. Low pulse current densities enabled the formation of prismatic textures while high current densities lead to the pyramidal one. Further investigations were performed by means of FIB-SEM and EBSD, analyses in order to study the epitaxial link between the substrate and the first growth steps.

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The study of Zn-Co-CeO_2 coating electrodeposition

Marija Riđošić[1], Eva Garcia Lecina[2], Asier Salicio Paz [2], Ljiljana Živković[3], Jelena Bajat[1]

[1]Faculty of Technology, University of East Sarajevo, Zvornik, Republic of Srpska,
[2]CIDETEC Surface Engineering, E-20014, San Sebastian, Spain, [3]The Vinča Istitute for Nuclear Sciences, University of Belgrade, P.O. Box 522, 11001 Belgrade,
[4]Faculty of Technology and Metallurgy, University of Belgrade, P.O. Box 3503, 11120 Belgrade, Serbia
e-mail: marija.ridjosic@tfzv.ues.rs.ba

Various metal matrix composites (MMCs) have shown to provide enhanced properties, like corrosion stability, hardness, wear resistance. Among other methods MMCs could be obtained by electrodeposition, when solid micro or nano particles are added into the plating bath. The main draw-back in the particles incorporation via electro-codeposition processes is the low dispersion stability of particles in plating baths due to their high ionic strength. Consequently, the agglomeration of particles in such media is difficult to avoid. The mostly used methods in minimizing particle agglomeration are: magnetic and mechanical stirring, wet ball milling, both prior and/or during electrodeposition. Lately, ultrasonic (US) assisted electrodeposition has emerged as promising method for promoting the deagglomeration of particles and, consequently, the enhancement of the particle incorporation, as well as their dispersion into the metal matrix.

According to literature, metal oxide particles are mostly introduced in the plating bath through powder nanoparticles, having a tendency for agglomeration. In this work ceria sol, consisted of already uniformly dispersed nanoparticles, as Ce source in codeposition was used. Two methods of minimizing particle agglomeration were simultaneously applied: ultrasound and utilizing ceria sol in the bath, thus avoiding commonly used CeO_2 powder.

The effect of the CeO_2 source (powder and sol), its concentration in the bath and deposition current density on the current efficiency, coating composition, phase structure and morphology was investigated. In order to determine the potential range where metal deposition takes place at rates common in industrial plating, polarization diagrams were recorded in the plating solutions. It was shown that the compact coatings were obtained by US horn assisted deposition, which was also favorable for incorporation of higher amounts of Co and Ce, that were uniformly distributed in the composite coating.

Acknowledgments: *This research was financed by the Ministry of Science and Technological Development, Republic of Serbia, contract No. III 45019.* The authors acknowledge networking support by the COST Action MP1407.

Smart anti-corrosion electro-galvanized composite nanocoatings

Farzad Nasirpouri, Katayoon Alipour, Behzad Poursattar, Vahid Kardan

Faculty of Materials Engineering, Sahand University of Technology, Tabriz, Iran

Abstract:

We will present our works on the electrodeposition of smart corrosion-resistant zinc-based composite coatings containing SiO2 nanoparticles and mesoporous silica (MCM-41), impregnated with molybdate. The molybdate functionalization, which is known as a common corrosion inhibitor, was added as an “anti-corrosive self-healing” agent to the coating to be released during the corrosion process. The dispersion and bonding of the functional MCM-41 particles in the electrodeposition solution were both improved by adding 3-mercopropyltrimethoxysilane (MPTMS). Zinc metal base was co-deposited galvanostatically with the MCM-41 particles under conditions that were varied to achieve the smoothest and most corrosion-resistant films. The open circuit potential of Zn–MCM-41–SH–Mo (SH: silane, Mo: molybdate functionalization) in a chloride solution increases as a function of time owing to the release of Mo as an anodic inhibitor which makes the self-healing functionality in the coating. Based on electrochemical impedance spectroscopy and potentiodynamic polarization tests, it was observed that the corrosion resistance increases in the order: Zn–MCM-41–SH–Mo > Zn–MCM-41–Mo > Zn–MCM-41 > Zn [1]. Other recent works on Zn-Ni alloy matrix and effect of roughness and morphology of the smart nanocoatings will be also presented.

