CSI 2022

CLUSTER-SURFACE INTERACTION WORKSHOP

CONFERENCE BOOK

About the Event

CSI 2022 is the latest in a series of topical international conferences on clusters on surfaces, which began in its present form in 2010 at Stratford-upon-Avon, UK. The CSI Workshop is the main venue for discussion of results about different aspects of clusters on surfaces, with special emphasis on:

- the growth of clusters in the gas phase and their deposition on surfaces
- cluster dynamics and electronic structure on surfaces
- the properties and applications of deposited clusters

Both experimental and theoretical modelling aspects are treated.

CSI 2022 is held at Hotel Regina Elena in Santa Margherita Ligure, Italy on April 1-4, 2022.

Conference Chairs

- **Riccardo Ferrando**, University of Genoa, Italy

- **Richard E. Palmer**, Swansea University, UK

Scientific Committee:

Richard E. Palmer (Swansea University, UK)
Scott L. Anderson (University of Utah, USA)
Riccardo Ferrando (University of Genoa, Italy)
Paolo Milani (University of Milan, Italy)
Atsushi Nakajima (Keio University, Yokohama, Japan)
Stefan Vajda (CAS Prague, Czech Republic)

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Cesare Roncaglia (University of Genoa, Italy)

Scientific Secretariat:

Mariachiara Lupi

Conference Venue

Hotel Regina Elena, Santa Margherita Ligure, Italy

Program

Friday, April 1st

17:30 – 19:00	Arrival and registration
19:00 – 20:00	Welcome cocktail
20:00 – 21:00	Dinner
21:00 – 23:00	Poster set-up and discussion

Saturday, April 2nd

09:00 – 09:10	Opening
Session 1	Chair: Riccardo Ferrando
09:10 – 09:35	**Richard E. Palmer** (Swansea University, UK) Clusters in the real world
09:35 – 10:00	**Konstantin Neyman** (University of Barcelona, Spain) DFT modelling of oxide-supported metal clusters and nanoparticles relevant to catalysis
10:00 – 10:15	**Mykhailo Vaidulych** (CAS Prague, Czech Republic) Novel cluster deposition instrument for building Cu cluster-based catalysts for the selective oxidative dehydrogenation of cyclohexene
10:15 – 10:30	**Pablo Álvarez-Zapatero** (University of Valladolid, Spain) A Neural Network potential for describing the energy landscape of clusters and nanoalloys. Application to ZnMg nanoalloys of interest in corrosion processes
10:30 – 11:00	Coffee break
Session 2	Chair: Christine Mottet
11:00 – 11:25	**Ueli Heiz** (TU Munich, Germany) Photochemistry and photocatalysis of alcohols on bare and metal cluster-loaded $TiO_2(110)$
11:25 – 11:50	**Pascal Andreazza** (University of Orléans, France) Substrate and deposition sequence effect in the stability of Co-Ag nanoalloys: a real-time experimental and numerical analysis
11:50 – 12:15	**Ewald Janssens** (KU Leuven, Belgium) Cluster-decorated graphene as a platform for studying molecular adsorption and desorption kinetics
12:45 – 14:00	Lunch
Session 3	Chair: Alessandro Fortunelli
14:30 – 14:55	**Stefan Vajda** (CAS Prague, Czech Republic) Subnanometer bimetallic clusters as oxidation and dehydrogenation catalysts
14:55 – 15:20	**Veronique Dupuis** (ILM/CNRS, Lyon, France) Properties of B2 FeRh clusters on surface
15:20 – 15:45	**Sergio D'Addato** (University of Modena, Italy) Plasmonic metal@oxide, core@shell nanoparticles: interaction with reducible oxides and applications in photovoltaic materials
15:45 – 16:00	**Christopher Heard** (Charles University in Prague, Czech Republic) Insights into cluster-zeolite dynamics from kinetic modelling and machine learning
16:00 – 16:30	Coffee break
16:30 – 20:00	Free time
20:00 – 21:00	Dinner
21:00 – 23:00	Poster session and discussion

Sunday, April 3rd

Session 4	Chair: Pascal Andreazza
09:00 – 09:25	**Riccardo Ferrando** (University of Genoa, Italy) Competition between kinetic trapping and equilibrium driving forces in the growth of metallic nanoparticles
09:25 – 09:50	**Paolo Milani** (University of Milan, Italy) Electrical conduction in nanogranular cluster-assembled metallic films
09:50 – 10:15	**Christine Mottet** (CINaM/CNRS, Marseille, France) Influence of an oxide substrate on the structure and morphology of metallic clusters
10:15 – 10:30	**Alberto Giacomello** (Sapienza Università di Roma, Italy) Structural transitions in Au nanoclusters via rare event methods
10:30 – 11:00	Coffee break
Session 5	Chair: Luca Gavioli
11:00 – 11:25	**Scott L. Anderson** (University of Utah, USA) Tuning sub-nano cluster catalysis and electrocatalyis
11:25 – 11:50	**Emanuele Panizon** (ICTP, Trieste, Italy) Rotational and translational friction at crystal interfaces
11:50 – 12:15	**Vladimir Popok** (Aalborg University, Denmark) Gas-phase aggregated silver and copper nanoparticles for applications in sensing and detection
12:15 – 12:30	**Enrico Lavagna** (University of Genoa, Italy) Amphiphilic nanoparticles aggregation on lipid membranes
12:45 – 14:00	Lunch
Session 6	Chair: Lidia Martinez
14:30 – 14:55	**Panagiotis Grammatikopoulos** (Guangdon Technion – IIT, China) Cluster nanoportals for hydrogen storage and single-nanoparticle electrochemistry applications
14:55 – 15:20	**Heinz Hövel** (TU Dortmund, Germany) Photoelectron spectra for clusters on surfaces: how can they be compared to free cluster spectra
15:20 – 15:35	**Letizia Savio** (IMEM-CNR, UOS Genova, Italy) 2D Ni nanoclusters on ultrathin MgO/Ag(100)
15:35 – 16:05	Coffee break
Session 7	Chair: Konstantin Neyman
16:05 – 16:30	**Atsushi Nakajima** (Keio University, Yokohama, Japan) Plasmonic silver nanoclusters for sensitizing surface plasmon polaritons propagating at buried organic/metal interfaces
16:30 – 16:50	**Kari Laasonen** (Aalto University, Finland) CO oxidations on MgO(100) supported Au_7C_{23} and $Au_{23}Cu_7$ clusters
16:50 – 17:10	**Scott M. Woodley** (University College London, UK) Predicting and modelling isolated and supported clusters
20:00 – 23:00	Social dinner at Strainer restaurant in Portofino

Monday, April 4th

Session 8	Chair: Letizia Savio
09:00 – 09:25	**Alessandro Fortunelli** (ICCOM-CNR, Pisa, Italy) Theoretical approaches to catalyst design
09:25 – 09:50	**Lidia Martinez** (CSIC Madrid, Spain) Gas-phase synthesis of new carbon nanoarchitectures from atomic precursors
09:50 – 10:05	**Maria Sygletou** (University of Genoa, Italy) Plasmonic Au nanoparticles and transparent-conductive oxides: a tale of interaction
10:05 – 10:20	**Malcom Dearg** (Cardiff University, UK) Classification of fluctuating gold clusters using convolutional neural networks
10:20 – 10:50	Coffee break
Session 9	Chair: Richard E. Palmer
10:50 – 11:15	**Luca Gavioli** (Università Cattolica del Sacro Cuore, Brescia, Italy) Influence of roughness, porosity and grain morphology on the optical properties of nanogranular Ag films
11:15 – 11:40	**Marcel Di Vece** (University of Milan, Italy) Persistent quantum confinement in a germanium quantum dot ensamble
11:40 – 11:55	**Rafael Cintra Hensel** (Università di Padova, Italy) Optical and impedance spectroscopy of Ag nanoparticles embedded in LbL polymer films for (bio)sensing
11:55 – 12:10	Closing
12:30 – 14:00	Lunch

Poster session

1. **Jose Eduardo Barcelon** (University of Parma, Italy)
   Surface assisted synthesis, characterization and electronic properties of pristine and oxygen-exposed graphene nanoribbons on Ag(110)

2. **Alexander Boucher** (Cardiff University, UK)
   Data-oriented approach for the design of Pd-based catalysts

3. **Sonia Cambiaso** (University of Genoa, Italy)
   Modeling metal and oxide surfaces and nanoparticles at coarse-grained level

4. **El yakout El koraychy** (University of Genoa, Italy)
   Unravelling the key atomic-level mechanisms that induce the formation of multiply twinned structure from crystalline seeds

5. **Tonggih Kang** (University College London, UK)
   Predicting and modelling clusters

6. **Alexander Kononov** (TU Dortmund, Germany)
   Growth of clusters on $Al_2O_3||Ni_3Al(111)$ thin film by annealing a sub monolayer amount of bismuth. STM and UPS studies of clusters size and shift of the $5d_{5/2}$ bismuth core level state.

7. **Filip R. Krzymieniecki** (Swansea University, UK)
   Nanoparticle fillers for photoresists in semiconductor fabrication

8. **Diana Nelli** (University of Genoa, Italy)
   Unexpected diffusion pathways in icosahedral nanoparticles

9. **Rikke Plougmann** (TU Denmark)
   Activity and stability of AuTi nanoparticles for CO oxidation

10. **Filippo Profumo** (University of Milan, Italy)
    Development of an artificial neuromorphic network based on nanostructured Au/ZrOx films for interfacing biological neuronal systems

11. **Cesare Roncaglia** (University of Genoa, Italy)
    Regression and clustering algorithms for AgCu nanoalloys: from mixing energy predictions to structure recognition

12. **Agustin Salcedo** (University of Lyon, France)
    DFT study of the oxidative redispersion of Pt nanoparticles supported on ceria

13. **Marija Stojkovska** (University of Genoa, Italy)
    Formation of 2D networks by deposition of the Pd-cyclometallate C22H14Br2Cl2N2Pd2 on Ag(110)

Oral communications

Clusters in the real world

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Abstract:

Compared with the notional case of an isolated cluster at T=0, as addressed in some foundation theoretical treatments, two factors will shape the behaviour of clusters in the real, that is to say, experimental, world: (i) the radiative environment (including temperature and charged beams) and (ii) the material environment (including pressure, reactive gas and support). We will discuss five examples of the influence of these (coupled) factors; the work is mostly unpublished.

(1) Aberration-corrected electron microscopy at elevated temperature probes the melting and isomeric energy differences of arrays of size-selected gold clusters bound to point defects on a carbon surface (while subject to irradiation by 200keV electrons) [1,2].

(2) Video imaging of a <u>single</u> cluster at room temperature (plus beam heating) under conditions as (1) shows fluctuations between isomers, enabling both equilibrium properties and dynamical behaviour (branching ratios) to be explored.

(3) The case of 1 nm silver clusters (on carbon) stored in vacuum versus exposed to ambient shows dramatic differences in the isomer proportions (fcc dominant versus Ih dominant), probably due to the effect of sulphur contaminants on the structural energetics.

(4) For clusters assembled on the carbon surface from sputtered gold atoms, the transition from 2D to 3D morphology versus size appears to be delayed substantially compared with the free cluster.

(5) Implantation of lead clusters from the scaled-up MACS cluster beam into porous carbon supports provides a means to create an electrode architecture, illustrated by the electrochemical generation of oxidising species for water treatment.

References:

[1] D.M. Foster, R. Ferrando, R.E. Palmer, *Nature Comms.*, 2018, 9, 1323.
[2] D.M. Foster, T. Pavloudis, J. Kioseoglou, R.E. Palmer, *Nature Comms.*, 2019, 10, 2583.

