

O 29: Nanostructures at Surfaces III: Dots, Particles, and Clusters

Time: Tuesday 10:30–13:00

Location: H25

O 29.1 Tue 10:30 H25

Negative differential resistance in the electron-transport through cuprous oxide thin films — ●ALEXANDER GLOYSTEIN and NIKLAS NILIUS — Institute of Physics, Carl von Ossietzky University, 26111 Oldenburg, Germany

Copper nano-islands grown on Cu₂O(111) thin films have been investigated by scanning tunneling microscopy and spectroscopy. The latter reveals pronounced lateral quantization effects in the Cu 4sp states, reflecting the finite island size. Below the onset of the quantized states, a wide region of negative differential resistance (NDR) opens up in the tunneling spectra. The effect is explained with the development of p-type conductance in the Cu₂O films below the ad-copper, which promotes electron transport at small negative bias but leads to a sudden closure of transport channels below a critical bias of -1.0 V. The resulting NDR effect exhibits an on/off current that is larger than in common molecular junctions and might qualify this inorganic system for applications.

O 29.2 Tue 10:45 H25

Ultrafast librations of supported nanoclusters studied with femtosecond electron diffraction — ●THOMAS VASILEIADIS¹, EMANUEL SKOUNTZOS², DAWN FOSTER³, SHAWN COLEMAN⁴, DANIELA ZAHN¹, VLASIS MAVRANTZAS², RICHARD PALMER⁵, and RALPH ERNSTORFER¹ — ¹Fritz-Haber-Institut, Faradayweg 4-6, 14195 Berlin, Germany — ²Department of Chemical Engineering, University of Patras — ³Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom — ⁴US Army Research Laboratory, Weapons and Materials Research Directorate — ⁵College of Engineering, Swansea University, Bay Campus, Fabian Way, Swansea SA1 8EN, United Kingdom

Femtosecond electron diffraction (FED) [1] can be used to probe ultrafast atomic motions in laser-excited bulk solids and nanoscale heterostructures [2]. In this work we show that, due to the sensitivity of diffraction in the crystal orientation, FED is sensitive to rotations of nanoclusters on a membrane. The investigated samples are size-selected Au nanoclusters with a partial (111) orientation on few-layer graphite. Optical excitation brings the nanoclusters and the substrate in non-equilibrium conditions. Due to substrate phonons, Au NCs perform ultrafast, constrained rotations, termed librations, which change the relative intensities of the various diffraction peaks in the picosecond timescale. References: [1] Waldecker et al. JAP 117, 044903 (2015). [2] Vasileiadis et al. ACS Nano 12 (8),7710-7720 (2018).

O 29.3 Tue 11:00 H25

Virtual Plasmonic Dimers of Silver Nanoparticles on Si(111)-(7x7) unraveled by Size-Correlated Single-Object Photoemission — ●KEVIN OLDENBURG¹, HANNES HARTMANN¹, JEAN LERME², KARL-HEINZ MEIWES-BROER¹, SYLVIA SPELLER¹, and INGO BARKE¹ — ¹University of Rostock, Institute of Physics, 18059 Rostock, Germany — ²Université de Lyon, Institut Lumière Matière, 69622 Villeurbanne Cedex, France

Single object spectroscopy is capable of unravelling individual features of clusters at surfaces. Here we show that for highly polarizable substrates the frequently applied picture of an "effective" dielectric medium surrounding each particle falls short due to coupling of the particle plasmon with its image dipole [1,2]. Silver nanoparticles deposited on Si(111)-(7x7) are investigated by using PEEM, thus probing a large number of particles simultaneously. We show that even for sizes as small as 10 nm the dipole approximation breaks down, because the system inherently creates higher-order multipole modes [3]. Model calculations based on Generalized Mie theory [2] reveal that the formation of multipole modes is extremely sensitive to the local geometry on the scale of one Angström, expressed by the effective intra-dimer separation. On the one hand this leads to a fundamentally limited control over particle plasmon energies. On the other hand selective excitation enables tailored energy transfer into molecular aggregates by utilizing certain metal nanoparticles as nanoscopic light sources.