Keywords: Functional materials, electrodeposition, Zn, SiO2

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Poster contributions

Ir/TiO2 nano-catalysts applicable as anode materials in electrolyzers

Nina Dimitrova[1]*, J. Georgieva[1], S. Sotiropoulos[2], Tz. Boiadjieva-Scherzer[3]

[1]*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

[2]*Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece*

[3]*CEST Kompetenzzentrum für elektrochemische Oberflächentechnologie GmbH, Wiener Neustadt, Austria*

Email: ndimtirova@ipc.bas.bg; tel. +359 2 979-39-38

Abstract

A facile, alternative method was developed to combine the properties of TiO2 with the electrocatalytic activity of IrO2 for oxygen evolution reaction. Ir was depositied on the surface of TiO2 powder by UV photodeposition from appropriate Ir salt aqueous solutions.

The resulting of Ir/TiO2 composites have been characterized by transmission electron microscopy (TEM), energy-dispersive spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS). Depending on preparation conditions, both metallic and oxide forms of IrO2 were detected. The electrochemical characterization of the resulting composites was carried out by cyclic voltammetry (to identify the surface electrochemistry of the catalyst) and linear sweep voltammetry to test their catalytic activity.

Acknowledgments:

Financial support of project: “National program support for young scientists and PhD students, Bulgarian Academy of Sciences - 17-52”. CEST Austria in the frame of the COMET program is also acknowledged.

Novel functionalized nanomaterials for acrylamide sensing

Anja Drame[1,2], Špela Trafela[1,2], Sašo Šturm[1,2], Kristina Žužek Rožman[1,2]
Department for Nanostructured Materials,
"Jozef Stefan Institute", Jamova 39 1000 Ljubljana
anja.drame@ijs.si

[1] *Department for Nanostructured Materials, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*

[2] *Jožef Stefan International Postgraduate School, Jamova 39, SI-1000 Ljubljana, Slovenia*

Acrylamide is industrially widely used the organic compound. In nature, it can be found as a contaminant originating from polyacrylamide – polymer which is used in wastewater treatment, paper and textile industries, and as a monomer in cigarette smoke and in heat-treated food [1]. Due to its neuro and genotoxicity [2] and classification as a potential human carcinogen [3], it is essential that we are able to detect its presence, especially in food products. Primarily used techniques for detection of acrylamide are ICP-MS, GC, HPCL, which are all expensive and time-consuming [1, 4]. However, nowadays, the desire is to have cheaper, more accessible and more operator friendly methods. The potential to fit this gap are autonomous sensors based on the electrochemical detection.

Molecularly imprinted polymers are synthetic polymers with recognition sites for specific binding of and are presenting a low cost and easy technique that provides high stability to harsh chemicals and physical conditions and reusability [5]. The screent printed carbon nanotubes and gold-based electrodes were modified with noble metals nanostructures (Au) and covered with polyaniline in which specific sites for acrylamide were imprinted. Sensing of acrylamide was carried out by using electrochemical methods for measuring the electrochemical response of a liquid solution of $K_3Fe(CNO)_6$) or solid ($Ni(OH)_2/NiO(OH)$) redox probe. The constructed receptor element presents a good base for a sensitive and selective small, portable, cost-efficient sensor which allows a real-time measurements.

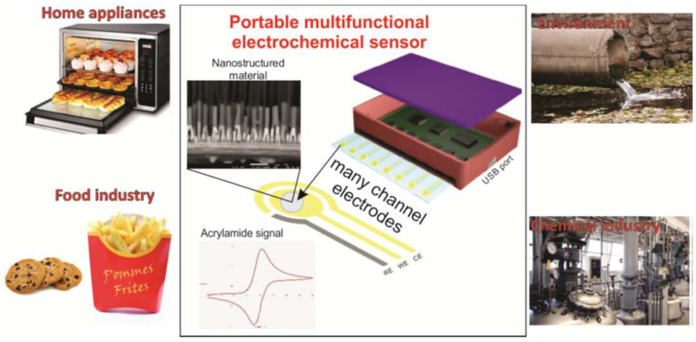

Figure 1: Potential usage of sensor in different industries

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Magnetic field controlled mass transport in fuel cell related electrocatalysis

