



2 – 5 September 2024

IMN 2024

International Meeting on Nanoalloys

Physics Department and Chemistry Department
of the University of Genoa, Italy

<https://nanoalloys-irn.cnrs.fr/imn-2024>



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The **International Meeting on Nanoalloys 2024 (IMN 2024)** is the fifth meeting of the IMN series, which started with IMN 2018, held in Orléans, and then continued with IMN 2019 (Genoa), IMN 2021 (Leuven, online) and IMN 2023 (Orléans). The IMN meetings have been organized with the support of the **International Research Network (IRN) "Nanoalloys"** of CNRS.

IMN 2024 brings together experimentalists and theoreticians from several European and extra-European countries, giving them the opportunity to present cutting-edge research, reinforce exchanges of ideas and foster collaborations in the field of alloy nanoparticles.

Research in nanoalloys is highly interdisciplinary, with aspects related to chemistry, physics and material science and it is conducted both by experimental and theoretical/computational methods. Collaborations between experimental and modelling groups are very active.

IMN 2024 will cover all aspects related to alloy clusters and nanoparticles, including

- multi-component systems and high-entropy nanoalloys;
- environmental effects;
- growth and ageing;
- chemical reactions on nanoalloys; and
- magnetic and optical properties.

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Monday, 2 September

- 08:30 Registration
- 08:50 Introductory remarks
Riccardo Ferrando (Università di Genova, Italy)
- 09:00 Manipulating Metal Atoms in Clusters and Nanoalloys to Control Catalysis
Richard E. Palmer (Swansea University, UK)
- 09:45 Under Pressure: MD Simulation of Primary Particle Coalescence during Gas-Phase Synthesis
Panagiotis Grammatikopoulos (Guangdong Technion-Israel Institute of Technology, China)
- 10:30 Coffee break
- 11:00 Chemical Ordering and Structural Evolution of Carbon-Supported Pt-based Nanoalloys
Claudia de Melo (Université d'Orléans, CNRS, ICNM, France)
- 11:30 Machine Learning Improved Embedded Atom Model Potentials: a Compromise Between Flexibility and Physical Meaning
Ralf Meyer (Graz University of Technology, Austria)
- 12:00 PdZn Nanoalloy Catalysts for CO₂ Hydrogenation to Methanol
Imran Abbas (KU Leuven, Belgium)
- 12:30 A New Strategy for the Design of Multi-Shell Nanoalloys
Diana Nelli (Università di Genova, Italy)
- 13:00 Lunch
- 14:30 CoNiCuCrS Alloy Nanoparticles Synthesis and Microscopy Characterization
Carlos Rufino da Silva (Northern Arizona University, USA)
- 15:00 Atomic Diffusion on the Surface of Metal Nanoparticles
Nicolò Canestrari (Università di Genova, Italy)
- 15:30 Domain Walls in Bimetallic Nanoparticles Driven by Elastic Relaxations
Grégoire Breyton (Université Paris Cité-CNRS, France)
- 16:00 Ceria-Based Nanoclusters: Composition, Size, and Phase Transition Insights
Carina Peraça (São Paulo Institute of Chemistry, Brazil)

Manipulating Metal Atoms in Clusters and Nanoalloys to Control Catalysis

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ABSTRACT

“But I am not afraid to consider the final question as to whether, ultimately - in the great future - we can arrange the atoms the way we want; the very atoms, all the way down! What would the properties of materials be if we could really arrange the atoms the way we want them? They would be very interesting to investigate theoretically. I can't see exactly what would happen, but I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do”.

So wrote Feynman in 1959 and the words are so amazing you never tire of reading them. In fact it was Don Eigler, with his manipulation of atoms in the STM, that made this quotation famous. Yet cluster physics competes favourably in the matter of arranging the atoms, and it is much more scalable than STM – various labs are now envisaging cluster deposition at the gram and even kg scale (as I will show), suggesting real industrial possibilities. And nanoalloys offer even more scope.

In this talk I will survey some recent advances in the quest to arrange the atoms in clusters, and its consequences – as enabled by new experimental production methods, probed by state-of-the-art measurement techniques, like aberration-corrected electron microscopy and photoemission with synchrotron radiation, and manifested in satisfying functional performance. The emphasis will be on supported clusters and alloys of noble metal atoms.

First [1,2], the arrangements and dynamics of size-selected (mainly Au and Pt) clusters, deposited on surfaces, are revealed by time-resolved single-cluster TEM imaging, and their energetics by the new variable-temperature version of the same method. Secondly, core-level photoemission of these same systems distinguishes smooth screening effects from a size of about 1000 atoms down to 50, while non-scalable quantum effects kick in at smaller sizes. Thirdly, mixing different kinds of atoms (eg Ag and Pd) inside a nanocluster tunes the chemical performance (via the electronic states), as illustrated by photocatalytic transformations of alcohols.

Together, the measurement provide a snapshot of the progress towards realizing Feynman's vision in the world of clusters and nanoalloys.

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Under Pressure: MD Simulation of Primary Particle Coalescence during Gas-Phase Synthesis

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ABSTRACT

The coalescence of primary particles (PPs) fabricated in the gas phase is a fundamental growth mechanism determining their shapes, sizes, compositions, and structures, with resultant effects on practically all of their physical and chemical properties. Its dependence on various physical parameters (e.g., temperature, number of PPs, PP size, orientation, crystallinity, shape, or composition, etc.) is a very active field of investigation. However, most computational studies on coalescence to date are performed in vacuum. This is due to many computational studies complementing inert-gas condensation experiments, which typically happen at high vacuum, and because a simulation set-up in vacuum is simpler and computationally less costly.

Here, I will present classical molecular dynamics investigations on the effect (or lack of) of gas pressure, as well as of other parameters on the early stages of coalescence between metallic PPs using the most sophisticated scheme for inert-gas cooling to date, a methodology relevant for both inert-gas condensation in high vacuum and aerosol synthesis in standard atmospheric conditions [1]. Multiple linear regression analysis confirmed temperature as a key factor; relative angular momenta direction was revealed as yet another important contributor. The effect of pressure was deemed insignificant for early coalescence stages. I will also elaborate on interesting atomistic mechanisms, aspiring that this study may indicate potential strategies for both gas-phase synthesis methods.

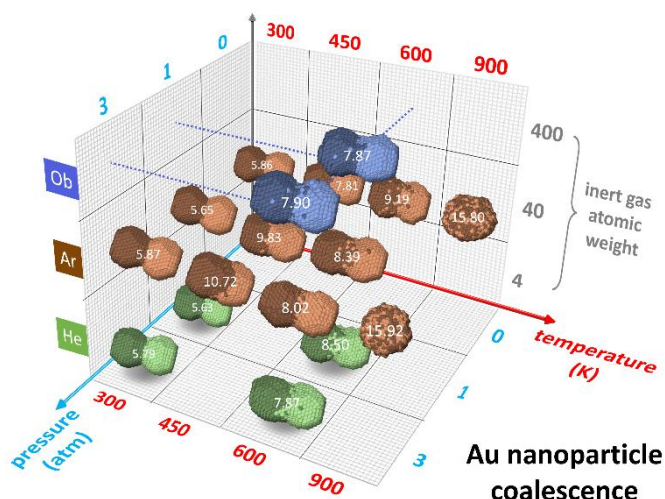


Fig. 1 : Schematic summary of final dimeric NPs corresponding to an exemplar configuration and their dependence on various parameters. The dominance of the effect of temperature is clear. The statistical variation is also evident, however, as coalescence at 450 K appears more pronounced than in 600 K under 1 and 3 atm Ar-gas atmospheres (but not in vacuum).

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Chemical Ordering and Structural Evolution of Carbon-Supported Pt-based Nanoalloys

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ABSTRACT

Pt-based binary alloys are potential candidates for catalysis, in particular they are considered very promising materials for the oxygen reduction reaction (ORR) in fuel cells [1]. In the case of Pt-based nanoalloys, the size reduction combined with synergistic effects allows a higher degree of tunability and, in some cases, a performance that far exceeds that of the individual components. Controlling the composition, structure, and chemical ordering in Pt-based nanoalloys is particularly important to optimize the catalytic activity while reducing the amount of Pt [2].

In this work, we explore the stability and chemical ordering of carbon supported Pt-based nanoalloys, ranging from binary PtNi to ternary PtNiCu systems. Two approaches were employed: simultaneous co-deposition or sequential growth of the different metals. While the chemical composition of the nanoparticles was verified by X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry (RBS) measurements, their morphology and structural evolution were studied *in-situ* by wide and small angle X-ray scattering in grazing incidence (GIWAXS/GISAXS) during growth and ageing (Fig. 1a). The goal was to examine how composition, size, and temperature influence the structure and chemical ordering ($L1_2/L1_1/L1_0$) or disordering (A1) of these nanoalloys. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images revealed local chemical order in the bimetallic nanoalloys, but GIWAXS experiments showed no superlattice peaks, indicating a low overall degree of order. This is probably because the annealing temperature required to promote ordering is close to the critical order/disorder temperature. Increasing the annealing time, rather than the temperature, can promote a higher degree of order.

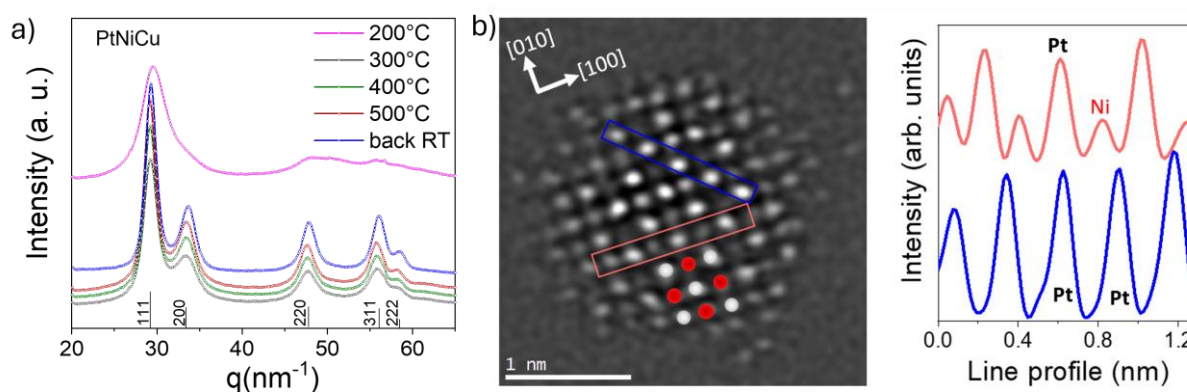


Fig. 1 : Typical GIWAXS spectra showing the structural evolution of PtNiCu nanoalloys during annealing (a). HAADF-STEM micrograph of a PtNi nanoparticle, and intensity line profiles showing the chemical ordering (b).

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Machine Learning Improved Embedded Atom Model Potentials: a Compromise Between Flexibility and Physical Meaning

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ABSTRACT

Analytical interatomic potentials are used for many tasks in the computational modeling of nanoalloys because density functional theory (DFT), the workhorse of theoretical material science, is computationally very expensive: the non-periodic nature, the number of atoms, and the vast configurational space of typical multimetallic nanostructures makes this class of materials particularly challenging. While many different variants of interatomic potentials have been suggested, most of them can be formulated as so-called many-body or 'embedded atom model' (EAM) potentials. Prominent examples include the second-moment approximation to the tight-binding (SMATB)¹, the Finnis-Sinclair², and the Sutton-Chen³ potentials. Common to all of these potentials is a relatively low number of parameters, which can be fitted to experimental data available for the bulk. However, it remains unclear if interatomic potentials designed for bulk systems can adequately describe the complex potential energy surface (PES) of structures at the nanoscale.

An alternative are so-called machine learning (ML) interatomic potentials, in which the PES is represented in a high-dimensional descriptor space, and ML methods such as neural networks or kernel-based methods learn the mapping from descriptor space onto the actual PES. Besides the fact that ML potential fitting requires very large amounts of computationally costly reference calculations since thousands of parameters are involved, another problem are the uncharted regions of the PES. Highly flexible, but fully uninformed ML approaches may predict entirely unphysical behavior in regions where reference data points are scarce.

Therefore, in this work, we propose a hybrid approach: ML techniques are not only used to provide novel interatomic potential expressions, but also to model and evaluate known, physically interpretable interaction terms of EAM-style potentials. The obtained models are built from a significantly reduced number of parameters, which we fit to DFT energies and forces. Furthermore, the low-dimensional nature of the fitted interaction terms also allows for an easy verification of correct limiting behavior and physically reasonable predictions over the entire PES.

