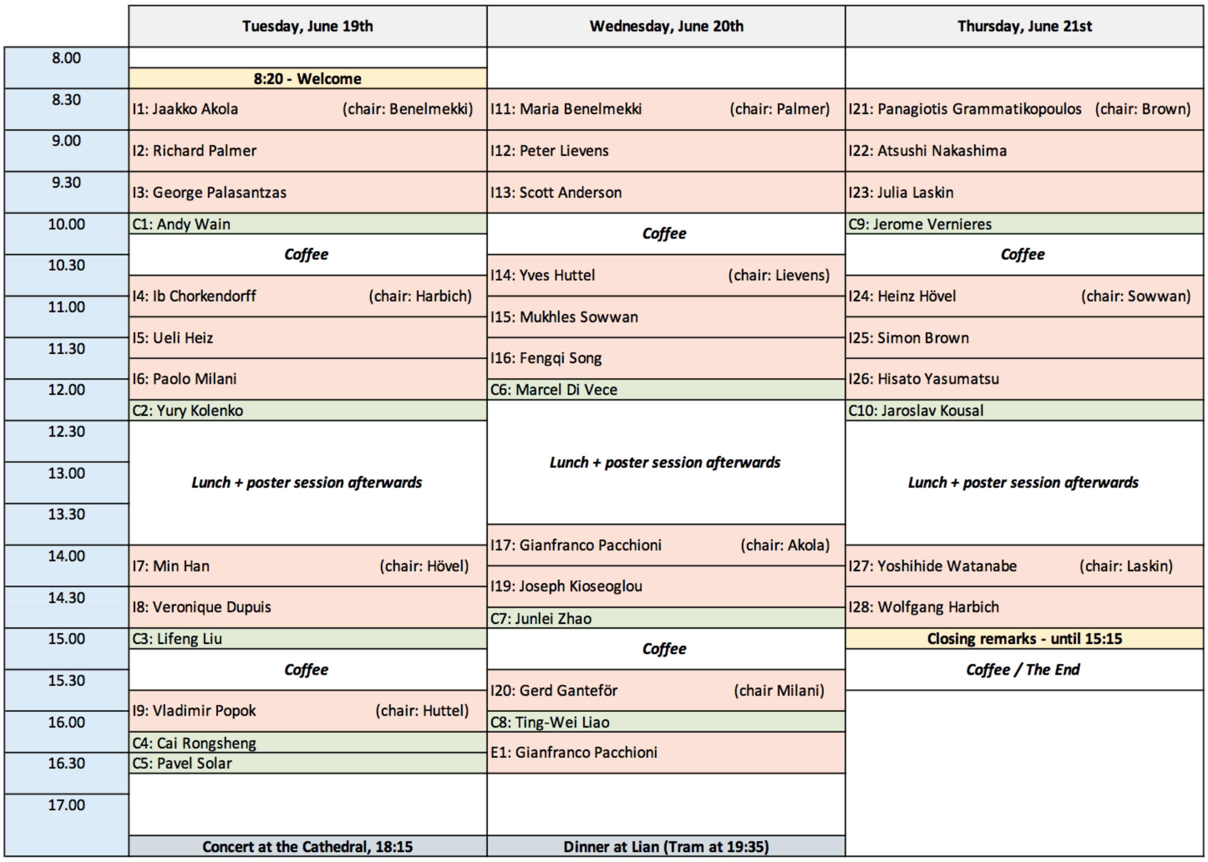
Book of Abstracts

Cluster-Surface Interactions Workshop, 18.-21.6.2018, Clarion hotel, Trondheim

Program overview:



	Tuesday, June 19th	Wednesday, June 20th	Thursday, June 21st
8.00	8:20 - Welcome		
8.30	I1: Jaakko Akola (chair: Benelmekki)	I11: Maria Benelmekki (chair: Palmer)	I21: Panagiotis Grammatikopoulos (chair: Brown)
9.00	I2: Richard Palmer	I12: Peter Lievens	I22: Atsushi Nakashima
9.30	I3: George Palasantzas	I13: Scott Anderson	I23: Julia Laskin
10.00	C1: Andy Wain *Coffee*	*Coffee*	C9: Jerome Vernieres *Coffee*
10.30	I4: Ib Chorkendorff (chair: Harbich)	I14: Yves Huttel (chair: Lievens)	I24: Heinz Hövel (chair: Sowwan)
11.00	I5: Ueli Heiz	I15: Mukhles Sowwan	I25: Simon Brown
11.30	I6: Paolo Milani	I16: Fengqi Song	I26: Hisato Yasumatsu
12.00	C2: Yury Kolenko	C6: Marcel Di Vece	C10: Jaroslav Kousal
12.30	*Lunch + poster session afterwards*	*Lunch + poster session afterwards*	*Lunch + poster session afterwards*
13.00			
13.30		I17: Gianfranco Pacchioni (chair: Akola)	
14.00	I7: Min Han (chair: Hövel)	I19: Joseph Kioseoglou	I27: Yoshihide Watanabe (chair: Laskin)
14.30	I8: Veronique Dupuis	C7: Junlei Zhao	I28: Wolfgang Harbich
15.00	C3: Lifeng Liu *Coffee*	*Coffee*	Closing remarks - until 15:15 *Coffee / The End*
15.30	I9: Vladimir Popok (chair: Huttel)	I20: Gerd Ganteför (chair Milani)	
16.00	C4: Cai Rongsheng	C8: Ting-Wei Liao E1: Gianfranco Pacchioni	
16.30	C5: Pavel Solar		
17.00			
	Concert at the Cathedral, 18:15	Dinner at Lian (Tram at 19:35)	

I = Invited talk

C = Contributed talk

P = Poster presentation

E = Extra talk

Posters (P1-P21) will be available for the whole workshop duration.

Invited Oral Presentations

I1: Rational Design of Transition Metal Nanocatalysts (H2020 – CritCat)

Jaakko Akola[1,2]

[1]Department of Physics, NTNU Trondheim, Norway
[2]Laboratory of Physics, Tampere University of Technology, Finland

jaakko.akola@ntnu.no

Abstract:

The H2020-project CritCat (www.critcat.eu) aims to provide solutions for the substitution of critical metals, especially rare platinum group metals (PGMs), used in heterogeneous and electrochemical catalysis. CritCat explores the properties of ultra-small transition metal (TM) nanoparticles to achieve optimal catalytic performance with earth-abundant materials. The emphasis is on industrially-relevant chemical reactions and emerging energy conversion technologies in which PGMs play an instrumental role, particularly in the context of hydrogen energy. The goal is to tailor optimal nanoparticle catalysts for selected (electro)chemical reactions.

The CritCat project includes all the aspects for rational catalyst design including novel catalyst synthesis, characterization, and performance testing together with large-scale computational simulations of the relevant catalysts, substrates and model reactions using the latest computational methods. The DFT data is collected in a descriptor database and used for materials screening at later stages. We have developed new machine learning algorithms for neural network (NN) force fields for generating catalyst structures, descriptor-based efficient hydrogen adsorption site scanning and prediction, and effective charge and energy level prediction based on xyz-files. The new tools pave way for much more efficient catalyst simulations with DFT accuracy.

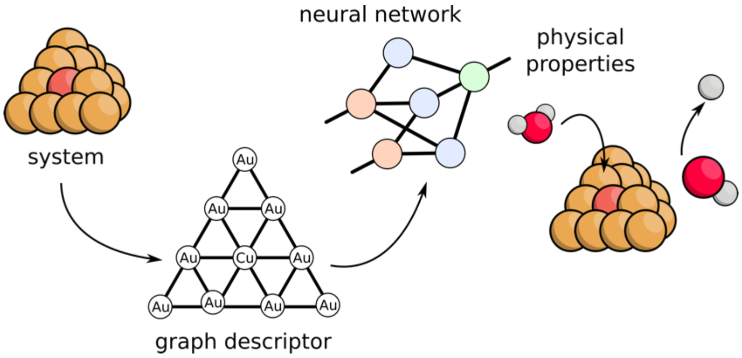


Figure 1: *Schematic presentation of the machine learning process starting from the system and its properties (descriptors), mapping to the neural network framework, and training to match the targeted physical properties.*

I2: The Route To Materials Manufacturing Incorporating Cluster Deposition

Richard E. Palmer

Nanomaterials Lab, College of Engineering, Swansea University,
Swansea SA1 8EN, UK

If we imagine a "factory of the future" in which cluster beam deposition (CBD) is integrated into the production of advanced materials or devices, then the control parameters of the advanced materials engineering process translate into a set of research challenges for the CBD science community. These include control of cluster composition, size, quantity (scale-up), atomic configuration on the support, response to the system environment, formulation engineering and performance validation. The prize is a set of applications ranging from theranostics and water treatment to catalysis and memristors. Compared with colloidal synthesis of nanoparticles, the cluster beam approach is green: it involves no solvents and no effluents; particles can be size-selected; and challenging combinations of metals (nanoalloys) can readily be produced. Here I will discuss 4 of these research challenges: environment (temperature), scale-up, formulation engineering and performance.

1) Environment - aberration-corrected Scanning Transmission Electron Microscopy (STEM) is used to investigate the behaviour of deposited clusters at elevated temperatures, including structural transformations and (core and surface) melting.
2) Industrial catalysis R&D typically requires a gram of catalyst, or 10 mg of clusters at 1% loading on a suitable catalyst support. The "Matrix Assembly Cluster Source" (MACS) is based on ion beam sputtering of a rare gas matrix into which metal atoms are pre-loaded. A scale-up of 5 orders of magnitude in cluster intensity has been achieved. I will also address the mechanism of cluster formation in the matrix.
3) I will discuss several means by which size-controlled clusters may be presented in a form matching the desired functional application, e.g., catalysis and theranostics. These examples of "formulation engineering on the nanoscale" include direct deposition of metal cluster beams onto micron-scale oxide powder support particles; bottom-up synthesis of novel cluster-decorated carbon powders; and functionalisation of deposited clusters to achieve biological compatibility.
4) Finally I will illustrate the validation challenge that we need to meet if we want to show that cluster-based functional materials are superior to advanced materials created by more traditional routes. I will focus on the hydrogenation (in both gas and liquid phases) of organic molecules over cluster catalysts as a basis for applications in the fine chemicals and pharmaceuticals sectors.

For refs see: https://scholar.google.co.uk/citations?hl=en&user=2pnEX-YAAAAJ&view_op=list_works

I3: Gas phase nanoparticles to control wetting, energy storage, and nanomagnetism

George Palasantzas

Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG
Groningen, the Netherlands

Abstract:

Nowadays monometallic and bimetallic nanoparticles (NPs) have emerged as key materials for important modern applications for example in energy storage, surface wetting, nanomagnetics, biodiagnostics, plasmonics, and catalysis. Consequently the control of NP structural motifs with specific shapes can provide increasing functionality and selectivity for related applications. However, producing bimetallic NPs with well controlled structural motifs still remains a formidable challenge. In my talk I will address the issues of a methodology for gas phase synthesis of Mg-Ti bimetallic NPs with distinctively different structural motifs, where emphasis will be given to Hydrogen storage systems involving Mg-Ti [1, 2]. Furthermore, I will discuss issues related to roughness controlled superhydrophobicity on single nanometer length scale with metal/non-metal (Cu, C, GST) nanoparticles. Indeed, independent of the exact details, our approach to alter the wetting state and induce droplet trapping is straightforward without involving special micro/nano (hierarchical) structuring facilities but instead using direct nanoparticle deposition onto any type of surfaces (hydrophilic and/or hydrophobic) [3, 4]. Finally, magnetic Force Microscopy (MFM) has been used to probe the magnetic properties of individual Fe-oxide/Fe core shell nanoparticles (NPs), and provide precise and localized information of their magnetic structure and magnetization orientation [5].

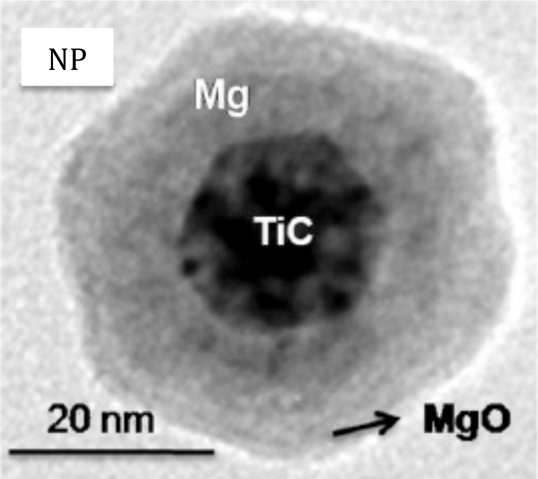


Figure 1: *Mg-Ti core/shell nanoparticle [1].*

References:

[1] Gopi Krishnan, Sytze de Graaf, Gert H. ten Brink, Marcel A. Verheijen Bart J. Kooi and George Palasantzas, Nanoscale 10, 1297 (2018)

[2] Gopi Krishnan, Sytze de Graaf, Gert H. ten Brink, Per O.A. Persson, Bart J. Kooi and George Palasantzas, Nanoscale 9, 24, 8149 (2017)

[3] G. H. ten Brink, N. Foley, D. Zwaan, B. J. Kooi and G. Palasantzas, RSC Adv., 5, 28696 (2015)

[4] G. H. ten Brink, P. J. van het Hof, B. Chen, M. Sedighi, B. J. Kooi, G. Palasantzas, Appl. Phys. Lett. 109, 234102 (2016)

[5] Lijuan Xing, Gert H ten Brink, Bin Chen, Franz P Schmidt, Georg Haberfehlner, Ferdinand Hofer, Bart J Kooi and George Palasantzas, Nanotechnology 27, 215703 (2016); L. Xing, Submitted.

I4: Mass-selected Nanoparticles for Conversion of Sustainable Energy

Ib Chorkendorff

SurfCat, Department of Physics, Technical University of Denmark (DTU),
Fysikvej, Building 312, DK-2800 Kongens Lyngby, Denmark.

ibchork@fysik.dtu.dk

Abstract:

In this presentation, I will give an overview of some our recent progress in making nanoparticles alloys and intermetallic compounds for catalysis, particularly in relation to conversion of sustainable energy [1]. We shall demonstrate how mass-selected nanoparticles synthesized can be used to elucidate the activity for processes related to electrolysis and the reversible process in fuel cells. The electrochemical Oxygen Reduction Reaction, is the limiting reaction in Proton Exchange Membrane Fuel Cells. Here we have found entirely new classes of electro-catalysts by alloying Pt with early transition metals [2] or the lanthanides [3]. We have shown that it is possible to make mass-selected nanoparticles of these alloys with very good activities [4] and PtGd alloys [5] although direct translation of such results to fuel cells is difficult [6]. We shall demonstrate that as similar approach can be used for studying size dependence and efficiency for catalysts related to water splitting [7, 8] and evaluate the scalability of scarce and expensive elements like Platinum and Ruthenium. Size dependence and isotope labelled experiments will be presented for NiFe nanoparticles for oxygen evolution under alkaline conditions [9]. Here we shall demonstrate a new principle for dynamic detection of gas evolution [10]. This has also been used to investigate electrochemical CO hydrogenation on mass-selected Copper nanoparticles to study the dynamical influence of surface oxygen on the selectivity for electrochemical methane/ethene production [11].

References:

[1] Z. W Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov, T. F. Jaramillo, Science (2017) 355
[2] J. Greeley,. I. Chorkendorff, J. K. Nørskov, Nature Chemistry. 1 (2009) 522
[3] M. Escudero-Escribano, … I. E.L. Stephens, I. Chorkendorff, Science 352 (2016) 73.
[4] P. Hernandez-Fernandez, , …, I. Chorkendorff, Nature Chemistry 6 (2014) 732.
[5] A. Velázquez-Palenzuela…. I. Chorkendorff, J. Catal. 328 (2015) 297.
[6] I. F. L. Stephens, J. Rossmeisl, I. Chorkendorff, Science 354 (2016) 1378
[7] E. Kemppainen, .. I. Chorkendorff, Energy & Environmental Science, 8 (2015) 2991.
[8] E. A. Paoli, F. … I. E.L Stephens, I. Chorkendorff, Chemical Science, 6 (2015) 190.
[9] C. Roy, …J. Kibsgaard, I. E. L. Stephens, and I. Chorkendorff; Submitted (2018).
[10] D. T. Bøndergaard, .. I Chorkendorff and P. C. K. Vesborg, Electrochem. Acta (2018) doi.org/10.1016/j.electacta.2018.02.060
[11] S. B. Scott, …. P. C. K. Vesborg, Jan Rossmeisl, and I. Chorkendorff, submitted (2018).

I5: Tuning cluster properties through modification of cluster-surface interactions

Friedrich Esch, Martin Tschurl, Ueli Heiz

Technische Universität München, Catalysis Research Center, Lehrstuhl für Physikalische Chemie, Lichtenbergstr. 4, 85748 Garching, Germany

ulrich.heiz@mytum.de

Abstract:

In this presentation, we highlight two examples of how to tune cluster properties through modification of the cluster-surface interaction. In a first study, we present strategies for optimizing cluster stability through structuring the cluster support materials. We show that for reducing Ostwald ripening, both, the binding of the clusters to the surface and that of the individual atoms must be controlled. Such tuning of the interactions is achieved through the judicious selection of surfaces with laterally modulated wettability. Furthermore, we observed that the broadening of cluster size distribution induced by Ostwald ripening is efficiently suppressed even under reaction conditions when using size-selected cluster samples. In a second study, we present results on the hydrogenation of ethylene on Pt_n clusters, where we observed an onset of reactivity when going from Pt_9 to Pt_{10}. Pt_{13} or Pt_{14} are the most active cluster sizes when interacting with MgO or amorphous SiO_2, respectively. The origin of the size dependent reactivity is the local charging of the reactive atoms in the cluster [1], which can be modulated by changing support acidity, support stoichiometry and support doping. [2,3]

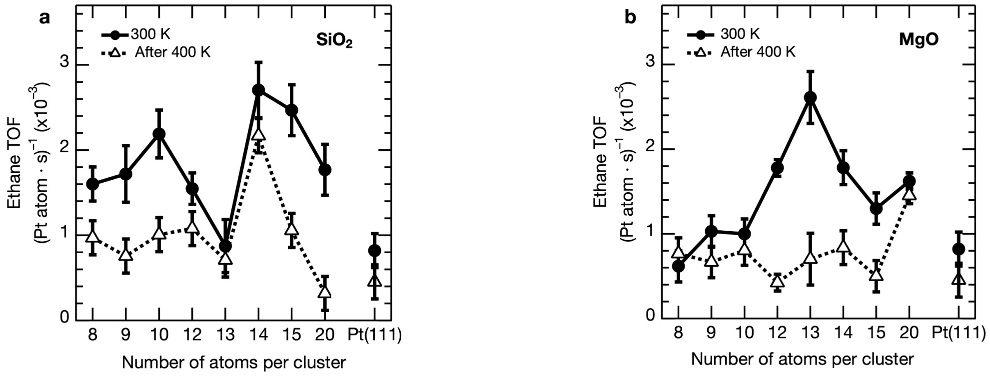


Figure 1: *Ethane formation on size-selected Pt clusters supported on SiO_2 (a) and MgO (b) measured at two different temperatures.*

References:

[1] Crampton, A., et. al.; Nature Communications, 2016, 10389
[2] Crampton, A. et. al., ACS Catalysis, 2017, 6738-6744
[3] Crampton, A., et.al. Angewandte Chemie Int. Ed. 55 (31), 2016, 8953-8957

I6: Resistive Switching in Cluster-assembled Nanogranular Devices

Chloé Minnai[1], Matteo Mirigliano[1], Simon A. Brown[2], Paolo Milani[1]

1CIMAINA and Dipartimento di Fisica,
Università degli Studi di Milano, via Celoria 16, 20133 Milano, Italy
2The MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Physics and Astronomy, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand.

paolo.milani@mi.infn.it

Abstract:

We report the realization of a resettable resistive switching device based on a nanostructured film fabricated by supersonic cluster beam deposition of gold clusters on plain paper substrates [1]. Through the application of suitable voltage ramps, we obtain, in the same device, either a complex pattern of resistive switchings, or reproducible and stable switchings between low resistance and high resistance states, with amplitude up to five orders of magnitude. Our device retains a state of internal resistance following the history of the applied voltage similarly to that reported for memristors. The two different switching regimes in the same device are both stable, the transition between them is reversible, and it can be controlled by applying voltage ramps or by mechanical deformation of the substrate. The device behavior can be related to the formation, growth and breaking of junctions between the loosely aggregated gold clusters forming the nanostructured films [2]. The fact that our cluster-assembled device is mechanically resettable suggests that it can be considered as the analogue of the coherer: a switching device based on metallic powders used for the first radio communication system.