Markus Kratz[1], Kristina Tschulik[1]

[1] Micro- & Nano-Electrochemistry, Center for Electrochemical Sciences (CES),
Ruhr-Universität Bochum, Universitätsstr. 150, ZEMOS, 44801, Bochum, Germany

Abstract

To achieve a global transition in energy politics and a deceleration of climate change, an extensive development and investigation of sustainable energy production and storage technologies is essential. In this context, the use of hydrogen, as an environmentally friendly and nearly unlimited available energy carrier, is main topic of recent research.

In electrochemical hydrogen production the high kinetic hindrance of the reaction and the mass transport of species is limiting catalysts efficiency. Thus, it has been shown that the enhancement of mass transport of reactants from the bulk to the electrode and of the product away from the electrode, to avoid blocking of the active sites can be achieved by superimposing magnetic fields.

It has been shown that by performing an electrochemical reaction like the hydrogen evolution reaction (HER) in the presence of an external magnetic field (e.g. by approaching a strong permanent magnet), magnetic forces are induced. These can induce convection and therefore influence the mass transport at the electrode/electrolyte interface, which is known as magnetohydrodynamic (MHD) effect.[1-3] It is also known that the magnetic field can be templated and focused by introduction of ferromagnetic materials e.g. iron, nickel or cobalt-iron alloy nanowires between the magnet and the electrode.[4] With the use of nanowires, higher magnetic gradients are generated which results in increased mass transport of species to and from the electrode. The induced convection can facilitate bubble desorption from the surface and therefore results in decreased surface blocking. Additionally, the significantly improved catalytic activity of nanowires is a result of the high surface area.[5]

The goal of the present research is to combine both, the effect of enhanced nano-electrocatalysis and magnetically enhanced mass transport, for further investigation and improvement of new HER systems to increase its activity and efficiency by applying an external magnetic field.

Firstly, the design and construction of an anodized aluminium oxide (AAO) nanowire growth setup is planned. By electrochemical oxidation of ultrapure aluminium, a highly ordered porous network is formed on the aluminium surface. Subsequently, metal and alloy materials are electrodeposited into the alumina pores. These nanowire arrays can then be used for generation of localized high magnetic gradients which therefore influence the reaction. A wide range of parameters can be changed to find a more active catalyst system for the HER. The size, shape, material, position and catalytic coating of the nanowires is changed. Additionally, a suitable combination of electrolyte, concentration, magnetic field strength and orientation, etc. will be optimized to obtain a better understanding of the magnetic field induced effects on mass transport and reaction rates to improve the electrochemical HER efficiency.

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Shape-Selective Electroless Plating

Falk Muench,[1,2]*, Alexander Vaskevich,[1] Wolfgang Ensinger,[2]

1: Weizmann Institute of Science, Department of Materials and Interfaces,
Herzl Street 234, 7610001 Rehovot, Israel

2: Technische Universität Darmstadt, Department of Materials and Earth Sciences,
Alarich-Weiss-Straße 2, 64287 Darmstadt, Germany

*Corresponding author. E-mail: muench@ma.tu-darmstadt.de

Electroless plating is traditionally employed to provide work pieces with protective or electrically conducting coatings, and produces smooth, compact metal films. On the contrary, typical application fields of metal nanomaterials tend to benefit from roughness, porosity and / or specific nanostructure. The conventional way of producing complex nanostructures with electroless plating is to exploit the method's excellent conformity to define the product structure via substrate replication. However, such template-assisted routes necessitate additional processing steps, and typically result in materials without distinct internal nanostructure.