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PdZn Nanoalloy Catalysts for CO₂ Hydrogenation to Methanol

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ABSTRACT

PdZn bimetallic catalysts show significant potential for CO₂ hydrogenation to methanol, but understanding their structure under reaction conditions and the role of each element in the nanoalloy remains challenging due to the complexity of heterogeneous catalysts¹⁻⁴. To address this, we synthesized PdZnO_x nanoparticles using a laser ablation gas aggregation source⁴ and deposited them under ultra-high vacuum conditions on carbon paper. Alloying and oxidation levels were tuned by controlling the O₂ (0-5%) content in the He condensation gas during production. For comparison, Pd nanoparticles were also produced and deposited on ZnO powder, which was then dry-coated also onto carbon paper.

CO₂ hydrogenation activity tests carried out in a high-pressure microreactor with sensitive gas analytics show that a minute concentration of Pd nanoclusters (0.1 wt%) on ZnO enhances methanol formation rates by 10 times compared to bare ZnO, while the PdZn nanoalloy produced in 1% O₂/He condensation gas is the most active catalyst, with a methanol selectivity reaching 90% (Fig. 1).

Operando X-ray Absorption Fine Structure (XAFS) spectroscopy at the Pd and Zn K edges under CO₂ hydrogenation conditions, combined with transmission electron microscopy (TEM) of the as-prepared samples, revealed strong alloying-dealloying dynamics in the bimetallic catalysts. EXAFS analysis of Pd clusters on ZnO shows that their Pd-Pd coordination decreases while their Pd-Zn coordination increases highlighting changes in the nanoalloy composition during the reaction (Fig. 2). Differences in the evolution of Pd-Zn bond distances in PdZn, PdZnO_x, and Pd/ZnO catalysts show the formation of α and/or β phases in the PdZn nanoalloy that could be directly related to their different catalytic activities and selectivities.

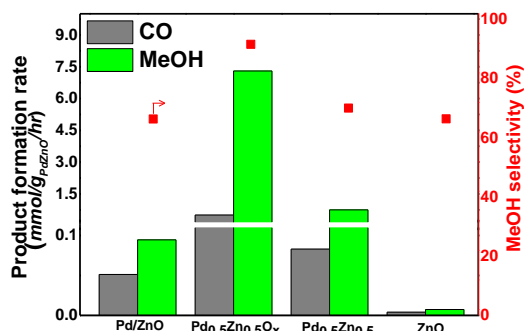


Fig. 2 : Methanol productivity and selectivity of prepared catalysts at 240°C and 40 bar.

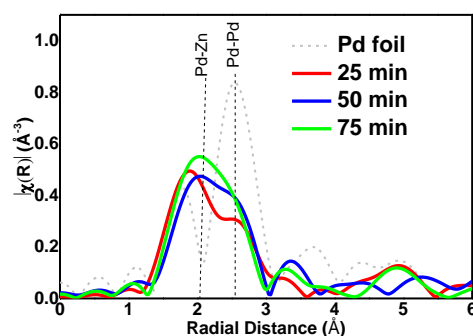


Fig. 3 : Phase-uncorrected Fourier Transforms of k³ weighted Pd K-edge EXAFS spectra of Pd/ZnO during reaction.

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A New Strategy for the Design of Multi-Shell Nanoalloys

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ABSTRACT

Multi-component metal nanoparticles are being intensively researched, due to their tunable properties and promising applications in various fields. Although interest is increasingly focusing on high-entropy alloys, in which atoms of different elements are almost randomly intermixed, ordered and symmetrical structures continue to play a prominent role. At present, synthesis techniques allow to finely tune the chemical ordering of the growing nanoalloy, thus achieving highly ordered arrangements. On the theoretical side, a very important task is the prediction stable and favorable configurations, which are expected to be durable under operating conditions. Such task becomes more and more challenging as the number of different metal components increases. At present, few results are found in the literature; in particular, there is no general theory for the design of stable multi-component nanoalloys, which would be very useful for the community.

Here we try to fill this gap by propose a design strategy for the design of multi-shell aggregates, in which atom of different types are placed in concentric shells of icosahedral symmetry [1]. Different shells can be built, of both achiral and chiral types. Such shells have the same arrangement of protein capsids of icosahedral viruses, and have first been studied and rationalized in the field of structural biology [2]. Here we show that the same shell types can be used to build stable metal nanoparticles, and we provide, for the first time, clear rules for assembling them into compact aggregates. A wide variety of icosahedral structures can be generated, with new series of icosahedral magic numbers. We show that the size-mismatch between atoms in adjacent icosahedral shells is key for the stability of the aggregate, and we provide simple formulas for evaluating the optimal mismatch.

Our design strategy is validated by molecular dynamics simulations of the growth of alkali and transition metal clusters up to ~1000 atoms, with two, three or four different metal species. The simulations show that atoms naturally self-assemble into the icosahedral shell sequences predicted by our theory. Moreover, DFT calculations confirm the stability of the new icosahedral magic structures at small sizes.

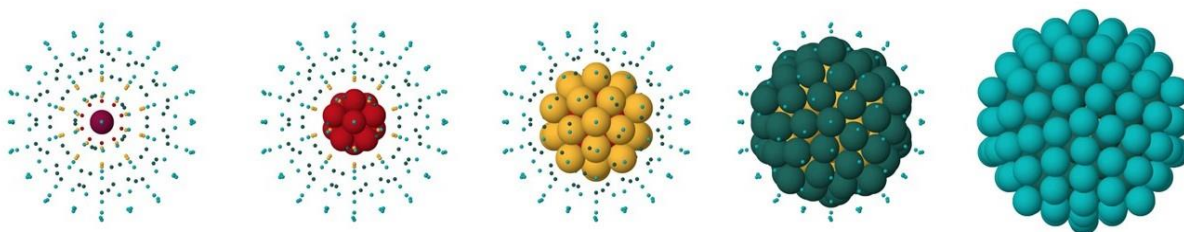


Figure: Shell sequence of a new icosahedral magic structure of 239 atoms, alternating achiral and chiral shells.

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CoNiCuCrS Alloy Nanoparticles Synthesis and Microscopy Characterization

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ABSTRACT

Multimetallic alloys (MMA) show a variety of structure-property relationships which make them important candidates for applications in modern materials science industry [1-3]. However, it is often challenging to produce suitable samples for atomically resolved characterization. Techniques like electropolishing and mechanical milling can potentially damage samples, not allowing to produce an appropriate large workpiece [4,5]. Another common technique is focused ion beam, but it might introduce radiation-induced defects to the sample due the Ga⁺ beam [6,7]. With nanoparticles, thin enough samples of MMA can be produced for atomic resolution imaging, overcoming the above-mentioned difficulties. In this work, we present the synthesis and characterization of CoNiCuCrS nanoparticle alloys using Scanning Transmission Electron Microscopy (STEM) techniques. Atomic resolution STEM imaging reveals hexagonal shaped platelets, and an ordered FCC crystal structure, in agreement with a (CuCo)₆Ni₃Cr₁S_{13.333} intermetallic phase. This research provides direct experimental evidence of the strain distribution at the atomic scale, confirming the presence of small but significant strains in High Entropy Alloys (HEA). This work demonstrates that nanoparticles can be used as a model for studying bulk properties of HEA, providing insights into local strain effects, and crystal growth dynamics.

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Atomic Diffusion on the Surface of Metal Nanoparticles

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ABSTRACT

We studied the diffusion of single atoms on a surface of the same chemical species. Depending on the shape of the surface, the movement of an atom can be made easier or more difficult. Particularly, we are interested in the surface of nanoparticles having different facets, and in the study of jumps between one facet and the next. We begin by considering the difference between a Mackay icosahedral and chiral icosahedral surface. This also relates to the growth of chiral nanoparticles which we have studied elsewhere. The energy barrier that must be overcome we recover both by the drag method and by a statistics of jumps analyzed by the Arrhenius plot.

We then extend our results by considering differently shaped nanoparticles and specifically tetrahedral and truncated octahedral ones. We study these with the drag method, and consider both the jumps between one facet and the other and the exchanges of the one moving atom with one of those on the border.

We find that mobility on the surface is easier when the borders are either very smooth or very sharp.

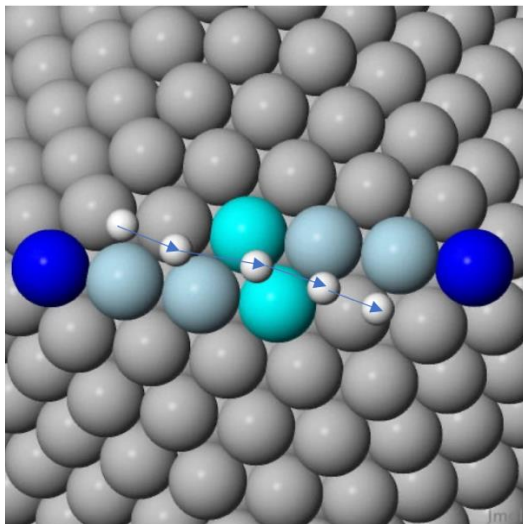


Fig. 4 : Path of facet-crossing for a chiral icosahedron. Colours are for symmetry.

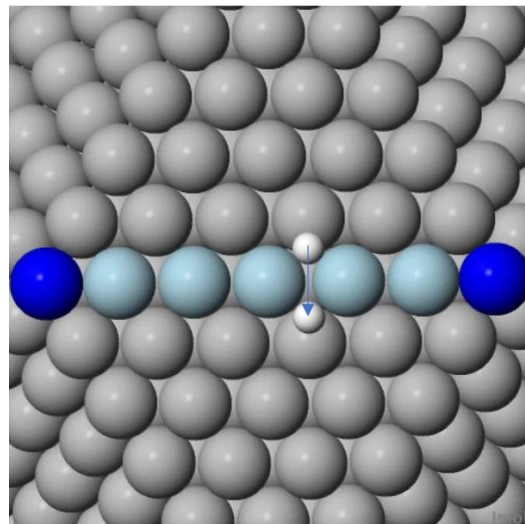


Fig. 5 : Path of facet-crossing for a Mackay icosahedron..

Domain Walls in Bimetallic Nanoparticles Driven by Elastic Relaxations

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ABSTRACT

In bulk A_xB_{1-x} binary alloys, microstructural investigations naturally reveal the presence of multi-domain walls emanating from heterogeneous nucleation sites within the material. In the case of nanoparticles (with diameters ranging from 2 to 10 nm), structural studies have always considered the presence of a single domain, which could be justified by correlation lengths that are far too long to give rise to the formation of multi-domains at the nanoscale. In fact, this hypothesis has never been confirmed, as there is currently no complete and accurate study to characterise the presence of such domains in nanoparticles (NPs). To clarify this issue, we have undertaken a detailed structural analysis of $Cu_{0.5}Au_{0.5}$ NPs for sizes ranging from 2 to 6 nm by combining transmission electron microscopy (TEM) experiments and atomic-scale simulations.

On an experimental level, we have determined the atomic-scale structure of $Cu_{0.5}Au_{0.5}$ NPs grown epitaxially on a NaCl (100) surface in the shape of a truncated octahedron by coupling high-resolution STEM images, spectroscopy and electron diffraction in an aberration-corrected electron microscope. For small NPs, we clearly observe the presence of a single domain characteristic of an $L1_0$ structure. In the case of large NPs, the electron diffraction results for the whole nanoparticle surprisingly show an $L1_2$ -type structure, while chemical analysis clearly indicates a NP with an equiatomic composition. By carrying out local electron diffraction analyses, we have revealed the presence of multi-domain walls (Figure 1) whose sum of contributions gives rise to an $L1_2$ -type structure in agreement with the global analysis. In order to identify the origin of these mechanisms, we have performed numerical studies at the atomic scale by coupling Monte Carlo (MC) modelling and HR-STEM image simulations. Our MC simulations showed that the presence of multi-domain walls is only observed for large NP sizes (Figure 2) as it is the case experimentally. By comparing the stress distribution within the NP between mono- and multi-domains, our complete study highlights how the formation of multi-domains for large NPs enables the system to relax elastically.

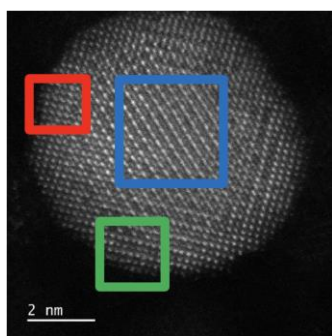


Fig. 6 : HR-STEM images of a CuAu NP where multi-domain walls are identified

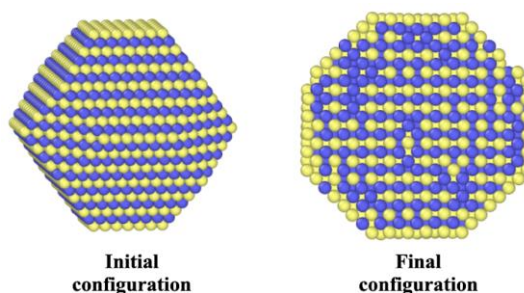


Fig. 7 : Monte Carlo simulations showing the presence of multi-domain walls within the NP.