References:

[1] C. Minnai, M. Mirigliano, S.A. Brown, P. Milani, Nano Futures 2, 01102 (2018)
[2] C. Minnai, A. Bellacicca, S.A. Brown, P. Milani, Sci. Rep. 7, 7955 (2017)

I7: Manipulating the localized surface plasmons in closely spaced metal nanocluster arrays

Min Han[1], Peng Mao[1], Yanyue Ding[1], Jian Chen[1]

[1] National Laboratory of Solid State Microstructures, College of Engineering and Applied Sciences, Nanjing University, Nanjing 210093, China

sjhanmin@nju.edu.cn

Abstract:

There has been considerable interest recently in metal nanoparticle based surface plasmon resonant (SPR) structures, for their fascinating optical properties, and potential applications. The SPR depends strongly on the nanoparticle composition, size, shape and the medium or environment, which allow tunability of both the plasmon resonance frequency as well as the strength of the plasmonic enhancement. The ability of fine-tune the SPR properties has been a key factor in advancing and optimizing these applications. In this contribution, we will report on some functional plasmonic nanostructures based on dense nanocluster assemblies. We demonstrate that gas phase cluster beam deposition provides a facile way for controllable fabrication of high density metal nanocluster arrays with a widely adjustable SPR frequency. We show that the plasmonic properties of the closely spaced nanocluster assembles can be seriously tuned by a precise control on the nanocluster-nanocluster spacing as well as nanocluster-surface spacing, which determines the strength of the near field-coupling. Some examples of application of such structures will also be shown.

References:

[1] L. B, He, X. Chen, Y. W. Mu, F. Q. Song and M. Han, Nanotechnology 21, 495601(2010)

[2] L. B. He, Y. L. Wang, X. Xie, M. Han, F. Q. Song, B. J. Wang, W. L. Chen, H. X. Xud and L. T. Sun, Phys. Chem. Chem. Phys. 19, 5091(2017)

I8: Size and Interface Effects on Magnetism of Chemically Ordered FePt and FeRh Clusters Prepared by MS-LECBD

P. Capiod, F. Tournus, L. Bardotti, D. Le Roy, A. Tamion, C. Albin,
O. Boisron and V. Dupuis
ILM, UMR 5306 CNRS & Université Lyon 1, 69622 Villeurbanne cedex

veronique.dupuis@univ-lyon1.fr

Abstract:

The major importance of surface atoms in small nanoparticles (NPs) offers the opportunity to tailor their magnetic properties by playing with the interface between nanomagnet and its surrounding. The systems FePt and FeRh has attracted a lot of attention because, when they are chemically ordered (resp. in $L1_0$ and B2 phase), they respectively present an huge magnetic anisotropy and an antiferromagnetic to ferromagnetic order (AFM-FM) transition close to room temperature in bulk phases. This paper deal with structural and intrinsic magnetic properties of such nanomagnets, prepared using Mass-Selected Low Energy Cluster Beam Deposition (MS-LECBD) embedded in carbon matrix, at the PLYRA platform of Institut Lumière Matière at Lyon. Recently $L1_0$ FePt clusters have been organized on epitaxially grown graphene on Ir(111), while B2 FeRh clusters have been deposited on a crystalline BaTiO3 layer epitaxially grown on a Nb-doped SrTiO3 layer. In this paper, their morphologies and physical properties are compared to their intrinsic ones[1-3] taken into account both size and interface effects.

References:

[1] F. Tournus et al. "Multi-$L1_0$ domain CoPt and FePt nanoparticles revealed by electron microscopy" Phys. Rev. Letters 110 (2013) 055501

[2] V. Dupuis et al., "Magnetic moments in chemically ordered mass-selected CoPt and FePt clusters", Journal of Magnetism and Magnetic Materials 383 (2015) 73

[3] A. Hillion et al., "Low Temperature Ferromagnetism in Chemically Ordered B2 FeRh Nanocrystals" Phys. Rev. Letters 110 (2013) 087207

I9: Metal cluster deposition on polymers and formation of nanoscale patterns

Florian Ceynowa[1,2], Manohar Chirumamilla[1,3], Vladimir Zenin[4], and Vladimir Popok[1]

[1]Aalborg University, 9220 Aalborg, Denmark
[2]Kiel University, 24098 Kiel, Germany
[3]Hamburg University of Technology, 21073 Hamburg, Germany
[4]University of Southern Denmark, 5230 Odense, Denmark

vp@mp.aau.dk

Abstract:

Metal nanoparticles (NPs) are widely used in research and industry for a variety of applications. New functionalities can be obtained if NPs are deposited on or embedded in a matrix. Polymers, as low-cost, flexible and easily processed materials, are very attractive hosting media for NPs. One of the areas of practical interest is related to plasmonic properties of coinage metal NPs giving raise to characteristic extinction and strong local electric fields which can be used for optical sensing and surface enhanced Raman scattering (SERS) applications. It has recently been shown that forming specific spatial architectures of NPs can tremendously enhance sensing capabilities [1].

In this work, main approaches for cluster deposition or embedding on/in polymers using cluster beam technique will be briefly overviewed. The physical mechanisms of cluster immersion into soft matrices will be analysed and the dynamics of NP embedding will be discussed using the examples of thermal annealing of size-selected copper and silver clusters soft-landed on thin polymer films. This approach opens great capabilities for the formation of polymers with controlled both surface coverage of NPs and ratio of embedment as well as production of thin composite layers with tunable filling factor of NPs. Plasmonic properties of copper and silver NPs pinned or embedded to/into polymers and issues of stability will be discussed.

Second part of the work addresses the formation of NP arrays by combining electron beam lithography, cluster deposition and thermal annealing. Several examples on use of Cu and Ag clusters for the production of stripes with variable width and periods will be presented and properties of these patterned structures will be discussed. The suggested approach is considered to be a promising way for formation of plasmonic architectures for nanoscale optics, sensing and SERS.

References:

[1] N.A. Brazhe, A.B. Evlyukhin, E.A. Goodilin et al., Sci. Rep. 5, 13793 (2015).

I10: Simplifying the Creation of Pd@Pt core-shell nanoclusters with well controlled shell-layer thickness for electrochemical oxygen reduction

Yafeng Zhang[1], Qianru Liu[1], Deying Leng[1], Juan Qin[1], FengQi Song[2], Feng Yin[1]*
[1]Laboratory of Low Dimensional Condensed Matter Physias, Shaanxi Normal University, Xi'an 710119, China
[2]National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China
E-mail: fengyin@snnu.edu.cn

Pd@Pt core-shell clusters has been achieved great attention due to the high activity and stability toward the oxygen reduction reaction (ORR), which is primarily ascribed to high dispersion and the strain effect from between two metals [1]. In this paper, we synthesized successfully Pd@Pt core-shell clusters with one-pot solvothermal method. The shell thickness could be well controlled by simply controlling the reaction temperature. The TEM and EDS results shows that the thickness of the Pt shell increased from ~3 layers to 12 layers when the temperature increase from 140ºC to 180ºC (3 layers/ ~10 degrees), Fig. 1. The mass activity of outermost layer Pt shell increases with increase of thickness shell and the get the maximum value when the thickness Pt shell is ~11 layers.

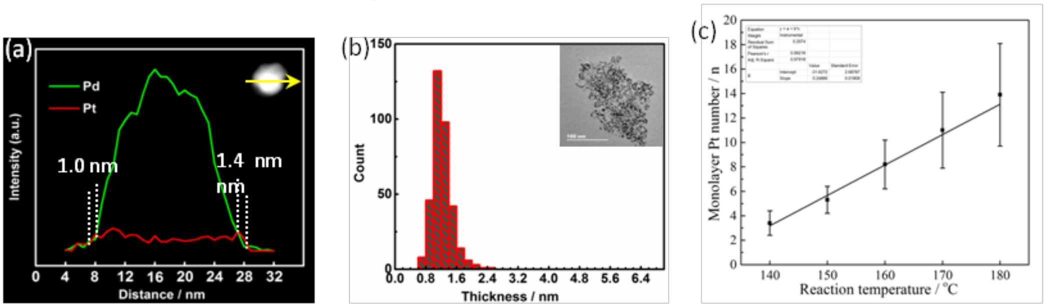


Fig. 1 (a) EDS line profiles and (b) The thickness distribution of Pd@Pt core-shell clusters prepared at 150ºC; (c) Relationship between reaction temperature and thickness of Pt shell.

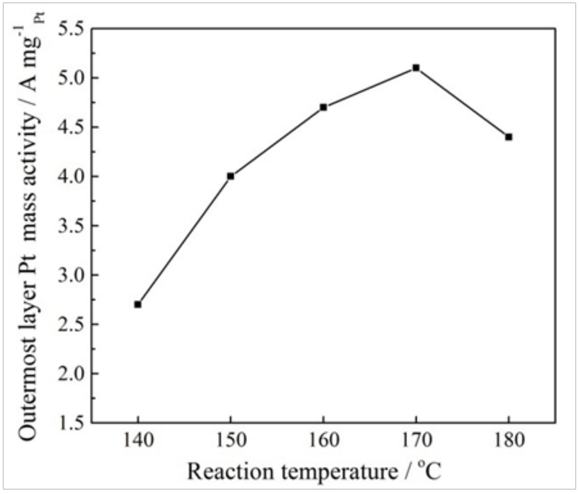


Fig. 2 Correlation curve between outermost layer Pt mass activity and thickness of Pt shell.

Reference:

[1] Shao, M., et al. Chemical Reviews, 2016. 116: p.3594-3657.

Acknowledgement:

This work was supported by Supported by the Fundamental Research Funds for theCentral Universities(Grant nos. GK201501004) and National Laboratory of Solid State Microstructures, Nanjing University, China (M28029).

I11: Bottom-up synthesis of multifunctional carbon nanoscrolls

Maria Benelmekki
Department of materials science and engineering
Norwegian University of Science and Technology, NTNU
Trondheim, Norway

maria.benelmekki@ntnu.no

Abstract:

Hybrid inorganic nanomaterials that combine two or more component into one nanostructure have experienced a substantial progress in terms of the design and synthesis processes. Such complex structures have the potential to combine magnetic, plasmonic, semiconducting and other physical or chemical properties into a single object, allowing enhanced and often new functionalities. In particular, carbon nanomaterials, such as graphene, graphite nanosheets, and nanoscrolls have been attracting considerable interest due to their high surface area, light weight, superior electronic function, thermal conductivity, and robust physical stability. Distinct from carbon nanotubes (CNTs), carbon nanoscrolls (CNS) are open tubular carbon structures with tuneable interlayer gaps between thin films and their radius, endowing higher molecular accessible surface areas than nanosheets and nanotubes, and thus making them robust in harsh environments, such as heat, humidity, and aggregation. Because CNS architectures comprise interlayer corridors, which are created by wrapping a C-nanofilm into a helical structure, the scroll topology allows their properties to significantly discriminate from those of either single or multi-walled CNTs.

Herein, we present a novel method for generating magneto-plasmonic carbon-nanofilms and nanoscrolls using a combination of two gas-phase synthetic techniques. Ternary Fe@Ag@Si nanoparticles (NPs) are produced by a magnetron-sputtering-inert-gas-condensation source and are *in-situ* landed onto the surface of carbon-nanofilms, which were previously deposited by a DC-arc-discharge technique. Subsequently, a polyethyleneimine-mediated chemical exfoliation process is performed to obtain carbon-nanoscrolls (CNS) with embedded NPs. The carbon nanofilms undergo an interfacial transition upon deposition of NPs and become rich in the sp^2 phase. This transformation endows and enhances multiple functions, such as thermal conductivity and the plasmonic properties of the nanocomposites. The obtained nanocomposites were evaluated as a Surface-Enhanced-Raman-Scattering (SERS) agents for ATP biomolecules, and showed a high Enhanced Factors (EF) allowing the detection of ATP molecules at concentrations of 10^{-10} M. In addition, CNSs-NPs showed an enhanced single- and two-photon fluorescence, in comparison with pristine CNSs and NPs.

References:

[1] M. Benelmekki et al. Nanoscale (2014), 6 (7), 3532 – 3535
[2] M. Benelmekki et al. Mater. Chem. Phys. 151 (2015) 275-281
[3] J.H. Kim and M. Benelmekki ACS Appl. Mater. Interfaces 2016, 8, 33121-30

I12: Scanning tunnelling microscopy imaging of gold and cobalt clusters on NaCl/Au(111) surfaces

Peter Lievens

Department of Physics and Astronomy, Faculty of Science, KU Leuven, Belgium

peter.lievens@kuleuven.be

Abstract:

Probing structure and properties of very small clusters on surfaces with subatomic precision is a long standing challenge that currently is within reach using state-of-the art scanning probe microscopy. Here, recent progress will be discussed using high resolution scanning tunneling microscopy (STM) at liquid helium temperature of clusters deposited on few-layers NaCl on Au(111).

In order to create nanostructures of atomic vacancies across atomic lattices we have used STM to create individual Cl vacancies and subsequently to laterally manipulate them across the surface of ultrathin NaCl films [1]. This allows monitoring the interactions between two neighboring vacancies with different separations. The lateral manipulation of atomic vacancies opens up a new playground for the investigation of fundamental physical properties of vacancy nanostructures of any size and shape, and their coupling with the supporting substrate.

Preformed Co clusters were produced in the gas phase and deposited under controlled ultra-high vacuum conditions. The three-dimensional atomic structure of the Co clusters is visualized by high-resolution STM using a functionalized tip that can be obtained on the NaCl surface [2,3].

Au clusters in a size range from a few up to several hundreds of clusters were deposited on thin layers of NaCl on Au(111) both without size selection and after size selection with atomic precision. The morphology of the observed species – on top of the surface, partially penetrating the NaCl layer, and below the NaCl – demonstrates a size dependent sieving behavior for metal clusters. This sieving behavior shows dependence on the film thickness and demonstrates that defect-free NaCl films on a Au(111) support act as size-dependent membranes for deposited Au nanoclusters [4].

References:

[1] Z. Li et al., Lateral manipulation of atomic vacancies in ultrathin insulating films, *ACS Nano* **9**, 5318 (2015)

[2] K. Schouteden et al., Probing the atomic structure of metallic nanoclusters with the tip of a scanning tunneling microscope, *Nanoscale* **6**, 2170 (2014)

[3] Z. Li et al., Size-dependent dissociation of small cobalt clusters on ultrathin NaCl films, *Nano Res.* **10**, 1832 (2017)

[4] Z. Li et al., Size-dependent penetration of gold nanoclusters through a defect-free, nonporous NaCl membrane, *Nano Letters* **16**, 3063 (2016)

I13: Improving the chemical and sinter stability of supported cluster catalysts

Timothy Gorey,[1] Eric Baxter,[1] Ashley Cass,[1] Guangjing Li,[1] Mai-Anh Ha,[2]
Huanchen Zhai,[2] Anastassia Alexandrova,[2] and Scott Anderson[1]

[1]Department of Chemistry
University of Utah
315 S. 1400 E.
Salt Lake City, UT 84112
[2]Department of Chemistry and Biochemistry
University of California, Los Angeles
607 Charles E. Young Drive East, Box 951569
Los Angeles, CA 90025-1569
anderson@chem.utah.edu

Abstract:

Materials containing supported size-selected clusters are interesting systems for exploring factors that affect the chemical and physical/thermal stability of catalysts. We have been exploring the effects on catalyst activity, selectivity, and stability, of doping Pt clusters with boron and tin atoms, and also of modifying/doping the oxide support with heteroatoms. A combination of detailed experiments and electronic structure and molecular dynamics calculations are used to probe these issues. The effects will be illustrated using the competition between desorption and dehydrogenation for ethylene.

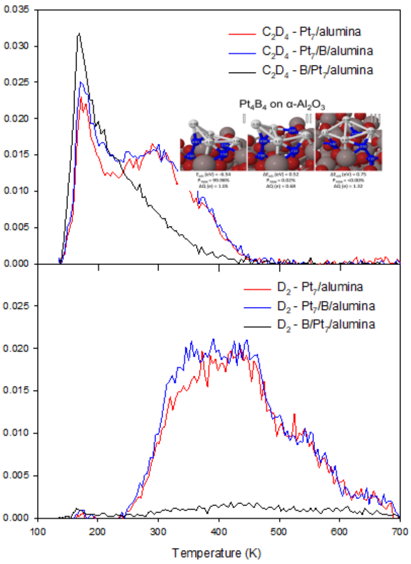


Figure 1: *Effect of borating Pt clusters, vs. borating the alumina support*

References:

[1] Ethylene Dehydrogenation on $Pt_{4,7,8}$ Clusters on Al_2O_3: Strong Cluster-Size Dependence Linked to Preferred Catalyst Morphologies, Eric T. Baxter, Mai-Anh Ha; Anastassia Alexandrova, and Scott L. Anderson, ACS Catalsis 7 (2017), 7, 3322–3335, DOI: 10.1021/acscatal.7b00409

[2] Boron Switch for Selectivity of Catalytic Dehydrogenation on Size-Selected Pt clusters on Al_2O_3, Mai-Anh Ha, Eric T. Baxter, Ashley Cass, Scott L. Anderson,* and Anastassia N. Alexandrova*, J. Am. Chem. Soc., 139 (2017) 11568-11575, DOI: 10.1021/jacs.7b05894

[3] Diborane Interactions with Pt_7/alumina: Preparation of Size-Controlled Borated Pt Model Catalysts with Improved Coking Resistance, Eric T. Baxter, Mai-Anh Ha, Ashley C. Cass, Huanchen Zhai, Anastassia N. Alexandrova,* and Scott L. Anderson*, J. Phys. Chem. C, 122 (2018), 1631–1644, DOI: 10.1021/acs.jpcc.7b10423

I14: Gas-Phase Synthesis of complex Nanoparticles and their interaction with surfaces

Y. Huttel[1], A. Mayoral[2,3], L. Martínez[1], J. M. García-Martín[4], I. Fernández-Martínez[5], M. García-Hernández[1]

[1] Instituto de Ciencia de Materiales (ICMM-CSIC), Cantoblanco, Madrid, Spain.
[2] Instituto de Nanociencia de Aragon (INA), Universidad de Zaragoza, Spain.
[3] School of Physical Science and Technology ShanghaiTech University 100 Haike Road, Pudong, Shanghai, 201210, China.
[4] IMN-Instituto de Micro y Nanotecnología (CNM-CSIC), Tres Cantos, Spain.
[5] Nano4Energy SLNE, Madrid, Spain.