In this contribution, we want to summarize our efforts in developing an alternative electroless plating strategy, in which the bath chemistry is tuned to directly create anisotropic metal nanostructures.[1-4] Similar to the mechanistically related colloidal nanoparticle syntheses, specific product shapes are realized by controlling the underlying nucleation and growth processes, not by spatially limiting metal deposition. This hybrid approach combines the advantages of electroless plating with those of shape-controlled nanoparticle synthesis, enabling the direct functionalization of surfaces with nanowires,[1] nanoplates[2,3] or nanospikes.[4]

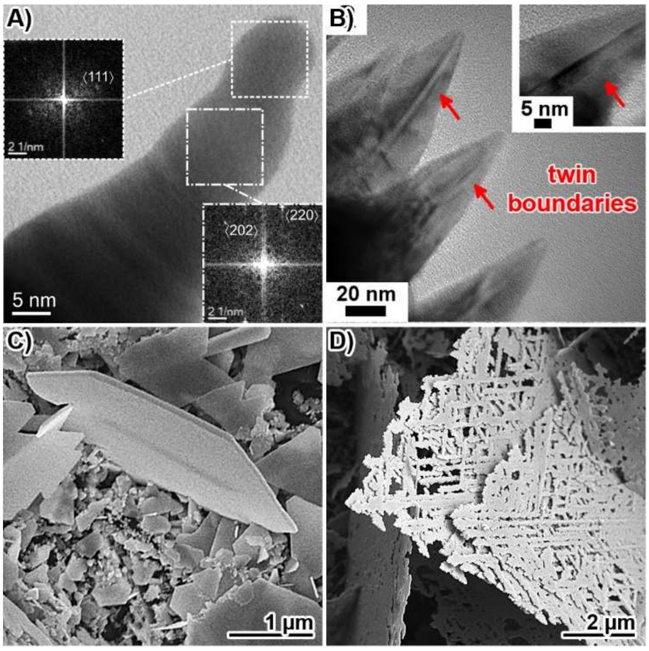

Figure 1. Electron micrographs of **A)** the tip of a Au nanowire, **B)** Ni nano-spikes growing along a central twin boundary, **C,D)** Ag nanoplates, all obtained by shape-selective electroless plating.

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Surface alloying during Pb underpotential deposition on Au(111)

Alicja Szczepanska[1,2]*, Neil A. Fox*[1,2,3] *and Natasa Vasiljevic*[1,2]

[1]Bristol Centre for Functional Nanomaterials, University of Bristol, United Kingdom
[2] School of Physics, University of Bristol, United Kingdom
[3] School of Chemistry, University of Bristol, United Kingdom

The advancement of miniaturised devices depends on the control of the structure and composition of new types of nanomaterials. Some of the candidates are two-dimensional (2D) nanomaterials such as thin films and alloys.[1] Particularly interesting are the spontaneously formed surface-alloys during deposition of one metal onto another, because they can exhibit a range of new chemical and physical properties that differ from their bulk counterparts. Moreover, surface-alloys can be created in systems with a very large lattice mismatch which do not have bulk counterparts, a so called immiscible system.

Spontaneous surface alloying during metal deposition has been widely studied in Ultra High Vacuum (UHV).[1] Although extensively explored, these new materials have not been exploited much in practical applications.[2] The surface alloying in an electrochemical environment is an ideal route to design functional materials because of the high control and scalability that would make the transfer to real and practical systems viable and versatile. The ideal systems to explore the electrochemically controlled nanoalloys formation are systems exhibiting phenomenon of underpotential deposition (UPD). The UPD process is the deposition of an epitaxial metal monolayer on a metal substrate at potentials positive from the equilibrium potential for the reduction of the bulk metal.

In this study we investigated the surface alloying process during Pb underpotential deposition (UPD) onto Au(111).[3] The electrochemical results suggest that Pb-Au alloying happens during potential cycling at partial monolayer coverage(s) of Pb.[4] Although Pb and Au are two immiscible metals, the surface alloying is driven by a very large lattice mismatch of ~21% and the elastic energy minimisation. The aim of the study is to establish the range of potential at which the alloy forms as well as its composition. The conditions of thermodynamic equilibrium at different coverages of Pb on Au (0-1 ML) during formation and the dissolution of Pb UPD ML have been explored and compared to establish the general conditions at which the surface alloy formation could be controlled. The effect of the potential polarisation time and multiple potential cycles on the surface-alloy structure and its stability have been explored as well.