Ceria-Based Nanoclusters: Composition, Size, and Phase Transition Insights

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ABSTRACT

Ceria-based materials play a crucial role in industrial applications, particularly in the field of catalysis [1]. Most of these applications are related to their capacity to store and release oxygen, a consequence of the reduction of Ce from Ce⁴⁺ (CeO₂) to Ce³⁺ (Ce₂O₃), which is also related to oxygen vacancy formation and diffusion [2]. The combination of CeO₂ with different metal oxides (CeO₂-MO_x), particularly for the formation of oxide nanoclusters (NCs), enhances the intrinsic properties of these materials by increasing structural defects and altering surface terminations, leading to opportunities to explore the effects of size, morphology, and chemical composition [3]. In this work we aim to provide a review of our investigations through mixed ceria-based nanoclusters, namely CeO₂-Gd₂O₃, CeO₂-La₂O₃, CeO₂-Ce₂O₃, and CeO₂-ZrO₂ with sizes from 1 up to 5 nm, focusing in the crystallization process, and vacancy formation as well as physico-chemical properties of these compounds. Thus, to obtain structural and electronic properties of these systems we combined molecular dynamics (MD) simulations, as implemented in Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package and density functional theory (DFT) calculations using the Vienna Ab Initio Simulation Package (VASP). These studies revealed that even at low concentrations, CeO₂ maintains its cubic fluorite structure and truncated octahedron morphology due to the high phase transition temperature of ceria [2]. The CeO₂-ZrO₂ structure was the only one to exhibit abrupt fluctuations in the phase transition temperature as a function of concentration [3]. Further investigation into the effects of composition (x) and size on Ce_{1-x}Zr_xO₂ NCs (1 to 3 nm) revealed structural phase transitions from disordered to ordered states in NCs larger than 108 cations and a linear relationship between the phase transition temperature and both size and composition [4]. Additionally, we observed that the introduction of M³⁺ cations in CeO₂-MO_x resulted in a decrease in the electrostatic potential, favoring vacancies near the surface. We then investigated the O vacancy formation in (La₄O₆)_n, (La₂Ce₂O₇)_n, and (Ce₄O₈)_n NCs (n = 10, 18), observing that mixing La₂O₃ with CeO₂ enhances the stability of CeO₂, increasing the formation energy of oxygen vacancies [5]. This comprehensive study highlights the critical influence of composition and size on the structural, energetic, and catalytic properties of CeO₂-based NCs, providing valuable insights for their optimized design in various applications. Additionally, we will discuss recent results obtained by DFT calculations La₂M₂O₇ nanoclusters.

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Tuesday, 3 September

- 09:00 Magnetic Behavior of Chemically Ordered and Disordered Nanoalloys
Jeff Shield (University of Nebraska-Lincoln, USA)
- 09:45 Photoabsorption and Dichroic Effects in Gold Based Nanoalloys
Mauro Stener (Università di Trieste, Italy)
- 10:30 Coffee break
- 11:00 Cobalt, Vanadium and Palladium Single Atom and Single Cluster Catalyst Supported on GDY and BGDY
Johanna Sandoval (University of Valladolid, Spain)
- 11:30 The Heating and Cooling of Core-Shell AgPt Nanoparticles
Haydar Arslan (Zonguldak Bulent Ecevit University, Turkey)
- 12:00 Surface Effects for FeRh Clusters: Reaching Metallic Nanomagnets on an Oxide Substrate
Sara Gonzalez – Florent Tournus (ILM, CNRS, Lyon, France)
- 12:30 Deep Learning Method for SMTB Potential Parametrization for Metallic Systems
Luca Benzi (Université d'Orléans, France)
- 13:00 Lunch
- 14:30 Low-Temperature ODH of Cyclohexene by Titania-Supported Pd, Pt and Pt-Pd Films
Mikhailo Vaidulych (Czech Academy of Sciences, Prague, Czech Republic)
- 15:00 Grain Boundary Migration in Nanoparticles
Manoj Settem (Sapienza Università di Roma, Italy)
- 15:30 Plasmonic Metal Nanostructures on Excitonic Systems for Nanothermometry
Emma Spotorno (Università di Genova, Italy)
- 16:00 Phase-Separation Transitions in Binary Nanoalloys and Beyond: Ternary & Quaternary
Micha Polak (Ben-Gurion University of the Negev, Israel)

Magnetic Behavior of Chemically Ordered and Disordered Nanoalloys

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ABSTRACT

Inert gas condensation (IGC), or gas aggregation, provides an opportunity to create nanoparticles with unique non-equilibrium atomic structures, such as extended solid solutions of immiscible metals or ordered atomic structures not observed in bulk alloys. Additionally, it is a good route to make hard-to-form phases between, for example, metals with much different melting temperatures.

We have fabricated unique structures in a number of alloy systems, and explored the magnetic behavior of these materials. For example, solid solution Fe-Au alloys were ferromagnetic in the as-deposited state over a range of composition (25 to 75 atomic percent Au). Heat treatment resulted in the formation of ordered atomic structures with the $L1_2$ or $L1_0$ structures, which were ferromagnetic or antiferromagnetic, depending on the Fe:Au ratio. Extended solid solutions have been formed in Co(Mo) alloys, with up to 35 atomic percent Mo dissolved in hcp Co (the equilibrium solubility is ~ 1 atomic percent). A dependence of coercivity with the amount of Mo dissolved in Co was observed (Fig. 1), consistent with an increase in magnetocrystalline anisotropy with the dissolution of 4d transition metals in Co [1].

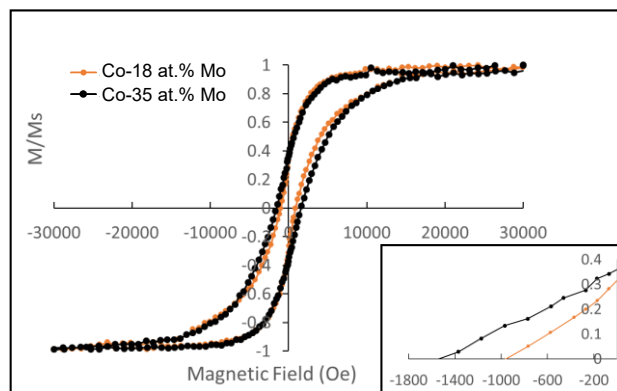


Fig. 8 : Hysteresis curves of Co(Mo) nanoparticles formed by IGC with 18 and 35 atomic percent Mo dissolved in hcp Co.

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Photoabsorption and Dichroic Effects in Gold Based Nanoalloys

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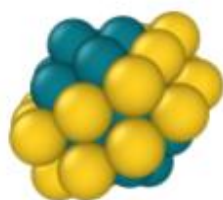
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ABSTRACT

We model the synthesis of AuRh nanoalloys by means of classical molecular dynamics calculations. We investigate the one-by-one growth process of Au over a Rh seed [1] and the coalescence of AuRh hybrid-structures, reminiscent of bimetallic nano-antennas. In both scenarios, the temperature is at 600K.

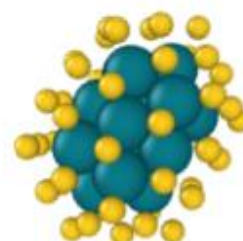
The two synthesis methods lead to different morphologies, with one-by-one favouring a core-shell formation while during the coalescence Janus-like are predominant mainly due to the slow diffusion of Au adatoms over Rh. Besides structural analysis, we estimate the optical properties at the TDDFT level of theory, and by employing classical electromagnetic calculations. TDDFT equations are solved using the polTDDFT algorithm [2], as implemented in the AMS/ADF program [3], for both photo-absorption as well as Electronic Circular Dichroism (ECD) [4]. Classical electromagnetic calculations are carried out through the pyGDM package [5]. At first, we compare the two approaches trying to determine at what size the classical approach becomes reliable. We would like to further check whether retrieving the dielectric constant from TDDFT and plug it into the pyGDM improves the accuracy of the classical approach.



Gold scarf



Ball cup



Chiral motif

Fig. 1 : Typical shapes and chemical orders of nanoalloys considered in the present work.

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Cobalt, Vanadium and Palladium Single Atom and Single Cluster Catalyst Supported on GDY and BGDY

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Nowadays, catalysis plays an important role in industrial chemical processes and Transition Metals (TM) are known to be excellent catalysts in many reactions, due to their different oxidation states, activity, selectivity, and unfilled d-orbitals. Carbon-based materials have been proposed as efficient support platforms for catalysis for their excellent electronic and mechanical properties, high superficial area, and low cost; a good choice of support platform can help to improve the catalytic efficiency due to the metal-support interaction and the performance of the catalysts can be tuned by varying the size of the supported metal nanoparticles.

DFT calculations have been performed to study the structural and electronic properties of single atom and single cluster catalysts of cobalt, palladium and vanadium adsorbed on Graphdiyne (GDY) and Boron-graphdiyne (BGDY) layers. The main objective is to investigate the effect of coverage. Our results suggest a strong dependence on the transition metal and the support.

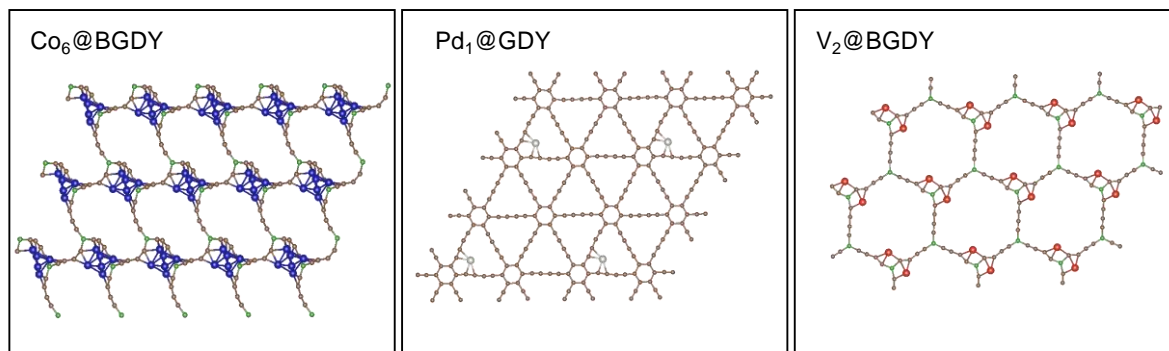


Fig. **Errore. Non è stata specificata alcuna sequenza.** : TM catalysts supported on BGDY and GDY layers. Boron and carbon atoms are represented by green and brown spheres, respectively. Transition metals are represented by, blue :

Work supported by Ministerio de Ciencia e Innovación of Spain MCIN/AEI/10.13039/501100011033 and FSE+(Grant PID2022-138340OB-I00).

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The Heating and Cooling of Core-Shell AgPt Nanoparticles

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ABSTRACT

The heating and cooling of nanoparticles are crucial processes that significantly impact their properties and applications. Nanoalloys, which are nanoparticles composed of two or more different metals, have unique chemical and physical properties due to their small size and the interactions between their constituent metals. Understanding the heating and cooling processes in nanoparticles is important for several reasons which are structural changes, melting behaviour, magnetic properties and catalytic activity. By understanding and controlling these thermal processes, scientists and engineers can tailor nanoparticles for a wide range of advanced applications, from catalysis and energy storage to biomedical technologies and nanofabrication [1-3].

For this purpose, the melting and freezing dynamics of core-shell bimetallic AgPt nanoparticles with different morphology (icosahedral and truncated octahedral) and sizes were investigated by molecular dynamics simulations. The AgPt system is particularly interesting with respect to their melting temperatures (2041 K for Pt and 1035 K for Ag). These nanoparticles have been studied at various heating and cooling rates. As a result, how the dynamical behavior of AgPt nanoparticles changes according to heating and cooling rates is revealed by caloric curve and root mean square displacement (RMSD) graphs.

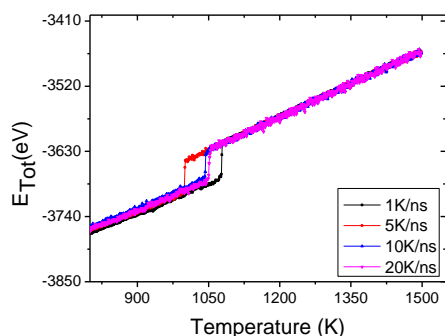


Fig. 9 : Caloric curve of $Pt_{561}Ag_{362}$ nanoalloy during the heating process from 600 K to 1500 K at various heating rates.