DFT modelling of oxide-supported metal clusters and nanoparticles relevant to catalysis

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Abstract:

Active metal components are commonly present in catalysts as nanoparticles containing thousands atoms. Such large particles are inaccessible for density-functional calculations. Yet, they can be quite realistically represented by computationally tractable smaller metal particles, whose surface sites marginally change the reactivity with increasing particle size. These models expose active sites, whose structure, geometric flexibility and reactivity are similar to those of the sites in customary catalysts. Calculations of model metal particles supported on regular (see Figure) and nanostructured oxide surfaces allow delineating elusive interface effects on the structure and reactivity of the catalysts [1-7]. The effects identified and quantified using our modelling will be discussed in relation with experimental observations of our co-authors.
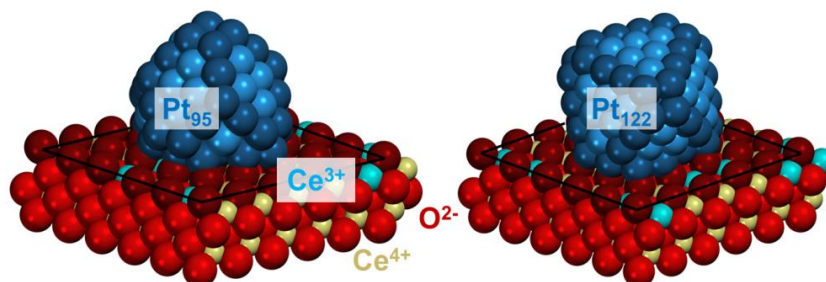
Figure 1: *Pt$_{95}$ and Pt$_{122}$ particles forming {100}/(111) and {111}/(111) interfaces with CeO$_2$(111) support [4,5].*

References:

[1] G. N. Vayssilov, Y. Lykhach, A. Bruix, F. Illas, K. M. Neyman, J. Libuda et al., *Nature Mater.*, 2011, 10, 310.
[2] A. Bruix, Y. Lykhach, V. Matolín, J. Libuda, K. M. Neyman et al., *Angew. Chem. Int. Ed.*, 2014, 53, 10525.
[3] Y. Lykhach, S. M. Kozlov, V. Matolín, K. M. Neyman, J. Libuda et al., *Nature Mater.*, 2016, 15, 284.
[4] S. M. Kozlov, K. M. Neyman, *J. Catal.*, 2016, 344, 507.
[5] Y. Suchorski, S. M. Kozlov, K. M. Neyman, G. Rupprechter et al., *Nature Mater.*, 2018, 17, 519.
[6] J. E. Quinlivan Domínguez, K. M. Neyman, A. Bruix, *submitted*.

Novel cluster deposition instrument for building Cu cluster-based catalysts for the selective oxidative dehydrogenation of cyclohexene

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Abstract:

In the first part of the presentation, a novel cluster deposition instrument will be introduced, which is utilized for the production of size selected supported catalysts, allowing to cover, without a gap, the mono-atom to subnanometer to few nanometer materials space. The instrument working principle is based on the condensation of atoms of metal vapors generated in magnetron sputtering source to form clusters and nanoparticles [1], followed by the collimation of the produced cluster cations in a coupled conical and linear octupole beam-line, and subsequent mass filtering of clusters of desired size on a quadrupole mass spectrometer (QMS) [2] comprised of an Extrel 9.5 mm Tri-Filter QMS operating at 440 kHz, allowing effective size-selection of clusters in the mass range (m/z) of 10 – 16000 with down to atomic precision.

In the second part of the presentation, selected results will be shown from a comparative study of the catalytic activity and selectivity of copper clusters, covering a range of supported Cu clusters of various sizes from Cu_1 to Cu_7, investigated in the oxidative dehydrogenation of cyclohexene at ambient pressure. In addition to cluster size effect, the effect of support on catalysts performance will be addressed as well, on the example of four commonly used technologically relevant metal oxide substrates TiO_2, SnO_2, Al_2O_3 and SiO_2. The obtained results reveal a strong dependence of the activity and selectivity on the size of clusters and the nature of substrate. Copper tetramer supported on TiO_2 is found to be the most active catalyst with 100% selectivity for benzene formation and with the rate of 4 $Cu\text{-atom}^{-1} \cdot s^{-1}$ at 400 °C. The same tetramer on SiO2 possesses 31% selectivity towards cyclohexadiene. Selectivity for the titania-supported clusters also shows odd-even oscillations with the atomicity. The even numbered Cu_4 and Cu_6 clusters produce only benzene and no CO_2, and the odd numbered Cu_5 and Cu_7 clusters produce considerable amounts of cyclohexadiene. [3]

References:
[1] H. Haberland et al., *J. Vac. Sci. Technol. A*, 1992, 10, 3266.
[2] C. Yin et al., *J. Chem. Phys.*, 2014, 140, 174201.
[3] S. Valtera et al., *submitted*.

Photochemistry and photocatalysis of alcohols on bare and metal cluster-loaded TiO₂(110)

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Abstract:

The energy transported as sunlight to the earth's surface is hardly utilized anywhere near its full potential by mankind, even though the total amount of energy reaching earth exceeds the demands of modern civilization by orders of magnitude. In this regard, heterogeneous photocatalysis is a potential key methodology for energy storage. For example, photocatalytic CO_2 reduction, water splitting, or decomposition of toxic organic compounds have been shown to be well feasible. However, a major drawback lies in the fact that the photocatalysts developed to this day lack efficiency, independent of the reaction they have been designed for. Their improvement is therefore strictly necessary for applicability, and potentially very rewarding given the possibilities. For example, hydrogen evolution by photo(electro)catalytic methods would be an economically competitive technology if the catalytic efficiency was sufficiently high.

Here we report on mechanistic investigations of the alcohol photo-oxidation on Pt and Ni cluster-loaded TiO₂(110) [1,2]. The photoreforming of alcohols is particularly interesting. Not only are alcohols hydrogen carriers and precursors for biomass; they also provide a rich chemistry due to a variety of different bonds, and their oxidation products are of considerable chemical and economical value.

References:

[1] M. Eder, C. Courtois, T. Kratky, S. Günther, M. Tschurl, U. Heiz, *Catalysis Science & Technology*, 2020, 10 (22), 7630-7639.
[2] C. Courtois, M. Eder, K. Schnabl, C. A. Walenta, M. Tschurl, U. Heiz, *Angewandte Chemie International Edition*, 2019.

Substrate and deposition sequence effect in the stability of Co-Ag nanoalloys: a real-time experimental and numerical analysis

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Abstract:

In the Ag-Co binary system, the existence of a surface induce systematically a strong segregation of silver since Ag presents lower surface energy and larger atom size (to minimize elastic-energy), in addition to the very large miscibility gap in wide ranges of temperature and concentration, without alloyed phases. On the nanometer scale, the size reduction favors a segregation behavior by surface and core contraction effects that can be opposed to kinetic trapping effects induced by the growth mode. In the UHV vapor deposition technique on the surface substrate, the mobility of Ag and Co (or Ni) atoms on the substrate and on the particles must be considered. In our works, stability of Ag-based supported nanoalloys (Ag and Ag-Co compared to Ag-Ni) were studied through modeling and experimental in situ investigations of structural arrangements. Especially, in our case, the effect of substrate and the kinetics of growth and annealing was followed as well as evolution of several configurations of deposition (simultaneous and sequential deposition of metals) until their equilibrium state obtained by thermal activation.

Experimentally, morphological and structural evolutions of clusters are studied by HRTEM/EFTEM/HAADF techniques combined with in situ and real time wide- and small-angle X-ray scattering in grazing incidence simultaneously (GIWAXS and GISAXS) combined with electron microscopy observations with the help of deep learning neural network analysis. In this paper, we explore to what extent this out-of-equilibrium structures are due to kinetic effects and the influence of the interaction of the particles with an amorphous carbon substrate by means of molecular dynamics simulations mimicking the experimental growth process, based on a tight-binding second moment approximation interatomic potential.

References:

[1] P. Andreazza, A. Lemoine, A. Coati, D. Nelli, R. Ferrando, Y. Garreau, J. Creuze, C. Andreazza-Vignolle, *Nanoscale*, 2021, 13, 6096.
[2] G.D. Förster, A. Castan, A. Loiseau, J. Nelayah, D. Alloyeau, F. Fossard, C. Bichara, H. Amara, *Carbon*, 2020, 169, 465.

Cluster-decorated graphene as a platform for studying molecular adsorption and desorption kinetics

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Abstract:

In view of the appealing catalytic properties of small clusters, understanding the adsorption and desorption kinetics of molecules on clusters is of significant fundamental and applied interest. However, experimentally it is difficult to obtain information about thermodynamic quantities of molecular adsorption like binding energies and entropy changes.

The sensitivity of graphene's transport properties to adsorbed particles has attracted widespread attention because of its potential for sensing applications [1]. This inspired us to develop a graphene field-effect transistor on which preformed size-selected clusters are deposited with a high control over the deposition energy and the deposited density. In situ electronic transport measurements on cluster-graphene devices demonstrate that cluster adsorption causes charge transfer, and hence doping, which is detectable in field-effect measurements [2] and in enhanced spin relaxation in nonlocal graphene spin valves [3]. The binding of molecular oxygen on Au_3-graphene and Au_6-graphene was studied and a pronounced cluster size dependence in the corresponding doping was found, in agreement with first-principles calculations [4].

Upon oxygen adsorption the doping of gold cluster decorated graphene changes sign from n- to p-doping, directly evidencing electron transfer to the oxygen molecules and hence their activation. Subsequently, the oxygen desorption can be induced by controlled current heating. In combination with a kinetics model, in situ measurements of the shifts of graphene's charge neutrality point provide quantitative information about the oxygen adsorption barrier, the desorption energy, and the entropy change during the desorption process [5]. This novel method can be applied to other systems and is expected to lead to new insights in the size-specific sorption kinetics of molecules on few-atom clusters.

References:

[1] F. Schedin et al., *Nat. Mater.*, 2007, 6, 652.
[2] J.E. Scheerder et al., *Nanoscale*, 2017, 9, 10494.
[3] W. Keijers et al., *J. Phys. Mater.*, 2021, 4, 045005.
[4] J.E. Scheerder et al., *Adv. Mater. Interfaces*, 2018, 5, 180274.
[5] G. Libeert et al., in preparation

A Neural Network potential for describing the energy landscape of clusters and nanoalloys. Application to ZnMg nanoalloys of interest in corrosion processes

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Abstract:

An accurate description of the potential energy surface landscape of moderate-sized nanoparticles is crucial to characterize their physical and chemical properties. While is common practice to use *ab-initio* methods, their computational requirements limit the complexity or size of the system at hand. Consequently, faster and cheaper empirical potentials are devised. Their reliability is often unsatisfactory nonetheless, and a combined empirical potential/*ab-initio* approach is mandatory to attain accurate results. Furthermore, the availability of this kind of potentials is not always guaranteed, as many interactions or characteristics are usually too intricate to be depicted with simple parametric models. An alternative to conventional empirical potentials is conceived from Machine Learning algorithms. Neural Network potentials have emerged as a reliable choice which offers unprecedented numerical accuracy. As non-parametric models, can be applied to represent the potential energy landscape of any system with any interactions.