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Synthesis and characterization of copper nanowire networks

Nils Ulrich[1,2]; M. Breiner[3], C. Gütz[3], S. Waldvogel[3], C. Trautmann[1,2] , M.E. Toimil-Molares[1]

1 Materials Research Department, GSI Helmholtz Centre, Darmstadt, Germany
2 Material- und Geowissenschaft, Technische Universität Darmstadt, Germany
3 Institut für Organische Chemie, Johannes Gutenberg-Universität Mainz, Germany

We present the synthesis and characterization of metallic copper nanowire networks with well controlled geometrical parameters by ion-track technology and electrochemical deposition. By sequential swift heavy ion irradiation of 30 µm thick polycarbonate foils from four different directions, interconnected latent tracks are generated. During the subsequent chemical etching process, the ion-tracks are selectively dissolved and enlarged to form an interconnected nanochannel network. By electrochemical deposition we synthesize copper nanowires in the channels. Deposition conditions and geometry are varied to obtain three-dimensional assemblies of embedded Cu nanowires displaying complete and homogeneous growth.

In this poster, we will present scanning electron microscopy (SEM) images that evidence how parameters such as wire diameter, wire density, interconnectivity, and surface morphology are tuned by adjusting the different processing steps. By varying nanochannel diameter and irradiation fluence, wire surface curvature and surface area of the nanowire network are tailored. Thus, for a network having a height of 30 µm, an area of 1 cm², and a nanowire diameter of 150 nm, a total surface area of ~330 cm² can theoretically be achieved. In addition, the nanowire networks are characterized by X-ray diffraction measurements and transmission electron microscopy. First results obtained on the implementation of these nanowire networks as electrodes for electrocatalysis and electrosynthesis will be presented.

Seebeck coefficient of $Bi_{1-x}Sb_x$ nanowire assemblies produced by electrodeposition in ion track-etched polymer membranes

M.F.P. Wagner[1,2,3], A.S. Paulus[1,2], P. Kuhn[1,2], J. Brötz[2], C. Trautmann[1,2], K.-O. Voss[1], F. Völklein[3], M.E. Toimil-Molares[1]

[1]Materials Research Department, GSI Helmholtz Center, Planckstr. 1, 64291 Darmstadt, Germany
[2]Department of Materials and Earth Sciences, Technische Universität Darmstadt, Alarich-Weiss-Straße 2, 64287 Darmstadt, Germany
[3]Institute of Microtechnologies, RheinMain University of Applied Sciences, Am Brückweg 26, 6542, Rüsselsheim, Germany

The unique properties of bismuth antimony ($Bi_{1-x}Sb_x$) nanostructures and the theoretical predictions on their enhanced thermoelectric efficiency two decades ago[1] triggered the development of a wide variety of growth and characterization methods aiming at measuring the thermoelectric properties of nanowires. Since then, several groups have studied the properties of $Bi_{1-x}Sb_x$ nanowires, and various size dependent effects have been highlighted[2-4]. However the experimental demonstration of a size dependent thermoelectric efficiency is still challenged by the difficulties to fabricate well-defined nanowire systems and to achieve reliable and stable electrical and thermal contacts.

Here we present the fabrication of $Bi_{1-x}Sb_x$ nanowire assemblies consisting of either parallel arrays or highly interconnected networks by using pulsed electrodeposition in ion track-etched polycarbonate membranes.[4-5] The wire diameter is determined by the dimensions of the host channel and was adjusted systematically between 30 nm and 160 nm. The composition was systematically varied as a function of the electrolyte composition. The Seebeck coefficient of both parallel and interconnected nanowire assemblies has been measured as a function of wire diameter and composition, and the results will be discussed.

