

O 46: Nanostructures and Clusters

Time: Wednesday 10:30–12:30

Location: H45

O 46.1 Wed 10:30 H45

***MSi_nH_n* aggregates: from simple building blocks to highly magnetic functionalized materials** — ●DENNIS PALAGIN and KARSTEN REUTER — TU München

The use of multi-doped endohedral Si clusters as building blocks for assembly at the nanometer scale has attracted much attention due to promising cage-like geometries and easy-to-tune electronic properties [1]. For instance, in these structures the high magnetic moments of transition metal dopants can be preserved through minimizing the cage-dopant interaction by hydrogen termination [2]. A variable amount of hydrogen atoms may be used to control the number of bonding sites of the cluster, to which another cage can be attached. With a tool box of monomers with differing numbers of "docking sites", it seems possible to build network architectures of any morphology. Here we scrutinize this proposition through density-functional theory based global geometry optimization. Our results show that, unlike in case of typical clathrate structures, *MSi₂₀H₂₀* clusters tend to aggregate through the formation of double Si-Si "bridges" between the monomers. Intriguingly, such aggregates possess very high magnetic moments due to their virtually isolated dopants. We screen a larger range of possible oligomers and critically discuss the resulting geometrical and electronic structures.

- [1] T. Iwasa and A. Nakajima, *J. Phys. Chem. C* **116**, 14071 (2012).
 [2] D. Palagin and K. Reuter, *Phys. Rev. B* **86**, 045416 (2012).

O 46.2 Wed 10:45 H45

A full-dimensional and reactive neural network potential for water clusters based on first-principles — ●TOBIAS MORAWIETZ and JÖRG BEHLER — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Artificial neural networks (NNs) provide an unbiased way to construct accurate interatomic potentials for a wide range of systems [1]. For this purpose a set of energies and forces obtained from electronic structure calculations is interpolated. The obtained NN potential can be evaluated several orders of magnitude faster than the underlying electronic structure data allowing to perform accurate simulations on extended length and time scales. Here, we report a full-dimensional NN potential for water clusters containing up to ten water molecules trained to density-functional theory (DFT) data [2,3]. Unlike other potentials for water based on first-principles, our potential is not constructed employing a truncated many-body expansion and is thus able to describe reactions involving proton transfer. Binding energies for global and local minima obtained with the NN potential typically deviate by less than 1% from the DFT values.

- [1] J. Behler, *PCCP* **13**, 17930 (2011).
 [2] T. Morawietz, V. Sharma, and J. Behler, *JCP* **136**, 064103 (2012).
 [3] T. Morawietz and J. Behler, submitted (2012).

O 46.3 Wed 11:00 H45

First-principles study of the interaction and charge transfer between gold clusters and TiO₂ nano-structures — ●CHUNSHENG LIU, RAN JIA, HARALD OBERHOFER, and KARSTEN REUTER — TU München, Germany

Recent experimental studies of catalysis on small (TiO₂)_m-Au_n hetero-clusters [*J. Phys. Chem. A* **115**, 11479 (2011)] have opened up a new direction in the search for efficient, yet stable (photo-)catalysts for reactions such as CO oxidation or water splitting. They have shown a strong dependence of the reactivity on the atomic stoichiometry of the catalyst clusters, including an especially pronounced even/odd behavior with respect to the number of Au atoms. In our contribution we discuss our findings - gained from *ab initio* global geometry optimization - leading to a theoretical understanding of the observed properties of nano-scale (TiO₂)_m-Au_n hetero-clusters. Analogous to experiment, we find an even/odd behavior of the coated clusters' HOMO-LUMO gap and charge transfer from the coating Au atoms, which in turn influences the clusters' reactivities. Finally, we compare these properties of the (TiO₂)_m-Au_n hetero-clusters to those of small gold Au_n particles adsorbed on extended TiO₂ surfaces, in order to gauge how much of the observed behavior is due to the limited size of the TiO₂ substrate cluster.

O 46.4 Wed 11:15 H45

Substrate-dependent dynamics of truly monodisperse Pd clusters under the STM — ●MICHAEL KÖNIG¹, BO WANG¹, YVES FUKAMORI¹, BOKWON YOON², FRIEDRICH ESCH¹, UELI HEIZ¹, and UZI LANDMAN² — ¹Chemistry Department, Technische Universität München, 85748 Garching, Germany — ²School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

We developed preparing truly monodisperse cluster-assembled materials via deposition of size-selected, soft-landed Pd clusters on epitaxial graphene to enable to fully complement STM with integral methods.

Our STM measurements show that the Pd clusters are well-dispersed on the graphene surface at room temperature (RT). Pd₁₉/Pd₂₀ clusters show both 2 and 3 monolayer high atomic structures, like clusters in the gas phase, but can be distinguished by slightly different height histograms. Neither cluster fragments, nor surface damage are observed, confirming a well-controlled soft-landing on the graphene surface [1].