We have developed a Neural Network potential for searching the atomic structures of pure and mixed nanoparticles with up to hundreds of atoms [1]. Both structural search and training protocols are reported. The ZnMg nanoalloy is studied under this strategy, using Density Functional Theory data to train the Neural Network model, involving energy and forces of clusters ranging from 10 to 100 atoms. This alloy poses a real challenge for any structural seeker, due to unexpected trends such as the coexistence of metallic and insulating bonds, or the segregation versus mixing tendencies. However, the resulting potential was capable of reproducing the *ab-initio* values of cluster energies and forces within chemical accuracy. Further development towards the simulation of the corrosion process on the ZnMg alloy is presented.

References:

[1] P. Álvarez-Zapatero, A. Vega, A. Aguado, *Acta Materialia*, 2021, 220, 117341.

Subnanometer bimetallic clusters as oxidation and dehydrogenation catalysts

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Abstract:

The effect of the size and composition of from molecular beams with atomic precision size- and composition-selected mixed supported subnanometer AgPt and CuPd clusters will be discussed in the catalytic oxidation of carbon monoxide and selective oxidative dehydrogenation of cyclohexene, and their performance compared with their monometallic analogs, along with the effect of technologically relevant oxide- and carbon supports, on the catalytic performance of these cluster-based catalysts.
The catalysts are tested under realistic working conditions of pressure and temperature. The paper will discuss the potential of using size/composition/support effects to tune the catalytic activity and selectivity and exploring ways of substituting precious metals in commonly used catalysts with more abundant and more economic metals.

References:

[1] C. Yin, F. R. Negreiros, G. Barcaro, A. Beniya, L. Sementa, E. C. Tyo, S. Bartling, K.–H. Meiwes-Broer, S. Seifert, H. Hirata, N. Isomura, S. Nigam, C. Majumder, Y. Watanabe, A. Fortunelli, S. Vajda, *J. Mater. Chem. A*, 2017, 5, 4923-4931.
[2] F. R. Negreiros, A. Halder, C. Yin, A. Singh, G. Barcaro, L. Sementa, E. C. Tyo, M. J. Pellin, S. Bartling, K.-H. Meiwes-Broer, S. Seifert, P. Sen, S. Nigam, C. Majumder, N. Fukui, H. Yasumatsu, S. Vajda, A. Fortunelli, *Angew. Chem. Int. Ed.*, 2018, 57, 1209 –1213.
[3] S. Valtera, A. Halder, J. Jašík, M. Vaidulych, M. Zlámalová, L. Kavan, S. Vajda, *in preparation.*

Properties of B2 FeRh clusters on surface

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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 FeRh has attracted a lot of attention because, in bulk phase when they are chemically ordered in B2 phase, they present an antiferromagnetic to ferromagnetic order (AFM-FM) transition close to room temperature. This paper deals 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 [1]. Very recently B2 FeRh clusters have been deposited on a crystalline $BaTiO_3$ (BTO) layer epitaxially grown on Nb-doped $SrTiO_3$ (STO) layer (see Figure). Their physical properties will be compared to their intrinsic ones taken into account both size and interface effects.
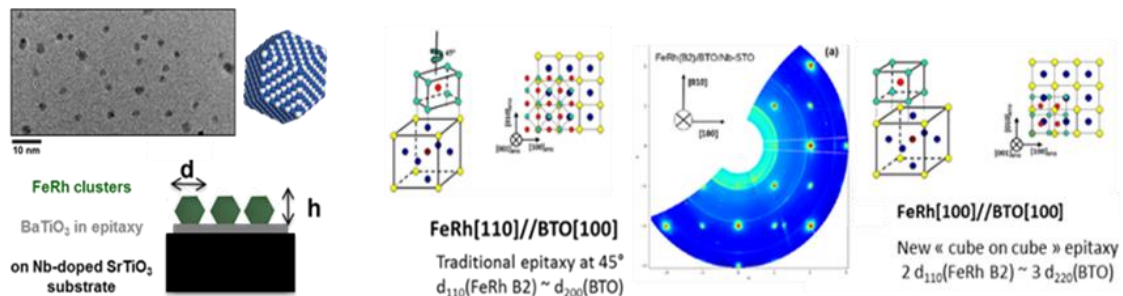
Figure 1: *Epitaxial relationships between faces of B2 FeRh and BaTiO₃ (001) surface*

References:

[1] A. Hillion, A. Cavallin, S. Vlaic, A. Tamion, F. Tournus, G. Khadra, J. Dreiser, C. Piamonteze, F. Nolting, S. Rusponi, K. Sato, T. J. Konno, O. Proux, V. Dupuis and H. Brune, *Phys. Rev. Letters*, 2013, 110, 087207.

Plasmonic metal@oxide, core@shell nanoparticles: interaction with reducible oxides and applications in photovoltaic materials

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Abstract:

During the last years different types of nanoparticles (NPs) grown with gas phase synthesis have been prepared and studied in our laboratory. Co-deposition and sequential layer deposition methods have been used to obtain core@shell NPs, realizing non-native oxide shells [1]. Recently, our group concentrated on the plasmonic properties of this class of NPs [2]. For instance, the coupling of wide band gap oxides with suitable plasmonic NPs has shown to be effective in providing materials with a light absorption range extending over the full solar radiation spectrum. This represents a promising strategy to obtain efficient functional materials, which convert solar into chemical or electric energy, relevant for a wide range of applications. The localized surface plasmon resonance (LSPR) decay, occurring on femtosecond time scales, involves a relevant energy transfer to the oxide, which may lead to modifications of the material properties on much longer time scales. Recent experiments involving time-resolved spectroscopies have been performed on Ag NPs embedded in a reducible wide bandgap oxide, namely CeO_x [3]. Another intriguing phenomenon is the increase of power conversion efficiency of photovoltaic cells by means of plasmonic NPs. This effect is particularly important in Perovskite Solar Cells (PSC), where an increase of their performances is a crucial factor for their commercial utilization. Ag@MgO NPs were synthesized and inserted in PSCs. After a full work of characterization and optimization, the Ag@MgO NPs engineered PSCs demonstrated an overall increase of 5% in terms of device power conversion efficiencies (up to 17.8%).

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Insights into cluster-zeolite dynamics from kinetic modelling and machine learning

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Abstract:

Atoms and clusters of Pt encapsulated by high-silica zeolites show surprising sintering resistance and reversible re-dispersion [1]. However, the interaction between metal and the zeolitic framework, and therefore the stabilization mechanism, is poorly understood. We tackle the problem of stabilizing encapsulated metal clusters within zeolite micropores via a combination of *ab-initio* global optimization calculations, kinetic modelling and dynamic simulations, using newly developed, reactive machine learning potentials of density functional quality [2]. The roles of metal element, cluster size, framework, heteroatom substituent and reducing adsorbates are investigated. Some recent findings include:

- Topology-specific local defect formation drives the stabilization of Pt atoms [3].
- Framework heteroatom substituents enhance sintering resistance by dramatically increasing inter-cage migration barriers, which are dependent on the Si:Al ratio.[3]
- Reducing adsorbates flatten the potential energy surface, promoting metal migration and severely inhibiting sintering resistance [4].

In this contribution, we will discuss our recent observations and the future directions of our work on the dynamics of zeolite-encapsulated metal clusters.
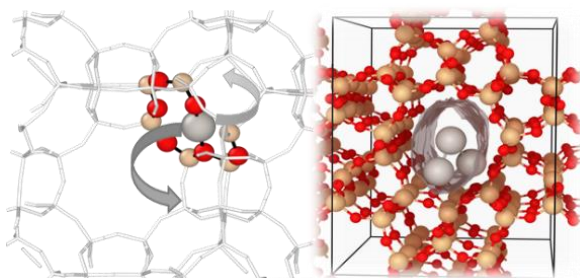
Figure 1: *Left: Global minimum of Pt₁@(Si)-LTA. Right: Diffusion trajectory of Pt₃@(Si)-TON from a 25ns MD simulation using neural network potentials.*

References:

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Competition between kinetic trapping and equilibrium driving forces in the growth of metallic nanoparticles

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Abstract:

The structures of metal nanoparticles and nanoalloys are often the results of complex formation pathways in which kinetic trapping effects and equilibrium driving forces are competing. The key atomic level mechanisms involved in these growth pathways are not trivial and difficult to pinpoint. In this regard, computer simulations are a very useful tool, because they can provide physical information at the atomic level. Here we present the results of molecular dynamics simulations applied to different growth experiments, including pure Pt [1] and pure Au [2] nanoparticles and Au-Pd [3] nanoalloys. In Pt and Au nanoparticle growth, our simulations reveal the key role of metastable defects that can cause symmetry breaking and subsequent shape changes. In Au-Pd nanoalloys, equilibrium driving forces related to surface stress relaxation cause a structural transition from fcc to icosahedral structures depending on composition.

Truncated Octahedron   Octahedron   Tetrahedron
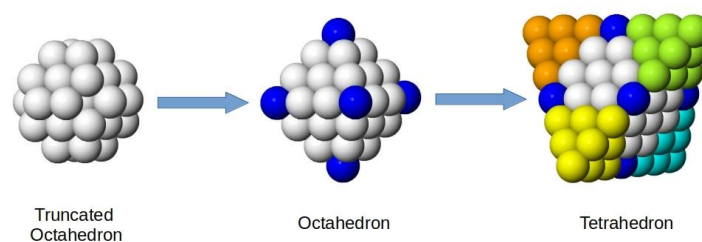
Figure 1: *Schematic representation of the growth pathway leading to the formation of a tetrahedral nanoparticle. From Ref. [1].*

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Electrical conduction in nanogranular cluster-assembled metallic films

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Abstract:

A film fabricated by the assembling of nanoparticles that retain, at least partially, their individuality is expected to show substantially different structural and functional properties compared to the case where atoms or molecules are used as building blocks. Although films assembled with metallic clusters or nanoparticles have been predicted to have unusual functional properties, it has been tacitly assumed that cluster-assembled metallic films have the same conduction behavior observed for polycrystalline metallic thin films grown from atoms. Unexpectedly, in the last decade several studies showed that nanogranular metallic films show a non-linear electric behavior, substantially different from their polycrystalline counterparts [1, 2]. Here I will discuss the electrical transport properties of cluster-assembled metallic films underlying the fundamental role of the extremely high density of defects and grain boundaries on the departure from ohmic behavior [3]. I will focus on the non-linear and non-local electrical conduction properties relevant for the fabrication of neuromorphic devices for data processing [4].