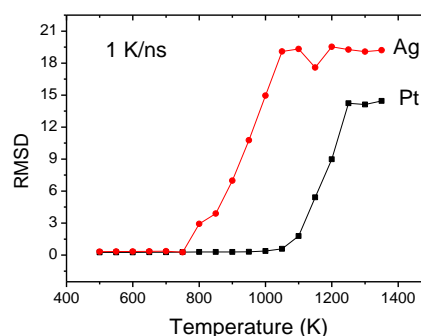


Fig. 10 : RMSD curve of $Pt_{561}Ag_{362}$ nanoalloy during the heating process for the 1K/ns heating rate.

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Surface Effects for FeRh Clusters: Reaching Metallic Nanomagnets on an Oxide Substrate

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ABSTRACT

Multiferroic composites are promising systems where the interfacial coupling between different ferroics can be driven by magnetic, voltage and strain mediation approaches to explore new technological applications [1]. Bulk FeRh alloy chemically ordered in the CsCl-type B2 phase, is characterized by a remarkable magneto-structural transition close to room temperature (~350 K) from an anti-ferromagnetic (AF) to a ferromagnetic (F) order. As in nanoscale systems, the magnetic order of FeRh is very sensitive to interfaces, strain and surface terminations [2, 3], we have deposited such nanocrystals (NCs) on perovskite oxides, SrTiO₃ (001) crystals (STO), where preferential orientation effects are met. Concerning the metallicity of Fe atoms, which is intimately linked to the magnetic properties, we observe that unprotected FeRh particles are (partially) oxidized but can be reduced by annealing at a moderate temperature, lower than the one necessary to promote the chemical order transition from the A1 to B2 phase of FeRh. This reversible process has been established using laboratory in situ X-ray photoelectron spectroscopy investigations (XPS), and has also been observed using X-ray absorption spectroscopy (SOLEIL synchrotron), simultaneously to X-ray magnetic circular dichroism (XMCD) measurements to follow the impact on the magnetic properties. In addition, the effect of in situ annealing and oxidation has been followed of the intensity of grazing incidence X-ray diffraction FeRh peaks, confirming that the oxidation is occurring at the outer surface of the metallic clusters rather than at the interface with the oxide substrate.

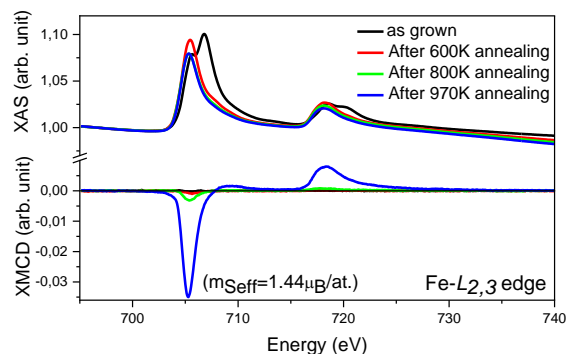


Fig. 11 : XAS (top) and corresponding XMCD (bottom) measurement follow the magnetic state of the particles during their reduction and the A1 to B2 transition under UHV annealing

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Deep Learning Method for SMTB Potential Parametrization for Metallic Systems

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ABSTRACT

Many-body atomic interaction potentials provide an accurate description of metallic systems with various lattice structures. Using the second-moment tight-binding (SMTB) approximation, it is possible to derive an accurate potential that has a simple and analytic expression. This potential allows for predicting the static and dynamic behaviour of a given metallic system¹. The Gupta formulation is particularly advantageous despite its dependence on a small number of parameters. It enables simulations of out-of-equilibrium conditions over relatively long time scales and facilitates the handling of large systems.

We have developed a procedure that utilizes machine learning techniques, specifically neural networks, to derive the parameters of the Gupta potential. This approach allows us to determine the parameters of the Gupta potential by using only a limited set of physical properties of the metal of interest, and it also considers thermodynamical properties for parameterization. This procedure is not only general, applicable to different metals with various lattice structures and properties, but also very fast; after training the neural network, the new parameterization can be generated within seconds.

The ultimate goal of our work is to describe high-entropy nanoalloys (HENAs). Therefore, we aim to extend this procedure to determine the parameters for interactions between different metals, allowing us to develop a set of potentials for our HENAs.

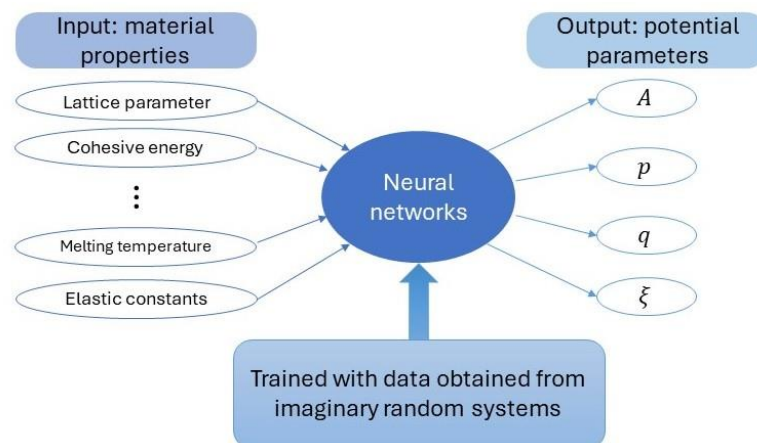


Fig. 1: Scheme of the of the procedure to derive the parameter of Gupta potential.

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Low-Temperature ODH of Cyclohexene by Titania-Supported Pd, Pt and Pt-Pd Films

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Federico Loi¹, Jan Hagen², Štefan Vajda¹

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ABSTRACT

Films of titania-supported monometallic Pd, Pt and bimetallic Pt-Pd catalysts made of metallic nanoparticles were prepared by magnetron sputtering and studied in the oxidative dehydrogenation of cyclohexene. Pd/TiO_x and Pt-Pd/TiO_x were found active at as low temperature as 150 °C and showed high catalytic activity with high conversion (up to 81 %) and benzene selectivity exceeding 97 % above 200 °C. In turn, the Pt/TiO_x catalyst performed poorly with the onset of benzene production at 200 °C only and conversions not exceeding 5%. The activity of bimetallic Pt-Pd catalysts far exceeded all the other investigated catalysts at temperatures below 250 °C. However, the production of benzene significantly dropped with a further temperature increase due to the enhanced combustion to CO₂ at the expense of benzene formation. In-situ NAP-XPS measurement of the Pt-Pd/TiO_x catalyst in the reaction conditions of the oxidative dehydrogenation of cyclohexene revealed Pd surface enrichment during the first temperature ramp. We assume that Pd surface enrichment is responsible for enhanced activity at low temperatures in the bimetallic catalyst. At the same time, the Pt constituent contributes to stronger cyclohexene adsorption and oxygen activation at elevated temperatures leading to changes in conversion and selectivity with a drop in benzene formation and increased combustion to CO₂. Both the monometallic Pd and the Pt-Pd-based catalysts produced a small amount of the second valuable product, cyclohexadiene, and below 250 °C produced only a negligible amount of CO₂ (< 0.2 %). Importantly, these catalysts were fabricated by utilizing proven methods suitable for large-scale production on extended surfaces.

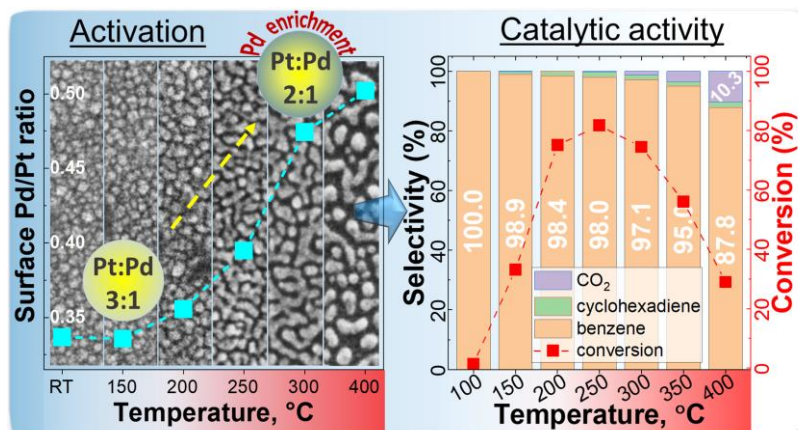


Fig. 12 : Graphic representation with (left) changes in the Pd/Pt ratio for the bimetallic catalyst during in-situ NAP-XPS measurements and (right) catalytic activity for Pt-Pd/TiO_x.

Grain Boundary Migration in Nanoparticles

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ABSTRACT

Grain boundary migration plays a significant role during nanoparticle coalescence and synthesis. It is known that a grain boundary migrates by generating step-like defects (Fig. 1) referred to as disconnections [1]. However, the migration mechanism is not entirely clear. Specifically, how are the disconnections generated and how do they move? Based on two-dimensional transmission electron microscope (TEM) images, local atomic shuffling is considered to be responsible for disconnection generation and propagation [2].

In this work, grain boundary migration in Pt nanoparticles is studied. The local atomic shuffling (observed in TEM images) is a result of atomic column shifts (or needle-shifts) and it is this atomic column shift which generates and also propagates the disconnections. First, a geometrical description of the needle-shift showing the nucleation and propagation of disconnection is provided. The needle-shift mechanism is then demonstrated in two cases: (i) grain boundary migration due to thermal energy, and (ii) grain boundary migration due to mechanical deformation.

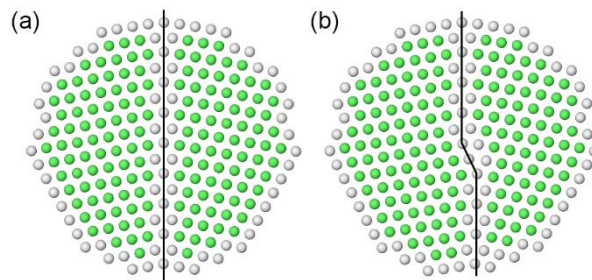


Fig. 1: (a) $\Sigma 11$ grain boundary. (b) Disconnection (indicated by the step) in $\Sigma 11$ grain boundary.

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Plasmonic Metal Nanostructures on Excitonic Systems for Nanothermometry

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ABSTRACT

With the ever-growing diffusion of nanotechnologies and nanodevices, the issue of heat propagation and dissipation within nanoscale systems has raised to attention. Indeed, while Fourier's law accurately describes heat diffusion in macroscopic system, it fails at the nanoscale. In these regimes, many phenomena such as ballistic transport, quantum and surface effects emerge, necessitating precise and localized thermal measurements. Therefore, developing non-invasive device to assess the temperature of nanoscale objects with high spatial resolution has become a crucial task.

We developed nano-systems to perform thermal measurements at the nanoscale that integrate heating and sensing in a single platform, employing light as a method of both heat generation and temperature readout. The system exploits the thermoplasmonic effect in Au nanoparticles for heat generation, and the temperature-dependent optical response of monolayer TMDC to measure the temperature less than 1 nm away from the particle surface. Nanoparticles are characterized by the localized surface plasmon resonance (LSPR), that can be excited by external radiation and locally generates heat upon non-radiative decay. On the top of the plasmonic nanoparticles we transferred a WS₂ monolayer encapsulated in h-BN, that acts as the nano-thermometer thanks to the temperature dependence of its photoluminescence.

The overall experimental set-up includes two different lasers, one to excite the plasmonic response of the NP and the other to excite the photoluminescence response of the TMDC material. Comparing the PL spectra with/without the LSPR excitation, a clear redshift by 10 meV can be observed, corresponding to a temperature variation of the WS₂ of approximately 35 K induced by the thermoplasmonics heating of the Au NDs. The hybrid plasmonic/excitonic system represents therefore a viable approach to measure the local temperature variation in nanosystems.

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Phase-Separation Transitions in Binary Nanoalloys and Beyond: Ternary & Quaternary

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ABSTRACT

The thermal stability of phase-separated cuboctahedral (O_h) **Pd-Ir** nanoparticles (NPs) is thoroughly explored over a wide range of temperatures using the highly efficient Free-energy Concentration Expansion Method [1] that is essential for the extensive computations of such *binary* systems and beyond. Thus, the results serve as a starting point for preliminary investigation of the effects of additional alloying, i.e., the **Pd-Ir-Pt** and **Pd-Ir-Rh** *ternaries*, and the *quaternary* **Pd-Ir-Pt-Rh** O_h NPs. The computations provide temperature-dependent variations in chemical order and the corresponding size-dependent nanophase separation diagrams (solid-solid “miscibility gaps”).