The clusters on graphene/Ru(0001) are exclusively adsorbed on the ring-fcc registry of the superstructure, indicating a strong carbon-metal interaction and a softening of the carbon-carbon bonding at this local registry. The STM study reveals that the cluster mobility depends on the cluster footprint, e.g. Pd₁₂ clusters show already at RT isomer-dependent diffusion [1]. Finally, the substrate and temperature dependent ripening processes were examined via variable temperature STM. [1]B. Wang, B. Yoon, M. König, Y. Fukamori, F. Esch, U. Heiz and U. Landman, *Nanoletters* **12**, 5907 (2012)

O 46.5 Wed 11:30 H45

A key to understanding gold nanoalloys: the interplay of fluxionality and electronic structure — ●LINN LEPPERT¹, RODRIGO Q. ALBUQUERQUE², ADAM S. FOSTER³, and STEPHAN KÜMMEL¹ — ¹Theoretische Physik IV, Universität Bayreuth, 95440 Bayreuth, Germany — ²Institute of Chemistry of São Carlos, University of São Paulo, 13560-970 São Carlos-SP, Brazil — ³Department of Applied Physics, Aalto University School of Science, P.O. Box 11100, FI-00076 Aalto, Finland

The high catalytic activity of Au nanoparticles (NP) is a prime example for the special properties of metal clusters. By alloying, e.g. with Pt, the properties of Au NP can further be significantly improved. Turnover rates in methanol fuel cells and other oxidation reactions are practically relevant examples. However, the fundamental question of why alloying improves the NP properties is still poorly understood. The finding that the high catalytic activity of Au-Pt nanoalloys is observed in a variety of reactions indicates that there is a combination of rather fundamental, basic properties that are not specific to certain chemical environments and that can be optimized by alloying. We show that electronic properties that are relevant for chemical reactivity, e.g. the density of states (DOS) at the Fermi level and the spatial orbital structure, can be associated with Pt. On the other hand we demonstrate that an increasing amount of Au increases the Au-Pt NP fluxionality. Thus, by combining Au and Pt both the DOS and the particle's fluxionality can be adjusted and a catalytically optimal interaction strength between catalyst and reactants be obtained.

O 46.6 Wed 11:45 H45

Mass selected copper and silver clusters on rare gas layers: Photoelectron spectroscopy with ultraviolet light — ●CHRISTOPH SCHRÖDER¹, NATALIE MIROSLAWSKI¹, PAUL SALMEN¹, BERND VON ISSENDORFF², and HEINZ HÖVEL¹ — ¹Fakultät Physik / DELTA, Technische Universität Dortmund, 44221 Dortmund, Germany — ²Fakultät für Physik, Universität Freiburg, 79104 Freiburg, Germany

Mass selected Cu_N and Ag_N clusters, with N=55,92,147 were soft landed at T=15K-25K on different substrates covered with rare gas layers. Up to 9 spots, with different cluster size and coverage, could be deposited on one and the same sample for better comparability. These spots were investigated by ultraviolet photoelectron spectroscopy using 11.6 eV photon energy in ultrahigh vacuum (UHV). In order to cut off the satellite of the ultraviolet light and achieving an UHV below 10⁻¹⁰ mbar we used a LiF window [1]. Caused by the low photon energy we obtained a size dependent cluster signal for energies in the s-p-band region which are discussed in respect of free beam experiments [2].

- [1] M. Budke and M. Donath, *Appl. Phys. Lett.* **92**, 231918 (2008); S. Suga et al., *Rev. Sci. Instruments* **81**, 105111 (2010)
- [2] Oleg Kostko, *Photoelectron spectroscopy of mass-selected sodium, coinage metal and divalent metal cluster anions*. PhD-thesis, Albert-Ludwig-Universität Freiburg (2007)

O 46.7 Wed 12:00 H45

The effect of oxygen on the morphology of Au nanoparticles

— •DARIUS POHL^{1,2}, ALEXANDER SURREY^{1,2}, LUDWIG SCHULTZ^{1,2}, and BERND RELLINGHAUS¹ — ¹IFW Dresden, P.O. Box 260116, D-01171 Dresden, Germany. — ²TU Dresden, Institute for Solid State Physics, Dresden, Germany.

We present an easy procedure for the synthesis of single crystalline gold nanoparticles with a mean diameter of 4 nm by using a DC-sputtering in an argon-oxygen gas mixture. Morphology population statistics for a large amount of particles have been determined to quantify the influence of oxygen. It is found that the particles undergo a structural transition from predominantly icosahedral to single crystalline particles with increasing amount of oxygen. Aberration-corrected HRTEM investigations prove that likewise prepared single crystalline nanoparticles are defect and oxygen free. In contrast, icosahedral particles prepared in pure argon atmosphere reveal the presence of edge dislocations pointing to an energetic disfavoring already at these relatively small particle sizes. The impact of oxygen on the early growth process of Au nanoparticles will be discussed in detail.

O 46.8 Wed 12:15 H45

XANES measurements on Ag clusters deposited in silica aerogel and ionic liquid — •DAVID ENGEMANN¹, SABRINA HOFFMANN¹, STEFANIE DUFFE¹, CHRISTIAN STERNEMANN¹, KRISTINA KVASHNINA², PIETER GLATZEL², RALPH WAGNER³, and HEINZ HÖVEL¹ — ¹Fakultät Physik / DELTA, Technische Universität Dortmund, 44221 Dortmund — ²ESRF, Grenoble, France — ³BU Wuppertal, Fachgruppe Physik-Materialwissenschaften, Wuppertal

Properties of clusters, in this case silver clusters, can differ widely from that of the corresponding bulk material. These differences correspond to the size of the clusters, their chemical environment and, in the case of deposited clusters, the supporting material. For most applications and measurements on deposited clusters it is necessary to deposit high amounts of clusters while protecting them from coalescence.

Silica aerogel is a very porous network (up to 99% empty space) of SiO₂ nanoparticles with interparticle distances of about 50 nm. Depositing clusters (high amounts up to several cluster monolayers) in the nano-porous surface can prevent them from coalescence.

Clusters deposited in these matrices are still in contact to the gases in their surroundings. Chemical reactions like sulfidizing were investigated with plasmon resonance measurements and X-ray Absorption Near Edge Structure spectroscopy (XANES).

Further experiments with Ag clusters deposited in Room Temperature Ionic Liquids (RTIL) are in progress.