Abstract

Since the seminal work of Haberland's group [1], magnetron based gas aggregation sources (GAS) have been used in an increasing number of nanoparticles studies. As compared to other GAS, the magnetron based GAS have gained popularity probably thanks to their relative ease to use, and to the fact that the majority of the generated nanoparticles are charged which allows their manipulation (filtering and deflection) [2].

In most experiments and experimental set-ups, the nanoparticles or clusters are deposited on substrates for their further use or study. Hence the interaction between nanoparticle/cluster and the surface of the substrate can play a role in the final properties of the system Nanoparticle/Surface. In this talk, through several examples, we will address such effects that arise from the interaction between the deposited nanoparticles and the substrates. In particular we will show that the charge of the nanoparticles (most of the nanoparticles generated by GAS are negatively charged) has a strong effect on the landing behavior of the nanoparticles and that the sticking coefficient of the nanoparticles is highly dependent on the chemical nature of the surface.

References

[1] H. Haberland, M. Karrais, M. Mall, Zeitschrift für Physik D Atoms, Molecules and Clusters 1991, 413-415; H. Haberland, M. Karrais, M. Mall, Y. Thurner, Journal of Vacuum Science and Technology A: Vacuum, Surfaces, and Films 1992, 10, 3266-3271.
[2] *Gas-Phase Synthesis of Nanoparticles*, Wiley, 2017, Ed. Y. Huttel.

I15: Nanoparticles by Design for Nanotechnology and Biomedical Applications

Mukhles Sowwan

Nanoparticles By Design Unit, Okinawa Institute of Science and Technology (OIST)
1919-1 Tancha, Onna Son,Okinawa 904-0495, Japan

Abstract:

One of the issues that has hindered the applications of nanotechnology has been the inability to develop nanoparticles with prescribed characteristics and with sufficient uniformity to be utilized with optimal success. These nanoparticles can exhibit unique structural, magnetic or catalytic properties.

In this talk I will address the synthesis and growth of mon-, bi- and multi-metallic nanoparticles using magnetron sputtering inert-gas condensation, and the direct integration of these nanoparticles into functional materials and devices.

References:

[1] Shaping the Future. https://www.oist.jp/news-center/news/2017/3/14/shaping-future.
[2] New ‘Ukidama’ Nanoparticle Structure Revealed. https://www.oist.jp/news-center/news/2016/6/10/new-ukidama-nanoparticle-structure-revealed.
[3] Nanoparticles by Design Unit. https://www.oist.jp/news-center/videos/nanoparticles-design-unit-introduction-video.

I16: Coherent transport of Dirac electrons decorated by metallic clusters

Shuai Zhang, Yuyuan Qin, Lu Cao, Guorui Hu and Fengqi Song

Second address National Laboratory of Solid State Microstructures, Collaborative Innovation
Center of Advanced Microstructures, and Department of Physics, Nanjing University,
Nanjing, 210093, P. R. China
songfengqi@nju.edu.cn

Abstract:

The Dirac electronic systems, such as graphene and topological insulators, are quickly rising recently due to possible application in low-dissipation electronics. A critical feature is their totally open structures, on which the external deposition might make full control of the electrical transport. Atomic clusters, with controlled sizes and species, are ideal candidates for these deposition control.

Here we report our experiments on the graphene and topological insulator nanodevices, on which the Pd, Co, Ir nanoclusters are deposited. We find, 1) Pd clusters may improve the coherent time of graphene while suppressing its electrical mobility. This is attributed to a saturation limit of the coherent time dependent on the carrier density. 2) Ir clusters may induce Kane-Mele desired spin orbit interaction in graphene, as demonstrated by the Elliot-Yafet spin relaxation and suppressed weak localization. 3) Co clusters may delay the Landau quantization of the topological electrons by broadening the Landau levels and inducing a Zeeman gap. This is demonstrated by the renormalized group theory analysis.

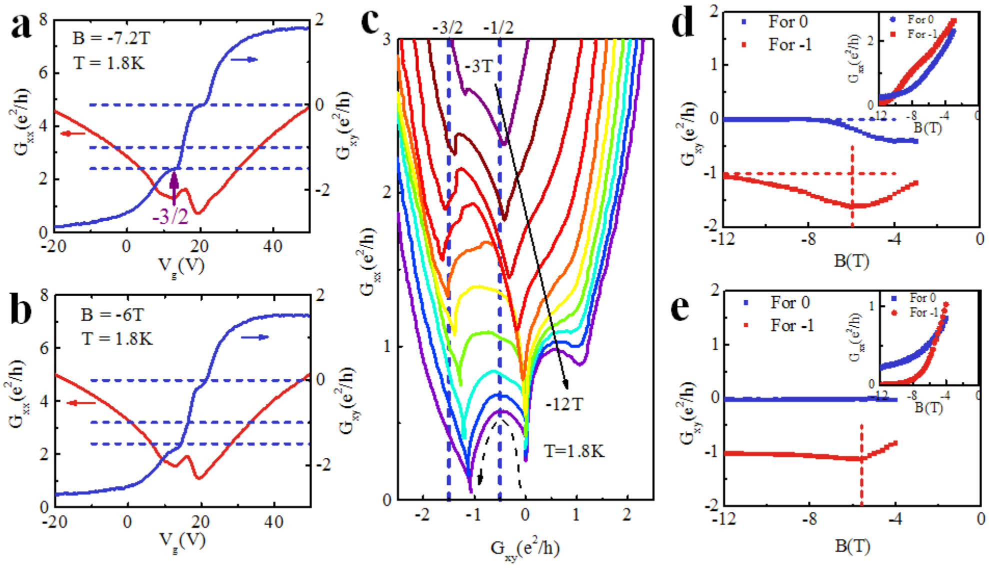


Figure 1. Renormalization group flow diagram analysis with the result of quantization trajectory of a single Dirac channel.

References:

[1] Shuai Zhang, et al Nature Communications 8, 977 (2017).
[2] Yuyuan Qin et al Applied Physics Letters, 106(2), 023108 (2015).
[3] Yuyuan Qin et al Applied Physics Letters, 108(20), 203106 (2016).

I17: Direct versus Inverse Catalysis: Role of Metal-Oxide Interface

Gianfranco Pacchioni

Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca,
via R. Cozzi, 55 - I-20125 Milano, Italy
E-mail: gianfranco.pacchioni@unimib.it

Abstract:

Nanoparticles deposited on an oxide support, or nanostructured oxides grown on a metal surface may result in new efficient catalysts, either direct (metals on oxides) or inverse (oxides on metals). We will show that nanostructured oxides in the form of ultra-thin films deposited on a metal may result in completely different properties of supported metal clusters. Here we will discuss the case of ZnO graphitic-like bilayers supported on Cu, Ag, and Au metals and of gold clusters adsorption [1,2]. We will show the occurrence of a spontaneous charge transfer that results in specific shapes of the supported clusters. We will also discuss the important role of the metal/oxide interface, referring to the nature of classical direct catalysts. In particular, we will show the high reactivity of the oxygen atoms at the boundary region between an Au nanoparticle and the oxide surface in CO oxidation [3-5]. TiO_2 and ZrO_2 supports will be considered to provide compelling evidence that the reaction occurs at specific sites of the Au/oxide interface and that even a non-reducible oxide such as ZrO_2 can become reducible when interfaced with gold.

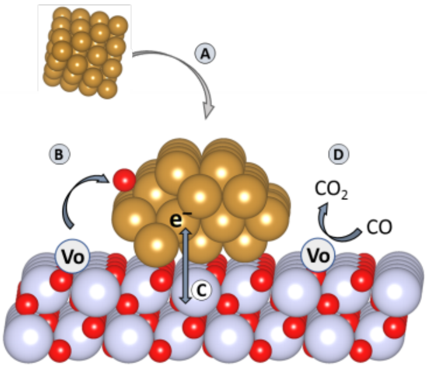


Figure 1: *Role of gold nanoparticles of oxide surface reactivity*

References:

[1] S. Tosoni, C. Li, P. Schlexer, G. Pacchioni, "CO adsorption on graphite-like ZnO bilayers supported on Cu(111), Ag(111) and Au(111) surfaces", ***J. of Physical Chemistry C***, 121, 27453 (2017).
[2] H. Thang, S. Tosoni, G. Pacchioni, "Evidence of charge transfer to atomic and molecular adsorbates on graphitic-like ZnO/X(111) (X = Cu, Ag, Au) ultrathin films", ***ACS Catalysis***,submitted.
[3] A. Ruiz Puigdollers, P. Schlexer, S. Tosoni, G. Pacchioni, "Increasing oxide reducibility: the role of metal/oxide interfaces in the formation of oxygen vacancies", ***ACS Catalysis***, 7, 6493 (2017).
[4] A. Ruiz-Puigdollers, G. Pacchioni, "CO oxidation on Au nanoparticles supported on ZrO_2: role of metal/oxide interface and oxide reducibility", ***ChemCatChem***, 9, 1119 (2017).
[5] P. Schlexer, D. Widmann, J. Behm, G. Pacchioni "CO oxidation on a Au/TiO_2 nano-particle catalyst via the Au-assisted Mars-van-Krevelen mechanism", ***ACS Catalysis***, submitted.

I18: Equilibrium and Metastable Structures in Metal Nanoparticles

Riccardo Ferrando

Chemistry and Industrial Chemistry Department, University of Genoa, Italy

ferrando@fisica.unige.it

Abstract: Clusters and nanoparticles are very often experimentally produced in metastable structures. Disentangling equilibrium and non-equilibrium effects may however be difficult, so that computer simulations can be of great help in understanding this issue. Here we consider a series of gas-phase and surface-supported systems, first searching for their lowest-energy structures [1-3], and then comparing these structures with those obtained by the evolution from metastable configurations. The systems studied here comprise pure Au clusters (in gas phase), and AgNi, AuCu, and AuCo nanoalloys (in gas phase and supported on MgO(100)).

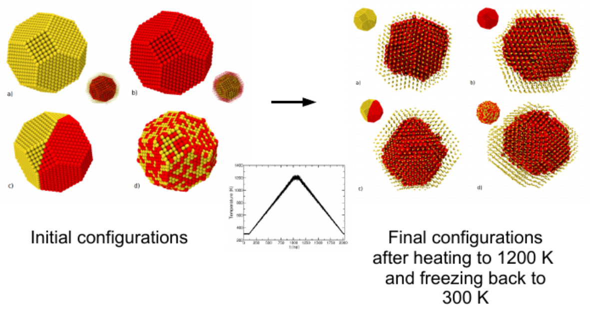


Figure 1: Molecular-dynamics simulation of heating-freezing cycles of AuCo nanoalloys (From Ref. [3]).

References:

[1] J.-Q. Goh, J. Akola, R. Ferrando, J. Phys. Chem. C 121, 10809-10816 (2017).
[2] D. Bochicchio, R. Ferrando, E. Panizon, G. Rossi, J. Phys. Condens. Matter 28, 064005 (2016).
[3] J.P. Palomares-Baez, E. Panizon, R. Ferrando, Nano Letters 17, 5394 (2017).

I19: Advances in understanding of atomic scale phenomena on nanoclusters by ab initio and molecular dynamics simulations

Joseph Kioseoglou

Department of Physics, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece

sifisl@auth.gr

Abstract:

Core/shell metallic nanoclusters and clusters/surface interactions, in which different materials are involved, offer a way to relax the strain induced by the lattice parameter mismatch and create defect-free interfaces, owing to their large surface to volume ratio. Moreover, a variety of structural phenomena such as coalescence, nanoalloy segregation, and diffusion of atoms are identified during their growth and/or the landing process on the surface. *Ab initio* calculations and interatomic potential based Molecular Dynamics(MD) and Monte Carlo (MC) simulations as well as computational methods in electron microscopy are employed to investigate the structural, kinetics, equilibrium and non-equilibrium metastable processes of a variety of nanocluster's related cases.

By the use of atomistic simulations, materials analysis and design is implemented on defects, surfaces, interfaces and nanoclusters at the atomic scale taking into account the experimentally identified growth conditions and the temperature dominated phenomena. Based on the aforementioned methodology technologically important cases are analyzed:

- The bi-metallic Ag-Cu NPs studied by MD and MC simulations, and in particular the formation of Janus or Ag@Cu core/shell metastable structures on the grounds of in-flight mixed NP coalescence.[1]
- Pd NPs on Mg nanofilms in a promising configuration for hydrogen storage.[2]
- Embedded B2-FeSi nanoclusters in [100]-oriented Si substrate.[3]

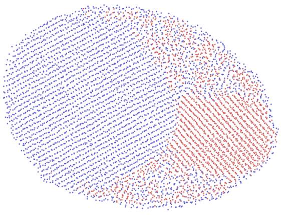


Figure 1: *Coalescence of Ag(blue) and Cu(red) nanoclusters. Cu subsurface diffusion.*

References:

[1] P. Grammatikopoulos, J. Kioseoglou, A. Galea, J. Vernieres, M. Benelmekki, R.E. Diaz, M. Sowwan, (2016) Nanoscale, 8 (18), pp. 9780-9790.

[2] S. Kumar, T. Pavloudis, V. Singh, H. Nguyen, S. Steinhauer, C. Pursell, B. Clemens, J. Kioseoglou, P. Grammatikopoulos, M. Sowwan, (2018) Advanced Energy Materials, 8 (4), art. no. 1701326

[3] C. Cassidy, J. Kioseoglou, V. Singh, P. Grammatikopoulos, C. Lal, M. Sowwan (2014) Applied Physics Letters, 104 (16), art. no. 161903.

I20: Long-lived excited states in metal clusters

Gerd Ganteför

Department of Physics, University of Konstanz, Konstanz, Germany

gerd.gantefoer@uni-konstanz.de

Abstract:

Electronically excited states govern the response of materials to an external stimulus and therefore are key parameters as far as applications are concerned. Long-lived excited states are responsible for phenomena such as fluorescence and photocatalysis. In this regard, nanoscience opens up new perspectives. In bulk metals excited state lifetimes are extremely short because of the ultrafast energy dissipation among the conduction electrons. Accordingly, metals are ineffective photocatalysts and in general do not exhibit fluorescence. Metal clusters have been shown to be different. The electron density might be smaller because of charge spillout and the density of states is discontinuous. However, contrary to expectation, long-lived excited states are a rarity in bare metal clusters. Only some clusters of a few elements exhibit excited states with lifetimes longer than a picosecond. Notably, this are always clusters with narrow peaks in their photoelectron spectra. We propose a concept explaining why long-lived excited states are so rare and why there is this correlation with the average width of the peaks in the photoelectron spectra. In addition, clusters of heavy elements such as Au and Pb seem to be more likely to exhibit long-lived excited states. We propose an explanation for this correlation, too. Both effects together would explain why Au clusters are so special.

E1: The Overproduction of truth. Passion, competition, and integrity in modern science

Gianfranco Pacchioni

Dipartimento di Scienza dei Materiali
Università di Milano Bicocca
Via R. Cozzi, 55 – 20125 Milano, Italy

Gianfranco.pacchioni@unimib.it

Abstract

The way science is done has changed radically in recent years. Scientific research and institutions, which have long been characterized by passion, dedication and reliability, have increasingly less capacity for more ethical pursuits, and are pressed by hard market laws. From the vocation of a few, science has become the profession of many — possibly too many. These trends come with consequences and risks, such as the rise in fraud, plagiarism, and in particular the sheer volume of scientific publications, often of little relevance. We will critically review and assess the present-day policies and behaviours in scientific production and publication. We will touch on the tumultuous growth of scientific journals, in parallel with the growth of self-declared scientists over the world. We will investigate the loopholes and hoaxes of pretend journals and non-existent congresses, so common today in the scientific arena, and discuss problems connected to the incorrect use of bibliometric indices, which have resulted in large part from the above distortions of scientific life. The solution? A slow approach with more emphasis on quality rather than quantity that will help us to rediscover the essential role of the responsible scientist.

Reference

G. Pacchioni, *The Overproduction of truth. Passion, competition, and integrity in modern science*, Oxford University Press, Oxford 2018.

I21: Atomistic Simulation of Trimetallic Nanoparticle Growth by Cluster Beam Deposition

Panagiotis Grammatikopoulos

Nanoparticles by Design Unit, Okinawa Institute of Science and Technology (OIST) Graduate University, 1919-1 Tancha, Onna-Son, Okinawa 904-0495, Japan

pgrammatikopoulos@oist.jp

Abstract:

Cluster beam deposition (CBD) is a versatile method where one can control the chemical composition of fabricated nanoparticles by suitably adjusting the powers of neighbouring sputtering targets [1]. Multi-metallic or hybrid nanoparticles thus grow as a result of coalescence of primary single-element clusters [2].

The nucleation and growth mechanisms of both the elementary primary clusters and the final mixed nanoparticles may be too complicated to be extracted directly from characterisation of the deposited samples. To shed light to the atomistic nature of the condensation process, computer simulation methods such as molecular dynamics (MD) and Monte Carlo (MC) are ideally suited, since the spatial and temporal scales involved are within their resolution capabilities.

Here, we will present the growth of trimetallic Au-Pt-Pd nanoparticles grown by concurrent co-sputtering of independent targets from the simulation point of view. We will show which parameters dictate the individual growth rate of each species, and how this determines the resultant composition and chemical order of the deposited nanoparticles. Further, we will expand on how the simulated nanoparticles show a remarkable agreement with experimentally fabricated ones in shape, structure, and composition.

References:

[1] P. Grammatikopoulos, S. Steinhauer, J. Vernieres, V. Singh, M. Sowwan, Advances in Physics: X 1(1) (2016) 81-100.
[2] P. Grammatikopoulos, J. Kioseoglou, A. Galea, J. Vernieres, M. Benelmekki, R. E. Diaz, M. Sowwan, Nanoscale 8 (2016) 9780-9790.