The binary: Vibrational-entropy and short-range order (SRO) significantly destabilize separated Quasi-Janus (QJ) asymmetric configurations of the NP core (beneath stable Pd surface layer), This configuration transforms to symmetric, solid-solution-like, mixed nanophases at higher temperatures. Nanosize-induced shifts in the phase-separation critical

temperature ($t_c \equiv 1 - \frac{T_c^{nano}}{T_c^{macro}}$) are modeled using a wide range of 22 NP sizes (147-49,049

atoms) by introducing an atomistic concept of site-specific contributions to the shift (SSCS). It is associated with several types of coordination in O_h and truncated-octahedral NPs [2]. In particular, deviations of t_c from the quite common inverse-size power-law of finite-size-scaling (FSS) are elucidated by considering face, edge, and vertex contributions, which are proportional to the relative fraction of each type of these surface sites.

The ternaries and quaternary: Chemical order and miscibility gaps computed for 1415-atom O_h exhibit composition-dependent distinct deviations from the *binary* case. These deviations are associated with the combined tendencies of demixing (separation) of the respective elemental pairs (Pd/Ir, Pd/Rh, Pt/Ir), and, to a lesser extent, weaker mixings (Pd/Pt, Rh/Pt, Ir/Rh), and Pd/Pt competitive surface co-segregation. (Computed concentration profiles along the Pd-Ir-Pt-Rh [111] axis reveal systematic Pt/Pd and Ir/Rh compositional correlations).

The transition-temperature drop with the increased number of alloying elements found for most compositions seems to originate also from augmented mixing entropy, contributing to the solid-solution-like phase stabilization.

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Wednesday, 4 September

- 09:00 A Laser Synthesis Route to Multifunctional Nanoalloys for Theranostic and Biomedical Applications
Vincenzo Amendola (Università di Padova, Italy)
- 09:45 Enhanced Reactivity of Oxide-Supported Bimetallic and Single Atom Sites: Insights from the Local Atomic Environment
Talat Rahman (University of Central Florida, USA)
- 10:30 Coffee break
- 11:00 Solid Solution Extension in Co(Mo) Nanoparticles
Sunil Dhapola – Jeff Shield (University of Nebraska-Lincoln, USA)
- 11:30 Chemical Ordering in Ni-Pt And Co-Ni-Pt Nanoalloys
Pamela Camilos (Aix-Marseille University CNRS, CINAf, France)
- 12:00 Coexistence of Miscibility and Segregation in Gold-Silver Nanoalloys
Murilo Moreira (Université del Lyon, ILM, CNRS, France)
- 12:30 Understanding Structural Transitions in Nanoclusters via Neural Variables
Emanuele Telari (Sapienza Università di Roma, Italy)
- 13:00 Lunch
- 14:30 Free time
- 16:30 Visit of the Renaissance palaces of the University of Genova (via Balbi 4 and via Balbi 5)
- 18:00 Cocktail (terrace of via Balbi 2)
- 20:00 Social dinner (Mercato del Carmine, piazza del Carmine)

A Laser Synthesis Route to Multifunctional Nanoalloys for Theranostic and Biomedical Applications

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ABSTRACT

In recent years, alloy nanoparticles containing noble and not-noble metals have been investigated for their range of innovative properties and unconventional structural behaviors. In particular, metastable nanoalloys have offered the opportunity to introduce functions which are not found in single element nanosystems and which show up only in complex environments such as the biological organisms. Here we show how laser ablation in liquid (LAL) has contributed to accessing several examples of metastable nanoalloys and we will specifically describe the case of magnetic antibacterial nanoparticles designed for interfering with bacteria biofilms¹ and of boron-doped gold nanoparticles designed for X-ray radiotherapy and boron neutron capture therapy assisted by CT imaging.² Due to the out-of-equilibrium nanoscale mixing of immiscible elements, these LAL synthesized nanosystems provided inherent advantages compared to single element counterparts, overall indicating the multiple possibilities available for metastable nanoalloys, despite the challenges of their production, characterization and modelling.

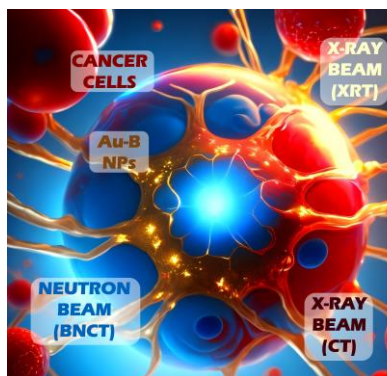


Fig. 13 : Pictorial scheme representing the multifunctionality of boron-doped gold nanoparticles for theranostic applications.

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Enhanced Reactivity of Oxide-Supported Bimetallic and Single Atom Sites: Insights from the Local Atomic Environment

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Singly dispersed transition metal atoms on oxide surfaces, the so-called single atom catalyst (SAC) have recently been shown to attain chemical activity and selectivity for several technologically important reactions that surpass those of Pt single crystal surfaces, the prototype exemplary catalyst but with a large price tag. Apart from being cost-effective, single atom catalyst offer excellent opportunities for tuning their local environment and thereby their oxidation state, local coordination, and electronic structure. In this talk, I will present results of collaborative work of our research group with several experimental groups on transition metal atoms anchored on surfaces, with and without ligands, that have the potential to be cost-effective catalysts with high activity and product selectivity. Examples will include Pd and Pt atoms anchored on ZnO that form a bimetallic local environment consisting of one Pd/Pt and three Zn atoms with high catalytic activity for generation of H₂ through methanol partial oxidation (MPO) [1,2], larger than that of Pt-Zn nanoalloys. Then there is the case of Pt atoms stabilized in specific fine-tuned local coordination environments that exhibit strikingly distinct catalytic behaviors in reactions as varied as CO oxidation and NH₃ oxidation [3]. I will also pay attention to the special role played by ligands (1,10-phenanthroline-5,6-dione (PDO)) in emergent catalytic properties of Pd single atoms stabilized on ceria surfaces [4]. I will draw attention to some factors that control the emerging functionalities of the above systems in controlled confinement.

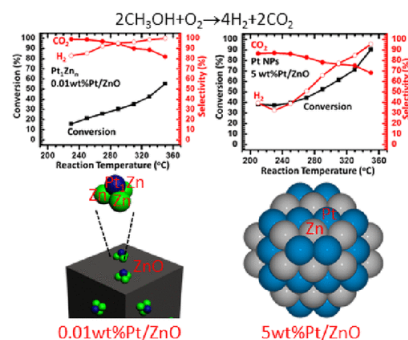


Fig. 14 : Enhanced reactivity of bimetallic Pt/Zn sites as compared to that of Pt/Zn nanoalloys (from Ref. 2) .

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Solid Solution Extension in Co(Mo) Nanoparticles

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ABSTRACT

Developing new multicomponent nanoscale materials are integral to obtaining unique catalytic, magnetic, electrical, or optical properties. We created new solid solution alloys in systems which are immiscible in bulk by forming nanoparticles by Inert Gas Condensation (IGC). Co-Mo nanoparticles with extended solubility of Mo in Co were produced by IGC using both 2 and 3 Mo plugs inset in a Co target. Sputtering power and aperture size were varied to observe the effect of processing parameters on the structure and size of nanoclusters. EDS spectra from TEM showed an elemental composition of approximately 82 at. % Co and 18 at. % Mo and 65 at. % Co and 35 at. % Mo for the 2 and 3 plug targets, respectively. HAADF STEM images displayed uniform contrast in the nanoparticles, suggesting homogenous mixing of Mo and Co, even up to 35% Mo.

For the 2 plug system, HRTEM images showed predominantly single-crystalline hcp structures. Nanoclusters were about 7-15 nm in diameter. Co-Mo nanoclusters were ferromagnetic at room temperature, and coercivity was observed to be related to nanoparticle size.

For the 3 plug system, HRTEM images showed poorly crystalline structures. Co-Mo nanoclusters were ferromagnetic at room temperature, and coercivity for both aperture sizes was similar. Overall, the coercivities observed for 3 plugs system were higher than 2 plugs systems, suggesting the formation of the hcp structure. The higher coercivity with higher Mo dissolution into the hcp Co can be correlated to the magnetocrystalline anisotropy enhancement caused by 4d dissolution into hcp Co [1]. Figure 1 (a,b) shows the structural differences between 2 and 3 plug system and (c) demonstrates homogenous mixing of Mo in Co.

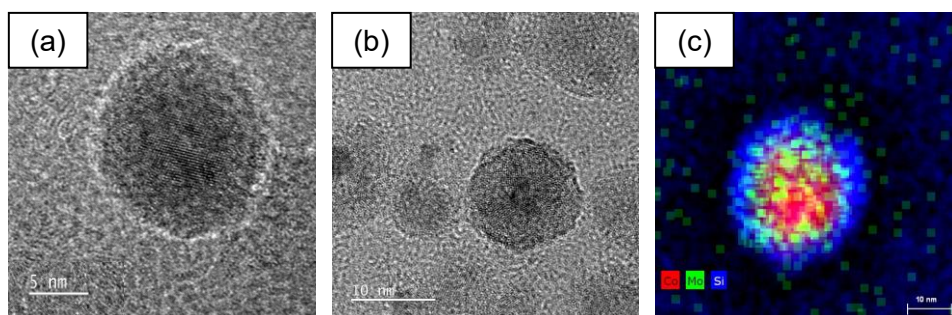


Fig. 15 : Co-Mo nanoparticles formed by IGC: (a) HRTEM image of 2 plug system showcasing single crystalline structure. (b) HRTEM image of 3 plug system representing poorly crystalline structure. (c) Composition maps demonstrating homogenous mixing of Mo in hcp Co. Si is part of the capping layer deposited to prevent oxidation.

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Chemical Ordering in Ni-Pt And Co-Ni-Pt Nanoalloys

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ABSTRACT

The extension of medium and high entropy alloy concepts to finite size systems, such as nanoparticles (NPs), is an emerging research area with potential applications in catalysis and mechanical properties [1]. In this work we focus on Ni-Pt and Co-Ni-Pt nanoparticles. These alloys are model medium entropy alloy systems of transition metals with FCC structure, where the binary subsets have both ordering (Co-Pt and Ni-Pt) and mixing (Co-Ni) tendencies at low temperature, making it interesting to discover the phases emerging from this complexity.

Describing the interactions between different species with a homemade semi-empirical potential, we perform extensive Monte Carlo simulations to find the equilibrium states. This allows us to study the effect of composition, temperature, shape and size on the chemical ordering in the core and on the surfaces of the NPs. Ad hoc short and long range order parameters are defined to identify both different phases and order/disorder transition temperatures.

In binary NPs, core and surface ordering are similar to the bulk and infinite surface slabs, which are not always compatible and create ordering frustrations. In ternary systems, we find more complex and exotic ordered structures and multi-phase domains, and discuss the role of each element. Pt surface segregation, which is important for catalysis, shows an interesting inverse behavior with temperature, driven by ordering effects. In particular, we find an enhanced stress-induced segregation in icosahedral NPs compared to octahedral NPs, which could explain their experimentally observed higher catalytic activity [2]. The approach developed here for the Co-Ni-Pt ternary system could be generalized to FCC high entropy alloy NPs with higher number of components.

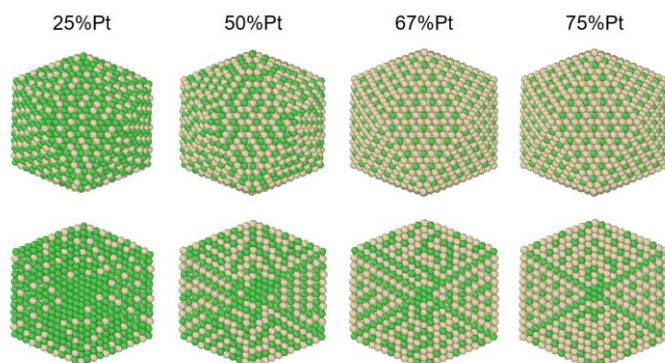


Fig. 16 : Icosahedral Ni-Pt nanoparticles with 5083 atoms at different compositions and after thermal equilibration at 300K, showing the chemical ordering from a shell view (top) and a cutting view (bottom). Green atoms represent Ni and beige atoms represent Pt.