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Influence of an oxide substrate on the structure and morphology of metallic clusters

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Abstract:

Cluster – Surface Interaction is a subject that is sometimes underestimated because it comes in addition to the complexity of nanocluster structure and properties. However, nanoparticles need to be supported and even the substrates with the weaker expected interaction (for example amorphous substrates) can contribute to the structure, morphology and properties of nano-sized systems [1,2].
We therefore wanted to simulate the effect of different substrates (MgO(100), □-SiO$_2$) on the structure and morphology of metallic clusters and study their properties at finite temperature to follow solid/liquid transition (Fig. 1) [2,3] and growth conditions [4]. The metal-oxide interaction comes from *ab initio* calculations on model interfaces giving inputs to fit an empirical potential to be used in intensive molecular dynamics simulations in order to reproduce realistic conditions of melting and recrystallization with equilibrium shapes and also atom-by-atom growth on a substrate as in ultra-vacuum experiments.
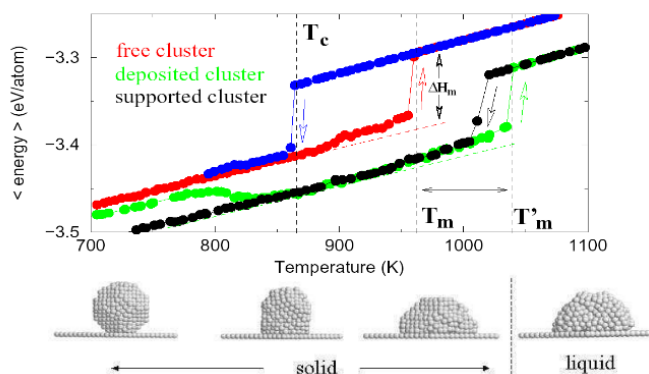
Figure 1: *Molecular dynamic simulations in canonical ensemble for melting and freezing of free or supported metallic nanocluster: red/blue curves for melting/freezing of free cluster, green curve for melting a deposited cluster starting with free cluster morphology and black curve for freezing a supported cluster.*

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Structural transitions in Au nanoclusters via rare event methods

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Abstract:

In this work we first explore the equilibrium structures of gold nanoclusters in the temperature range from 0 K to melting using Parallel Tempering Molecular Dynamics complemented by Harmonic Superposition Approximation [1]. The identified phenomenology is particularly rich, displaying a size- and temperature-dependent competition between the global energy minimum and other structural motifs. In the case of Au90 and Au147, the global minimum is also the dominant structure at finite temperatures. In contrast, the Au201 cluster undergoes a solid–solid transformation at low temperatures (<200 K). Building upon these results, the free energy landscape is computed for Au147 as a function of two collective variables, the Steinhardt order parameter Q_6 and the Relative Shape Anisotropy k^2. The structural transitions between the six minima identified at 400 K are characterized in terms of free-energy barriers and pathways, see Fig. 1. A critical discussion of the rare-event methods used for exploring structural transitions is presented.
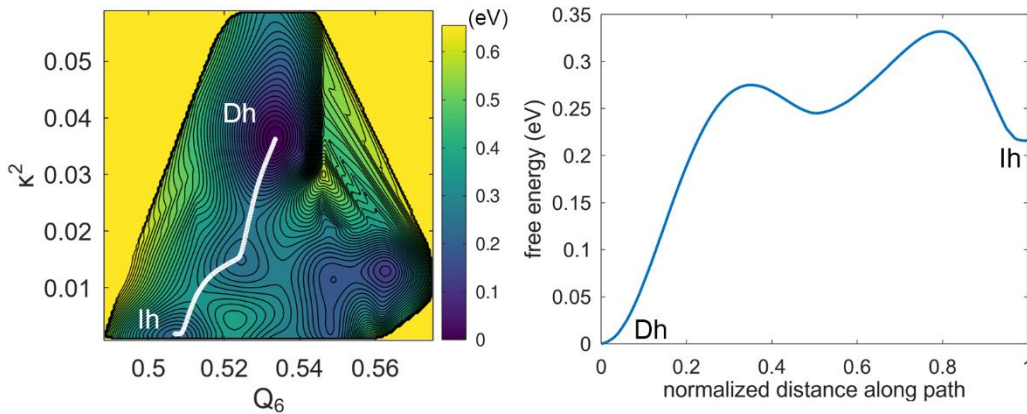
Figure 1: *Free energy landscape for Au147 at 400 K as a function of Q_6 and k^2 including a representative path between decahedron (Dh) and icosahedron (Ih). The free energy profile along the path is shown on the right*.

References:

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Tuning sub-nano cluster catalysis and electrocatalyis

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Abstract:

Alloying of sub-nano supported Pt clusters can dramatically improve catalytic selectivity and stability against sintering and poisoning/coking. The example of Pt_nSn_m/alumina and Pt_nGe_m/alumina catalysts will be used to illustrate the effects and mechanisms. In the case of Sn alloying, coking is completely inhibited, but sintering is only partially suppressed. For Ge, a very specific self-limiting coking process is actually key to producing the final, highly stable catalyst.

The talk will also discuss size effects on electrocatalysis, including HER on clusters ranging down to single atoms, and alcohol oxidation, where size seems to affect both activity and selectivity.
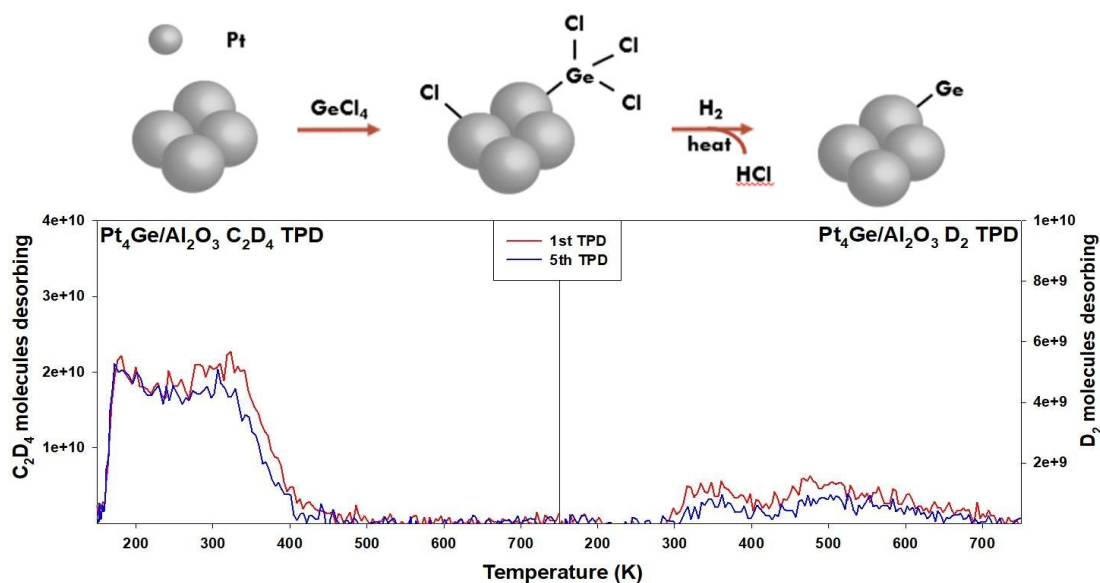
Figure 1: *Illustration of method used to selectively prepare Pt₄Ge₁/alumina, and effects on stability.*

Rotational and translational friction at crystal interfaces

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Abstract:

When two contacting solid surfaces are set into relative motion, their dynamics is governed by the frictional processes occurring at the interface. Such a subject is both of fundamental importance for engineering reasons and a fascinating topic of deep and complex non-equilibrium physics.

In recent works we realized that even at the seemingly trivial level of overlaid perfectly *rigid* crystalline layers, novel surprising phenomena can emerge. Relative motion can still vary from *superlubric*, i.e. showing vanishing friction with size, *directionally locked* [1, 2], i.e. with preferential directions of motion, or even *directionally superlubric*, i.e. with preferential directions with vanishing friction. Moreover, we were able to demonstrate at this scale a universal coupling between rotational and translational friction.

All these phenomena – found in experiments with colloidal clusters and reproduced in simulations – do not depend on the details of the systems. On the contrary we show that are connected to simple geometrical features of the crystals (even *quasi*crystals) and mathematically described in terms of the moiré patterns of the superposed lattices. We explain all regimes theoretically by simple arguments in terms of matching conditions between crystal lattices. We further demonstrate that the same arguments which should hold only for perfect matching and infinite large crystals, hold for (realistically) mismatched contacts *only* in the regime of finite sizes. The general nature of this phenomena and the strong effect of finite sizes make the understanding of such frictional regimes potentially very relevant at the nanoscale.

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Gas-phase aggregated silver and copper nanoparticles for applications in sensing and detection

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Abstract:

Gas-phase aggregation of metal nanoparticles (NPs), in particular using magnetron sputtering, is a widely used method for formation of matrixes to improve sensing and detection. One of the areas is surface enhanced Raman spectroscopy (SERS), where strong local electric fields generated by metal NPs, exhibiting localized surface plasmon resonance (LSPR) on interaction with laser light, lead to a tremendous increase of detection efficiency [1]. Another field of application is matrix assisted laser desorption ionization (MALDI) mass spectrometry (MS) [2, 3]. Use of nanoscale materials significantly facilitates analysis of thermally labile biomolecules. However, the mechanisms facilitating the detection enhancement are poorly studied: in particular, of heat absorption by the NPs and following transfer to the analyte; of analyte ionization and the role of metal ions. It is argued in recent publications that LSPR can play an important role in the enhancement [4].

In the current work, utilization of Ag and Cu NPs for enhanced sensing is discussed. The NPs are produced by magnetron sputtering cluster apparatus, MaSCA [5]. Advantages of the setup are in the formation of very pure monocrystalline NPs, the ability of size selection and good control of NP surface coverage.

In the first part, the results on LSPR stability of size-selected Ag and Cu NPs in ambient atmospheric conditions over time are presented. The evolution of plasmonic properties is explained based on the investigation of structure and composition of the NPs. Practical recommendation on utilisation of the NP matrixes for SERS are elaborated.

In the second part, the results on application of Ag NP matrixes in MALDI are presented. The role of particle size and laser energy in the enhancement of detection of particular biomolecules is described and possible physical mechanisms are discussed. The results of structural evolution of the matrixes under the laser irradiation are presented.

References:

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Amphiphilic nanoparticles aggregation on lipid membranes

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Abstract:

Metal nanoparticles (NPs), functionalized by an organic ligand shell, are promising theranostics agents. Functionalized Au NPs, in particular, are interesting because of their versatility and flexibility at synthesis stage, both in size and ligand shell composition[1]. One of the crucial steps of NP interactions with our organism is the interaction with the cell membrane, a soft, self-assembled planar interface whose structural constituents are lipids. In this work we address the collective behavior of Au NPs adsorbed on membrane surfaces. We show[2] that Au NPs, functionalized by an anionic, amphiphilic shell, spontaneously aggregate in fluid zwitterionic lipid bilayers. Using Molecular Dynamics, we observe that the thermodynamics of aggregation is different depending on the state of penetration of the NPs in the bilayer: adsorbed, semi-embedded, fully embedded[3]. We disentangle the short-range and long-range driving forces of aggregation. At short inter-particle distances, ion-mediated, charge-charge interactions (ion bridging) stabilize the formation of large NP aggregates, as shown by cryo-EM microscopy data. At long-range, lipid depletion and membrane curvature are the main membrane deformations driving NP-NP attraction. Ion bridging, lipid depletion, and membrane curvature stem from the configurational flexibility of the nanoparticle shell. Our simulations show, more in general, that the aggregation of same-charge membrane inclusions can be expected as a result of intrinsically nanoscale effects taking place at the NP-NP and NP-bilayer soft interfaces.
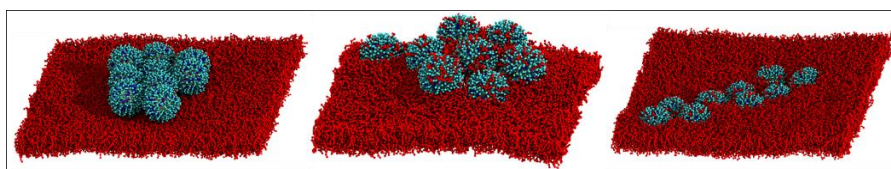
Figure 1: *Aggregates of functionalized Au NPs on a DOPC membrane*

References:

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Cluster nanoportals for hydrogen storage and single-nanoparticle electrochemistry applications

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Abstract:

What is the hydrogen flux into storage media at any given time and experimental parameters? Can there be a universal, facile method to assess, and potentially boost it? In my presentation, I will propose a nanoarchitecture that may help answer these questions. Using magnetron sputtering inert-gas condensation we deposited homogeneous, non-aggregated Pd nanoparticles (NPs) on Mg thin films with precisely adjusted surface coverage and forming clear interfaces. We, thus, designed nanoportals selectively allowing hydrogen flow into the underlying Mg films. We scrutinized all possible cluster-surface interactions theoretically, and proved the decoupling of all potential mechanisms, which enables individual portal investigation.