I22: Superatom Chemistry of Metal-Encapsulating Tetrahedral Silicon-Cage (METS) Immobilized on C_{60} Surface

Atsushi Nakajima[1,2]
[1] Department of Chemistry, Faculty of Science and Technology, Keio University
[2] Keio Institute of Pure and Applied Sciences (KiPAS), Keio University

nakajima@chem.keio.ac.jp

Abstract:

One of the challenges in cluster science is to develop the novel research field of solid-state chemistry and material science using gas-phase-synthesized superatomic clusters. Among various superatoms, the greatest advantage of the central-atom-encapsulating binary superatoms, such as $M@Si_{16}$, is that their electronic structures can be designed by optimizing the central atom while retaining the geometrical symmetry of the cage [1]. We have systematically investigated the surface immobilization of the $M@Si_{16}$ cations and anions. Initial products prepared via the surface immobilization of $M@Si_{16}$ cluster ions on solid surfaces terminated with monolayer films of C_{60} molecules were investigated using scanning tunneling microscopy (STM) [2,3] and X-ray photoelectron spectroscopy (XPS) [4,5]. Furthermore, we have developed a large-scale synthesis method for $M@Si_{16}$ (M = Ti and Ta) by scaling up the clean dry-process with a high-power impulse magnetron sputtering (HiPIMS, nanojima ®) [6,7] and by a direct liquid embedded trapping (DiLET) method [8]. The spectroscopic results reveal that the structures of soft-landed and isolated $M@Si_{16}$ superatoms are the metal-encapsulating tetrahedral silicon-cage (METS) as shown in Figure.

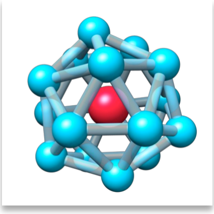


Figure. Tantalum Atom-encapsulating tetrahedral silicon-cage cluster (METS); $Ta@Si_{16}$.

References:

[1] K. Koyasu, A. Nakajima, *et al.* J. Am. Chem. Soc. 127 (2005) 4998.
[2] M. Nakaya, A. Nakajima, *et al.* Nanoscale 6 (2014) 14702.
[3] M. Nakaya, A. Nakajima, *et al.* J. Phys. Chem. C 119 (2015) 10962.
[4] M. Shibuta, A. Nakajima, *et al.* J. Am. Chem. Soc. 137 (2015) 14015.
[5] T. Ohta, A. Nakajima, *et al.* J. Phys. Chem. C 120 (2016) 15265.
[6] H. Tsunoyama, A. Nakajima, *et al.* Chem. Lett. 42 (2013) 857.
[7] C. H. Zhang, A. Nakajima, *et al.* J. Phys. Chem. A 117 (2013) 10211.
[8] H. Tsunoyama, A. Nakajima, *et al.* J. Phys. Chem. C 121 (2017) 20507.

I24: High-Coverage Deposition of Mass-Selected Cluster Anions: Fundamentals and Applications

Venkateshkumar Prabhakaran[1], Grant E. Johnson[1], Pei Su[2], and Julia Laskin[2]

[1]Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA, USA
[2]Department of Chemistry, Purdue University, West Lafayette, IN, USA

jlaskin@purdue.edu

Abstract:

Soft-landing of mass-selected ions is a powerful tool for precisely-controlled preparation of cluster-based interfaces. We have developed a high-intensity electrospray ionization source that delivers nanoamperes of mass-selected cluster ions onto surfaces. This capability allows us to efficiently populate two- and three-dimensional (2D and 3D) interfaces with cluster ions. We are particularly interested in studying the deposition of stable anionic species, which efficiently retain their ionic charge on surfaces. For example, we examined soft-landing of a polyoxometalate Keggin anions (POM) onto self-assembled monolayer (SAM) and carbon surfaces. POM are stable anionic species with multielectron redox activity, which retain their negative charge following deposition on surfaces. Cyclic voltammetry (CV) experiments indicate that soft-landed POM anions maintain their electrochemical activity. Furthermore, a substantial increase in the electrochemical capacitance and stability of carbon electrodes was observed after soft-landing of $PMo_{12}O_{40}^{3-}$ POM anions (MoPOM).[1] Detailed characterization of electrode surfaces indicates that the observed improvement in the carbon electrode performance is attributed to a uniform deposition of anions and elimination of inactive counter cations from the electrochemical interface. Soft-landing of POMs into more complex porous carbon materials demonstrates that the electric field generated by accumulated anions promotes ion penetration into 3D materials. Detailed understanding of the kinetics and mechanisms of interfacial processes occurring at electrochemical interfaces prepared using ion soft-landing is obtained using a new in situ electrochemical cell. The three-electrode cell is fabricated using a nanostructured ionic liquid-based solid membrane with excellent transport properties, which enables measurements both in vacuum and in controlled environments of inert and reactive gases.[2] Comparison of the redox activity of different POM anions using the in situ cell helped identify the best composition of the redox-active species for designing high-performance electrodes. These studies provide important insights into the activity of soft-landed ions at complex interfaces.

References:

[1] Prabhakaran, Mehdi, Ditto, Engelhard, Wang, Gunaratne, Johnson, Browning, Johnson, Laskin, "Rational Design of Efficient Electrode-Electrolyte Interfaces for Solid-State Energy Storage Using Ion Soft Landing." *Nat. Commun.* 7, 11399 (2016)
[2] Prabhakaran, Johnson, Wang, Laskin, "In situ solid-state electrochemistry of mass-selected ions at well-defined electrode–electrolyte interfaces." *PNAS* **113**, 13324-13329 (2016).

I25: Cluster Assemblies Produced by Aggregation of Preformed Ag Clusters in Ionic Liquids

Stefanie Roese[1], Alexander Kononov[1], Janis Timoshenko[2], Anatoly I. Frenkel[2,3]
and Heinz Hövel[1]

[1] Fakultät Physik/DELTA, Technische Universität Dortmund, 44227 Dortmund, Germany
[2] Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, NY 11794, USA
[3] Division of Chemistry, Brookhaven National Laboratory, Upton, NY 11973, USA

heinz.hoevel@tu-dortmund.de

Abstract:

Room temperature ionic liquids (RTILs) can be used as electrosterical stabilizers for nanoparticles without adding stabilizing agents. However, the nanoparticle stability and its mechanisms are still in discussion. We deposited pre-formed 2 nm ± 0.6 nm silver clusters into the ionic liquid $C_4MIM\ PF_6$ using in-situ UV/Vis absorption to monitor the deposition process [1]. The time- and temperature-dependent cluster aggregation process was studied with ex-situ UV/Vis absorption spectroscopy analyzed with electrodynamic calculations using Generalized Mie Theory. On an atomistic level the sample structure was investigated using EXAFS and a neural network based analysis of XANES. The combination of all methods shows that an aggregation of the original 2 nm clusters without coalescence takes place, which can be controlled or stopped by choosing an appropriate sample temperature [2]. This approach allows the controlled production of chain-like cluster aggregates in RTIL, promising for a number of applications.

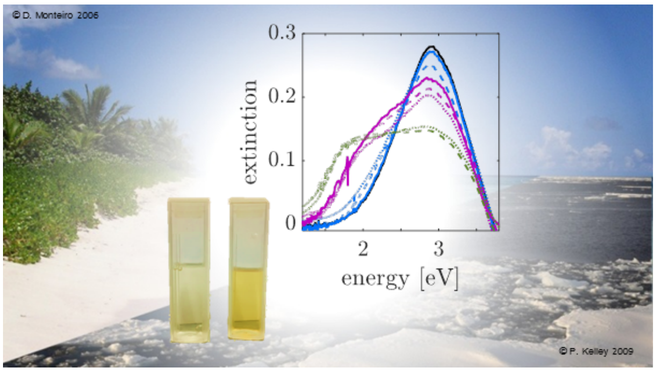


Figure 1: *Sample storage at different temperatures: 293K (solid lines), 277K (dashed lines), 253K (dotted lines). The colors denote the different aggregation phases. The cuvettes show a visual indication of the sample aggregation.*

References:

[1] D.C. Engemann, S. Roese, H. Hövel, J. Phys. Chem C **120**, 6239 (2016).
[2] S. Roese, A. Kononov, J. Timoshenko, A.I. Frenkel, H. Hövel,
Langmuir (2018), accepted for publication, **DOI:** 10.1021/acs.langmuir.7b03984

I26: Bi and related nanostructures - spectroscopy, topological states, and jumping islands

S. A. Brown[1], P. J. Kowalczyk[2], T. Maerkl[1], I. V. Mahajan[1], M. Le Ster[1], G. Bian[3], X. Wang[4], T.-C. Chiang[5], F. Genuzio[6], T. O. Mentes[6], A. Locatelli[6]

[1] The MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Physics and Astronomy, University of Canterbury, Christchurch, New Zealand
[2] Department of Solid State Physics, University of Lodz, Poland
[3] Department of Physics and Astronomy, University of Missouri, USA
[4] College of Science, Nanjing University of Science and Technology, Nanjing, China
[5] Department of Physics, University of Illinois at Urbana-Champaign, USA
[6] Elettra - Sincrotrone Trieste S.C.p.A., Basovizza, Trieste, Italy

simon.brown@canterbury.ac.nz

Abstract:

Recently topological insulators have emerged as a new class of matter in which surface and / or edge states are protected from backscattering by a combination of spin orbit interactions and time reversal symmetry. The simple deposition techniques developed by the cluster community over the last 20 years turn out to be ideal for the growth of topological nanostructures, and allow the study of outstanding fundamental issues. Of particular importance is the question of whether or not topological states found in bulk or 2D structures survive in nanoscale structures.

Bulk $Bi_{1-x}Sb_x$ alloys were the first 3D topological insulators (in the critical alloy concentration range of x~0.07-0.22) and so nanostructures of these alloys are an obvious target. Here we present an overview of recent experiments that include detailed STM studies of the structure and electronic properties of both $Bi_{1-x}Sb_x$ alloy and pure Bi nanostructures, as well as sequentially deposited (layered) van der Waals heterostructures (VDWHs). These VDWHs allow the observation of new allotropes of both Bi and Sb.

We will present the first ARPES data from single topological nanostructures of pure Bi and compare them with DFT calculations that reveal the presence of novel Dirac cones in the bandstructure. Finally we present the first images / movies of the growth of these nanostructures via LEEM, revealing a major surprise: large islands comprising more than 100,000 atoms are observed to be mobile and undergo a unique shuttling motion - they jump back and forth over distances of hundreds of nanometers.

I27: Low-temperature catalysis of NO reduction and CO oxidation on size-selected platinum cluster disk bound to silicon substrate surface

Hisato Yasumatsu[1] and Nobuyuki Fukui[2]

[1]Cluster Research Laboratory, Toyota Technological Institute: In [2]East Tokyo Laboratory,
Genesis Research Institute, Inc. Ichikawa, Chiba 272-0001, Japan

yasumatsu@clusterlab.jp

Abstract:

For sustainable development of combustion engines, lean combustion at larger air-to-fuel ratios suppresses fuel consumption due to its high heat efficiency. Accordingly, its exhaust gas is cooler, so that poisonous species such as NO and CO included there must be converted catalytically to N_2 and CO_2, respectively, at lower temperatures under the oxygen-rich condition. We are tackling this crucial issue with new materials, i.e. size-selected Pt cluster disks bound to a Si substrate, Pt_N/Si (N=10 - 60), prepared by cluster-impact deposition [1]. It has been found in our STM observation that electrons are accumulated at the sub-nano interface between Pt_N and the Si substrate [2,3], where it is expected that molecules are promoted with high efficiency. In this talk, their prominent low-temperature catalytic activities in the NO reduction and the CO oxidation are presented on a basis of surface-chemistry experiments such as turnover-rates (TOR) measurements under quasi-steady-state and transient conditions as well as temperature-programed desorption (TPD) mass spectroscopy.

We have found that the CO oxidation on the Pt_{30}/Si disks starts at 130 K [4,5], which is lower by 150 K than that on the Pt(111) single-crystal surface [6]. This is explained by low-temperature dissociative adsorption of O_2 on the Pt_N/Si owing to the accumulated electrons. The NO reduction also proceeds on the Pt_N/Si at lower by 70 K than that on the Pt(100) single-crystal surface. The low-temperature catalytic activity was confirmed further in the TOR measurements under the quasi-steady-state condition. Furthermore, it shows high chemical selectivity such that only N_2 but neither N_2O nor NO_2 are produced even in oxygen-rich environment, mimicking the exhaust gas of the lean combustion. It is probable that dissociative adsorption of NO on Pt_N/Si, which is the rate-determining step in the current reaction, also starts to occur at lower temperature. The selectivity of the NO reduction is also explained by the lower-temperature dissociation of NO than its oxidation.

References:

[1] H. Yasumatsu, *Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry*, ed. Klaus Wandelt (Editor-in-Chief), Elsevier, in press (2018); Book ISBN: 9780128097397.
[2] H. Yasumatsu, T. Hayakawa and T. Kondow, *Chem. Phys. Lett.* **487**, 279 (2010).
[3] H. Yasumatsu, P. Murugan and Y. Kawazoe, *Phys. Stat. Solidi B* **6**, 1193 (2012).
[4] H. Yasumatsu and N. Fukui, *J. Phys. Chem. C* **119**, 11217 (2015).
[5] H. Yasumatsu and N. Fukui, *Catal. Sci. Technol.* **6**, 6910 (2016).
[6] J. Yoshinobu and M. Kawai, *J. Chem. Phys.* **103**, 3220 (1995).

I28: Cluster-support interactions control the morphological transitions and catalytic activities of size-selected Pt clusters supported on metal oxides

Yoshihide Watanabe[1], Syed Mohammad Fakruddin Shahed[1], Hirohito Hirata[2] and Atsushi Beniya[1]

[1]Toyota Central R&D Labs., Inc., 41-1 Yokomichi, Nagakute, Aichi 480-1192, Japan
[2]Toyota Motor Corporation, 1200 Mishuku, Susono, Shizuoka 410-1193, Japan

ywatanabe@mosk.tytlabs.co.jp

Abstract:

Pt clusters were produced by dc magnetron sputtering with an inert gas condensation technique and mass-selected by a quadrupole mass-filter [1]. Size-selected Pt$_n$ clusters were deposited on TiO_2(110) [2], Al_2O_3 /NiAl(110) [3] and CeO_2(111)/Ru(0001) [4] and show the transition from a planar structure to a three-dimensional (3D) bi-layer structure and from 3D bi-layer to 3D tri-layer structure occurred at the different cluster size.
The morphological transition of Pt$_n$ clusters deposited on Al_2O_3 /NiAl(110) was shown in Figure 1as an example. The transition from a planar structure to a 3D bi-layer structure occurred at the cluster size of 19 atoms [2] and the transition from 3D bi-layer to 3D tri-layer structure occurred at the cluster size of 26-30 atoms.
We investigated the chemical states of Pt$_n$ clusters by infrared reflection absorption spectroscopy (IRAS). Two ontop CO species were assigned as adsorbed CO on neutral and slightly cationic Pt atoms. Despite of the first layer Pt atoms, the Pt clusters are composed of the two kinds of Pt atoms. With increasing cluster size, the number of neutral Pt atoms increases. Oxygen prefers to adsorb on the neutral Pt atoms. CO prefers to adsorb on the cationic Pt atoms [3]. CO_2 production by temperature-programed reaction (TPR) of CO + O_2 perfectly matches the ratio of the number of the neutral Pt site to the cationic one. These findings suggest the cluster-support interaction controls cluster-morphology and catalytic activity by perturbing the electronic states of Pt clusters.

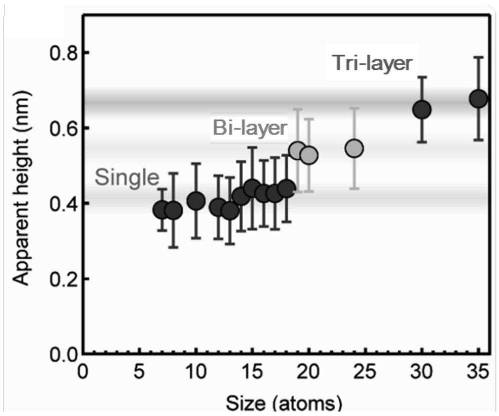


Figure 1: *Morphology of Pt$_n$/Al_2O_3/NiAl(110)*

References:

[1] Y. Watanabe, N. Isomura, J. Vac. Sci. Technol.A 27, 1153 (2009).
[2] Y. Watanabe, X. Wu, H. Hirata, N. Isomura, Catal. Sci. Technol. 1, 1490 (2011).
[3] A. Beniya, N. Isomura., H. Hirata, Y. Watanabe, Phys. Chem. Chem. Phys.16, 26485 (2014).
[4] S. M. F. Shahed, A. Beniya, H. Hirata, Y. Watanabe, J. Chem. Phys., 148(11) , 114702 (2018).

I29: Morphology and reactivity of Pt and Fe clusters on hexagonal (h)-BN/Rh(111)

Hamed Achour, Wolfgang Harbich, and Harald Brune

Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL),
CH-1015 Lausanne, Switzerland
wolfgang.harbich@epfl.ch

Abstract:

The stability and reactivity of Pt and Fe clusters supported on h-BN/Rh(111) is investigated. h-BN forms a strongly corrugated single sp^2 bonded atomic honeycomb layer. This corrugation provides trapping centers for molecules and clusters. We find that Pt clusters are thermally stable up to 700 K, above, intercalation of the Pt under h-BN takes place. Energetic cluster impact allows for intercalation at low surface temperatures as well as the formation of Pt/h-BN/Pt/Rh(111) sandwich layers. We discuss the influence of the morphology on the stability of the clusters and their reactivity. CO oxidation over Pt and NH_3 synthesis over Fe clusters are discussed.

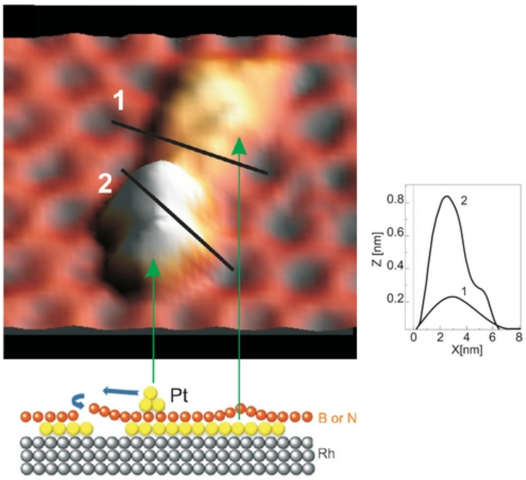


Figure 1: *STM image of supported Pt_7.on intercalated Pt on h-BN/RH(111)*

Contributed Presentations

Oral presentations: C1-C10

Posters: P1-P21

C1: Influence of Anodic Potential Limit on the Electrocatalytic Performance of Size-Selected Platinum Clusters

Jo J. L. Humphrey[1], Patrick J. Harrison[2], Quanmin Guo[2],
Richard E. Palmer[3] and Andrew J. Wain[1]

[1]National Physical Laboratory, Hampton Road, Teddington, TW11 0LW, UK
[2]Nanoscale Physics Research Laboratory, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK
[3]College of Engineering, Swansea University, Bay Campus, Fabian Way, Swansea, SA1 8EN, UK

andy.wain@npl.co.uk

Abstract:

Nanoparticles deposited *via* cluster beam methods have attracted significant attention as potential catalyst materials for a wide range of applications [1,2]. The atomic precision with which clusters may be produced using mass selection techniques offers a substantial advantage over traditional chemical routes, allowing structure and size dependencies to be explored systematically with unprecedented control. Particular efforts have focused on the development of catalysts for green electrochemical energy conversion devices such as fuel cells and electrolysers, which typically rely on the use of critically scarce and expensive platinum group metals (PGMs). Cluster beam synthesis provides an efficient route to minimizing the PGM content in such electrocatalysts through tightly-controlled surface optimization and the potential for introducing Earth-abundant substitutes.