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Coexistence of Miscibility and Segregation in Gold-Silver Nanoalloys

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Among the most studied nanosystems are gold-silver alloys, known for their catalytic, plasmonic, and photocatalytic properties. While gold and silver are completely miscible in bulk, their nanoscale behavior involves additional factors like particle surface and possible segregation, leading to unique structures. Despite the high number of experimental and theoretical articles published on AgAu nanoparticles, the controversy about whether intrinsically one of the two metals preferentially segregates at the surface or not is still unresolved. In this context, we aim to contribute to this discussion by providing statistically reliable quantitative chemical profiles of AgAu BNPs, using high signal-to-noise ratio and resolution hyperspectral images (HSI) obtained by Energy Dispersive X-ray Spectroscopy (EDS) and Scanning Transmission Electron Microscopy (STEM), analyzing 118 AgAu BNPs. To ensure analysis in the chemical ground state, the BNPs were protected by a thin amorphous carbon layer and annealed at 300°C. Unsupervised machine learning methods, including Principal Component Analysis (PCA) and Nonnegative Matrix Factorization (NMF), were employed to identify latent information on composition variations. This robust statistical analysis confirmed the radial composition changes (chemical gradients) indicated by the EDS spectra. We also used azimuthal integration of pixels from BNPs' region to enhance signal-to-noise ratio (SNR). Our findings demonstrate the capability to quantify chemical composition within BNPs ranging from 4-10 nm in diameter, revealing Ag enrichment towards the surface of every BNP. This study combines well-defined model samples, robust EDS-TEM analysis, and machine learning for statistical validation, resolving the controversy on nanoscale miscibility in the AgAu system. While Au and Ag are miscible in the core of BNPs as small as 4 nm in diameter, with a core of 2 nm (<400 atoms), a consistent surface enrichment of silver by about 10% is observed, revealing that the question related to elemental distribution of gold-silver alloys is complex with the coexistence of both, elemental miscibility and segregation within the BNPs. Our work also paves the way for extending these methods to environmental and tomographic studies of multimetallic nanostructures, such as high entropy alloys.

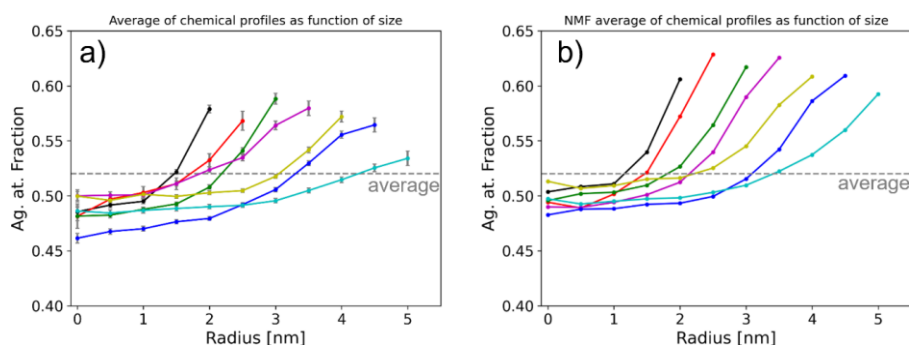


Fig. 1: Chemical gradients for different AgAu BNP diameters. Left: averaged raw data; right: NMF denoised and averaged data. No error bars are displayed for the NMF denoised data as their calculation does not yet follow a recognized and well accepted procedure. The dashed lines represent the mean Ag fraction as averaged over the entire BNP ensemble.

Understanding Structural Transitions in Nanoclusters via Neural Variables

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ABSTRACT

The structural landscape of nanoclusters is extremely multi-faceted and hard to describe in terms of a limited number of variables.

A general method to obtain a representation of this complex landscape in terms of a reduced number of variables is proposed. Starting from the approach proposed in [1], a different strategy, based on the coupling via neural networks of the thermalized descriptions of the system with their inherent structures, has been developed to generate a low dimensional description of nanoclusters structural landscape. The neural variables enable the description in molecular simulations of both equilibrium phenomena, allowing for the computation of free-energies and transition rates, and non-equilibrium ones, such as melting and freezing. The method has been tested over a particular elemental gold nano cluster composed of 147 atoms, of which free energy for its complete structural landscape has been computed and several freezing simulations have been performed in order to perform polymorph selection. While the method has been tested on an elemental nanocluster, it shows promise as a general strategy to describe structural transitions for all types of nanoparticles, including nanoalloys.

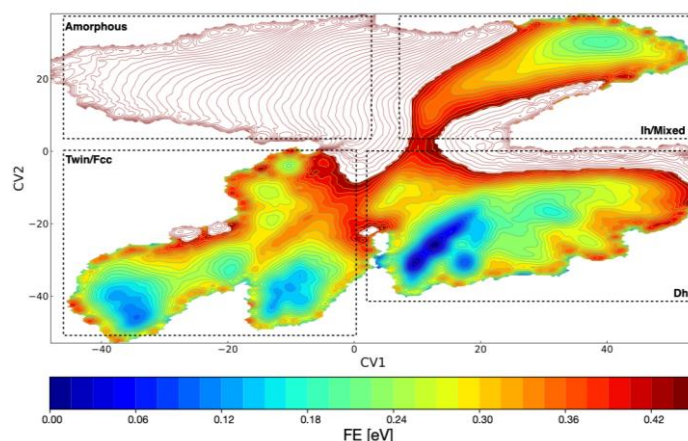


Fig. 1 : Free energy landscape of a system composed of 147 gold atoms at 396 K, obtained performing umbrella sampling simulations exploiting neural variables

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Thursday, 5 September

- 09:00 Exploring the Effects of Reactive Species over the Composition in Au-Fe Non-Equilibrium Alloy NPs Obtained by the Laser Ablation in Liquid
Vito Coviello (Università di Padova, Italy)
- 09:30 Solid Solution and Segregated Alloy Nanoparticle Structures by Laser Ablation in Liquids (LAL)
Christoph Rehbock (University of Duisburg-Essen, Germany)
- 10:00 Thermal Stability of High Entropy Alloy Nanoparticles: an Atomic Scale Study
Anissa Acheche (ONERA-CNRS, Chatillon, France)
- 10:30 Coffee break
- 11:00 Exploring the Importance of Dynamics in Metals Using Advanced Computational Methods
Matteo Cioni (Politecnico di Torino, Italy)
- 11:30 The Effect of Surface States Accumulation on Photo-Electrochemical Performances of Bi₂₄Fe₂O₃₉ Grown by Supersonic Beams
Skexho Osmani (Università Cattolica del Sacro Cuore, Brescia, Italy)
- 12:00 Do We Know the Spectra of Small Al Clusters? Pitfalls and Solutions in TDDFT
Hans-Christian Weissker (Aix-Marseille Université, CNRS, CINAM, France)
- 12:30 Correlating Plasmonic and Structural Properties of In₂Au Nanoparticles
Matthias Hillenkamp (Université de Lyon, CNRS, iLM, France)
- 13:00 Concluding remarks
Riccardo Ferrando (Università di Genova, Italy)
- 13:15 Lunch

Exploring the Effects of Reactive Species over the Composition in Au-Fe Non-Equilibrium Alloy NPs Obtained by the Laser Ablation in Liquid

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ABSTRACT

Controlling the size, shape, and composition of alloy nanoparticles (NPs) is crucial in developing a tailor-made nanomaterial for a specific application. In this context, bimetallic alloy NPs having non-thermodynamically stable compositions, i.e. Au-Fe, play a pivotal role in venturing into the new generation of multifunctional nanomaterials.^{1–4}

Laser ablation synthesis in liquid (LAL) is one of the most suited synthetic techniques for obtaining Au-Fe alloy NPs, as their syntheses occurs rapid formation times and non-equilibrium synthetic approaches.⁵

To achieve compositional control, this study examines the environmental effects of LAL synthesis on the ultimate composition of non-equilibrium Au-Fe alloy nanoparticles. The NPs syntheses were performed in two distinct pure solvents, as well as in their solutions containing reactive gas sources such as O₂, N₂, and H₂ (Figure 1a). The presence of these gases affects the outcome of LAL synthesis, as they can lead to variations in the thermodynamical paths and physicochemical conditions of the ablation processes.⁶ This investigation focuses on the early stages of the ablation process, specifically the shock wave propagation and cavitation bubble evolution, to assess the underlying nature of the effect that gaseous reactive species have on the NPs' composition. Shadowgraph imaging allows for the direct visualization of laser-induced shock waves and cavitation bubbles, enabling the study of their dynamics (Figure 1b).^{7,8} The characterization of these phenomena provides qualitative and quantitative clues regarding the solvent's major effect on the synthesis thermodynamic conditions and therefore on the final composition of the NPs (Figure 1c).

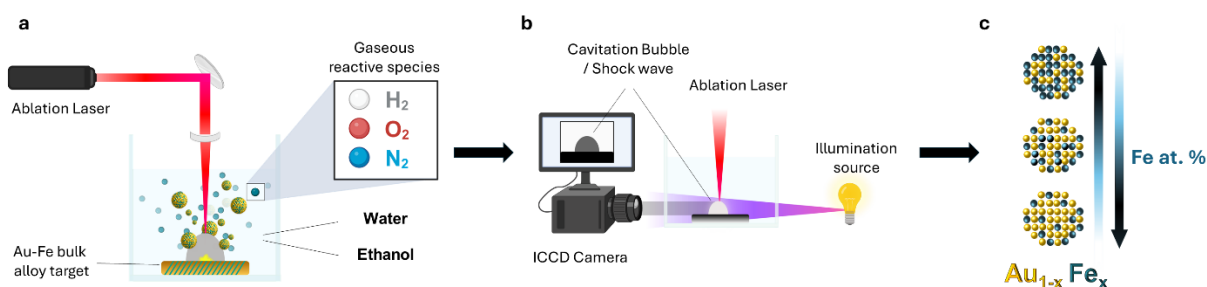


Fig. 1 : a) Sketch of the Laser Ablation in Liquid synthesis. Alloy nanoparticles were obtained in water and ethanol as pure solvents and with the addition of gaseous reactive species. b) Sketch of the shadowgraph imaging technique. The characterization of the ablation processes allows a deeper understanding of the environmental effects on the final alloy NPs composition. c) Au-Fe alloy NPs with various compositions are obtained by varying solvents and the present gaseous reactive species.

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Solid Solution and Segregated Alloy Nanoparticle Structures by Laser Ablation in Liquids (LAL)

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ABSTRACT

Laser-generated alloy nanoparticles (NPs) exhibit unique structures, highly interesting in many applications from catalysis to biomedicine [1], and they may be generated using either alloyed targets or pressed pellets from metallic micropowder mixtures [1, 2]. Especially the binary gold-silver system has been very well studied, where LAL synthesis gives access to AgAu NPs with compositions and optical properties well controlled by the target and ideal solid solution crystal structures and full elemental miscibility on a single NP level [3], while recent studies highlight that the outer surface-near volume is enriched by the minor element [1]. However, more complex structures emerge when we switch to bimetallic systems with pronounced miscibility gaps and oxidation susceptibility. We particularly studied the FeAu system in great detail, where we could observe the formation of a unique metastable iron core, gold-iron alloy shell structure [4]. Interestingly, formation of core-shell ultrastructures was disfavored upon utilization of ultrashort laser pulses [5], a phenomenon probably associated with a limited elemental mixing during the initial stages of NP formation by LAL, currently highlighted by atomistic modeling [6]. While observing transferability towards other non-miscible bimetallic systems like AuCo and PtCo we could deduce a set of core-shell formation rules, namely an immiscibility in the bulk, a defined NP diameter and a mismatch in melting temperature and surface energy, which favours formation of core-shell ultrastructures [7]. We further demonstrated transferability of LAL to multicomponent high entropy alloy (HEA) NPs, with focus on the FeCoNiCrMn (Cantor alloy). Here we could synthesize crystalline HEA NPs with diameters <10 nm and a homogeneous elemental distribution on a single particle level [8], which exhibited high performance in electrocatalysis. Recently, we also synthesized fully amorphous HEA metallic glass nanoparticles, favored by carbon implementation into the metal core [9].

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Thermal Stability of High Entropy Alloy Nanoparticles: an Atomic Scale Study

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ABSTRACT

Recently, HEAs have been synthesized in the form of nanoparticles (HEA-NPS). First reports on the tuneable properties of HEA-NPs have shown their promising catalytic activity in many reactions. A critical first step towards optimizing the potential of HEA-NPs for medium or high temperature application, beyond catalysis, is to develop a better understanding of their thermal behavior and their structural stability. In this contribution, we have performed Molecular Dynamics (MD) simulation coupled with in situ aberration-corrected Scanning Transmission Electron Microscopy (STEM) observations to gain atomic-level fundamental insights into the thermal stability of CoNiCuPtAu HEA-NPS.

On an experimental side, the CoNiCuPtAu HEA-NPs were first deposited on a SiN support by pulsed laser deposition as in [1]. Their atomic and chemical structures were then followed at single particle level and atomic scale during in situ STEM heating up to 1000K under vacuum ($\sim 10^{-6}$ Pa). Evaluation of NP stability by in situ STEM imaging, shows that some particle coalescence is activated around 700K. X-ray spectroscopy revealed that particle coalescence occurred concomitantly with Au and Cu surface segregation. As the temperatures is raised to 1000K, we additionally observed the simultaneous depletion of the latter two elements from the NPs, leading to ternary CoNiPt. To gain fundamental insights into the atomic and kinetic/thermodynamic origin of the temperature-driven structure transition observed experimentally, we performed MD simulation, using the LAMMPS code based on the Zou et al potential [2], to investigate the structure of CoNiCuPtAu NPs under thermal stimuli.