[1] Knight et al., Nano Letters 9, 2188 (2009) [2] Lermé et al., J. Phys. Chem. C 117, 6383 (2013) [3] Oldenburg et al., under review

O 29.4 Tue 11:15 H25

In-situ monitoring of nanoparticle generation in plasma — ●OLEKSANDR POLONSKYI, JONAS DREWES, ALEXANDER VAHL, THOMAS STRUNSKUS, and FRANZ FAUPEL — Chair for Multicomponent Materials, Faculty of Engineering, Kiel University, Germany

The unique properties of nanoparticles (NPs) associated with their dimensions make them very attractive for the growing field of nanotechnology. The methods of their synthesis allowing a simple and reliable tuning of NP dimensions as well as chemical structure are in a high demand. Here, we focus on a plasma based approach for generation of metallic NPs utilizing a magnetron sputtering operating at a relatively high gas pressure (~100 Pa). This method became very attractive for NP generation providing the ability to deposit various types of NPs with good control over size and size distribution. However, the processes during NP formation in plasma are not fully understood yet and require more advanced in-situ methods to follow NP growth. Here we report on the investigation of the initial stages of metallic NP growth in a gas phase by broadband transmission UV-Vis spectroscopy. We demonstrate that due to their strong particle plasmon resonance, small clusters and NPs can be monitored by UV-Vis spectroscopy in-situ during growth and transport. We found that small clusters are already generated in the region close to the magnetron target surface. Our measurements indicate that a high concentration of nanoparticles is located near the magnetron because of trapping in a plasma volume.

O 29.5 Tue 11:30 H25

Elucidating morphology changes in MgO supported Palladium nanoparticles — ●JAN-CHRISTIAN SCHOBER^{1,2}, SIMON CHUNG¹, VEDRAN VONK¹, and ANDREAS STIERLE^{1,2} — ¹Deutsches Elektronensynchrotron Hamburg — ²Universität Hamburg, Fachbereich Physik

Noble metals are of great importance in heterogeneous catalysis of CO oxidation and NO_x reduction. While already existing practical applications usually consist of oxide supported nanoparticles, oxidation behaviour and the precise catalytic processes occurring are still not completely understood on the atomic scale.

It was shown that at elevated temperature and in oxygen atmosphere palladium nanoparticles undergo a reversible shape change [1], however the time-scale and energetics of this process are still unknown. We aim to build on the results of this study and elucidate the formation and diminishing of the {112} facets in oxygen atmospheres ranging from ultra-high-vacuum to 1 bar and temperatures from 300 K to 900 K in order to establish a phase diagram of the particle morphology. Observing the intensity of the {111} and {112} facet in a diffraction experiment allows to determine the conditions at which the phase change occurs as well as the relative size of the facets.

[1] P. Nolte et al., Nano Lett. 1, 4697-4700 (2011)

O 29.6 Tue 11:45 H25

Understanding charge transfer and electronic polarization of Au nano-catalysts supported on reduced TiO₂(110) surfaces — ●SU-HYUN YOO¹, NIKLAS SIEMER², MIRA TODOROVA¹, DOMINIK MARX², and JÖRG NEUGEBAUER¹ — ¹Department of Computational Materials Design, Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany — ²Lehrstuhl für Theoretische Chemie, Ruhr Universität Bochum, 44780 Bochum, Germany

Gold nanoparticles on TiO₂(110) surfaces containing oxygen vacancies are of great interest due to their catalytic activity respective oxidation reactions, such as the water gas shift reaction, the CO oxidation reaction and others. Despite extensive studies, the nature of the interactions between oxygen vacancy, substrate and the gold nanoparticle remains controversial, which hampers an understanding of the catalytic mechanism. Combining ab-initio molecular dynamics calculations with methods developed in semiconductor physics to study defects, we investigate the interactions between the vacancy and the nanoparticle for a representative set of density-functionals theory (DFT) exchange-correlation functionals (PBE, PBE+U and two hybrid functionals). The obtained band diagrams allow us to discuss the direction of charge transfer between the nanoparticle and the substrate. Despite the differences of the constructed band diagrams from the employed functionals, we consistently find the absence of charge transfer between the vacancy and the cluster, as well as a positive charging of the Au nanoparticle.

The obtained results and their implication for the role of the vacancy in the catalytic system will be discussed.

O 29.7 Tue 12:00 H25

Template-Guided Programmable Janus Heteronanostructure Arrays for Efficient Plasmonic Photocatalysis — ●ZHIQIANG ZENG, RUI XU, and YONG LEI — Institut für Physik & IMN Macro-Nano* (ZIK), Technische Universität Ilmenau, 98693, Ilmenau, Germany

Abstract: Janus heteronanostructures (HNs) could facilitate synergistic coupling of diverse functions inherited by their comprised nanocomponents. Nowadays, synthesizing deterministically targeted Janus HNs remains a challenge. Here, a general yet scalable technique is utilized to fabricate an array of programmable Janus HNs based on binary-pore anodic aluminum oxide templates. The binary-pore anodic aluminum oxide templates provide high degrees of design freedom for both nanocomponents of the Janus HNs, including morphologies, compositions, dimensions, and interfacial junctions. Arrays of TiO₂-Au and TiO₂/Pt NPs-Au Janus HNs are prepared and demonstrated about 2.2 times photocurrent density and 4.6 times hydrogen evolution rate of that obtained from their TiO₂ counterparts. The enhancement was mainly due to localized surface plasmon resonance induced direct hot electron injection and strong plasmon resonance energy transfer near the interfaces of TiO₂ nanotubes and Au nanorods. This study may represent a promising step forward to pursue customized Janus HNs, leading to novel physicochemical effects and device applications.