The same concept can also be utilised in a variety of electrochemical applications. It is known that the electrochemical response of a nanocatalyst consisting of an ensemble of NPs depends both on their individual structure and on properties of the ensemble itself (e.g., NP spacing). A comprehensive understanding of the intrinsic electrocatalytic activity of NPs is of paramount importance; hence the emergence of single-NP electrochemistry as a promising branch of the field. Here, I will also utilise the Pd-NP Mg-film nanoportal architecture for the design of uncoupled single-NP electrodes (SNPEs) that facilitate the study of their individual electrochemical performances via ensemble measurements and averaging. The high degree of control associated with gas phase synthesis is again crucial, circumventing limitations associated with traditional ensemble measurements.

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Photoelectron spectra for clusters on surfaces: how can they be compared to free cluster spectra

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Abstract:

For free beam clusters photoelectron spectroscopy is a powerful tool to analyze their electronic structure. In combination with calculations also information on geometric structure of the clusters can be extracted.

Clusters deposited on surfaces will be needed for almost all applications of the special size-dependent cluster properties in technology. Therefore, the study of the cluster surface interaction is a crucial step. Even if one realizes soft-landing conditions with low kinetic energy for the deposition of mass selected clusters the interaction with the surfaces changes the cluster shape significantly in most cases and the cluster electronic structure in almost all cases.

We use scanning tunneling microscopy/spectroscopy (STM/STS) in combination with ultraviolet photoelectron spectroscopy (UPS) for cluster/surface systems. While STM/STS allows the investigation of individual clusters, the interpretation of the results is often difficult for example due to the significant influence of the tip properties for measurements on clusters. With UPS the data is taken in most cases for a large ensemble of clusters which often averages information for different cluster sizes or isomers. The interpretation of UPS avoids the difficulties due to the unknown STM tip properties, but several other mechanisms must be considered. Some of them are connected to the photoemission process itself.

These topics will be discussed with different cluster / surface combinations.

2D Ni nanoclusters on ultrathin MgO/Ag(100)

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Abstract:

Sub-monolayer MgO films grown on Ag(100) with different morphology are often reported in literature. By combining STM and XPS information with DFT calculations, we could rationalize this finding and demostrate that the final morphology of the single layer [1] and its appearance [2] in STM images depend on the accumulation of oxygen at the MgO/Ag(100) interface. If separated MgO islands form, interfacial oxygen concentrates at their centre; vice versa, on the ultra-flat MgO/Ag(100) monolayer it is evenly distributed.

We used this latter system as an insulating substrate for the deposition of Ni clusters up to 30 Å in diameter at 100 K $\leq$T$\leq$300 K. At 200 K both small Ni_xO_y aggregates and 2D Ni NP of average size close to 12 Å form. The former result from the spontaneous oxidation of the smallest Ni nanoclusters due to segregation of oxygen available at the MgO/Ag(100) interface [3]. The larger clusters, on the contrary, have a metallic nature and efficiently catalyze CO dissociation at 200 K due to the high density of undercoordinated atoms [4].
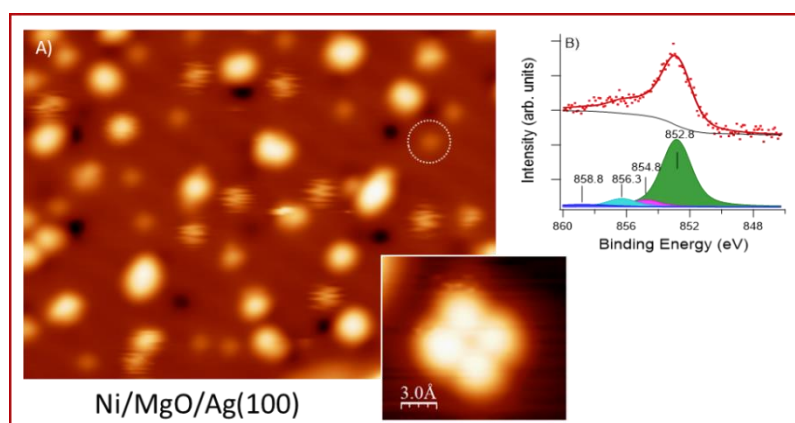
Figure 1: A) *STM image of MgO/Ag(100) covered by Ni clusters. The inset shows the details of a Ni_xO_y aggregate as the one marked by the dotted circle. B) XPS spectrum of the Ni 2p region, showing the mainly metallic nature of the Ni NPs.*

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Plasmonic silver nanoclusters for sensitizing surface plasmon polaritons propagating at buried organic/metal interfaces

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Abstract:

Electronic and optical phenomena utilizing plasmonic effects have recently attracted considerable attention for their promising applications to functional devices of the next generation, for example plasmonic lasers and optical circuits. Particularly, surface plasmon polaritons (SPPs) propagating along organic/metal interfaces are of interest for their efficiency in confining and/or transporting light fields beyond the Abbe's diffraction limit. Although there are several experimental approaches in investigating the SPP properties of surface systems (e.g. electron energy loss spectroscopy, THz spectroscopy), dual-color photoemission electron microscopy (2P-PEEM) with femtosecond laser light is one of the most powerful tools for imaging SPPs in a non-destructive manner [1,2].

We have employed 2P-PEEM to visualize SPPs propagating along a chemically modified organic/metal interface of alkanethiolate self-assembled monolayers (SAMs). In 2P-PEEM, near-infrared photons around 900 nm generate SPPs at the interface of SAMs/Au(111), which interfere with the remaining light field [3]. However, when the thickness of the organic overlayer becomes thicker, the photoemission efficiency is drastically decreased due to the finite electron mean free path. The inherent limitation of SPP imaging with the 2P-PEEM can be overcome by depositing small amounts of plasmonic silver nanoclusters (NCs); size-selected Ag_{21} NCs (~0.1 ML) on the top layer enhance the photoemission with the NIR and UV photons. For 10 ML C_{60} film/Au (111), which is an example of "buried organic/metal interfaces", we demonstrate the visualization of SPP propagation at the "buried" C_{60}/Au(111) interface with negligible modification by Ag_{21} NC sensitizers [4].

Furthermore, plasmonic behaviors of Ag_n ($n = 3−55$) on a C_{60} film are size-selectively investigated by hot electron generation dynamics using time-resolved two-photon photoemission (2PPE) spectroscopy. By tuning the NC size and the polarization of the femtosecond excitation photons, the plasmonic behavior is characterized by 2PPE intensity enhancement by $10−100$ times magnitude, which emerge at $n \geq 9$ for Ag_n NCs [5].

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# CO oxidations on MgO(100) supported Au_7C_{23} and $Au_{23}Cu_7$ clusters

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Abstract:

We have performed DFT calculations of CO oxidations on MgO(100) supported Au_7C_{23} and $Au_{23}Cu_7$ clusters [1]. The adsorption of reactants, O_2 and CO, and O_2 dissociation have been investigated in detail. The MgO(100) surface is modified with F-center, V-center vacancies. The total charge on Au_7Cu_{23} and $Au_{23}Cu_7$ is negative on all supports, regardless of the presence of vacancies, but the effect is significantly amplified on the F-center. Au_7Cu_{23}/MgO(100) and $Au_{23}Cu_7$/MgO(100) with an F-center are the only systems to bind O_2 more strongly than CO. In each case, O_2 can be dissociate to 2×O atoms with low barrier. The different reaction paths based on the Langmuir–Hinshelwood and Eley–Rideal mechanism for CO oxidation have been explored on the Au_7Cu_{23} and $Au_{23}Cu_7$ clusters on F-center MgO. These results are similar with the previous findings for $Au_{15}Cu_{15}$ [2]. Overall, the reaction barriers are small, but the changes in the Au:Cu ratio tune the reactant adsorption energies and sites considerably, showing also varying selectivity for CO and O_2. The microkinetic model built on these results shows a pronounced CO_2 production rate at low temperature for the clusters on F-center.
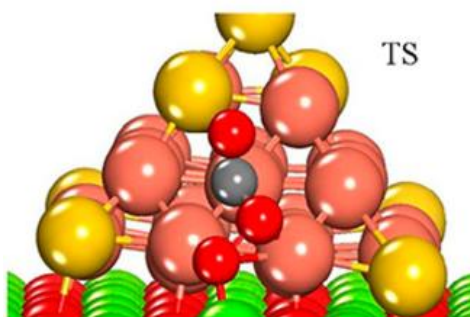
Figure 1: *Transition state of O_2 and CO reaction on MgO supported $Cu_{23}Au_7$ cluster*

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Predicting and modelling isolated and supported clusters

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Abstract:

We are interested in modelling clusters isolated in vacuum [1] and on surfaces [2,3]. Our focus in this area is that of predicting the atomic structures of clusters, using a global optimization scheme that first searches for local minima (LM) on the energy landscape defined using interatomic potentials, which are subsequently refined using a DFT approach[*]. This approach relies on the success of the global optimization procedure for finding LM and the availability and quality of the interatomic potentials to reproduce both the DFT LM and the DFT energy ranking of the LM. Thus, we develop both the global optimization algorithm[1] and interatomic potentials [2]. Here, we present recent results of both activities, for example, we will show results of modelling Cu clusters supported on ZnO and a novel *sp*-lone pair potential for lead and tin oxide clusters.
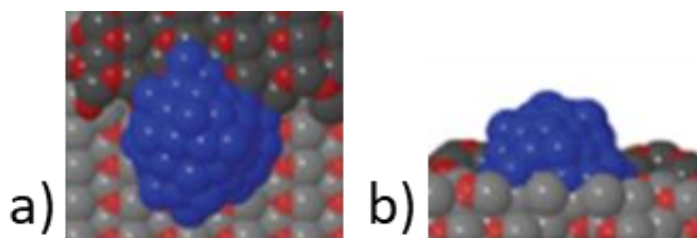
Figure 1: *Relaxed Cu_{55} cluster on a ZnO structure as viewed from (a) above and (b) the side. Blue, red and grey spheres represent Cu, O and Zn atoms.*

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Theoretical approaches to catalyst design

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Abstract:

We will present our research in the development of theoretical methods to arrive at a predictive design of nanocatalyst (NC) systems, along with selected examples of applications. We start with the description of the support. The interplay between the chemico-physical features of NC and of supports which are invariably amorphous represents a complex challenge presently in strong need of theoretical and experimental clarification. As a step in this direction, we describe a novel method to derive atomistic structures of carbonaceous amorphous materials. We use atomistic simulations based on Reactive Force Fields [1] and develop a simulation protocol based on a combination of Potential Energy Surface (PES) transformations and global optimization (GO) searches [2]. Hence, we derive a set of candidate atomistic configurations which span a wide set of structural descriptors, phases that compare well with experimental data [3]. Next step, we present experimental and theoretical evidence of how interaction with the support can be decisive in stabilizing the NCs, focusing on the case of Pt NC supported on amorphous carbon as catalysts in the oxygen-reduction-reaction (ORR). We then discuss approaches to the rational catalyst design in the case of complex reactions involving several potential rate-determining steps, where the simple Sabatier-principle-based volcano relationships in terms of a single controlling parameter no longer apply. One path is to introduce more than one descriptor in volcano theory, and analyze experimental and computational techniques in strict analogy/parallel to devise quantities with a precise correspondence between theory and experiment. We will illustrate this path using Pt-Ni catalysts for the ORR under acidic conditions [4]. A second path is high-throughput screening, illustrated via the case of ammonia synthesis Haber-Bosch (HB) process over Fe bcc facets. We start from a computational protocol combining Density-Functional Theory plus dispersion to unveil mechanistic steps at the atomic level with kinetic Monte Carlo (kMC) modeling to predict steady-state catalytic reaction rates, validated against experimental kinetic data, to derive a Hierarchical High-Throughput Screening (HHTS) approach to explore optimal modifications of the catalyst, such as alloying [5].

