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How US-funded research is driving innovation

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Building up

Dr Stanko R Brankovic explains the background to his research into the nanofabrication of metallic structures, as well as the importance of investment in the education of tomorrow's scientists

To begin, could you offer an overview of your research project?

The proposed career development programme represents a unique synergy between the fundamental science of metal deposition via surface limited red-ox replacement (SLRR) reaction, dealloying and surface electrochemistry and their application to the related fields of electrocatalysis, thin films, sensors and nanofabrication. For the first time the most important thermodynamic quantities controlling deposit morphology obtained via SLRR will be identified and studied in great detail. Additionally, the kinetic aspects of electrochemical thin film growth will be examined and the dominant atomistic processes defining the thin film morphology will be revealed. The dealloying of binary alloys will be examined as the fabrication method for synthesis of the ultrasound sensor materials.

How does your work build on previous breakthroughs in the field?

The proposed research plan capitalises on advantages that metal deposition via SLRR reaction provides to produce model system for studies of fundamentally important questions in electrocatalysis and surface science, which until this moment were mostly confined to experiments in vacuum. The proposed work will study metallic low-dimensional and nano-porous structures and evaluate their application through the scope of advanced nanoscale catalyst design, and ultrasound sensor fabrication.

In which direction would you like to take your research in the future?

The future direction of my research will be driven by the quest for new materials and their application in energy harvesting. This means electrochemical synthesis of new materials for harvesting energy of the sun, understanding the corrosion processes responsible for the reliability of nuclear plants, design of catalyst materials for isotope separation, and understanding fundamental questions related to the morphological stability of the metal-solution interface at conditions far from equilibrium (battery applications).

Your project incorporates various educational elements. Could you outline the graduate and undergraduate components?

The research work provides topics for three PhD theses in the field of interfacial electrochemistry, nanofabrication, thin film deposition and electrocatalysis. The new knowledge acquired throughout this research programme will be incorporated into the lecture material of three graduate courses; Electrochemical Nanofabrication Technology, Alternative Energy Storage and Energy Conversion Systems, and The Material Science of Thin Films. This project will provide a base for sophistication and advancement of the undergraduate nanofabrication course, Introduction to Design and Fabrication of Nanoscale Devices. The undergraduate students of Chemical, Electrical Engineering and Chemistry Departments will have the opportunity to participate in this project through the topics of their undergraduate research or directly working in my research group.

How have high school students been a part of your activities?

The outreach programme to high school chemistry students of the North Shore Senior High is also a part of the educational component of this research. This programme involves high school students visiting my research lab and actively participating in lectures and laboratory exercises in the field of electrochemistry and corrosion. As an outreach to scientific community, many results of this work will be embedded into the educational material for Electrochemical Society Short Courses which I routinely instruct at The Electrochemical Society fall meetings. The most recent one is 'Electrodeposition for Energy Application', which was offered in fall, 2011 (Boston) and will be offered in fall, 2012 (Honolulu).

How important is the nurturing of young scientists to the development of research in the physical sciences? To what extent do you feel as though your research has contributed to this?

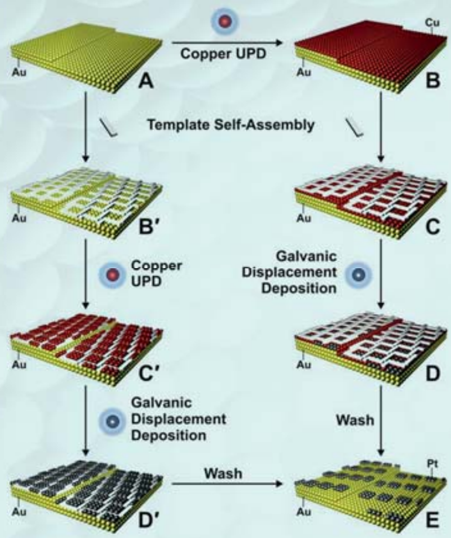
Research-based education is as crucial as classroom education in elevating the quality and diversity of scientists and engineers in the US. My deep belief is that every academic faculty must endeavour towards excellence while building a progressive programme that is sustainable and original, impacting education and career development for future generations. The main criteria followed in education of engineers for 21st century should be based on their ability to perform systematic work, to adopt structured knowledge and to demonstrate an independent thinking. Together with an effort to provide students with the best possible technical education and research experience, the academic faculty must take an active role in elevating moral and ethical standards of young generations to ever-increasing levels. This research programme encompasses all these aspects making sure that the road to success for future engineers and scientists in our country is paved by the steps of their mentors.