O 29.8 Tue 12:15 H25

Structure and surface energies of nanoparticles from atomistic simulations — ●DAVID HOLEC¹, FRANZ FISCHER², and DIETER VOLLATH³ — ¹Department of Materials Science, Montanuniversität Leoben, Austria — ²Franz-Josef-Strasse 18 — ³NanoConsulting, Stutensee, Germany

Nanoparticles are fascinating objects not only from the point of view of diversity of their applications but also from the basic research perspective. In this contribution we review our recent activities directed towards revealing structure and surface energy of Au₅₅ nanoparticle. It turns out that an amorphous structure possesses lower energy than a crystalline or well ordered structure. In this context, the two step process to increase the thermal stability should be mentioned. This process is a new, until now, never described phenomenon. Further on, we shown that surface energy changes dramatically as a function of the radius, in particular for a particle with small effective radius such as Au₅₅. This small change of radius is physically corresponding to the presence of an electronic cloud surrounding atomic radii. By calibrating our calculations to bulk fcc Au mass density we propose that the radius should be about increased by 0.13 nm as compared to convex hull of only ionic positions. Eventually, this correction of the surface energy radius makes is possible to put the contradictory trends from theory (surface energy increases with decreasing particle

size) and experiment (surface energy decreases with decreasing particle size) onto a common ground, finally yielding only a slight-to-no particle size dependence.

O 29.9 Tue 12:30 H25

Soft Epitaxial Superlattices of PbS Nanocrystals — ●SANTANU MAITI^{1,2}, ALEXANDER ANDRÉ³, SONAM MAITI^{2,3}, MARTIN HODAS², MACIEJ JANKOWSKI⁴, MARCUS SCHEELE³, and FRANK SCHREIBER² — ¹Institute of Complex Systems, Forschungszentrum Jülich, Germany — ²Institute of Applied Physics, University of Tübingen, — ³Institute of Physical and Theoretical Chemistry, University of Tübingen, Germany — ⁴ID10, European Synchrotron Radiation Facility, France

We prepare templates of atomically coherent, ordered superlattices of PbS NCs, coupled with copper tetraaminophthalocyanines (CuTAPc) molecules [1,2]. PbS NCs of different sizes/shapes are deposited on the surface of templates and the adlayer superlattices are further functionalized with CuTAPc [2]. Here, we investigate the structure of the templates as well as the adlayer NC assemblies by using grazing-incidence small angle x-ray scattering (GISAXS), grazing incidence x-ray diffraction (GIXD) and electron microscopy [3]. The deposited NCs self-assemble not only into ordered superstructures (sc, bcc), but also into a preferred atomic orientation with respect to the templates. Moreover, after functionalization, the bcc superlattices undergo a remarkable orientational change from [110]SL to [100]SL via lattice reconstruction. These results provide new insight into the coherent design of epitaxial nanostructures with desired crystallographic orientation [4,5]. [1] M. Scheele et al, PCCP 2015, 17, 97; [2] S. Maiti et al, JPCL 2018, 9, 739-744; [3] S. Maiti et al, JPCM 2017, 29, 095101; [4] S. M. Rupich et al, Nat Commun. 2014, 5, 5045; [5] M. X. Wang et al, ACS Nano 2017, 11, 180-185.

O 29.10 Tue 12:45 H25

Studying Copper Growth on Zinc Oxide Utilizing a Neural Network Potential — ●MARTÍN LEANDRO PALEICO and JÖRG BEHLER — Universität Göttingen, Theoretische Chemie, Tammannstr. 6, 37077 Göttingen, Germany

The catalyst used in the industrial synthesis of methanol is composed of large copper and zinc oxide nanoparticles. Studying this system requires a simulation method capable of handling thousands of atoms with ab initio accuracy, but with computational efficiency comparable to classical force fields. For this purpose, a Neural Network Potential (NNP) has been trained to reproduce the potential energy surface of the system, making use of DFT calculations as reference data.

The current work focuses on results for model ternary copper-zinc oxide system. Specifically, we investigate the growth of copper clusters and films on zinc oxide surfaces using both grid and grid-free basin hopping Monte Carlo simulations, entrenching of clusters at elevated temperatures and under an indentation force, and the behavior of copper and zinc oxide interfaces at high temperatures.