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Electrochemical studies for the preparation of Fe-Co/Cu multilayers with GMR

D. Zalka, L. Péter, I. Bakonyi*
Wigner Research Centre for Physics, Hungarian Academy of Sciences
H-1121 Budapest, Konkoly-Thege út 29-33, Hungary
**Corresponding author. E-mail: bakonyi.imre@wigner.mta.hu*

In the past years, several studies have been reported about the preparation and giant magnetoresistance (GMR) of electrodeposited Fe-Co/Cu multilayer films [1-2]. However, relatively little amount of information is available about the optimization of the electrochemical parameters and the properties of the resulting multilayers. In our recent work [1], such an optimization has been carried out by using sulfamate type bath.

In the present work, this study was continued by carrying out more electrochemical characterization for the same bath as used in Ref. 1 (pH = 3.25 and pH = 1.25) and extending the study to three other bath formulations with commonly used solutes. The three new baths contained (i) just the sulfate salts of the metals and boric acid (pH = 2.8), (ii) sulfate salts, sodium citrate and boric acid (pH = 5.6) and (iii) sulfate salts and ammonium chloride (pH = 3.5). For each bath, two different Fe^{2+} ion concentrations were used (5 and 20 mol% with respect to the total magnetic ion concentration, $Fe^{2+} + Co^{2+}$) which resulted in 5 at.% and 35 at.% Fe-content in the magnetic layer, respectively.

As in Ref. 1, G/P pulse-plating method was applied for Fe-Co/Cu multilayer preparation (Fe-Co layer: galvanostatic control; Cu layer: potentiostatic control). For the deposition of the magnetic layer, two current densities (-20.7 mA/cm^2 and -34.5 mA/cm^2) were used. The Cu layer deposition potential was electrochemically optimized for all bath formulations as described in Ref. 3 at which neither the dissolution of the magnetic layer during the Cu deposition pulse, nor the codeposition of the magnetic elements in the non-magnetic layer (Cu) can occur. This also ensures that the actual layer thicknesses will be equal to the nominal ones calculated on the basis of Faraday's law by assuming 90% and 100% current efficiency for the magnetic and non-magnetic layers, respectively. It was a particular aim to study the effect of the various complexing agent additives on the optimal Cu deposition potential that was dependent on the bath formulation, Fe^{2+} ion concentration and pH.

The room-temperature magnetoresistance (MR) of the electrodeposited Fe-Co(5nm)/Cu(5nm) multilayers each with a total thickness of 1 μm has been measured up to H = 9 kOe. All the multilayers studied exhibited GMR in that both the longitudinal and transverse MR components were negative for all magnetic fields. The MR(H) curves have been decomposed into ferromagnetic and superparamagnetic contributions according to the procedure described in Ref. 1. Larger GMR was observed at the smaller Fe-content for each bath.

This work was supported by the Research Group Linkage Programme (Project Ref. 3.4 – 1001292 – HUN - IP) of the Humboldt Foundation, Germany

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The specific grain boundary resistivity of Ni from an analysis of the grain size dependence of the resistivity of electrodeposited nanocrystalline Ni

I. Bakonyi[1,*] , V.A. Isnaini[1], T. Kolonits[2], Zs. Czigány[2], J. Gubicza[3], L.K. Varga[1],
E. Tóth-Kádár[1], L. Pogány[1], L. Péter[1] and H. Ebert[4]

[1]Wigner Research Centre for Physics, Hungarian Academy of Sciences.
H-1121 Budapest, Konkoly-Thege út 29-33, Hungary
[2]Institute for Technical Physics and Materials Science, Centre for Energy Research,
Hungarian Academy of Sciences, Budapest, Hungary
[3]Department of Materials Physics, Eötvös Loránd University, Budapest, Hungary
[4]Department Chemie, Ludwig-Maximilians-Universität München, Germany

**Corresponding author. E-mail: bakonyi.imre@wigner.mta.hu*

New results are presented on the room-temperature electrical resistivity of nanocrystalline (nc) Ni metal produced by electrodeposition with various grain sizes which were deduced from X-ray diffraction (XRD) line profile analysis and/or from direct imaging by transmission electron microscopy (TEM). From a systematic analysis of all available resistivity data reported on nc-Ni, the specific grain boundary resistivity (ρ_{SGBR}) value was evaluated for Ni.