Minute **metals**

A team of researchers at the **University of Houston in Texas** are investigating functional surfaces and metallic nanostructures in their Electrochemical Nanofabrication project work, which is set to revolutionise the use of metals

HUMANS HAVE WORKED metals for over 7,000 years, and the general trend has been for ever finer scales of work and increasing levels of technological accomplishment. Continuing this trend, a team at the University of Houston have been investigating the technologies around electrochemical interfaces, giving them the ability to work at the nano level of their materials, producing novel functionality and application. The processes they are examining are numerous, and include organic adsorption, de-alloying, deposition, etching, oxidation and electropolishing. These allow the team to form organised hetero-epitaxial metal overlayers and oxide nanostructures, a minute layering of crystalline substances over substrates, as well as the production of materials with functional surfaces of alternative properties and uses. The current focus of their work is the organic phase and hydroxide incorporation into magnetic matrices during the electrodeposition process. This is multifaceted work, which includes studying the organics and hydroxide incorporation effect on the morphology of the deposits, the resultant corrosion and magnetic properties, and a number of other physical outcomes of changes in the interaction. The team hopes that their examination of metals on this superfine scale will help to improve understanding of how manufacturing processes adjust the properties of the materials and nanostructrues produced.

Seeking to gain knowledge of changes at the nanoscale, the team have concentrated their strategies on extremely high levels of detail. In order to focus on the thermodynamics of metal deposition via surface limited red-ox replacement (SLRR) – the process at the centre of their current work – they have systematically use scanning tunnelling microscopy and sophisticate image processing. This incredibly fine work has required the team to be extremely methodical, closely examining the morphology of the deposits and linking this to the particular nature of the SLRR reaction which occurred. Alongside this work, the team have employed conventional electrochemical techniques to quantify the thermodynamic

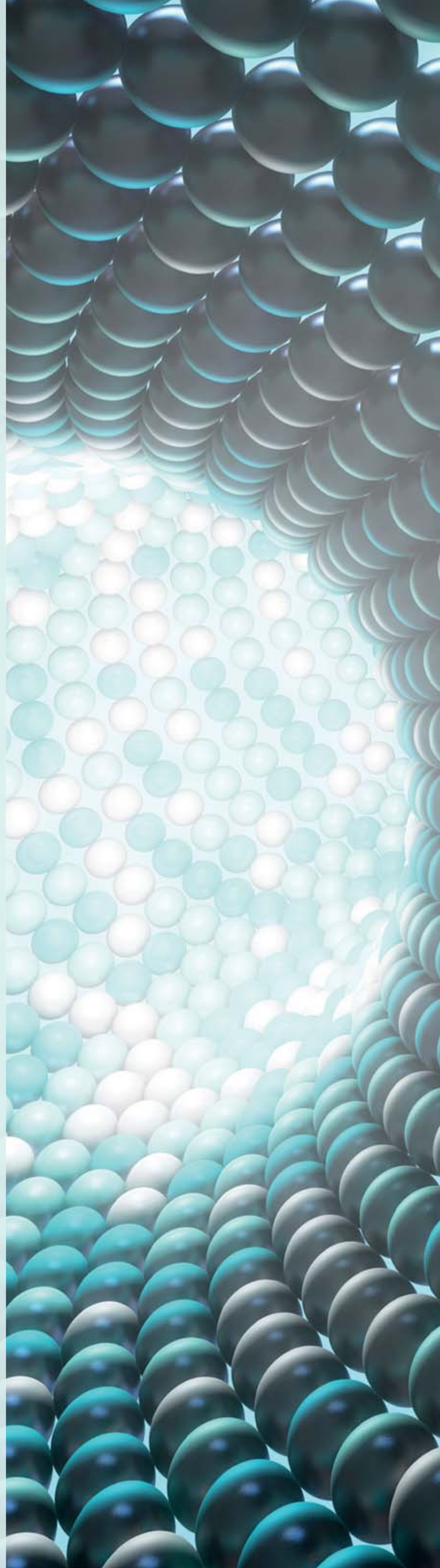


SLRR AND SUPRAMOLECULAR TEMPLATE SELF-ASSEMBLY STEPS TO PRODUCE ORDERED MONOLAYER PT CATALYST. PATH 1: A-B'-C'-D'-E, PATH 2: A-B-C-D-E

parameters of the SLRR process. By keeping the driving force in the red-ox process constant but producing a varied amount of deposited metal, the team is able to investigate the nucleation kinetics at work in the SLRR reaction. Similarly, the catalytic properties of monolayers obtained by SLRR are studied by a combination of scanning tunnelling microscopy, IR spectroscopy as well as electrochemical measurements of relevant reaction kinetics including hydrogen oxidation, oxygen reduction and others. Since studying epitaxial processes requires such minute measurements, the team must be entirely meticulous in their work, driving the innovations in thin films science, and electrocatalysis.