In this work we explore the application of size-selected magic number Pt clusters ranging from Pt_{147} to Pt_{2057} (~1 – 4 nm diameter) as electrocatalysts for the hydrogen evolution reaction. We demonstrate that the electrochemical behavior and catalytic activity of the clusters are highly dependent on the potential treatment prior to performance testing. Cycling the potential to increasing anodic limits results in a broad improvement in the observed catalytic performance metrics, attributed to a combination of cluster restructuring and the removal of organic contaminants from the catalyst surface. Small variations in behavior are observed across the various cluster sizes, suggesting subtle differences in their susceptibility to these effects.

References:

[1] Palmer *et al.*, *J. Phys. Chem. C*, 2012, 116, 26295-26299
[2] Chorkendorff *et al.*, *Angew. Chem. Int. Ed.*, 2012, 51, 4641-4643

C2: Acetylene Semi-Hydrogenation over Alumina-Supported Pd Clusters: Experiment and Theory

L. P. L. Gonçalves[1], S. Vinati[2], E. Barborini[2], X.-K. Wei[3], M. Heggen[3],
J. Wang[4], J. Akola[4,5], and Yu. V. Kolen'ko[1]

[1]International Iberian Nanotechnology Laboratory, Braga 4715-330, Portugal.
[2]Tethis S.p.A., Milan 20143, Italy.
[3] Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany.
[4]Tampere University of Technology, Tampere 33101, Finland.
[5]Norwegian University of Science and Technology, Trondheim 7491, Norway.

yury.kolenko@inl.int

Abstract:

The selective semi-hydrogenation of acetylene to ethylene ($C_2H_2 + H_2 = C_2H_4$) is important industrial process to remove traces of acetylene in the ethylene feed for the production of polyethylene. This purification process, however, should be very selective in order to omit the consecutive hydrogenation of ethylene to ethane ($C_2H_4 + H_2 = C_2H_6$). Promoted nanosized palladium supported on alumina (Pd/Al_2O_3) is an industrial catalyst for the semi-hydrogenation of acetylene, since it has good activity, selectivity and durability in this reaction. Notably, Pd catalysts have modest selectivity at high levels of acetylene conversion, since they can also simultaneously catalyze the further hydrogenation of ethylene to ethane. Hence, the current research trend is aiming at better understanding of the catalytic process over Pd in order to achieve high selectivity at high conversion rates.

In this contribution, we will first introduce synthesis and characterization of palladium clusters supported on alumina (Figure 1) as catalysts for semi-hydrogenation of acetylene, followed by the activity and selectivity evaluation of the resultant materials. We will then showcase our recent progress in catalytic understanding of the role of Pd clusters in semi-hydrogenation of acetylene using synergetic tandem of experimental and theoretical considerations.

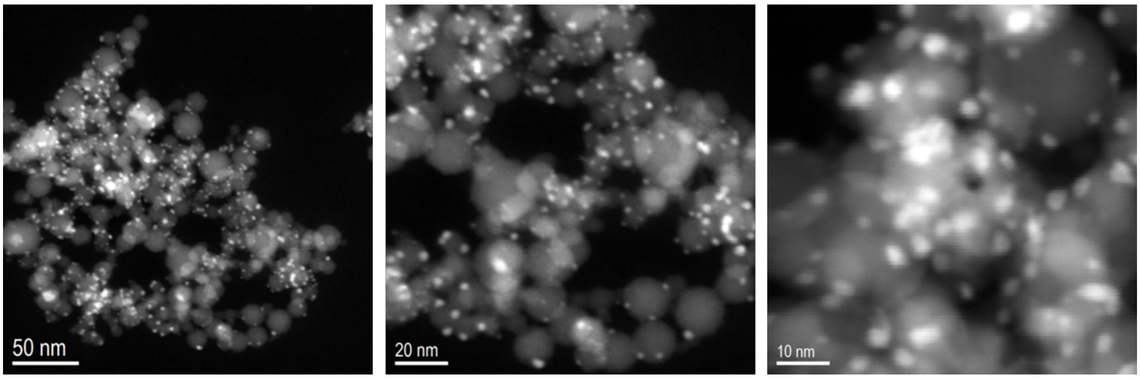


Figure 1: *HAADF-STEM images of the 5%wt Pd/Al_2O_3 catalyst.*

C3: Trends in activity for the oxygen evolution reaction on transition metal (M = Fe, Co, Ni) phosphide cluster pre-catalysts

Junyuan Xu[1], Bingsen Zhang[2], Yuefeng Liu,[2] and Lifeng Liu[1]

[1]International Iberian Nanotechnology Laboratory (INL), 4715-330 Braga, Portugal
[2]Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Science, Shengyang, China

lifeng.liu@inl.int

Abstract:

Transition metal phosphides (TMPs) have recently emerged as a new class of pre-catalysts that can efficiently catalyze the oxygen evolution reaction (OER). However, how the OER activity of TMPs varies with the catalyst composition has not been systematically explored. Here, we report the alkaline OER electrolysis of a series of nanoparticulate phosphides containing different equimolar metal (M = Fe, Co, Ni) components. Notable trends in OER activity are observed, following the order of FeP < NiP < CoP < FeNiP < FeCoP < CoNiP < FeCoNiP, which indicate that the introduction of a secondary metal(s) to a mono-metallic TMP substantially boosts the OER performance. We ascribe the promotional effect to the enhanced oxidizing power of bi- and tri-metallic TMPs that can facilitate the formation of MOH and chemical adsorption of OH^- groups, which are the rate-limiting steps for these catalysts according to our Tafel analysis. Remarkably, the tri-metallic FeCoNiP pre-catalyst exhibits exceptionally high apparent and intrinsic OER activities, requiring only 200 mV to deliver 10 mA $cm^{-2}$and showing a high turnover frequency (TOF) of ≥0.94 s^{-1} at the overpotential of 350 mV [1].

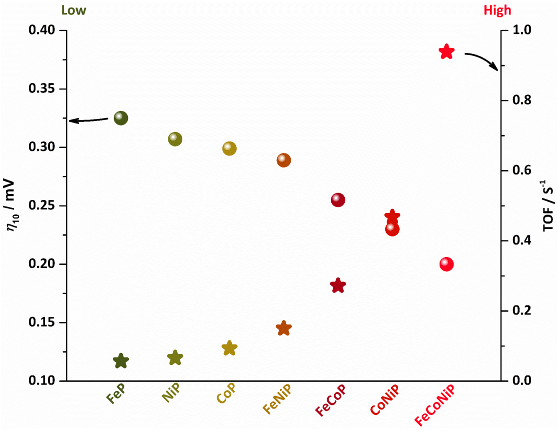


Figure 1: *Trends in OER performance of transition metal phosphide clusters.*

References:

[1] J.Y. Xu, et al. Chemical Science, 2018, DOI: 10.1039/C7SC05033J

C4: Cluster beam deposition of preformed metal clusters for liquid and gas phase catalysis

Rongsheng Cai[1], Peter R. Ellis[2], Jinlong Yin[3], Christopher M. Brown[2], Kevin Cooke[3], Peter T. Bishop[2], Richard E. Palmer[1]

[1] College of Engineering, Swansea University, Bay Campus, Fabian Way, Swansea SA1 8EN, UK
[2]Johnson Matthey, Blount's Court, Sonning Common, Reading RG4 9NH, UK
[3]Teer Coatings Ltd., Berry Hill Industrial Estate, Droitwich, Worcestershire WR9 9AS, UK

rongsheng.cai@swansea.ac.uk

Abstract:

The deposition of preformed cluster beams onto suitable supports represents a new paradigm for the precise preparation of heterogeneous catalysts. Compared with traditional chemical methods, it exhibits a range of unique advantages including good size (and composition) control, no toxic reagents needed, absence of chemical ligands etc. However, for a long time the feasibility of cluster-beam deposited catalysts for reactions under realistic conditions has been limited by the low production rate. Based on our successful scale-up of the cluster flux [1], we present here two experimental validations of cluster catalysts, for liquid phase and vapour phase reactions, respectively. i) Au/Cu nanoalloy clusters of variable compositions on MgO powder supports, created by a dual-magnetron sputtering gas condensation cluster source, are found to be highly active for the catalytic reduction of 4-nitrophenol in solution [2]. The interplay between the Au and Cu atoms at the cluster surface appears to enhance the catalytic activity via the binding energies of product and reactant. In addition, the physically deposited clusters with Au/Cu ratio close to one show a 25-fold higher activity than a Au/Cu reference sample made by chemical impregnation. ii) Size-controlled Pd clusters deposited on diced graphite tapes from the Matrix Assembly Cluster Source (MACS) [3] are found to be much more active than a Pd reference sample made by wet impregnation in the vapour phase 1-pentyne selective hydrogenation reaction. Aberration-corrected scanning transmission electron microscopy of the cluster size evolution before and after reaction reveals that the superior activity derives from the smaller cluster size and better stability against sintering compared with the Pd reference sample. Thus the addition of Au atoms to the Pd clusters, which increases cluster diffusion and sintering, decreases the catalytic activity.

References:

[1] Peter R. Ellis et al, Faraday Discuss., 2016, 188, 39.
[1] Rongsheng Cai et al, Small, 2018, 1703734
[2] Palmer R.E. et al, Rev. Sci. Instrum. 2016, 87, 046103.

C5: Heterogenous metal/plasma polymer nanoparticles and their potential applications

H. Biederman, A. Shelemin, D. Nikitin, P. Pleskunov, P. Solar, A. Choukourov, O.Kylián, J. Hanus, M. Cieslar, D. Slavínská

Charles University, Faculty of Mathematics and Physics, V Holešovičkách 2, Prague 8, 180 00, Czech Republic

bieder@kmf.troja.mff.cuni.cz

Abstract:

In recent years, considerable attention has been paid to the vacuum-based production of multicomponent NPs in which metals and/or metal oxides were alloyed or mixed in heterogeneous structure. Recently, hybrid core@shell NPs were introduced that combine a metal core and an organic envelope made of plasma polymer. This was achieved by a DC magnetron-based gas aggregation cluster source (GAS) built in-line with an RF glass tubular reactor for plasma polymerization. Beams of Ag NPs were produced in the GAS and subsequently passed through the glow discharge in an Ar/organic precursor mixture (*n*-hexane, acetone). Core@shell Ag@C:H NPs were successfully synthesized with the 16 nm mean diameter of the metallic core and 1-2 nm thickness of the plasma polymer shell [1]. Plasma polymers as highly cross-linked carbonaceous networks could act as stable supports for linker-free immobilization of bioactive cargo especially if they are functionalized with electrophile (e.g. NH_2) or nucleophile (e.g. COOH) groups. Recent studies point to the feasibility of bio-loaded plasma polymer NPs in drug/gene delivery systems [2].

In this study, we present two alternatives to the above production of hybrid core@shell NPs. The first approach utilizes the same DC magnetron-based GAS and takes advantage of introducing hexamethyldisiloxane (HMDSO) vapors directly to the aggregation chamber. STEM and HRTEM measurements show that sputtering of Ag in Ar without HMDSO results in the production of spherical NPs with the mean diameter of 30 nm (Ar pressure 150 Pa, magnetron current 600 mA). The introduction of 1.32% of HMDSO to Ar results in the formation of smaller (~10 nm) NPs, yet enveloped by thin organosilicon shell. At 4.00% of HMDSO and above, multicore@shell NPs are produced consisting of numerous Ag cores embedded in a single plasma polymer shell.

The second approach employs an RF magnetron-based GAS with a composite Cu/nylon target. The RF sputtering is performed in Ar at the pressure ranging from 20 to 150 Pa and RF power reaching up to 80 W. The first results of heterogeneous NPs are presented. In conclusion potential applications are discussed.

References

[1] O. Kylian et al., Plasma Process Polym. 2018,15,1700109

[2] M. Santos et al., Applied Nano Mater. 2018, 1, 580-594

Acknowledgments: This work was supported by the grant GACR 17-22016S from the Czech Science Foundation

C6: A proof of principle quantum dot solar cell fabricated with a magnetron sputtering cluster source

Jonathan Cardoso[1], Sarita Marom [1], Justin Mayer [1], Ritika Modi [1], Alessandro Podesta [1],
Xiaobin Xie [2], Marijn A. van Huis [2], and Marcel Di Vece[1]

[1] Interdisciplinary Centre for Nanostructured Materials and Interfaces (CIMaINa) and Physics Department, University of Milan, Via Celoria 16, 20133, Milan, Italy
[2] Soft Condensed Matter, Debye Institute for Nanomaterials Science, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands

Marcel.divece@unimi.it

Abstract:

Radiation from the sun is an attractive source of energy to reduce our current fossil fuel dependence. Solar cells are available for many decades, but only recently the price per kWh is becoming competitive. To further stimulate the use of solar energy, the efficiency and cost of solar cells need to be increased and reduced, respectively. Quantum dots are an interesting form of matter because their band gap is tunable by controlling the size of the semiconductor[1]. Quantum dot based solar cells are currently not commercially available, but research provides a steady increase of efficiency and stability of laboratory devices[2]. Since quantum dots are small particles in the order of a few nm, it is interesting to use a gas aggregation nanoparticle source to fabricate such quantum dots for solar energy harvesting. In this work we present the first quantum dot solar cell made with a gas aggregation nanoparticle source. The atoms of the semiconductor target were released by magnetron sputtering. UV-Vis spectroscopy revealed quantum confinement and spectral response of the solar cell confirmed the presence of large and small band gap optical absorption due to a mix of particle sizes. Some of the particles were small enough to have substantial quantum confinement while others were so large that they had bulk like properties. The diverse particle sizes and shaped were inventoried by HRTEM. This first quantum dot solar cell made with a gas aggregation nanoparticle source demonstrates the technological potential for research and applications combining these fields.

References:

[1] Alivisatos A P 1996 Perspectives on the Physical Chemistry of Semiconductor Nanocrystals *J. Phys. Chem.* **100** 13226–39
[2] Jabbour G E and Doderer D 2010 Quantum dot solar cells: The best of both worlds *Nat Photon* **4** 604–5

C7: Formation and emission mechanisms of Ag nanocluster, AuAg and AuPd nanoalloy in Ar matrix assembly cluster source

Junlei Zhao[1], Lu Cao[2], Richard E. Palmer[2,3], Kai Nordlund[1] and Flyura Djurabekova[2]

[1]Department of Physics and Helsinki Institute of Physics, University of Helsinki, P.O. Box 43, FIN-00014 Helsinki, Finland

[2]Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Birmingham B15 2TT, England, United Kingdom

[3]College of Engineering, Swansea University, Bay Campus, Fabian Way, Swansea SA1 8EN, Wales, United Kingdom

junlei.zhao@helsinki.fi

Abstract:

We study the mechanisms of growth of Ag nanoclusters in a solid Ar matrix and the emission of these nanoclusters from the matrix by a combination of experimental and theoretical methods. The molecular dynamics simulations show that the cluster growth mechanism can be described as "thermal spike-enhanced clustering" in multiple sequential ion impact events. We further show that experimentally observed large sputtered metal clusters cannot be formed by direct sputtering of Ag mixed in the Ar. Instead, we describe the mechanism of emission of the metal nanocluster that, at first, is formed in the cryogenic matrix due to multiple ion impacts, and then is emitted as a result of the simultaneous effects of interface boiling and spring force. We also develop an analytical model describing this size-dependent cluster emission. We further study the formation of AgAu and PdAu nanoalloys. The phase segregation of PdAu nanoalloy can be explained from kinetic origin by the different melting points of Pd and Au.

References:

[1] Zhao, J., Cao, L., Palmer, R. E., Nordlund, K., & Djurabekova, F. (2017). Formation and emission mechanisms of Ag nanoclusters in the Ar matrix assembly cluster source. *Physical Review Materials*, *1*(6), 066002.

C8: Composition-tunable self-organization in Au_xAg_{1-x} phase segregated nanostructures

Ting-Wei Liao[1], Anupam Yadav[1], Kuo-Juei Hu[1,2], Johan van der Tol[1],
Salvatore Cosentino[1], Francesco D'Acapito[3], Richard E. Palmer[4], Cristina Lenardi[5],
Riccardo Ferrando[6], Didier Grandjean[1] and Peter Lievens[1]

[1]Laboratory of Solid-State Physics and Magnetism, KU Leuven, Celestijnenlaan 200D - Box 2414, 3001 Leuven, Belgium.
[2]Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Birmingham, B15 2TT, United Kingdom.
[3]CNR-IOM-OGG c/o ESRF LISA CRG - The European Synchrotron CS 40220, 38043 Grenoble Cedex 9, France.
[4]College of Engineering, Swansea University, Bay Campus, Fabian Way, Swansea SA1 8EN United Kingdom
[5]CIMaINa and Physics Department, Università degli Studi di Milano,Via Celoria 16, 20133 Milano, Italy
[6]Dipartimento di Chimica e Chimica Industriale dell'Università di Genova, IMEM/CNR, via Dodecaneso 31, 16146 Genova, Italy

tingwei.liao@kuleuven.be

Abstract:

Bimetallic Au_xAg_{1-x} nanoparticles with various compositions ($x = 0.2$ to 0.9) are synthesised in the gas phase with precise composition control prior deposition and then the nanoparticles are deposited on amorphous SiO_2 wafers and TEM grids for structural investigations by HAADF-STEM, XPS and Refl-XAFS techniques. It is shown consistently from all the techniques that a systemic inversion of chemical ordering takes place by going from Au-rich to Ag-rich compositions, with the minority element always occupying the nanoparticle core, and the majority element enriching the shell. With the aid of DFT calculations, this composition-tunable chemical arrangement is rationalized in terms of a four-step growth process in which the very first stage of cluster nucleation plays a crucial role: first, Au and Ag plasma is generated by laser ablation; second, small Au-Ag binary aggregates are formed; third, few atoms binary aggregates form nuclei; forth, the majority material condense on the nuclei, hence resulting in composition dependent shell inversion. The four-step growth mechanism is based on mechanisms of a general character, likely to be applicable to a variety of binary systems besides Au-Ag.

References:

[1] R. Ferrando, in Frontiers of Nanoscience, ed. F. Riccardo, Elsevier, 2016, vol. Volume 10, pp. 131-183.
[2] T.-W. Liao, A. Yadav, K.-J. Hu, J. van der Tol, S. Cosentino, F. D'Acapito, R. E. Palmer, C. Lenardi, R. Ferrando, D. Grandjean and P. Lievens, Nanoscale, 2018, 10, 6684-6694.