In this context, 309 to 3871-atom CoNiCuPtAu HEA-NPs in equiatomic composition were considered. Particle size were comparable to those probed experimentally (approximately 2 to 5 nm diameter). The investigation of their structural properties over the temperature range from 400 to 1500 K, results in a number of significant conclusions. Firstly, in good agreement with experimental observation, a temperature-dependent segregation of gold and copper at the NP surface is highlighted. Furthermore, the analysis of the local atomic energy of the different elemental species confirms the strong tendency of Au and Cu atoms to segregate at the surface. The Au and Cu surface atoms have the lowest energy and are therefore highly susceptible to evaporation, which may explain their depletion in the NPs at high temperature as observed experimentally. Lastly, the diffusion studies of the constituent elements demonstrated that the presence of interfacial area in coalesced NPs favors Au mobility and thus its segregation [3].

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Exploring the Importance of Dynamics in Metals Using Advanced Computational Methods

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Understanding the dynamic behavior of materials at the microscopic level is essential for explaining their macroscopic properties. However, capturing complex atomic/molecular dynamics and translating them into a comprehensive understanding of material properties is challenging. This study focuses on metals, exploring the non-trivial atomic dynamics within them.

Initially, we investigate copper surfaces¹ using deep-potential molecular dynamics simulations with a neural network potential trained on DFT calculations, resolving their complex dynamic behaviors. Additionally, we explore gold nanoparticles (NPs) to characterize their atomic dynamics at different temperatures². By extending our previous approach, we demonstrate that our analytical framework is applicable to various metal systems, providing insights into the intrinsic atomic dynamics shaping NP properties. This progress led to a collaboration with experimental groups, combining advanced computational and experimental techniques to characterize these systems with unprecedented resolution, overcoming the limitations of each method when used separately.³

At the core of our approach, we utilize high-dimensional structural descriptors, such as SOAP³, and unsupervised machine learning techniques to identify and track atomic environments across metal systems. This reveals the dynamic equilibrium between native and non-native AEs, offering a new perspective on the "statistical identity" of metals.

Overall, this general approach unravels and characterizes the intricate dynamics of metal systems. By examining microscopic dynamics, we can accurately determine macroscopic properties, enhancing our understanding of metal surface behaviors under relevant conditions. Shifting from static to dynamic perspectives, our approach advances the understanding of complex systems, providing comprehensive insights into the behavior of metals and other materials.

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The Effect of Surface States Accumulation on Photo-Electrochemical Performances of Bi₂₄Fe₂O₃₉ Grown by Supersonic Beams

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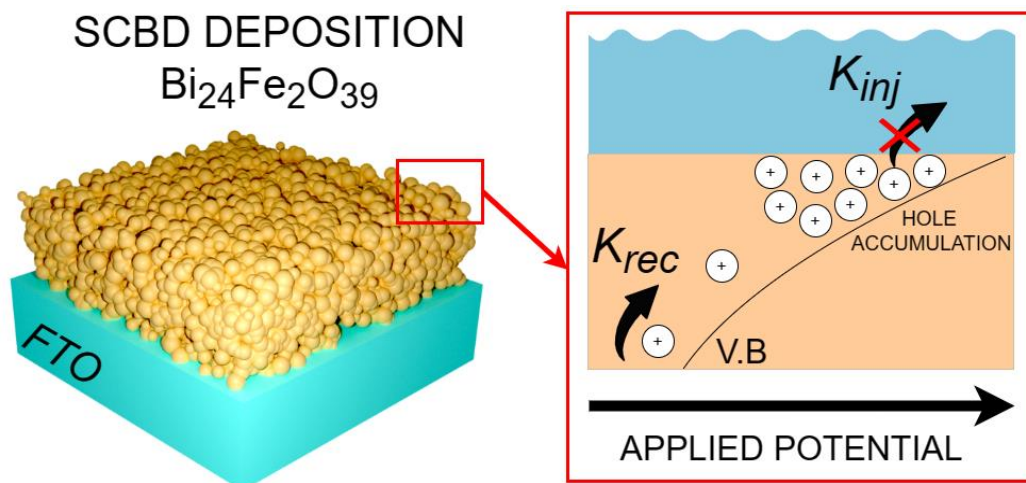
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ABSTRACT

Holes accumulation on the surface of bismuth ferrite oxides (BFO) photoanodes for photoelectrochemical (PEC) water splitting (WS) is one of the major issues limiting the overall cell efficiency. However, among the various BFO crystal structures, no evidence of this mechanism has been reported for Bi₂₄Fe₂O₃₉, a scarcely investigated phase. Herein we characterize the morphological, structural and PEC properties of 100 nm thick nanogranular films of a Bi₂₄Fe₂O₃₉ single phase synthesized by supersonic cluster beam deposition. The films were tested as photoanodes for the WS reaction in KOH and Na₂SO₄ + Na₂SO₃ electrolytes. The PEC data provide direct evidence of holes accumulation on the surface of the material with increasing applied biases. The interesting performances of this material at low biases suggest a possible use as photocatalyst under visible light irradiation.



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Do We Know the Spectra of Small Al Clusters? Pitfalls and Solutions in TDDFT

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ABSTRACT

Alloying of Ag nanostructures with aluminum or indium promises a possible extension of plasmonic applications into the UV. Aluminum itself has been studied as an unconventional material for plasmonics since some time [1]. The advantages of Al are its low cost as well as the fact that the surface plasmon for nanoparticles occurs far in the UV, unlike in the more traditional plasmonic materials like Ag and Au. A disadvantage is certainly the high sensitivity to oxidation which poses enormous problems for the experimental fabrication of small Al nanoparticles and clusters. In addition, optical measurements high in the UV are likewise very difficult.

However, also for theory the situation is difficult. Taking the presumably simple cluster Al_{13} as an example, a brief review of the literature shows that while there are several optical spectra published in different contexts, they are entirely contradictory and do have no similarity between them, in some cases.

The reason can be traced back to the high energy of the plasmon, above the ionization energy, and to the fact that the transitions that contribute involve states which are largely part of the continuum, in particular for the anion.

In the present work we show how we can describe the system properly. To this end, we combine jellium calculations using the octopus code [2], where the calculation domain is finite, with calculations using the spherical jellium model where no box is imposed and, in addition, the polarizability can be expressed in terms of only the occupied states. This comparison allows us to determine the proper parameters for absorbing boundaries [3] which in turn produce correct spectra for all charge states, +1, neutral, and -1, of the Al_{13} clusters. This, in turn, allows us to calculate the size-dependence of the surface-plasmon resonances.

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Correlating Plasmonic and Structural Properties of In_2Au Nanoparticles

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ABSTRACT

Alloying noble and trivalent metals in nanoparticles has been shown a feasible way to shift the Localized Surface Plasmon Resonance (LSPR) further into the UV spectral range, opening the way for applications in UV photocatalysis, sensing and the generation of high energy hot electrons. Here we show that In_2Au is a good candidate as it shows an LSPR at wavelengths below 300 nm and an improved stability against oxidation as compared to other alloy combinations. The distinct crystalline structure (CaF_2) allows for an unambiguous identification of the metallic phase in transmission electron microscopy. We investigate the chemical structure of the bimetallic nanoparticles using energy-dispersive x-ray spectroscopy in a scanning TEM and separate metallic from oxidized phases using machine learning techniques such as principal component analysis (PCA) and non-negative matrix factorization (NMF).

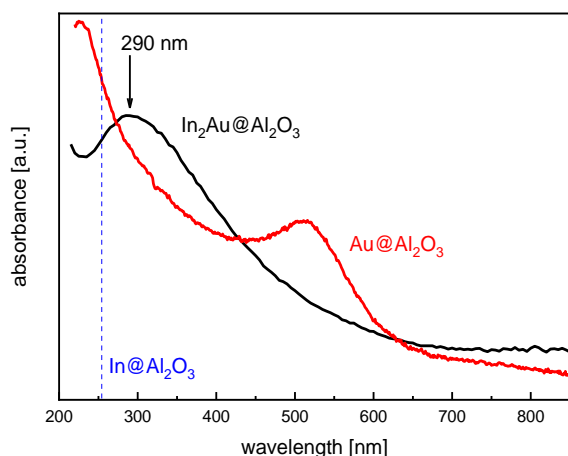


Fig. 17 : Optical absorption of alumina-embedded In_2Au nanoparticles (black). For comparison are shown the LSPR of pure gold and the calculated Mie LSPR of pure Indium.

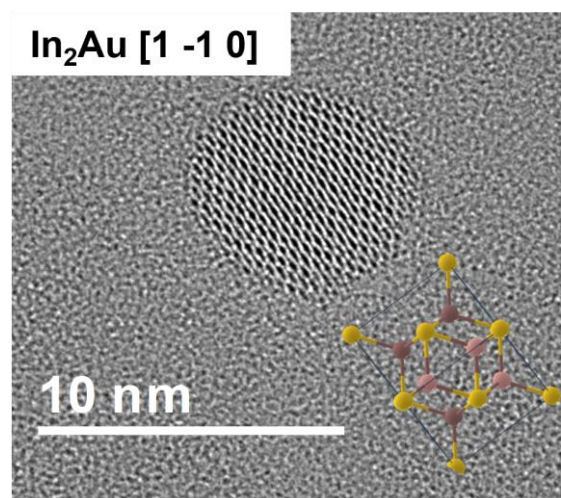


Fig. 18 : High-resolution TEM image of a In_2Au particle protected in amorphous carbon. The crystalline structure corresponds to the CaF_2 structure along the $[1, -1, 0]$ orientation.

Poster session

1. **Pascal Andreazza** (University of Orléans, France)
Strongly and Weakly Miscible Bimetallic Nanoalloys Based on Pt and Ag: Some Tendencies
2. **Aryan Aryan** (University of Orléans, France)
Effect of a Secondary Plasma on Copper Nanoparticles Synthesized by a Gas Aggregation Source
3. **Giovanni Barcaro** (Pisa Research Unit, Italy)
Grouping At Work: New Strategies in the Global Optimization of NanoAlloys
4. **Emmanuel Cottancin** (University of Lyon 1, France)
Towards Stable Nanoalloys Mixing Au or Ag With Al or In With Localized Surface Plasmon Resonances In The UV Range
5. **Véronique Dupuis** (University of Lyon 1, France)
Finite Size Effects on the Metamagnetic Phase Transition in B2 FeRh Nanoclusters
6. **Alberto Giacomello** (Sapienza University of Rome, Italy)
Charting Nanocluster Structures via Convolutional Neural Networks
7. **Wilken Aldair Misael** (University of Aix Marseille, France)
Theoretical Investigation of Interband and Plasmonic Excitations in Mono-Metallic In and Bi-Metallic AgIn Nanoclusters
8. **Christophe Petit** (Sorbonne University, France)
The Contribution of XPS to the Problem of Nucleation-growth of Nanoparticles: the Case of Cobalt and its Derivatives
9. **Elina Mkrtchian** (University of Genoa, Italy)
Highly Active Ni–Fe Bi-Metallic Catalysts on DRM and RWGS Reactions
10. **Morgan Rees** (Swansea University, UK)
Energy Differences Between Structural Isomers of Deposited, Size-Selected Au Nanoclusters
11. **Rocca Mario** (UOS Genova, Italy)
Cross-coupling of Pd-cyclometallated complexes on Ag(110)
12. **Thantip Roongcharoen** (Consiglio Nazionale delle Ricerche)
Presenting Pt-Mn Catalyst for Methanol Aqueous-Phase Reforming and a CSCP Approach for Catalytic Processes: Theoretical Studies
13. **Carlos Rufino Da Silva** (Northern Arizona University, USA)
Decahedral Shaped Nanoparticles
14. **Anshika Singh** (University of Allahabad, India)
Interfacial Engineering Enables Polyaniline-Decorated Bismuth Sulfide Nanorods towards Fast UV-Vis Photodetector
15. **Robert Stuckert** (University of Duisburg-Essen, Germany)
Structure of Cantor and Noble Metal High-Entropy Alloy Nanoparticles Produced by Laser Ablation in Liquid

16. **Songül Taran** (Duzce University, Turkey)
Investigation of Size Dependence for the Properties of NiCoRh Nanoalloys

17. **Florent Tournus** (Claude Bernard University of Lyon 1, France)
Preferential Orientations of FeRh Nanomagnets Deposited on a BaTiO₃ Epitaxial Thin Film

18. **Michele Vergari** (Università Cattolica del Sacro Cuore, Italy)
Characterization of Stoichiometrically Different BFO Thin Films for Photoanodes

19. **Yue Wang** (Guangdong Technion-Israel Institute of Technology)
Support-Induced Strain Engineering of the Chemical Ordering in Anchored Ni-Pt Nanoalloys

Strongly and Weakly Miscible Bimetallic Nanoalloys Based on Pt and Ag: Some Tendencies

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ABSTRACT

We can distinguish three main driving forces in order to predict the nature and the degree of mixing and segregation in a binary alloy: the differences in cohesive energies and radii of the two elements (mismatch-effect), and the mixing energy in the bulk. With respect to these features, two extreme systems are very interesting to investigate experimentally and theoretically: the weakly miscible systems and the strongly miscible systems. Considering the association of Pt or Ag with Co atoms in the equi-composition range, the tendencies at the nanoscale are clearly the mixing with a negligible surface segregation for PtCo since Pt and Co present a comparable surface energy and a strong mixing energy, and rather the phase separation for AgCo in a surface segregation of silver since Ag presents lower surface energy and larger size (to minimize elastic-energy), in addition to the very large miscibility gap in wide ranges of temperature and concentration, without alloyed phases.