PROBLEMS AND SOLUTIONS

The research has provided a number of challenges for those in the team, with its high complexity and precise nature. Dr Stanko Brankovic, who is leading the project, has taken the technical aspects in his stride but found other elements testing: “The greatest challenge in this research programme is its multidisciplinary nature which revolves around



the fields of electrocatalysis, sensors, materials science, nanofabrication and thin films". Moving between and beyond the individual fields has been an ongoing challenge for the team, and has also impacted on the educative work which they have completed. The ability of graduate and even undergraduate students to work across different fields is increasingly important, and the Texan team's educative role has helped to expose these young scientists to this new paradigm in creative thinking. Working between different fields has been difficult, but the work of the team has been assisted by the existence of preformed models which help to identify dominant processes on which to focus their attention. The Kinetic Monte Carlo simulations have been able to bring out the elements which control the morphology and size uniformity of the metal deposits which are made.

REVOLUTIONARY RESULTS

The problems of interdisciplinary work and the advantages of modelling, as well as the dedication of the team, lie behind a number of significant results which have been produced. The general finding is that the relationship between a catalyst's activity and its morphology centres on the relationship between the energy of the catalyst d-band centre and the value of surface strain in catalyst clusters. Brankovic is excited in particular by two results: "Our work illuminates several new details that are of wide importance when catalyst monolayer and submonolayer design is considered". The first of these focuses on reactions where the kinetics are improved by increasing the reactivity of the catalyst through tensile strain. In these processes, the coarsening of the submonolayer catalyst has a positive effect on the catalyst activity. From this detail, the team have calculated what the optimum morphology is for these catalysts. The second major finding regards reactions where catalysts are poisoned by intermediaries. In these, catalysts should be designed as submonolayer configuration, which provides a mechanism to fine tune the catalyst's selectivity, increasing its tolerance. These successes are inspiring the team to continue their work, pushing towards further significant results.

THE THIRD DIMENSION

In addition to the work on monolayers, part of the research has been the investigation of processes to create more complex nanostructures. These include SLRR reactions and dealloying, working towards the production of three-dimensional nanoscale metal structures. Brankovic has also been pushing this work forward: "The current research has realised the first three-dimensional nanostructures with unprecedented sensitivity towards upcoming ultrasound excitation in electrolyte," he highlights. This innovation represents a new class of ultrasonic sensing technology, formed of a material with inherent transducer properties limited only by the sensor design. The Houston team is also looking at how the spontaneous self-organisation of two- and three-dimensional nanostructures, demonstrates how uniform size and geometry are possible when the underlying processes are carefully controlled. It is their ultimate hope that an increased understanding of the thermodynamics and kinetic processes during SLRR will allow catalyst monolayers to be designed on a truly atomic scale.

INTERDISCIPLINARY IMPACTS

The challenges faced by the team in bridging opposed areas of research will be rewarded in the breadth of output which their investigations will have. The many applications of the research will allow an extension of their findings into numerous other scientific disciplines. Self organised two-dimensional metal structures, the design of catalyst monolayers and the managed growth of carbon nanotubes are all possibilities which are opened up by the work. This breadth also translates into the ways in which the research could impact new areas of investigation, opening up the potential for further breakthroughs. These outcomes connect intimately with the educative element of the work, which is a vital component, as Brankovic explains: "The long-term goal of this programme is to produce highly qualified scientists and engineers who will be able to carry out the technical challenges of the modern age". This aim is driving the Texan team to produce new results, providing the gems that will generate future research into the new possibilities of metallic structures.

Since studying epitaxial processes requires such minute measurements the team must be entirely meticulous in their work, driving the innovations in thin film science and electrocatalysis at the centre of their work

INTELLIGENCE

ELECTROCHEMICAL NANOFABRICATION – TRANSFORMATIVE CONCEPT TOWARDS SYNTHESIS OF NOVEL MATERIALS, FUNCTIONAL SURFACES AND METALLIC NANOSTRUCTURES

OBJECTIVES

To investigate the governing thermodynamics and kinetics processes controlling the morphology of the metal nanodeposit obtained via surface limited red-ox replacement reaction. In this novel deposition method, a single monolayer of less noble metal is oxidised-displaced by more noble metal cations which are simultaneously reduced-deposited on a substrate surface. The obtained metallic deposit has just a single atom in thickness as nanoclusters uniformly distributed over the substrate surface. Such nanodeposit will be used as model system to study structure-property relation of catalyst monolayers, their stability in different chemical reactions and their self-organisation.

KEY COLLABORATORS

Dr Ping Liu, Brookhaven National Laboratory • **Dr Peter Strasser**, Technical University of Berlin • **Dr Lars Grabov**, University of Houston • **Dr Ognjen S Miljanic**, University of Houston

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STANKO BRANKOVIC obtained his BE in Chemical and Biochemical Engineering in 1994 at the University of Belgrade and PhD in Science and Engineering of Materials in 1999 at Arizona State University, before joining the University of Houston in 2005. He spent two years at Brookhaven National Laboratory, New York (1999-2001) and four years at Seagate Research Center in Pittsburgh (2001-05). Brankovic's work has been acknowledged by Cullen College of Engineering Faculty Research Excellence Award (2009), University of Houston Research and Teaching Excellence Award (2010) and NSF CAREER (2010).

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