C9: Toward Multifunctional Fe-based Nanocubes Using Cluster Beam Deposition

J. Vernieres[1,2], M. Sowwan[2], R. E. Palmer[1]

[1]College of Engineering, Swansea University, Bay Campus, Fabian Way, Swansea SA1 8EN, UK
[2] Nanoparticles by Design Unit, Okinawa Institute of Science and Technology (OIST) Graduate University, 1919-1 Tancha, Onna-Son, Okinawa 904-0495, Japan

Jerome.vernieres@swansea.ac.uk

Abstract:

The field of nanotechnology applied to heterogeneous catalysis or nanomedicine is developing at a fast pace and is expected to provide solutions for novel catalyst powder architectures at the gram-scale or solutions for early diagnosis, targeted therapy, and personalized medicine. The unique structure-property relationship of nanoscale objects such as clusters offers numerous possibilities for scientists. Taking advantage of their individual and unique properties that are unavailable in bulk materials, and additional synergistic properties arising when combining different materials, greatly augments their potential for nanotechnology applications. To date, the realization of suitable nanomaterials is mostly based on chemical synthesis routes, which can require complex, time-consuming, and often costly solution-based techniques. In addition, wet-chemical procedures involve organic solvents and hazardous agents which poses the risk of residual contamination and can inhibit the catalytic. On the other hand, size- and shape-controlled cluster beam deposition (CBD) techniques have generally been accompanied by post-growth separation, such as time-of-flight or quadrupole mass filtration, which limits the prospect of upscaling. Here, we report a method based on CBD that favours accurately determined nanoparticles (NPs) sizes *during* growth, instead of producing a wide-size dispersion first only to narrow it down by mass filtration *afterwards*[1]. We introduce magnetic target thickness as a crucial parameter that controls the density and temperature of the sputtered atoms, producing Fe NPs[2] of tailored size, shape and crystallinity. Thus, we remove from the concept of NP size selection from the necessity of mass filtration. Using this approach, we were able to prepare percolating thin films for chemoresistive gas sensing applications, which show unprecedented high-sensitivity to the analyte NO_2 down to the 3-ppb level. We attributed this high performance to a morphological change in operando from Fe/Fe-oxide core/shell to specific hollow-nanocube structures. Finally, we will present recent progress on the design of multifunctional nanomaterials by doping the Fe nanocubes with noble metals, while keeping their uniformity in size and shape. Using different approaches, we were able to engineer FePd[3] and FeAu[1] alloy nanocubes, as well as Fe nanocube-Au cage morphology. The ability to synthesize such advanced nanomaterials using physical methods will open numerous possibilities for future nanotechnology applications, especially if the scale-up proves possible with the new generation of cluster sources[4].

[1] J. Vernieres et al. *Adv. Funct. Mater.* **27**, 1605328 (2017).
[2] J. Zhao et al. *ACS Nano* **10**, 4684-4694 (2016).
[3] S. Steinhauer et al. *Nanoscale* **9**, 7380-7384 (2017).
[4] Peter R. Ellis et al. *Faraday Discuss* **188**, 39 (2016).

C10: In-situ study of nanoparticles in a gas aggregation cluster source by small-angle X-ray scattering

J. Kousal[1], A. Shelemin[1], M. Schwartzkopf[3], J. Hanuš[1], P. Solař[1], O. Polonskyi[2],
M. Vaidulych[1], D. Nikitin[1], P. Pleskunov[1], I. Melnichuk[1], Z. Krtouš[1], A. Choukourov[1], T. Strunskus[2], F. Faupel[2], S. V. Roth[3,4], H. Biederman[1]

[1] Charles University, Prague, Czech Rep.
[2] Christian-Albrechts-Universität zu Kiel, Kiel, Germany
[3] Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany
[4] KTH Royal Institute of Technology, Stockholm, Sweden

jaroslav.kousal@mff.cuni.cz

Abstract:

Nanoparticles (NPs) produced using gas aggregation cluster sources (GAS) based on magnetron sputtering [1] from various materials are subject of numerous studies [2]. While the experimental data on the NPs themselves are usually reported, in-situ characterization of processes inside GAS is much less common [3].

In this work, growth and transport of metallic and metal-plasma polymer NPs was studied using small-angle X-ray scattering (SAXS) at P03 beamline of PETRA III synchrotron in DESY, Hamburg (Figure 1). Two size- and spatially-distinct populations of NPs have been observed and characterized inside GAS aggregation chamber. This presents important new insight into principles of GAS operation.

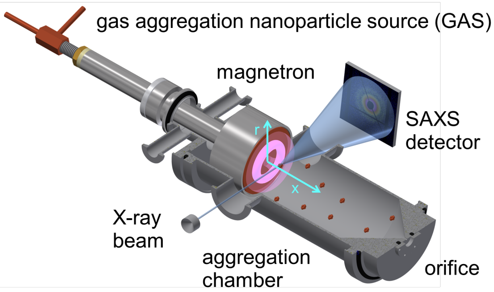


Figure 1: *General scheme of the experimental setup*

Acknowledgements:

This work was supported by the grant 17-22016S of the Czech Science Foundation.

References:

[1] H. Haberland, M. Karais, M. Mall, Y. Turner, J. Vac. Sci Technol A 10 (1992) 3266
[2] O. Kylián, M. Petr, A. Serov, P. Solař, O. Polonskyi, J. Hanuš, A. Choukourov, H. Biederman, Vacuum 100 (2014) 57-60
[3] J. Kousal, A. Kolpaková, A. Shelemin, P. Kudrna, M. Tichý, O. Kylián, J. Hanuš, A. Choukourov, H. Biederman, Plasma Sources Sci. Tech. 26 (2017) 105003

P1: Accelerating the Study on Nanocluster Catalysts with Machine Learning

Eiaki V. Morooka[1], Marc Jäger[1], and Adam Foster[1]

[1]Aalto University, takaari 1, Espoo, Finland

eiaki.morooka@aalto.fi

Abstract:

Platinum Group Metals (PGMs) are heavily used for catalysts that can withstand high acidic environments such as for fuel cells [1], however; there is a limited amount of supply [2]. We are studying characteristics of catalysts of nanoclusters using Machine Learning (ML) methods to automate the procedure of substituting expensive catalysts by rationally designing them with earth-abundant materials. We do so by eliminating redundant quantum mechanical calculations, classifying surface structures and interpolating adsorption energy using a state-of-the-art ML descriptor called Smooth Overlap of Atomic Positions (SOAP) [3].

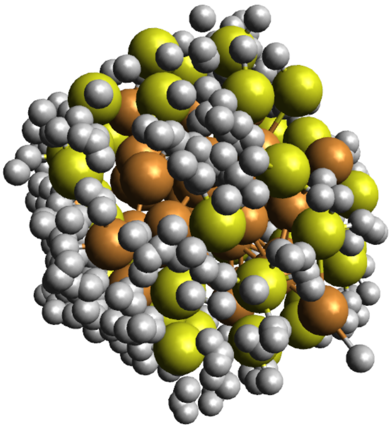


Figure 1: *Relaxed AuCu nanocluster with surface hydrogens that were selected uniquely with the SOAP measure differences.*

References:

[1] European Commision. Report on Critical Raw Materials for the EU, Ad hoc Working Group on defining critical raw materials. Technical report, (2014).
[2] https://newscientist.com/data/images/archive/2605/26051202.jpg (26.2.2018)
[3] Albert P. Bartók, Risi Kondor, and G. Csányi. On representing chemical environments. Physical Review B - Condensed Matter and Materials Physics, 87(18):1-19(2013).

P2: Efficient Scanning of Hydrogen Adsorption Energies on Nanoclusters

Marc Jäger[1], Eiaki Morooka[1] and Adam Foster[1,2]

[1] Aalto University, Helsinki, Finland
[2] Kanazawa University, Japan

marc.jager@aalto.fi

Abstract:

Nanoclusters differ from bulk metal behavior, their catalytic properties are sensitive to changes in size and morphology. We are interested in exploiting those properties in simple electrocatalytic reactions, such as hydrogen and oxygen evolution reaction (HER and OER). The vast amount of possible nanoclusters requires reduction and interpolation of DFT calculations using Machine Learning. Structural descriptors (ACSF[1], MBTR[2] and SOAP[3]) are used to describe the geometry of an adsorption site and to predict properties which indicate a high catalytic activity, in particular the adsorption free energy.

By merging the combinatorial space with the chemical compound space and applying machine learning on diverse datasets we were able to efficiently scan adsorption energies. It is also possible to predict properties without knowing the relaxed structure, only by using initial guesses of adsorbate positions and a large enough training set. Like that, optimizing the adsorbate-nanoclusters structure can be circumvented.

Furthermore, we showcase unsupervised learning to find patterns in nanoclusters. In particular, we visualize the local similarity of nanoclusters to Wulff-shapes, high-symmetry clusters (icosahedra, decahedra) and surface facets of low Miller-indices.

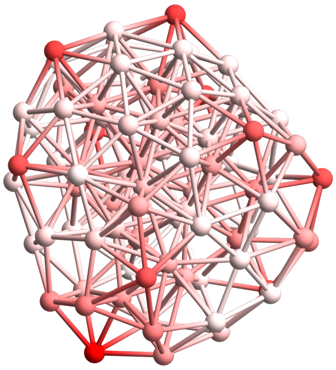


Figure 1: Local similarity (white-red) of a gold nanocluster with gold bulk and surface.

References:

[1] Behler, J. J. Chem. Phys. 2011, 134 (7), 74106.
[2] Huo, H.; Rupp, M. 2017, arXiv:1704.06439, (18.02.2018).
[3] Bartók, A. P.; Kondor, R.; Csányi, G. Phys. Rev. B - Condens. Matter Mater. Phys. 2013, 87 (18), 1–19.

P3: High-performance gas phase synthesized palladium nanoparticles for H_2O_2 sensing and methanol electro-oxidation

Jue Wang[1] and Min Han[1]

[1] National Laboratory of Solid State Microstructures and Department of Materials Science and Engineering, Nanjing University, Nanjing 210093,China

wjphoebe@163.com

Abstract:

In recent years, Pd nanoparticles (NPs) have attracted much research interests in H_2O_2 sensing and methanol electro-oxidation applications. Pd NPs used for electro-catalytic applications was commonly synthesized by chemical routes such as chemical reduction and electrodeposition. In each case, it is inevitable that the chemical solution would affect the catalytic activity. Recently, We used the gas phase cluster beam deposition process to fabricate Pd NP-deposited-glassy carbon electrode (GCE), which enabled highly selective amperometric detection of H_2O_2 at a sufficiently low applied potential (∼−0.12 V) [1]. In order to improve the response time and the linear response range, Pd NPs were deposited on chemical vapor deposition synthesized bilayer graphene films (BGFs) supported with GCEs in the gas phase. With the introduction of BGFs, the catalytic activity of Pd NP-modified electrodes toward H_2O_2 reduction was largely enhanced [2]. Because of outstanding catalytic activity of the Pd NPs, we fabricated Pd NPs supported on carbon supports and used them as the electro-catalysts for methanol oxidation reactions. The resulting Pd NPs/multi-walled carbon nanotubes/few-layer graphene sheets combination exhibits an ultrahigh electrocatalytic activity and unusual long-term durability for methanol oxidation [3]. These results indicate that the Pd NP catalysts produced by gas phase cluster beam deposition are promising applications in H_2O_2 sensing and methanol electro-oxidation.

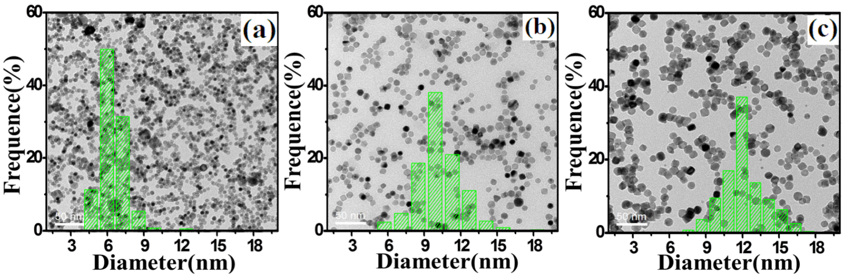


Figure 1: *TEM images of Pd NPs produced with argon gas pressure of (a) 90 Pa, (b) 110 Pa, and (c) 130 Pa and the corresponding size distributions.*

References:

[1] J. Wang, et al., Nanoscale Res. Lett. (2015) 10:311
[2] J. Wang, et al., Sensor. Actuat. B-Chem. 230 (2016) 690–696
[3] J. Wang, et al., Electrochim. Acta 251 (2017) 631–637

P4: Tuning Size Distribution of Germanium Nanoparticles Produced by High Pressure Gas Condensation

Xiaotian Zhu[1], Gert H. ten Brink[1], Bart J. Kooi[1] and George Palasantzas[1]

[1]Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands

xiaotian.zhu@rug.nl

Abstract:

Strong impetus has been given to the study of germanium nanoparticles (NPs) due to their unique size-dependent optical and electrical properties, which could be alternatives to classical II–VI and IV–VI quantum dots (QDs) containing toxic elements such as Hg, Cd and Pb[1, 2]. In our research, Ge NPs produced by high pressure magnetron sputtering gas condensation were studied by bright field transmission electron microscopy (TEM) and selected area electron diffraction (SAED) to provide information on size distribution and crystalline structure. Particles with a size smaller than the Bohr exciton radius λ_B (≈24.3nm) show strong quantum confinement, allowing bandgap widening and thus its control with particle size. The size of Ge NPs can be tuned from 5nm to 20nm. These Ge NPs adopted diamond structure indicted by SAED. The core-shell structure, composed of a Ge core surrounded by an oxide layer, was confirmed by high resolution TEM combined with Fast Fourier transform (FFT). Moreover, extensive analysis shows that the particle size strongly depends on the plasma density, which could be tuned by adjusting the thickness of the protective backing plate positioned in-between the target and the magnetron head. With increasing backing plate thickness, the particle size decreases. Based on finite element method simulations, it could been found that the decrease of NPs size with the increasing backing plate thickness can be attributed to a reduced magnetic field strength above the Ge target surface. These results pave the way to drastically control the NP size which allows adjusting the bandgap of Ge NPs by quantum confinement effect.

References:

[1] D. Carolan, Recent advances in germanium nanocrystals: Synthesis, optical properties and applications, Progress in Materials Science 90 (2017) 128-158.
[2] Y. Wang, N. Herron, Nanometer-sized semiconductor clusters: materials synthesis, quantum size effects, and photophysical properties, The Journal of Physical Chemistry 95(2) (1991) 525-532.

P5: Atomic-resolution imaging and *ab initio* modelling of surface and core melting of supported, size-selected Au nanoclusters

Th. Pavloudis[1], D.M. Foster[2], J. Kioseoglou[3] and R.E. Palmer[1]

[1]College of Engineering, Swansea University, Bay Campus, Fabian Way, Swansea, SA1 8EN, UK
[2]Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Birmingham, B15 2TT, UK
[3]Department of Physics, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece

Theodoros.Pavloudis@Swansea.ac.uk

Abstract:

There is much interest in how melting, one of the most familiar and visible phase transitions in the macroscopic world, changes at the nanoscale. The behavior of nanoclusters at elevated temperatures is both interesting from a fundamental perspective but also relevant to functionalities such as catalysis due to the applications of nanoclusters in modern catalysts. In this work, we observe surface melting in real space in individual size-selected Au clusters below 5nm supported on amorphous carbon films. We identify the formation of a solid core/liquid shell structure at elevated temperatures. The melting mechanism is consistent with the liquid nucleation and growth model but with higher melting temperatures and a notably larger solid-liquid coexistence region. We employ a novel very large-scale *ab initio* simulation approach that mimics the effect of the support by adopting a frozen-facet on the nanoclusters. The cluster-support interaction is consequently identified as a major source of the deviation between theoretical predictions and experimental observations. We obtain quantitative results that are in good agreement with the experiment. Moreover, we prove the existence of a solid core and a melted surface, and show the differences in size and placement of the core in free and frozen-facet nanoclusters. The Au clusters studied in this work lie in the catalytically active size regime, therefore the results may assist the design of novel nanocluster-based catalysts.

P6: Kinetic barriers and reaction energetics of oxygen evolution reaction on nitrogen-doped carbon nanotubes

Garold Murdachaew [1], Kari Laasonen[1], and Lauri Partanen[1]

[1]Department of Chemistry and Material Science, Aalto University, P.O. Box 16100,FIN-00076 Aalto, Finland

lauri.partanen@aalto.fi

Abstract:

We have investigated kinetic barriers and reaction energetics for the oxygen evolution reaction (OER) on singly and doubly nitrogen-doped single-walled carbon nanotubes (NCNTs). Our calculations combine DFT with the climbing image nudged elastic band (CI-NEB) method. Solvent effects have been included by a 45 water molecule droplet model. The sites for the CI-NEB calculations were chosen based on a simple thermodynamic model, which ignored both solvent effects and kinetic barriers [1]. One of these sites was located on a singly nitrogen-doped CNT, and the other was on a doubly-doped CNT. According to the thermodynamic model, the two sites were approximately equally suitable for OER. However, our reaction barrier calculations revealed a clear difference in the rate-determining *OOH formation step between the two systems, with barrier heights differing by more than 0.4 eV. Thus, the thermodynamic model may be insufficient for identifying optimal OER sites. Of the remaining three reaction steps of the four-step OER process, the two H_2O forming ones were barrierless in all cases. We also performed solvent-free barrier calculations on NCNTs and undoped CNTs. Substantial differences were found in the energies of the intermediates when the solvent was present. The low activation energy barriers observed for these reactions corroborate both theoretical and experimental research findings of the utility of NCNTs for OER catalysis.

References:

[1] Rossmeisl, J.; Logadottir, A.; Nørskov, J. K. Chem. Phys. 2005, 319, 178 - 184.

P7: “Planetary” silver nanoparticles held in orbit by electric charge

Sarita Marom[1], Ritika Modi[1], Michael Plesser[1], Nicola Manini[2] and Marcel Di Vece[1]

[1] CIMAINA and Dipartimento di Fisica, Università di Milano, Via Celoria 16, 20133 Milano, Italy
[2] Dipartimento di Fisica, Università di Milano, Via Celoria 16, 20133 Milano, Italy

Marcel.divece@unimi.it

Abstract:

In a gas aggregation cluster source, nanoparticles are formed by aggregation of single atoms to particles as well as by agglomeration of smaller particles to form larger particles. Because the small particles are often electrically charged, it is possible that particles are mutually attracted or repelled by electric forces. We report the observation of “planetary” bound multi-particle systems which are the result of the electrical and centrifugal forces acting on nanoparticles in a magnetron sputtering cluster source. Transmission electron microscopy analysis of deposited “planetary” nanoparticle systems exhibit characteristic interparticle distances and sizes, as well as different charge states of the particles. Simulations confirm the presence of stable planetary nanoparticle systems composed by up to at least 6/7 satellites. The discovery of such “planetary” nanoparticle systems inside a cluster source opens up possibilities for more research into their properties and how they can be further controlled and explored.

P8: Machine-learned potentials for Pt-TM nanoclusters

Filippo Federici Canova[1], Olli Ahlstedt[2], Jaakko Akola[2], David Z. Gao[1]

[1]Nanolayers Research Computing Ldt, 1 Granville Court, N12 0HL London, UK
[2]Tampere University of Technology, P.O. Box 527, 33101 Tampere, Finland

felix@nanolayers.com

Abstract:

Platinum is one of the most prominent materials in catalysts in automotive and fuel cell industries. Unfortunately, it is scarce and supply is largely dominated by few countries. Reducing the amount of Pt from catalysts, and eventually replace it entirely with cheaper and more accessible materials can have a significant impact on industry and society.