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Gas-phase synthesis of new carbon nanoarchitectures from atomic precursors

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Abstract:

In this work we present the formation of carbonaceous clusters and nanoparticles using a sputter gas aggregation source working in ultra-high vacuum. The sputtering of carbon atoms from a graphite target in a hydrogen atmosphere leads to a wide variety of morphologies, depending on the hydrogen dose employed. For low hydrogen doses, nanoparticle formation dominates. Amorphous nanoparticles are formed together with smaller alkane clusters (Figure 1a, b). By increasing the hydrogen dose, we start observing the formation of fibers with crystalline order up to 2.6 µm long and between 6 and 20 nm width (Fig. 1c, d). These fibers are only formed below a threshold hydrogen dose. Above it, new morphologies appeared. Bigger agglomerates of different sizes and shapes with graphitic nature are then formed. A growth mechanism of the different architectures found will be proposed.
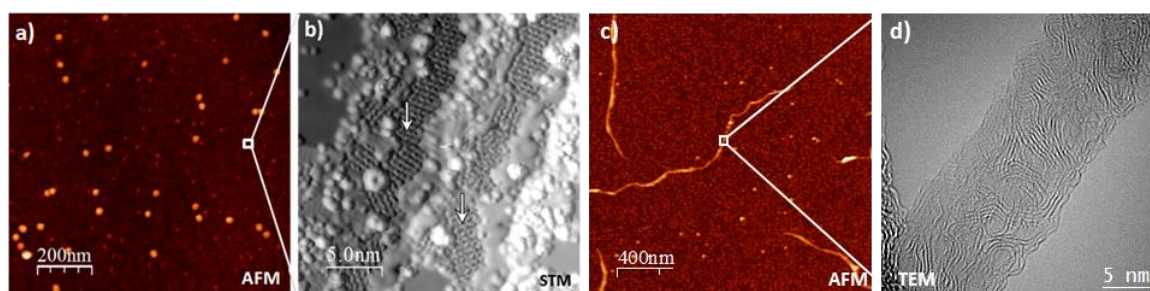
Figure 1: *Morphology of carbonaceous species. In low hydrogen atmosphere a) C-nanoparticles are formed together with b) small C-cluster film [1]. In medium hydrogen atmosphere c) fibers are predominantly formed d) with locally ordered regions [2].*

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Plasmonic Au nanoparticles and transparent-conductive oxides: a tale of interaction

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Abstract:

Understanding the interaction between plasmonic nanoparticles (NPs) and transparent conductive oxides (TCOs) is instrumental to the development of next-generation photovoltaic, optoelectronic, and energy-efficient solid-state lighting devices. In this work, we investigated the optical response of hybrid media composed of gold NPs deposited on aluminum-doped zinc oxide (AZO) thin films with varying doping concentration [1]. We focus on the evolution of the localized surface plasmon resonance (LSPR) of metallic NPs upon the doping level of AZO, leveraging on high-precision assessment of the dielectric characteristics of the whole system. We observed a systematic blueshift of the LSPR of gold NPs by increasing the dopant concentration of the TCO support (see Figure 1) which could be only partially attributed to the dielectric environment of the plasmonic NPs. We suggest a doping-dependent charge transfer between the substrate and the NPs as the responsible for the effect. This can have interesting implications in the design of either passively- or actively-tuned plasmonic/TCO systems, exploitable for a broad range of energy/environmental applications, such as in light harvesting and photo-catalytic devices.
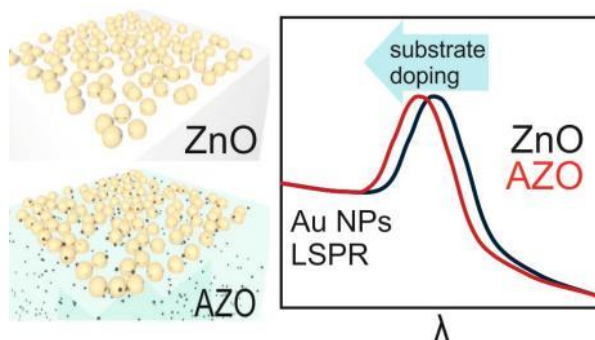
Figure 1: *Schematic of the doping-dependent optical response of the hybrid Au NPs/AZO film system.*

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Classification of fluctuating gold clusters using convolutional neural networks

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Abstract:

The exact atomic structure of nanoparticle surfaces is of great importance in catalysis. Typically, 1-5nm metal particles will adopt decahedral, icosahedral or fcc structures – with glassy structures also common. The structural isomer of a nanoparticle can be measured using high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) [1,2] in an aberration-corrected instrument. The isomer identification depends on comparison with a Simulation Atlas [1]. Here we investigate size-selected gold clusters produced by a magnetron sputtering, gas-condensation source [3]. One innovation is video imaging of the fluctuations of a single cluster over time; the second is an automated approach to classifying the structures – e.g., to determine their relative potential energies [1,2].

Machine learning has become popular in electron microscopy [4]. Here we turn this approach to the cluster structure classification problem. We use a convolutional neural network (CNN), a class of machine learning algorithm that can be trained to recognize image features [5]. Specifically, a CNN is trained using HAADF-STEM images of particles (simulated using the plane-wave reciprocal-space interpolated scattering matrix (PRISM) algorithm) to recognize the different shapes and patterns of nanocluster images from HAADF-STEM [6]. The neural network can rapidly determine the proportion of different isomers. The speed improvements afforded by the CNN approach will allow us to process multiple videos of individual clusters, determining the structure in each frame. This concept is demonstrated using the manual classification approach of Fig. 1. Video-rate imaging versus temperature [2] will determine both isomer energies and branching ratios (thus energy barriers) between the different structures.
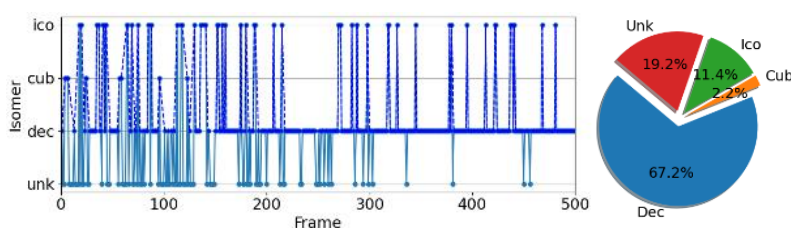
Figure 1. Manual classification results from an HAADF-STEM video of one Au309 cluster on carbon at room temp. Icosahedral (ico), decahedral (dec), cuboctahedral (cub), unknown/amorphous (unk).

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Influence of roughness, porosity and grain morphology on the optical properties of nanogranular Ag films

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Abstract:

Ag thin films are widely applied in plasmonic devices, photovoltaic cells, transparent conductive multilayers, optical and antimicrobial coatings [1]. In these systems, a key point is the interplay between the optical response and the nanoscale morphological structure, *e.g.* grain size and shape, porosity and surface roughness. Localized surface plasmon resonances are determined by the grain extension and crystallinity [2], and the film surface roughness acts as a scattering interface for electron propagation. This makes the determination of the optical constants – film morphology relationship complicated if one does not take into account the presence of pores and models the system with a uniform bulk layer. A recent review [2] indeed underlines the large differences in the dielectric function $\varepsilon(\omega)$ determined from experimental data obtained on nominally similar systems.

In this work we provide fundamental physical insights on the nanoscale morphology-optical correlation behavior for the paradigmatic case of ultrathin Ag films deposited on fused silica. The experimentally measured morphology and optical characteristics are quantitatively described by modelling reflectance and transmission spectra with a multi-layer BEMA configuration. The model, implemented through a new home-made code for ellipsometry, reflectance and transmission spectra computation and fitting (Determination of Effective Multilayer Optical constants for Nanotechnology – DEMON), provides the thickness and morphology dependence of the optical features, highlighting the role of the film roughness, nanoscale grain size and the presence of voids in the determination of the dielectric function of the films. The nanoscale morphology - dielectric function relationship is quantitatively described by comparing Ag films obtained by thermal evaporation with with those obtained by gas phase synthesis, which provides low density and high porosity films with a granular morphology. These results establish a milestone in the understanding of the nanoscale morphology effects on the dielectric funciton and open new perspectives in the interpretation of thin film properties and in the design of the optical response of a tailored system.
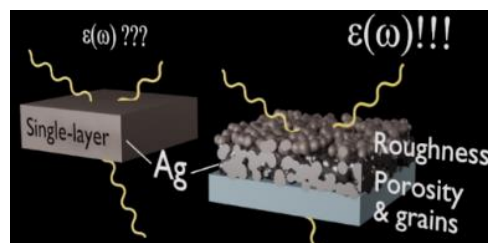
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# Persistent quantum confinement in a germanium quantum dot ensamble

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Abstract:

Quantum dot solar cells have the advantage that they can harvest the full spectrum of the sun by layers of quantum dots made out of the same semiconductor but with just a different size [1, 2]. This means that such quantum dots must maintain their quantum confinement and therefore their band gap, upon being in an ensemble in which all quantum dots are connected. When the quantum dot does not have a protective shell, which often hinders charge transport, the preservation of quantum confinement in a highly connected ensemble remains a question. We will present the work on a germanium quantum dot ensemble, which is investigated by probing the quantum dots with scanning tunnelling spectroscopy in which only one or few quantum dots are targeted for each interrogation. Besides the band gap, the discrete energy levels at the edges of the band gap, which accompany quantum confinement, are here used as a key-tool to investigate the quantum confinement. This work forms a next step in assessing how quantum confinement is highly persistent and understanding how it can be utilized in solar-cell architectures based on nanoparticle assemblies.
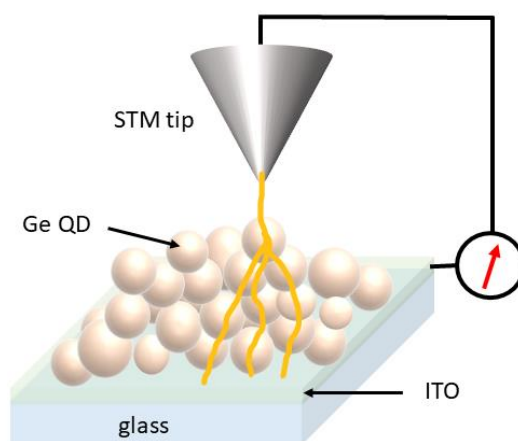
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Optical and impedance spectroscopy of Ag nanoparticles embedded in LbL polymer films for (bio)sensing

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Abstract:

The Layer-by-Layer (LbL) technique is a versatile method to grow polymer films. This method allows assembling of highly ordered nanostructures with different functionalities, which makes them suitable for a myriad of various applications. It has recently been demonstrated that both the sensitivity and the selectivity of electrochemical sensors based on LbL films is significantly enhanced by doping them with metal nanoparticles (NPs).[1] The mechanisms for this enhancement are, however, unclear, mainly because the implementation of wet-chemically prepared NPs allows no control over the particle interface, nor of their dispersion in the polymer matrix. We present here the implementation of surfactant-free silver NPs in prefabricated LbL films, which give us full and independent control over NPs size, composition and concentration. LbL films composed of polyallylamine hydrochloride (PAH) and poly(sodium 4-styrenesulfonate) (PSS) in $(PAH/PSS)_n$ architecture were grown on quartz substrates and gold interdigitated electrodes. Silver NPs fabricated in the gas phase in a magnetron cluster source are then implanted at controlled deposition energy. Optical plasmon spectroscopy allows us to distinguish between isolated and coupled NPs, up to the formation of (discontinuous) metallic films. *In situ* impedance measurements are performed to keep track of the electrical properties of the hybrid material during NP deposition. The electrical AC response during continuous NPs deposition into the polymer matrix gives us crucial information on how the electrical properties of the nanostructured film can be tuned for future implementation in electrochemical (bio)sensors. First proof-of-principle experiments with the impedance sensor in an electronic tongue show improved discrimination of analytes as compared to the undoped sensor.
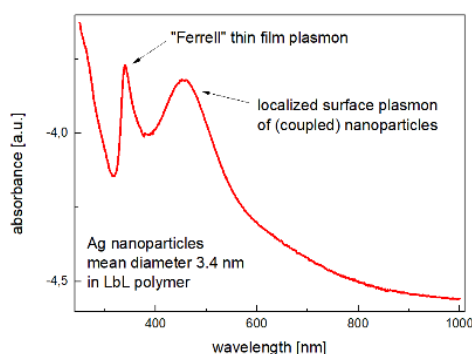
Figure 1: *Absorption spectrum of an LbL polymer thin film with implanted Ag nanoparticles. Visible are the signals (coupled) individual NPs and a continuous Ag film.*

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Poster communications

Surface assisted synthesis, characterization and electronic properties of pristine and oxygen-exposed graphene nanoribbons on Ag(110)

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Abstract:

Graphene is well-known for its exceptional electronic, mechanical, and thermal properties [1,2], yet its intrinsic zero-gap reduces its potential for applications in nanoelectronics [3]. Graphene-based nanostructures such graphene nanoribbons (GNRs) possess semiconducting properties due to one-dimensional electron confinement and edge structure effects [4]. Some of us succeeded in growing ordered arrays of GNRs with alternate zig-zag and armchair edges and monodispersed in width, by surface assisted polymerization of a suitable precursor, namely 1,6-dibromopyrene [5]. Here we characterise the electronic band structure of these GNRs scanning tunnelling spectroscopy, showing the presence of a distinct band gap with well-defined states within it. Moreover, we address the modifications of the GNRs/Ag(110) system upon oxygen exposure by scanning tunnelling microscopy and X-ray photoemission spectroscopy. Our results demonstrate that oxygen exposure deeply affects the overall system by interacting both with the nanoribbons and with the substrate; this factor must be considered for supported GNRs under operative conditions [6].
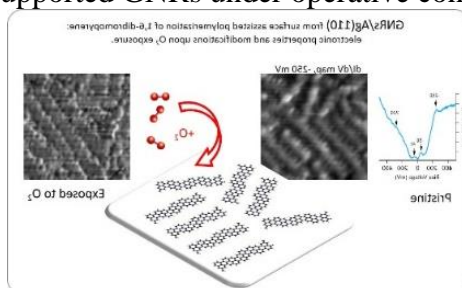
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Data-oriented approach for the design of Pd-based catalysts

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Abstract:

Catalysts are key elements in most industrial processes, e.g., synthesis of goods and pharmaceutics and air and water cleaning. In particular, heterogeneous catalysts have been known and used for more than a hundred years [1]. Even though, substantial progress is required to achieve a resilient and environmentally friendly industry.

The ever-growing computational power available to scientist has allowed consistent improvement in the design of heterogeneous catalysts, leading to the synthesis of catalysts offering optimised performances in terms of reactivity and selectivity. However, there are still areas of surface science relatively poorly understood. A major obstacle toward building an ideal catalyst, high efficiency during a long lifetime, is the loss of activity, mainly driven by the catalyst sintering. Sintering is described as the motion of nanoparticles and eventual coalescence on a support [2, 3].

As computational methods largely proved their reliability to predict physical and chemical properties, this project aim at providing an atomistic approach for the prediction of supported nanoparticles sintering. This bottom-up approach is based on the relationship between atomic physical descriptors in nanoparticles (e.g., the coordination number and chemical environment) with a computationally accessible observables (e.g., the adhesion energy of a particle on a support and its surface energy). Establishing such models allow for predictions on a variety of systems at a large scale (nanometric, possibly thousands of atoms) derived from a model built using much smaller systems (hence the term 'bottom-up'). The main advantage of this procedure is the almost instantaneous predictions of a property instead of having to run a large number of calculations on big systems to access it, which can be extremely time consuming and even unfeasible. So far, the model predicting the surface energy of a metal atom as a function its coordination number has been established. This model allows for an unprecedented on-site prediction of this property at the atomic level, a key descriptor of catalysts' stability and reactivity.

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Modeling metal and oxide surfaces and nanoparticles at coarse-grained level

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Abstract:

The study of nanoparticle (NP)/surface interfaces in complex environments at fully atomistic resolution is computationally challenging, due to intrinsic limitations in time and length scales. A strategy to overcome this limitation is exploiting coarse-grained (CG) models, which reduce the degrees of freedom by grouping several atoms in single interaction beads. We present the development of new, tailored CG interaction beads for the modeling of oxide and metal surfaces and NPs, within the framework of the popular Martini model [1]. The development of CG models relies on i) the identification of target properties, experimentally measured or quantified by means of higher-resolution approaches, ii) the tuning of the new bead size and interaction parameters to reproduce the target properties, and iii) the assessment of the new model against a validation set of material properties. Here, we show our results concerning the development of CG models for Au NPs [2,3], and present our preliminary data concerning the development of a model for bare and functionalized SiO_2 surfaces (H2020 SUNSHINE project, No 952924).
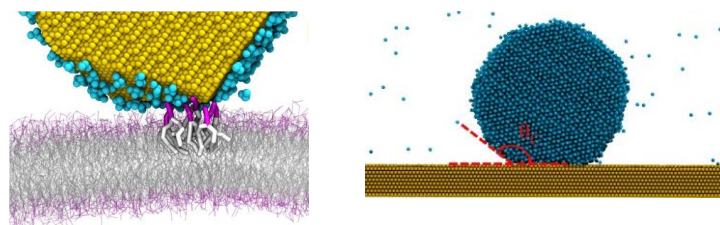
Figure 1: *Examples of complex surface-cluster interactions treated at CG level. Left: a Au cluster interacts with a solvent, a functionalizing agent and a soft lipid membrane. Right: a water droplet shows its contact angle θ_C on a hydrophobic surface.*

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Unravelling the key atomic-level mechanisms that induce the formation of multiply twinned structure from crystalline seeds

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Abstract:

We have employed molecular dynamics simulations to investigate the atomistic growth of decahedral and icosahedral twinned gold nanoparticles form tetrahedral seeds in the gas phase. Our investigation has revealed that the growth from a tetrahedron to a multiple twin can take place by different pathways: directly from a tetrahedron to a decahedron (Th→Dh pathway), directly from a tetrahedron to an icosahedron fragment (Th→Ih), from a tetrahedron to an icosahedron passing through an intermediate decahedron (Th→Dh→Ih). The simulations allow to determine the key atomic-level growth mechanism, which is common to all these pathways. This mechanism originates from the preferential nucleation of faulted atomic islands in the vicinity of facet edges, leading to the formation and stabilization of twin planes and of fivefold symmetry axes. This study provides that the identification of the key growth mechanisms of multiply twinned nanoparticles in the gas phase will be of great help in designing specific ligands with the aim of driving the growth towards specific multiply twinned nanoparticles.
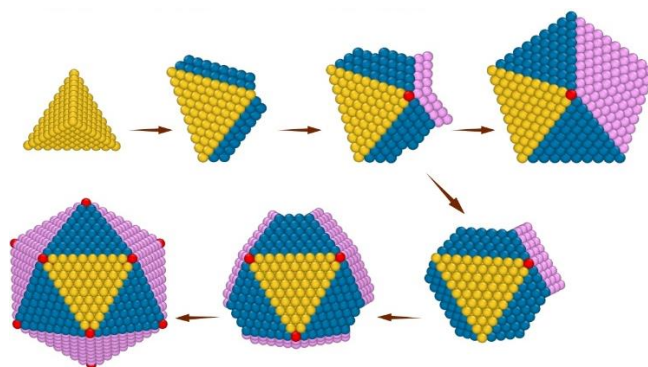
Figure 1: *Schematic representation of the stepwise evolution of multiply twinned gold nanoparticles from tetrahedral seeds.*

Predicting and modelling clusters

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Abstract:

We are interested in modelling clusters isolated in vacuum [1-3] and on surfaces [4,5], and one of the developers of a cluster database of predicted nanoclusters: http://hive.chem.ucl.ac.uk. Our focus in this area is that of predicting the atomic structures of clusters, using a global optimization scheme, as implemented as part of the KLMC code[6], that first searches for local minima (LM) on the energy landscape defined using interatomic potentials (IP), which are subsequently refined using a DFT approach[*]. To calculate the IP and DFT energies and perform the local optimizations, we use the GULP and FHI-aims software, respectively. This approach relies on the success of the global optimization procedure for finding LM and the availability and quality of the interatomic potentials to reproduce both the DFT LM and the DFT energy ranking of the LM. Thus, we develop and test the suitability of interatomic potentials for this approach to structure prediction.

Here we will present results from our investigation of different functions employed as IPs, show the match between IP and DFT landscapes for example inorganic clusters, including a metal fluoride, oxide, and nitride, and present analysis of a selection of the predicted atomic structures.

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Growth of clusters on $Al_2O_3\|Ni_3Al(111)$ thin film by annealing a sub monolayer amount of bismuth. STM and UPS studies of clusters size and shift of the $5d_{5/2}$ bismuth core level state.

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Abstract:

For bismuth quantum mechanical effects appear earlier than in common metals with decreasing dimension (from bulk over thin films to clusters), such as semimetallic-to-semiconductor transition in thin films with the thickness of a few tens nm [1] or superconductivity at a few Kelvin in bismuth clusters [2] (in contrast 0.5 mK for bulk bismuth [3]). Nevertheless, all these effects are highly controversial and not yet fully understood. For example, the substrate or embedding matrix seems to play an important role and must not be left out of the discussion [4]. Therefore, further experiments with different combinations of substrates and adsorbates are necessary.

A thin layer of Al_2O_3 film grown under controlled conditions in ultra-high vacuum by controlled oxidation on $Ni_3Al(111)$ shows large well-structured terraces in scanning tunneling microscopy (STM) images. Two structures become visible: the so-called network structure at tunneling voltage of 3.2V and the dot structure at 2.0V. The dot structure acts as a nucleation pattern in the growth of metallic clusters by atomic vapor deposition [5]. We present here the results of our experiments for bismuth clusters with ultraviolet photoelectron spectroscopy (UPS) and STM in ultra-high vacuum at low temperatures. The clusters are formed in sub monolayer regime by the gradual increase of temperature. We study the growth of the bismuth clusters (STM) and the resulting decrease of binding energy of the $5d_{5/2}$ core level state of bismuth (UPS HeII) in sub monolayer regime.