In an overall assessment, our new resistivity results matched fairly well with all previous data reported on nc-Ni as a function of grain size. However, when comparing all reported resistivity data on nc-Ni, it could be established that the evaluated value of ρ_{SGBR} depends on whether the grain size was determined by XRD or TEM and the difference can amount to a factor of about 2. It is pointed out that this difference of ρ_{SGBR} values is due to the fact that the XRD crystallite size is determined also by intragrain structural defects such as small-angle grain boundaries and twin boundaries which, on the other hand, have a very small contribution only to the resistivity. Therefore, the grain size obtained by direct TEM imaging is the appropriate parameter when accounting for the resistivity.

For the evaluation of ρ_{SGBR} from the experimental resistivity data, we have adopted the scheme suggested by Andrews [1] who noticed that the resistivity increases linearly with the grain boundary surface area per unit volume (S_{GB}/V). However, it will be pointed out here that since various values ranging from 2.37 to 3.24 are used in the literature for the proportionality factor k_{GB} relating quantitatively S_{GB}/V and the grain size, this gives an uncertainty of the ρ_{SGBR} values to the same extent. By considering this uncertainty in deducing ρ_{SGBR} from the reported grain size dependence of the resistivity, our ρ_{SGBR}(Ni) value matches fairly well the lastly reported calculated value for Ni metal [2].

This work was supported by the Research Group Linkage Programme (Project Ref. 3.4 – 1001292 – HUN - IP) of the Humboldt Foundation, Germany. The research was carried out also in the framework of the COST Action MP1407.

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Magnetic Tunnel Junctions for Molecular Spintronics

Nathan Missault, Prof. Walther Schwarzacher

H H Wills Physics Laboratory, Tyndall Avenue, Bristol BS8 1TL, UK

Magnetic tunnel junctions (MTJ) consist of ferromagnetic metal layers separated by an insulator of a few nm thick. As such, electrons can only travel between the two metals by tunnelling across the insulating barrier. Since tunnelling is spin-coherent, the resistance across the barrier depends strongly on the respective alignment of the magnetization of the metal layers, leading to very high magnetoresistance ratios. Inversely, a well characterized MTJ can be used to study spin coherence in organic molecules. An array of molecules can be deposited electrochemically over a MTJ pillar, effectively bridging the insulator along the outside. This provides a robust platform to study the magnetoelectric transport properties of the attached molecules, while maintaining electrochemical control.

As a proof of concept, polypyrrole was deposited across a 15 micron wide gap through cyclic voltammetry, showing both the moment the gap is bridged and the dependence of the molecular conductance on the electrochemical potential. In order to reduce the separation between the two metal layers sufficiently for them to be bridged by organic molecules, the bottom layer is electroplated with a thin film (< 10nm) of copper. Copper is chosen for its long spin-diffusion length compared to the barrier thickness, so any spin-scattering can be attributed to the molecular transport.

Data from these many-molecule measurements will be compared to single-molecule measurements using a scanning tunnelling microscope break junction (STM-BJ). For these experiments a fine metal tip is crashed into a metal substrate and retracted while measuring the current across the tip and the substrate. When done in a solution, nearby thiol-terminated molecules can bridge the tip and the substrate, enabling a measurement of the molecular conductance. This too is done under electrochemical control. This project will be able to identify molecules with promising magnetoelectronic properties for spintronics applications, while studying the limits of thin film electrodeposition.