Theoretical simulations, at the quantum level, can be used to predict the catalytic activity of binary Pt-TM nanoclusters and check for suitable replacements without recurring to expensive laboratory tests. However, accurate calculations are time-consuming and the chemical space of possible materials/structures is too vast to be explored.

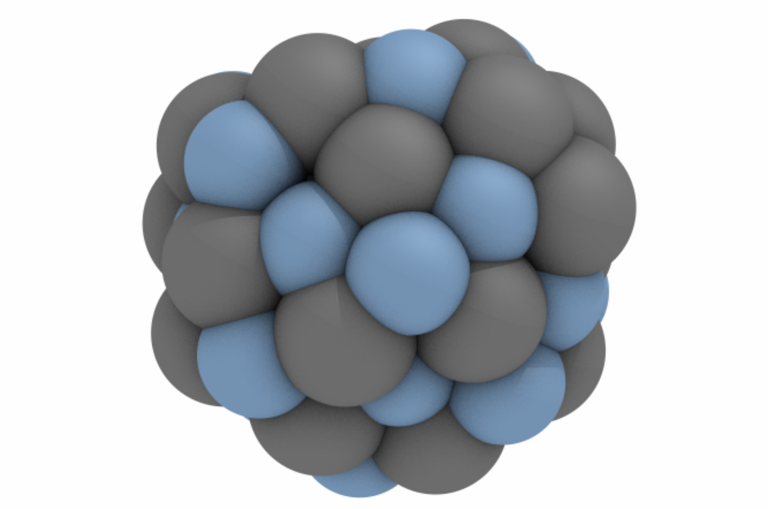


Figure 1: *Rendering of a candidate Pt-Ti nanocluster.*

Using neural networks [1] and atom centered symmetry functions [2], we attempt to fit the energy of Pt-TM nanoclusters from a database of DFT reference calculations. This machine-learning model can be used to screen candidate structures extremely fast, and eventually search optimal ones, to be further analyzed with quantum mechanical methods.

References:

[1] W. S. McCulloch and W. Pitts, *Bull. Math. Biophys.* **5**, 115 (1943)
[2] J. Behler, *J. Chem. Phys.* **134**, 074106 (2011)

P9: Core-shell W/Cu nanoparticles fabricated by means of gas aggregation source

Solař Pavel[1], Kylián Ondřej[1], Hanuš Jan[1], Cieslar Miroslav[1], Kúš Peter[1], Biederman Hynek[1]

Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, 180 00, Prague, Czech Republic

pawell.solar@seznam.cz

Abstract:

Since their introduction in the 90s of the last century gas aggregation sources (GAS) become routine means for production of single material nanoparticles (e.g. metallic, metal-oxide or plasma polymer ones). However, as demonstrated in recent studies GAS systems may also be adapted for fabrication of heterogeneous multicomponent nanoparticles, usually with core-shell structure. In the case of metal-metal nanoparticles three principal strategies were developed that are based either on the use of multiple magnetrons in one aggregation chamber, in-flight coating of nanoparticles in an auxiliary deposition chamber attached to GAS or utilization of a composite target. The last approach was used in this study for production of bimetallic system of copper and tungsten.

In order to homogenize the sputtering of copper and tungsten, the target was made of a Cu plate 3-inch in diameter with variable number of small W pellets (diameter 0.125 inch) inserted into the erosion track. This target was then mounted on the top of DC magnetron inserted into water cooled cylindrical aggregation chamber terminated with conical orifice 2.0 mm in diameter. The sputtering took place in argon atmosphere at pressures ranging from 20 to 210 Pa and magnetron current of up to 500 mA. It is shown that depending on the number of W pellets in the target and the deposition conditions (magnetron current, pressure and gas flow), nanoparticles with varying ratio between copper and tungsten were obtained. However, it was found that at certain conditions the nanoparticles were trapped in the discharge which greatly reduced their deposition rate. In order to overcome this limitation, a method based on pulsing of the DC power was developed.

Acknowledgements

This work was supported by the grant GACR 17-22016S from the Grant Agency of the Czech Republic.

P10: Chemical Characterization of Group 3-5 Metals Encapsulating Si_{16} Cage Nanoclusters on Organic Surfaces

Toshiaki Kamoshida[1], Masahiro Shibuta[2], Tsutomu Ohta[1], Hironori Tsunoyama[1],
and Atsushi Nakajima[1,2]
[1] Department of Chemistry, Faculty of Science and Technology, Keio University
[2] Keio Institute of Pure and Applied Sciences (KiPAS), Keio University

kamoshida@chem.keio.ac.jp

Abstract:

Metal atom-encapsulating Si_{16} cage nanoclusters ($M@Si_{16}$) are promising superatoms to be applied as functional nanomaterials. In addition to their geometric stability with caged framework, $M@Si_{16}$ is electronically stabilized owing to the superatomic electron-shell closure (68 e^-; each Si atom has 4 valence electrons). Hence, when the group 3 (Sc, Y, Lu), 4 (Ti, Zr, Hf), and 5 (V, Nb, Ta) atoms are chosen as the central metals, they show the halogen-, rare gas-, and alkali-like chemical properties, respectively. Here, we have characterized the chemical states and chemical stabilities for the soft-landed $M@Si_{16}$ (M = Lu, Ti, and Ta) on organic substrates by X-ray photoelectron spectroscopy (XPS).

Figure 1 shows the XPS spectra for $Ta@Si_{16}$ deposited on an *n*-type C_{60} fullerene substrate, where the deposition amount is about. 0.6 monolayer. The Si 2*p* and Ta 4*f* peaks of $Ta@Si_{16}$ are reproduced assuming a single chemical state within the experimental resolution. The result indicates that all Si atoms are homogeneously distributed around the central metal. In the alkali-like $Ta@Si_{16}$, the peak position of Si 2*p* shows the charge state of Si atoms is zerovalent (Si^0), while the Ta 4*f* peak indicates monovalent (Ta^{1+}). Therefore, the overall charge state of $Ta@Si_{16}$ is +1, implying that the deposited $Ta@Si_{16}$ is stabilized by a charge transfer (CT) complexation with *n*-type C_{60} as $(Ta@Si_{16})^+C_{60}^-$ [1]. For the $Ti@Si_{16}$, the overall charge state is in between 0 and +1, which indicates the rare gas-like $Ti@Si_{16}$ is also immobilized by moderate CT interaction with C_{60}. Unlike $Ta@Si_{16}$ and $Ti@Si_{16}$, broad XPS spectra were obtained for $Lu@Si_{16}$, suggesting that the halogen-like $Lu@Si_{16}$ is less stabilized on the *n*-type substrates of C_{60}.

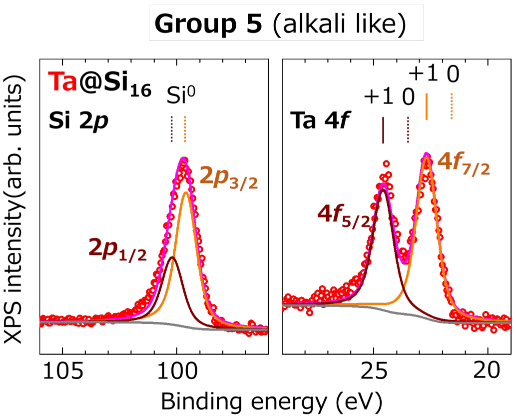


Figure 1. XPS spectra for $Ta@Si_{16}$ deposited on C_{60} substrate.

Reference: [1] T. Ohta, M. Shibuta, H. Tsunoyama, T. Eguchi, and A. Nakajima, J. Phys. Chem. C 120 (2016) 15265–15271.

P11: Silver cluster in ionic liquids of different viscosity – stabilisation and aggregation

Philippe Poulet[1], Florian Lippert[1], Stefanie Roese[1], Alexander Kononov[1] and Heinz Hövel[1]

[1] Fakultät Physik/DELTA, Technische Universität Dortmund, 44227 Dortmund, Germany

philippe.poulet@tu-dortmund.de

Abstract:

Due to their low vapor-pressure, enabling cluster deposition to liquids, Ionic Liquids (IL) gained interest for vacuum application [1]. Due to the relatively high viscosity of the IL at low temperature, the aggregation of deposited clusters is significantly slowed down and the clusters stay separated [2]. However, during cluster deposition a high viscosity hinders the mixing of the clusters into the volume of the IL. For ILs with high viscosity Ag-clusters are deposited by temperatures higher than room temperature to decrease the viscosity of the ILs and the temperature is decreased afterwards for storage.

Via UV/vis-spectroscopy, the aggregation of clusters is measured in-situ and ex-situ for different storage-temperatures. Therefore the refractive indices depending on the wavelength are measured via Fabry-Pérot-Interferometry for the ILs [BMIM] [PF$_6$], [BMIM] [BF$_4$], [BMIM] [TF$_2$N], [BMIM] [DCA], [OMIM] [BF$_6$] and [EMIM] [FAP]. Additionally the temperatures for the melting and freezing points of the above mentioned ILs are determined by measuring transmission.

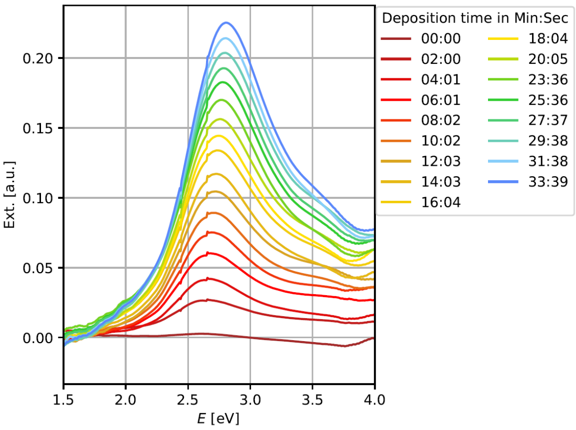


Figure 1: *In-situ UV/vis spectroscopy of Ag clusters deposited into [BMIM] [PF$_6$].*

References:

[1] D. C. Engemann, S. Roese, H. Hövel, J. Phys. Chem. C **120**, 6239, (2016).
[2] S. Roese, A. Kononov, J. Timoshenko, A.I. Frenkel, H. Hövel,
Langmuir (2018), accepted for publication, **DOI:** 10.1021/acs.langmuir.7b03984

P12: Examination of the aggregation of silver clusters in ionic liquids

David Mönkebüscher[1], Alexander Kononov[1] and Heinz Hövel[1]

[1] Fakultät Physik/DELTA, Technische Universität Dortmund, 44227 Dortmund, Germany

david.moenkebuescher@tu-dortmund.de

Abstract:

Nanoparticles offer interesting and different properties in comparison to their bulk version. Due to their instability, they have to be deposited in a stabilizing material.
Ionic liquids, e.g. BMIM-PF$_6$, delay the aggregation of nanoparticles due to their high viscosity and a formation of a cation layer around the clusters, which separates them electrosterically [1]. The temperature dependent aggregation of the nanoparticles can be measured in-situ and ex-situ via UV/vis-spectroscopy [2].
Two different methods are used to examine these silver clusters and their aggregation:
Via atomic force microscopy the nanoparticles in the ionic liquid are scanned on a gold on mica surface, which proves to be difficult due to the high viscosity of the ionic liquids.
Another method to examine the nanoparticles is an exchange of the solvent from the ionic liquid to a liquid with lower viscosity. This can provide information about the way the ionic liquids delay the aggregation, e.g. if a cation layer around the nanoparticles is adsorbed and stays around them, which would continue to delay the aggregation if the solvent is exchanged.

References:

[1] D. C. Engemann, S. Roese, H. Hövel, J. Phys. Chem. C **120**, 6239, (2016).
[2] S. Roese, A. Kononov, J. Timoshenko, A.I. Frenkel, H. Hövel,
Langmuir, (2018), accepted for publication, **DOI:** 10.1021/acs.langmuir.7b03984

P13: Electron Microscopy Characterization of Efficient and Stable Nickel Phosphide Electrocatalyst for Water Oxidation

Xian-Kui Wei[1], Junyuan Xu[2], Yury V. Kolen'ko[2], Marc Heggen[1] and Rafal E. Dunin-Borkowski[1]

[1]Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich GmbH, Jülich 52425, Germany
[2]International Iberian Nanotechnology Laboratory, Braga 4715-330, Portugal

E-mail: m.heggen@fz-juelich

Abstract

Full-water splitting, involving hydrogen and oxygen evolution reactions (HER and OER), provides a promising strategy towards the production of clean and renewable hydrogen energy. However, the implementation of water electrolysis (WE) is challenged by the slow kinetics of OER taking place at the anode. Furthermore, a large-scale implementation of the WE technology is limited by the cost of rare Pt-group-metal-based materials, including RuO_2 and IrO_2. Recently, transition-metal-containing compounds, e.g., oxides, hydroxides and phosphides [1], have been reported to show efficient and stable catalytic performance both in HER and OER, which makes large-scale application of Earth-abundant catalysts for WE more cost-efficient. In this study, the microscopic structures of Ni_2P-$(Mg,Ni)P_xO_y(OH)_z$ nanocomposite catalyst, which show high efficiency and long-time stability in alkaline solution [2], are investigated by using scanning electron microscopy (SEM) and probe-corrected transmission electron microscopy (STEM). Their phase structures and compositional changes are studied in detail by energy-dispersive X-ray spectroscopy (EDS) and other relevant techniques.

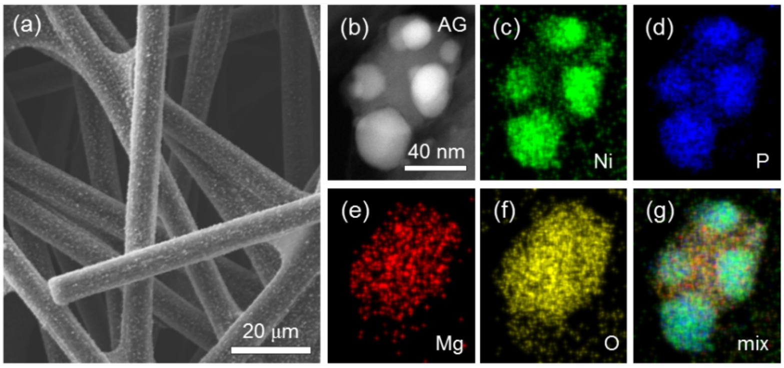


Figure 1. *(a) SEM image of the nanocomposite catalyst. (b) HAADF-STEM image of* Ni_2P *nanoparticles supported by the* $(Mg,Ni)P_xO_y(OH)_z$ *substrate. (c-f) Elemental maps of Ni, P, Mg and O. (g) Composite of the elemental maps.*

[1] Wang, Y., Kong, B., Zhao, D., Wang, H. & Selomulya, C. Strategies for developing transition metal phosphides as heterogeneous electrocatalysts for water splitting. *Nano Today* **15**, 26-55 (2017).

[2] Xu, J. *et al.* Interface engineering in nanostructured nickel phosphide catalyst for efficient and stable water oxidation. *Acs Catal.* **7**, 5450-5455 (2017).

P14: Reactivity of Cu Single Atoms and Mass-Selected Nanoparticles Correlated with their CO Electroreduction Activity

Jakob Ejler Sørensen[1], Niklas Mørch Secher[1], Søren Bertelsen Scott[1], Jakob Kibsgaard[1], and Ib Chorkendorff[1]

[1]Surface Physics and Catalysis, Department of Physics, Fysikvej, Building 312, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

jejsor@fysik.dtu.dk

Abstract:

Copper exhibits very interesting activity and selectivity in electrochemical reduction of CO_2 to products with two or more carbon atoms. This selectivity depends highly on the structure of the catalyst. In pursuit of understanding this, a module has been designed to make temperature-programmed desorption of CO (CO-TPD) on Cu samples prepared using a magnetron sputter head and mass-selection of gas-aggregated nanoparticles as done previously with Pt[1]. This will give a direct measure of the reactivity of the sample surface towards the first reaction intermediate. Coupled with elemental composition characterization using X-ray photoelectron spectroscopy (XPS) and low-energy ion scattering spectroscopy (LEIS), this gives a more unique fingerprint used for comparing the activity of individual samples. Based on the high CO binding energy and correlated activity of oxide-derived Cu[2], it is the hope that some unique fingerprints of model systems will be identified and correlated with the activity tested using electrochemistry – mass spectrometry (EC-MS)[3]. All characterization is done within the same UHV system and is only exposed to air intentionally or prior to activity testing. In this study, we focus on the reactivity of Cu single atoms and mass-selected nanoparticles on glassy carbon.

References:

[1] F. J. Perez-Alonso, D. N. McCarthy, A. Nierhoff, P. Hernandez-Fernandez, C. Strebel, I. E. L. Stephens, J. H. Nielsen, and I. Chorkendorff. The effect of size on the oxygen electroreduction activity of mass-selected platinum nanoparticles. *Angewandte Chemie*, 51:4641–4643, 2012. doi: 10.1002/anie.201200586.

[2] A. Verdaguer-Casadevall, C. W. Li, T. P. Johansson, S. B. Scott, J. T. McKeown, M. Kumar, I. E. L. Stephens, M. W. Kanan, and I. Chorkendorff. Probing the active surface sites for co reduction on oxide-derived copper electrocatalysts. *Journal of the American Chemical Society*, 137:9808–9811, 2015. doi: 10.1021/jacs.5b06227.

[3] D. B. Trimarco, S. B. Scott, A. H. Thilsted, J. Y. Pan, T. Pedersen, O. Hansen, I. Chorkendorff, P. C. K. Vesborg. Enabling real-time detection of electrochemical desorption phenomena with sub-monolayer sensitivity. *Electrochimica Acta*, 268:520-530, 2018. doi: 10.1016/j.electacta.2018.02.060

P15: Silica/Carbon dots-composites as detectors of pollutive organic substances

Asmira Delic[1], Erik Dobloug Roede[1], Maria Benemekki[1]

[1]Department of Materials Science and Engineering, NTNU Norwegian University of Science and Technology, NO-7491 Trondheim, Norway

asmira.delic@ntnu.no

Abstract:

Intrinsically fluorescent carbon dots may form the basis for a safer and more accurate detector technology for pollutive organic substances. This work presents a new generation of environmentally friendly nanodetectors based on carbon dots (CD) embedded in porous silica particles. When organic substance is trapped in the silica pores, the refractive index of the medium surrounding the CDs will change, inducing changes in the optical response of the CDs. These changes can be monitored and used to detect the presence of organic substances.

A facile two-step aqueous rout yields photoluminescent silica/carbon dots (SiO_2/CD) composite. First, porous silica is hydrothermally synthesized by a modified Stöber method, according to Benelmekki et al. [1]. Thereafter, carbon dots are hydrothermally synthesized, with citric acid and urea as precursors [2], on the surface and in the pores of the silica spheres.