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Nanoparticle fillers for photoresists in semiconductor fabrication

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Abstract:

It is predicted that nano-composite resist materials will play a key role in the continuing miniaturisation of semiconductors (Moore's Law) through photo-, EUV- and ebeam-lithography, for example by helping to increase the feature resolution [1]. Nano-fillers can be carbon-based, metal or metal oxides. Crucially, new nanofillers have the potential to accelerate the application of new semiconductor materials such as GaO and SiC. These high band gap, hard materials with applications in areas such as power electronics need high etch-resistance resists to achieve deep etching [1]. Nanoparticles can also enhance the dielectric properties of the resists [2]. Nanoparticle effects are size dependent and controlling their size remains a significant challenge. This work explores the potential role of a novel cluster beam generation system [3] to create nanoparticles with optimum characteristics. The poster will review this exciting field and latest results will be presented.

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Unexpected diffusion pathways in icosahedral nanoparticles

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Abstract:

The diffusion of atoms of the different species within the nanoparticle volume is the underlying process of chemical ordering transformations in nanoalloys. Diffusion is known to be enhanced at the nanoscale, as the result of the activation of specific diffusion mechanisms not accessible to bulk systems, in which the nanoparticle surface often plays a prominent role. Diffusion of inner atoms very often requires the presence of vacancies, so that atoms can diffuse by jumping to unoccupied neighboring sites. Usually, such vacancies first appear on the surface, where defects are created more easily, and then migrate inward through subsequent filling steps.

Here we study the diffusion of a single-atom impurity of Ag or Au within otherwise pure icosahedral clusters of Cu, Co, Ni, Rh and Pt, by means of two different computational techniques, i.e., molecular dynamics and metadynamics. The combination of the two methods allows us to identify a complete collection of possible evolution pathways, thus providing an overall view of the impurity diffusion process within the icosahedral matrix. Our simulations reveal unexpected diffusion pathways, in which the displacement of the impurity is coupled with the creation of vacancies directly in the central part of the cluster. We show that the observed mechanism is quite different from the vacancy-mediated diffusion processes identified so far, and we demonstrate that it can be related to the presence of non-homogeneous compressive stress in the inner part of the icosahedral structure and to the size mismatch between the impurity and the atoms of the icosahedral matrix [1,2].
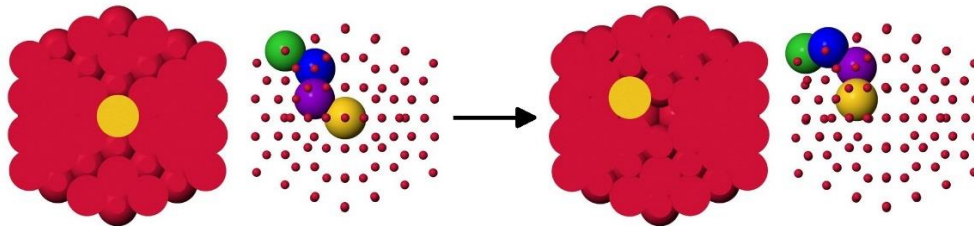
Figure 1: *Impurity diffusion mechanism in Au_1Co_{146}. The impurity moves from the center to the second shell of the perfect icosahedron, leaving a vacancy in the central site.*

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Activity and stability of AuTi nanoparticles for CO oxidation

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Abstract:

Alloying Au with Ti in a AuTi a nanoparticle (NP) form can overcome the issue of Au NP sintering [1]. This provides a possible route to utilize the excellent activity of Au NPs for CO oxidation at lower temperatures [2], while reducing catalyst degradation. In this work, we present the activity and stability of AuTi NPs for CO oxidation and give insight into their structure. Figure 1 shows the phase separated particles deposited from an Au/Ti 50/50 at% alloy target. We combine activity measurements on microreactor chips with XPS, ISS and electron microscopy data to fully understand these particles and their catalytic properties.
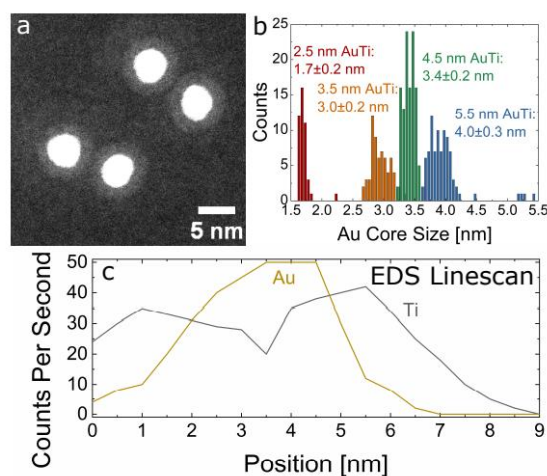
Figure 1: *a) STEM image of a 4.5nm AuTi NP on a lacey carbon CU TEM grid. b) Measured Au core sizes from STEM images of different sizes of NPs. c) EDS line scan of 5.5 nm AuTi NP showing core-shell structure of Au-Ti. Figure from [3].*

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Development of an artificial neuromorphic network based on nanostructured Au/ZrOx films for interfacing biological neuronal systems

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Abstract:

The creation of electronic devices that overcome the increasing limits of traditional electronics based on Von Neumann's architecture is a main research topic. The search for unconventional computation systems has prompted the development of neuromorphic computing architectures, that represent an attempt to emulate the human brain functions. A key factor for the implementation of neuromorphic computing is the development of new devices, emulating neurons and synapses behaviors by exploiting non-linear electrical properties of the device material. A first contribution to this purpose is represented by memristive technology [1], a peculiar non-volatile memory technology, whose memory effect is based on resistance changes induced by voltage application.

We exploited Supersonic Cluster Beam Deposition (SCBD) to fabricate planar devices based on cluster-assembled films made of gold-zirconia composites, deposited between two gold electrodes on a glass substrate. Starting from previously investigated gold cluster-assembled films electrical switching and spiking properties [2], we explored the electrical behavior of the composite ones. Interestingly, composite cluster-assembled films, when subjected to pulsed voltage stimuli, undergo to an increasing/decreasing in resistance depending on the positive/negative sign of the applied voltage. The new resistance state is maintained also when the sample is no longer biased. This memory effect is promising for developing neuromorphic devices to be interfaced with real biological neuronal systems, thanks to the biocompatibility of zirconia and gold nanostructured films, used as cell culture substrates for neurons and astrocytes [3].

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Regression and clustering algorithms for AgCu nanoalloys: from mixing energy predictions to structure recognition

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Abstract:

Machine learning landed rather recently in the field of nanoparticles, showing its abilities to perform complex task such as force field reconstruction and acceleration of energy landscape exploration [1]. Applications of these tools are indeed of some interest whenever physically meaningful models are not available. Thanks to basin-hopping-based global optimizations [2], we searched for the lowest-energy structures of AgCu nanoalloys for sizes 100 and 200 atoms, for different compositions. Even though the AgCu system is very weakly miscible in macroscopic samples, the mixing energy for these nanoalloys turned out to be clearly negative for both sizes, a result which is attributed to the stabilization of non-crystalline Cu@Ag core-shell structures at the nanoscale [3]. The mixing energy is a quantity nowadays unknown in its functional form, so that its prediction may take advantage of machine learning techniques. A Support Vector Regressor was then implemented to successfully predict the mixing energy of AgCu nanoalloys of both sizes. Moreover, with the help of unsupervised learning algorithms, it was shown that the automatic classification of such nanoalloys into different physically meaningful structural families is indeed possible. Finally, thanks to the Harmonic Superposition Approximation, the temperature-dependent probabilities of such structural families were calculated.

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DFT study of the oxidative redispersion of Pt nanoparticles supported on ceria

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Abstract:

Water-gas shift (WGS) is a key reaction in the production of pure H_2. Ceria-supported Pt is an active catalyst for the low-temperature WGS reaction. However, it suffers from sintering problems, forming large nanoparticles (NPs) with low surface area.[1] The catalytic performance is strongly structure-sensitive, favoring small Pt NPs (~1.4 nm) for CO oxidation.[2] Several strategies have been considered to minimize aggregation, including optimizing the Pt concentration and doping the support. Alternatively, the problem can be tackled by making use of the structural dynamics under operating conditions to tune the NP size. Oxidative treatments at ~500 °C promote the redispersion of large nanoparticles and might prove useful to obtain optimal catalysts.[3]

In this work, we propose a computational DFT study to gain atomic-level insight into the redispersion process of Pt NPs. According to microscopy experiments, the process takes place through Pt spillover, i.e. dissociation of atomic species from the metal and their capture on the support,[3] thus we focus the study on this phenomenon.

We consider a Pt_{147} cluster in its most stable high-symmetry homotope, namely a strongly-irregular truncated octahedron, exhibiting various types of facets. An ab initio thermodynamic analysis is performed to take into account the oxidative gas atmosphere. Subsequently we investigate the adsorption of the cluster on the $CeO_2(111)$ surface, and the spillover of Pt from the cluster to the support. This study sheds light into the effect of Pt oxidation on the stability of the adsorbed cluster and on the metal-support interactions.
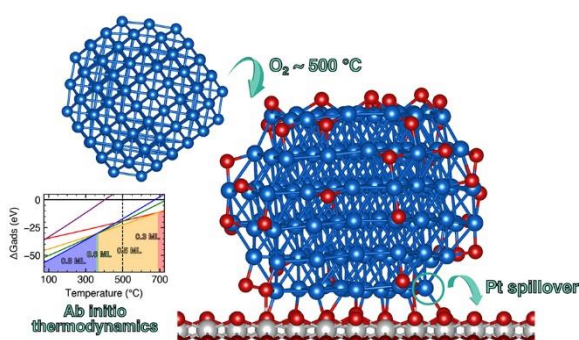
Figure 1: *DFT study of Pt spillover from an oxidized Pt_{147} NP to the $CeO_2(111)$ surface.*

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Formation of 2D networks by deposition of the Pd-cyclometallate C22H14Br2Cl2N2Pd2 on Ag(110)

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Abstract:

Cyclometallated complexes are attractive for numerous applications: catalysis, organic synthesis, and formation of biologically active compounds1. Particularly, palladium complexes have been extensively studied for several catalytic cross-coupling reactions [2,3]. Depositing such complexes on a metal surface is little explored and fundamental understanding of their properties is lacking. We investigated the interaction of a Pd cyclometallated compound [(2-[2-{3-bromopyridyl}] phenyl) palladium chloride tetramer] (C22H14Br2Cl2N2Pd2) with Ag(110) with the goal of exploiting their potential for the synthesis of ordered arrays of single metal atoms embedded in a carbon matrix. The choice of Ag(110) as a substrate due to its intermediate reactivity among coinage metals. The precursor was chosen for its planar structure and its thermal stability; moreover, brominated molecules dissociate on Ag surfaces at RT thus favoring the formation of new C-Ag or C-C bonds4,5. The system is characterized upon RT deposition of the molecules and following annealing up to 150 °C by combining STM, NEXAFS and XPS measurements. The adsorption model is validated by ab-initio calculations and comparison with simulated STM images. Our results indicate a complex surface chemistry: the substrate promotes dissociation of the Pd cyclometallate into two fragments. Each fragment is coordinated by an Ag atom from the substrate while the Pd atoms diffuse into the subsurface. The dissociated halogen atoms bind to Ag atoms provided by the surface. Though the final configuration is not the one originally foreseen and is not optimal for further catalytic studies, it opens new possibilities for this class of materials. Our results allow for an in-depth understanding of the basic interaction between metal atoms and organometallic complexes

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