Biomimetic bone growth on TiO_2 nanotubes for dental implant applications

Elnaz Moslehifard a,*, Iman Yousefi b, Farzad Nasirpouri b

a Department of Prosthodontics, Faculty of Dentistry, Tabriz University of Medical Sciences, Tabriz, Iran
b Faculty of Materials Engineering, Sahand University of Technology, Tabriz, Iran

The effect of structural and morphological aspects of TiO_2 nanotubes on their application in biomedical materials application such as implants is very interesting that has not been well documented. For example, it has been clarified that the morphology and composition of TiO_2 nanotubes influences the biocompatibility, bioactivity and bone cell/material interaction of titanium implants using in-vitro studies. Most of the studies have focused on the application of simulated body fluid (SBF) as an artificial source of bone growth to form calcium phosphate and hydroxyapatite coatings and other structures and have revealed substantial evidences to exploit TiO_2 nanotubes as a bioactive and biocompatible material for implant applications. However, further studies still are required to identify the effect of anodic oxidation voltages at critical temperature on morphology and their response to bone growth for biomedical applications.

The geometry and dimensions of TiO_2 nanotubes anodised under different voltages and temperatures in an organic electrolytewere manipulated to investigate themorphological, crystalline microstrcture and their response to soaking in simulated body fluid (SBF) for biomaterial implant applications. It was observed that high anodisation voltages up to 120 V increase the internal pore diameter. Hexagonally arranged nanotubes were achieved by anodisation of Ti in a lower temperature of 0 °C , while the geometry of nanotubes becomes circular at a higher temperature of 30oC. For biomaterial application in particular the bone cell/implant biomaterial interaction, we found that the nanotubes anodised at a voltage of 120 V and a temperature of 0 °C exhibited a better mineralisation than those obtained under other anodising conditions. This was mainly due to the rougher and sharper tube walls which provide more suitable places for the nucleation of bio-sediments. On the other hand, annealing of the nanotubes results in the formation of crystalline sediments the amount of which was decreased compared to the as-anodised nanotubes.

Electrodeposition and corrosion behavior of nanostructured Ni-Cr films for dental materials application

Elnaz Moslehifard[1], Hossein Firouzi[2], Farzad Nasirpouri[2]

Faculty of Dentistry, Tabriz University of Medical Sciences, Tabriz, Iran -1
Faculty of Materials Engineering, Sahand University of Technology, Tabriz, -2
iran

The electrochemical deposition of alloys is technically a more complex process than pure the metal deposition. Because in addition to more precise control of the electrolyte composition and deposition conditions, it also requires more detailed monitoring of these parameters, also have additional problems related to the performance of the anode. The electrochemical deposition, compared with other methods, is known as a unique low cost method for the production of nanocrystalline materials with an easy control of factors affecting grain size less than 20nm, high production speeds and more limited technological barriers to convert this process from laboratory to industrial state.

In this research, the electrochemical deposition of nickel-chromium alloy in a sulphate-chloride bath was performed by using two direct and pulsed current techniques on a copper substrate and the properties of the obtained coatings were compared. The effect of current type and pulsed current parameters including duty cycle, peak current density, and frequency on coating efficiency, composition variation, crystallite size, microhardness, morphology and corrosion properties of coatings, were investigated.

The results showed that the disposition with the pulse current increases the efficiency in comparison to the direct current (97 and 85% respectively). Elemental analysis showed that by increasing the peak flow density and duty cycle and decreasing the frequency, the amount of chromium in the alloy coating increases. The X-ray diffraction analysis showed that by increasing the amount of chromium in the alloy, the size of the crystallite decreases, and by increasing the chromium content by more than 24% Wt, a phase separation, and γ' phase formation were observed. The hardness of the deposited coatings increases with increasing chromium content. Field emission scanning electron microscope showed that the size of the spherical topological topological grains was in the range of 27-114 nm, and by increasing the amount of chromium, surface roughness increased and eventually, the micro-cracks emerged. In nickel-chromium alloy deposited by a pulsed current, active and inactive behaviors were observed in the potentiodynamic of polarization curves due to the formation of a passive $NiO.Cr_2O_3$ detected by X-ray diffraction analysis. By means of potentiodynamic polarization experiment it was indicated that the nickel-11.2% chromium alloy coating had the highest resistance to corrosion attack compared to other alloys, and with increasing chromium content, the corrosion resistance increased in the alloy coating, and by increasing the amount of chromium to more than 24%, corrosion resistance is reduced. These films have potential application in base metal dental alloys for their enhanced corrosion resistnce.