Characterization of the SiO_2/CD reveals successful loading of the carbon dots onto silica spheres. Transmission electron microscopy images show silica spheres with a diameter of 450 nm, decorated by carbon dots, 50 nm in diameter. The SiO_2/CD spheres were sliced with focused ion beam (FIB). Images of the interior were collected by scanning electron microscopy, showing hollow silica spheres. The UV-Vis absorption spectrum reveals absorption bands located at ~ 330 nm and at ~ 520 nm, attributed to the carbon dots and silica, respectively. Intense photoluminescence was observed from the SiO_2/CD composite material upon irradiation by a 356 nm UV lamp.

References:

[1] Benelmekki, M., et al., *Design and characterization of Ni2+ and Co2+ decorated Porous Magnetic Silica spheres synthesized by hydrothermal-assisted modified-Stöber method for His-tagged proteins separation.* Journal of Colloid and Interface Science, 2012. **365**(1): p. 156-162.

[2] Li, X., et al., *Engineering surface states of carbon dots to achieve controllable luminescence for solid-luminescent composites and sensitive Be2+ detection.* Scientific Reports, 2014. **4**: p. 4976.

P16: Electron Microscopy Characterization of GaN Nanowires grown on Graphene

Inger-Emma Nylund[1], Dingding Ren[2], Helge Weman[2], Bjørn-Ove Fimland[2],
and Antonius T. J. van Helvoort[3]
[1]Department of Materials Science and Engineering, NTNU, Trondheim, Norway
[2]Department of Electronic Systems, NTNU, Trondheim, Norway
[3]Department of Physics, NTNU, Trondheim, Norway
inger-emma.nylund@ntnu.no

Combining graphene with III-V semiconductors can result in a novel heterostructure interesting for device application [1]. Here we present a structural electron microscopy study of GaN nanowires (NWs) grown on graphene using molecular beam epitaxy (MBE). Scanning electron microscopy (SEM) and different transmission electron microscopy (TEM) techniques have been used.

To initiate the GaN NW growth on graphene, an AlN nucleation layer is used [2]. The NWs presented in this contribution have a distinct AlN nucleation particle at the bottom. The NWs were found to be quite evenly distributed on the substrate, and of approximately the same length (ca. 400 nm). Their cross-sectional shape varied from thin (< 40 nm) perfect hexagonal, to thicker (40~70 nm) distorted hexagonal, to coalesced into larger clusters. The AlN nucleation particles are dome-shaped with a typical height of 10-15 nm. Only limited GaN growth around the base of the AlN nucleation particles was observed compared to metal-organic vapor phase epitaxy grown GaN nanorods on an AlN nucleation layer [2]. It is assumed that the even distribution of AlN nucleation particles causes the even distribution of NWs. These findings indicate that the AlN particles can control the size, distribution, and shape of the GaN NWs. Although the AlN nucleation particles seem to be essential to initiate and control GaN NW growth on graphene, the relatively high band gap poses challenges for the use of these graphene/AlN/GaN NW heterostructures for device applications [2].

The studied single NWs can be categorized. The NWs of type I (diameter > 40 nm) and II (diameter < 40 nm) are considered to be closest to the targeted structure, with a single NW growing from a single nucleation particle. Furthermore, both types are defect-free wurtzite GaN above the nucleation particle. The type III NW is a single NW grown from multiple nucleation particles, creating a base of AlN particles. Type III has approximately the same length as type I and II, but the diameter is in general larger, and varies more (from ~40 nm to ~110 nm). The type III NWs are also defect-free wurtzite above the base.

Compositional analysis was performed using energy-dispersive spectroscopy, which confirmed the AlN composition of the nucleation particle. HAADF-STEM images and diffraction patterns were obtained at two different zone axes rotated 30° relative to each other for all the studied NWs. This approach gave additional structural and morphological information. For example, these tilt series could determine that the wurtzite GaN NW facets are {1100}, and not {2110} as commonly observed in Au-catalyzed wurtzite GaAs NWs [3].

References:

[1] A. Mazid Munshi and H. Weman, "Advances in Semiconductor Nanowire Growth on Graphene", physica status solidi (RRL) - Rapid Research Letters **7**, 713-726 (2013).

[2] M. Heilmann, A. M. Munshi, G. Sarau, M. Gobelt, C. Tessarek, V. T. Fauske, A. T. J. van Helvoort, J. F. Yang, M. Latzel, B. Hoffmann, G. Conibeer, H. Weman, and S. Christiansen, "Vertically Oriented Growth of GaN Nanorods on Si using Graphene as an Atomically Thin Buffer Layer", Nano Letters **16**, 3524-3532 (2016).

[3] J. Todorovic, "Correlated Transmission Electron Microscopy and Micro-photoluminescence Studies of GaAs-based Heterostructured Semiconductor Nanowires", *Doctoral thesis at NTNU, 2012:319*, NTNU-trykk, 2012.

P17: O_2 saturation on Cu_{55} cluster and CO oxidation with different oxygen coverages on Cu_{55}/Al_2O_3

Li Ma[1] and Jaakko Akola[1,2]

[1]Department of Physics, Tampere University of Technology, FI-33101 Tampere, Finland
[2]Department of Physics, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway

li.ma@tut.fi

Abstract:

The adsorption of multiple O_2 molecules on Cu_{55} cluster has been investigated by spin-polarized density functional theory. The optimal structure of each $Cu_{55}(O_2)_N$ (N = 1-20) complex is obtained systemically via a sequential adding of O_2 units. The number of O_2 units that binds molecularly and spontaneously dissociate on the cluster has been determined. Through the calculation of the adsorption energy for each successive O_2 addition, the fully saturated structure arrived at N = 19 with twelve molecular O_2 units and seven dissociated units $[Cu_{55}(O_2)_{12}(O)_{14}]$. The stepwise dissociation of O_2 has been considered further. The O_2 molecule dissociates easily on $Cu_{55}(O)_{2N}$ regardless of the oxygen coverage. Ab initial molecular dynamics simulations at 300 K confirm the easy dissociation of O_2 molecule and the easy movement of oxygen from surface to interior. Furthermore, CO oxidation reactions [1, 2] have been studied according to the different oxygen coverages. The isolated $Cu_{55}(O)_{2N}$ and the $Cu_{55}(O)_{2N}$ on Al_2O_3 substrate are considered to compare the supporting effect for the catalytic activity. The reaction barriers of CO oxidation decrease with the oxygen coverages increase on both $Cu_{55}(O)_{2N}$ and $Cu_{55}(O)_{2N}/Al_2O_3$. In addition, the lower reaction barriers on $Cu_{55}(O)_{2N}/Al_2O_3$ than those on $Cu_{55}(O)_{2N}$ indicate the importance of oxide support for the catalytic activity of metal clusters.

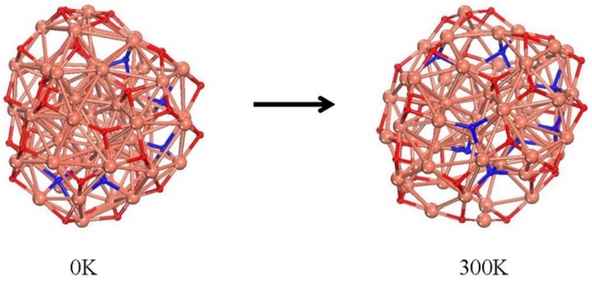


Figure 1: *Geometries of $Cu_{55}O_{40}$ with surface and endohedral oxygen atoms (red and blue color, respectively) at 0 K and 300 K.*

References:

[1] Bu Y, Niemantsverdriet J W H and Fredriksson H O A 2016 *ACS Catal.* **6** 2867.
[2] Ma L, Melander M, Laasonen K and Akola J 2015 *Phys. Chem. Chem. Phys.* **17** 7067.

P18: Ammonia decomposition over Ru/Al_2O_3 catalyst: Theoretical and experimental studies

Jianguang Wang[1], Hans Fredriksson[2], and Jaakko Akola[1,3,*]

[1] Tampere University of Technology, 33101 Tampere, Finland
[2]SynCat@DIFFER, Syngaschem BV, P.O. Box 6336, 5600 HH Eindhoven, Netherlands
[3] Norwegian University of Science and Technology, 7491 Trondheim, Norway

Email: jianguang.wang@tut.fi

Abstract:
Decomposition of NH_3 over Ru/Al_2O_3 catalyst for hydrogen and nitrogen production is studied theoretically and experimentally. A square-base pyramidal Ru_{30} cluster on γ-Al_2O_3 (100) surface, as a representative, is considered as a model structure catalyst used for the theoretical simulations. First-principles calculations is firstly performed to determine the adsorption of NH_x (x=0-3) and N_2H species, and identify the transition states of all considered reactions over Ru_{30}/Al_2O_3 catalyst. Comparing with the N recombination reaction, the energy barrier of generation N_2 molecule by the reaction of NH_2 attacking N_2H ($N_2H+NH_2=N_2+NH_3$) decreases greatly, ~1.20 eV. Thus, the N_2 formation is not the rate determining step in the present study. Microkinetic modeling is further applied to estimate the temperature dependence of NH_3 conversion, N_2 and N_2 yields according to the experimental conditions. The apparent activation energy obtained in this study (68.4 kJ/mol) is in good agreement with the previous experimental value (Ru/Al_2O_3 64.6 kJ/mol).[1] The theoretical simulation results are further verified from our experimental investigation.

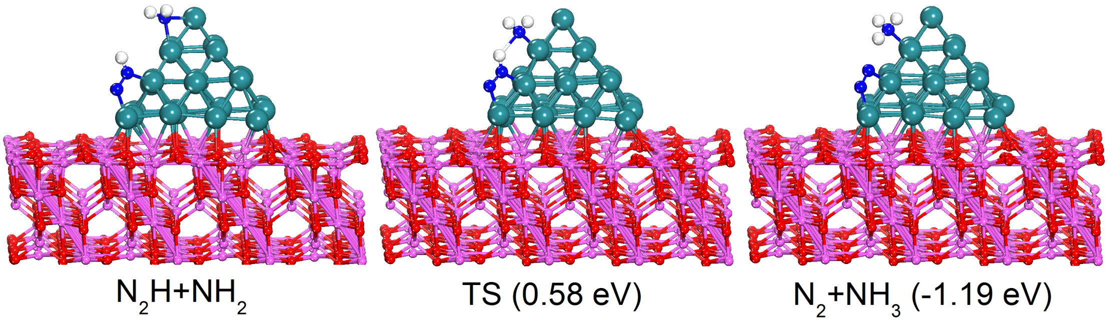


Figure 1. *The initial state, transition state, and final state of the lowest identified pathway for the reaction* $N_2H+NH_2=N_2+NH_3$ *on* $Ru_{30}/Al_2O_3(100)$ *with the energy changes with respect to the initial state. Color key: Ru, dark green; H, white; N, blue; O, red; Al, pink.*

References:

[1] S. Yin, Q. Zhang, B. Xu, W. Zhu, Z. Ng, and C. Au, J. Catal. **224** (2004) 384.

P19: Density functional study of hydrogen adsorption on 55-atom Pt-Ni nanoclusters

Olli Ahlstedt[1] and Jaakko Akola[1,2]

[1]Laboratory of Physics, Tampere University of Technology, 33720 Tampere, Finland
[2]Department of Physics, Norwegian University of Science and Technology, 7491 Trondheim, Norway

olli.ahlstedt@tut.fi

Abstract:

Density functional theory calculations were performed on small 55-atom Pt-Ni nanoclusters to study their activity towards the hydrogen evolution reaction (HER). Two Pt_nNi_{55-n} compositions, $Pt_{12}Ni_{43}$ and $Pt_{20}Ni_{35}$, were studied in the gas phase and on an Al_2O_3 support. The critical hydrogen coverages were determined using the method based on the differential free energy of hydrogen adsorption. The free energy of hydrogen adsorption, ΔG_{H*}, was used as a descriptor of the HER activity.

Ni_3 hollow sites were discovered to be the strongly binding sites for hydrogen. The clusters adsorb approximately four H atoms per facet before the hydrogen adsorption becomes endergonic, therefore the critical hydrogen coverages on the clusters are high. The obtained ΔG_{H*} descriptor values are smaller than 0.1 eV in the gas phase and on the support, suggesting that the clusters are catalytically active towards HER.

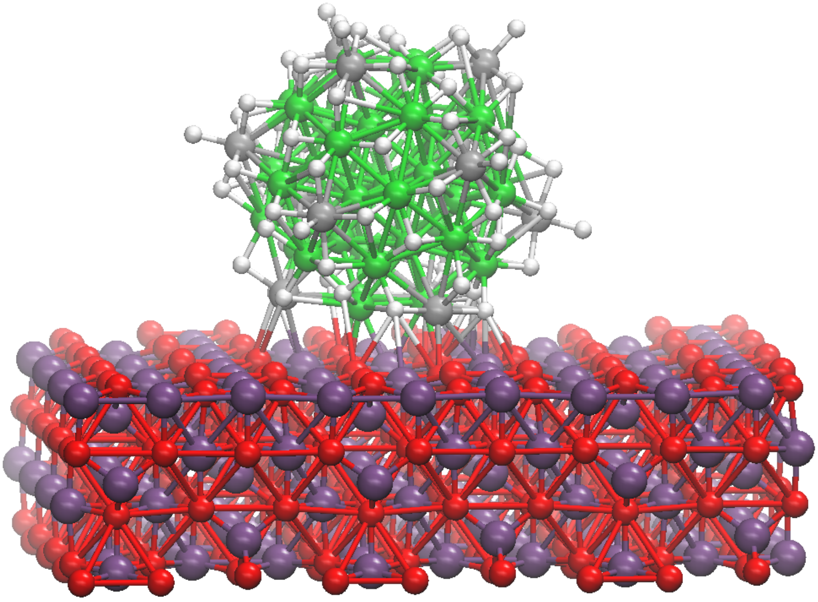


Figure 1: *The hydrogen covered $Pt_{12}Ni_{43}$ cluster aligned on the alumina support.*

P20: Magneto-plasmonic Nanoparticles for Biomedical Applications

Anuvansh Sharma and Maria Benelmekki

Department of Materials Science and Engineering, Norwegian University of Science and Technology (NTNU), 7491, Trondheim, Norway

anuvansh.sharma@ntnu.no

Abstract:

The use of magnetic and plasmonic nanoparticles (NPs) has substantially been explored in the medical industry. However, in order to extract multiple functionalities from a single nanoparticle, heterodimeric NPs have attracted immense interest as ideal materials for future biomedical applications[1]. Having multifunctional attributes, enable these materials to be used simultaneously for applications such as sensing[2], targeted drug delivery, imaging[3] and so on. Upon uniting the characteristic properties of individual entities into one particle, leads to precision and efficacy of therapeutics.

Combining the magnetic properties of iron oxide NPs as well as the optical properties of silver NPs would open new possibilities for precise crosschecking of the response signal, easier separation, increased reusability, to name a few, thereby reducing both measuring time and material wastage. The combination of optical and magnetic properties in a single composite nanostructure would enable simultaneous and precise diagnosis at each part. Many efforts have been dedicated to the synthesis of these heterogeneous NPs. However, the growth mechanism that plays a vital role in the coherent design and precise fabrication of such particles, for the desired end use, has not been largely explored. Herein, we try to understand the growth of silver on the surface of iron oxide (magnetite) NPs via the epitaxial growth model, thereby finally leading to heterodimeric (dumbbell) structures and their subsequent application.

References

1. Jiang, J., et al., Bifunctional Fe_3O_4–Ag Heterodimer Nanoparticles for Two-Photon Fluorescence Imaging and Magnetic Manipulation. Advanced Materials, 2008. **20**(23): p. 4403-4407.
2. Kumar, D.R., D. Manoj, and J. Santhanalakshmi, Au–ZnO bullet-like heterodimer nanoparticles: synthesis and use for enhanced nonenzymatic electrochemical determination of glucose. RSC Advances, 2014. **4**(18): p. 8943-8952.
3. Xie, J., et al., Manipulating the power of an additional phase: a flower-like Au−Fe_3O_4 optical nanosensor for imaging protease expressions in vivo. Acs Nano, 2011. **5**(4): p. 3043-3051.

P21: Single-atom and Dimer Pt Catalysts Supported by Graphene Nanomaterials: Quantum Chemical Calculations

Mehdi Mahmoodinia[1], Per-Olof Åstrand[1], and De Chen[2]

[1]Department of Chemistry, and [2]Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway

Mehdi.mahmoodinia@ntnu.no

Abstract:

In recent years, the research interest on materials for catalytic applications are focused on designing highly efficient catalyst with lower content of precious metals. Platinum (Pt)-based catalysts are among the most utilized catalysts in fuel cell technologies, despite their high price and poor utilization efficiency. To get a higher efficiency, downsizing of bulk catalysts to nanoparticles, small clusters, and even to single atom catalysts is highly desirable. Support materials play an important role for stabilizing these particles. A fundamental understanding of the interface between these particles and their support materials has been the subject of many theoretical and experimental works in recent years. We recently studied the structural, electronic, and catalytic properties of transition metal catalysts supported by graphene nanomaterials using density functional theory calculations [1-4]. The charge transfers through the interface and its impact on the catalytic properties of the supported catalysts were among the main challenges. It is found that functionalization of graphene support using oxygen-containing groups has a large effect on the stability and the catalytic activity of the Pt/C catalysts, and it can also be used as a method for improving their resistance toward CO poisoning.

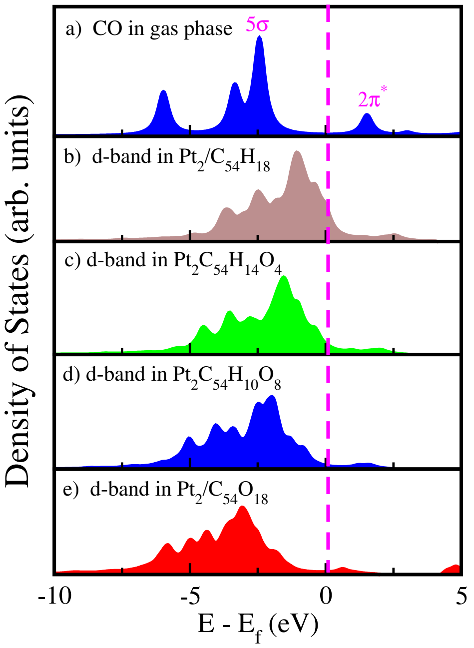


Figure 1: *Density of states of (a) gas phase CO molecule, d-band of the Pt dimer supported by (b) the polyaromatic hydrocarbons (PAH) surface, (c–e) the edge-oxidized PAH surfaces.*

References:

[1] M. Mahmoodinia, M. Ebadi, P.-O. Åstrand, D. Chen, et al., Phys. Chem. Chem. Phys. 2014, 16, 18586.
[2] M. Mahmoodinia, P.-O. Åstrand, D. Chen, J. Phys. Chem. C 2015, 119, 24425
[3] M. Mahmoodinia, P.-O. Åstrand, D. Chen, J. Phys. Chem. C 2016, 120, 12452.
[4] M. Mahmoodinia, P.-O. Åstrand, D. Chen, J. Phys. Chem. C 2017, 121, 20802.