As the Ni atoms are chemically and thermodynamically comparable to Co atoms, similar bulk phase diagram for PtNi and PtCo or between AgNi and PtNi, similar cohesive and surface energies for Ni and Co, similar atom size. the association with Pt or Ag could be expected very similar! However, at the nanometer scale, the growth technique influence, the kinetic effects or the environment effects can overcome the behaviors expected by the thermodynamics. In addition, in our case of UHV atomic deposition and condensation on a substrate, the nature of substrate (topologically and chemically) and the mobility of Pt, Ag, Co or Ni atoms on the substrate must be considered, leading to unexpected atom arrangement.

We will present the different results and comparisons on the morphological and structural evolutions of clusters 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). Several behaviors have been revealed in the structure evolution depending on the deposition modes, from the simultaneous or sequential metastable growth at room temperature up to their equilibrium state obtained by thermal activation.

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Effect of a Secondary Plasma on Copper Nanoparticles Synthesized by a Gas Aggregation Source

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ABSTRACT

A Gas Aggregation Source (GAS) is a system used to create nanoparticles by evaporating or sputtering a target material into a dense inert gas atmosphere. The gas cools the evaporated atoms, causing them to aggregate into nanoparticles [1]. Copper (and PtSn) nanoparticles (NPs) synthesized in a Gas Aggregation Source were successfully deposited on a silicon (Si) substrate. The CuNPs were introduced into a secondary plasma created in the vicinity of the substrate by applying a bias of +50 V. At the orifice of the GAS, the mixture contains negative, positive, and neutral atomic species and clusters that come under the influence of the secondary plasma to form larger clusters. The stability of this secondary plasma was examined at various bias potentials. From SEM analysis, it was observed that without the influence of the secondary plasma, a porous homogeneous film of smaller NPs (<10 nm) was deposited, while with the secondary plasma, the morphology of the film changed to larger clusters (50 nm).

For PtSn, Rutherford backscattering spectrometry (RBS) was used to examine the composition ratio, while XRD analysis was used to study the phase and micro-strain within the thin film. It will be crucial to examine the growth of these nanoclusters in the secondary plasma. The potential of this secondary plasma to improve the organization of NPs will be the subject of future investigations.

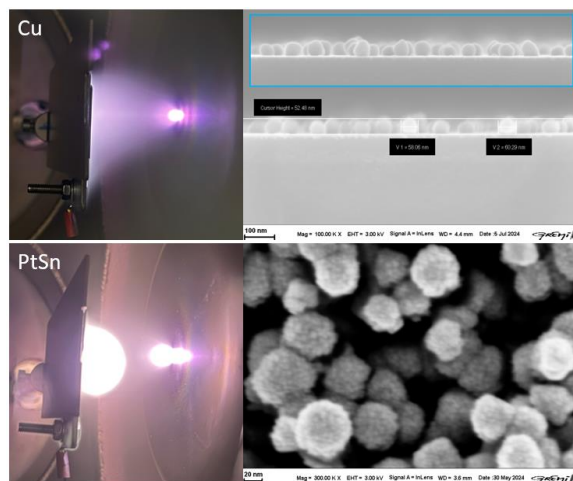


Fig. 1 : Presence of dusty plasma and the respective SEM images of nanoclusters.

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Grouping at Work: New Strategies in the Global Optimization of NanoAlloys

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ABSTRACT

Given the experimental difficulties in achieving a high-level atomistic characterization on alloyed nanoparticles, computational modeling can play a key role in elucidating structures and structure/properties relationships, in view of potential applications in many technological fields, like catalysis, sensing, optics, etc. At this purpose, we will present a free-source code based on global optimization statistical algorithms to efficiently single out low-energy structures of metallic nanoclusters made of two different elements (nanoalloys). The complexity of the problem stems from the need to explore simultaneously both the phase space of structural configurations and that of chemical ordering patterns, combining exhaustiveness and speed. A recent method [1] has demonstrated how “Grouping” methods can significantly improve the identification of chemical ordering patterns, maintaining a high level of exhaustiveness. Within this framework, we will present an improved computational code able to exploit an intertwined approach, achieved by implementing the Grouping method within an efficient engine for the Global Optimization of NanoAlloys previously developed at the Genoa University [2]. This project is part of the “National Center in High-Performance Computing, Big Data and Quantum Computing (CN-HPC)” of the Italian PNRR.

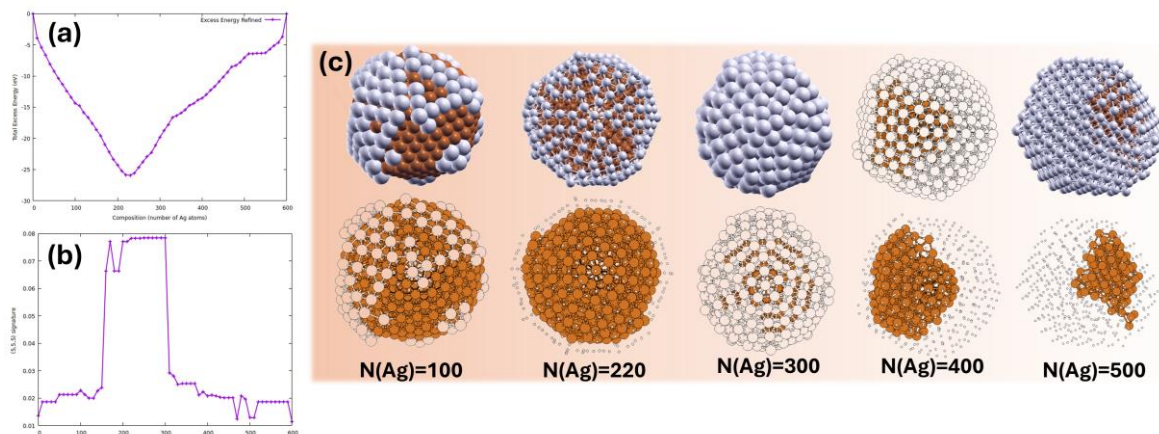


Fig. 1 : (a) convex hull and (b) (5,5) signature of the lowest-energy structures characterizing the AgCu alloy at size 600; (c) some characteristic low-energy structures covering the full compositional range of the alloy.

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Towards Stable Nanoalloys Mixing Au or Ag with Al or In with Localized Surface Plasmon Resonances in the UV Range

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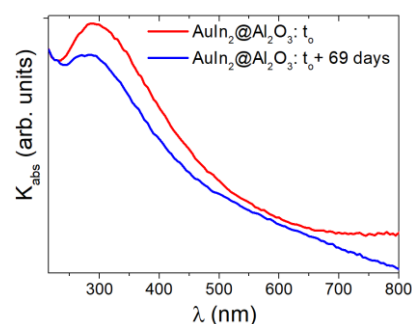
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ABSTRACT

Bimetallic nanoparticles (BNPs) are promising for fundamental research and applications, as their physicochemical properties can be tuned or enhanced with respect to the monometallic particles. In this context, the atomic and chemical structure and the optical response of A_xB_{1-x} BNPs combining gold or silver (A) with aluminium or indium (B) were investigated for various stoichiometries in order to examine if stable alloyed phases could exist and promote localized surface plasmon resonances (LSPR) in the UV range. [1, 2]

The structure and morphology of matrix embedded-BNPs of a few nanometers, produced by laser vaporization, were analysed by transmission electron microscopy (TEM) and optical absorption measurements compared with Mie calculations in the dipolar approximation. The BNPs' internal structure was further investigated by in situ x-ray photoelectron spectroscopy and synchrotron-based x-ray scattering techniques giving complementary information about the chemical state of the constituent elements and structural heterogeneities in the BNPs. The complementary techniques of characterization show that silica-embedded silver-based Ag-In and Ag-Al BNPs form metallic silver-rich alloyed cores surrounded by an indium or aluminium oxide shell. The initial LSPRs are in the UV range for both systems, but the difference in the kinetics of oxidation between indium and aluminium involves less blue-shifted LSPRs for Ag-Al BNPs. In the case of gold-based BNPs, we investigated the chemical structure of the gold-based BNPs in various matrices (carbon, silica, alumina) using energy-dispersive X-ray spectroscopy in a STEM and separated metallic from oxidized phases using unsupervised machine learning techniques such as principal component analysis (PCA) and non-negative matrix factorization (NMF). The characterization of the metallic structures was achieved by complementary imaging in HRTEM, STEM-HAADF and SAED. [3] Finally, by combining imaging, diffraction, and spectroscopy techniques, we show that In_2Au is a good candidate to correlate plasmonic and structural properties as it shows an LSPR in the UV range and improved stability against oxidation compared to other alloy combinations (see figure).



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Finite Size Effects on the Metamagnetic Phase Transition in B2 FeRh Nanoclusters

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ABSTRACT

Near equiatomic composition, FeRh bulk alloys in the CsCl-type (B2) chemically ordered phase present a metamagnetic transition from the antiferromagnetic (AFM) state at low temperature to the ferromagnetic state (FM) above a critical transition temperature of 370 K, accompanied by a 1% volume expansion. Despite the high FeRh material cost, the competition near room temperature between both magnetic orders holds great potential applications including magnetocaloric refrigeration and ultrafast spintronics. Beyond previous studies on continuous FeRh films, here we propose to explore metamagnetic phase transition in nanogranular film, made of FeRh clusters preformed in the gas phase using the Low Energy Cluster Beam Deposition (LECBD) technique [1]. We also present experimental results obtained on mass-selected FeRh clusters with 3 nm and 7 nm in diameter deposited on TiO₃ based substrate and subsequently UHV annealed at 700°C to reach the B2 phase [2]. We clearly observed epitaxial relationships from STEM-HAADF on single nanoparticle of B2 FeRh deposited on oxide perovskite substrate with carbon capping but also from grazing incidence X-ray diffraction (GIXRD) on clusters assemblies, which is also accompanied by a Fe (resp. Rh induced) magnetic moment evolution visible from X-ray magnetic circular dichroism (XMCD) measurements at Fe and at Rh L-edge under synchrotron facilities. The systematic study of such hybrid multiferroic nanostructures (0D/2D) reveals a strong interplay between surface chemical reactivity, configuration, morphology and magnetic state.

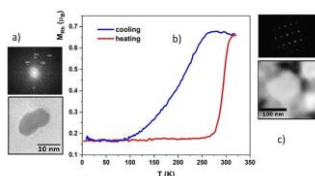


Fig. 19 : TEM (a), XMCD at Rh-L edge versus T under 7T (b) and STEM (c) on gradient-structured B2 FeRh film

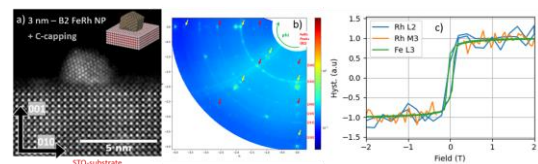


Fig. 2 : STEM HAADF(a) on 3nm B2 FeRh cluster in epitaxy on STO studied by GIXRD (b) XMCD at Fe and Rh edges (c)

This work is part of the PhD thesis of G. Herrera with financial support of VOLTage Control of NANOmagnet ANR VOLCONANO projet (2020-24) ANR-19-CE09-0023.

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Charting Nanocluster Structures via Convolutional Neural Networks

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ABSTRACT

A general method to obtain a representation of the structural landscape of nanoparticles in terms of a limited number of variables is proposed [1]. The method is applied to a large data set of parallel tempering molecular dynamics simulations of gold clusters of 90 and 147 atoms, silver clusters of 147 atoms, and copper clusters of 147 atoms, covering a plethora of structures and temperatures. The method leverages convolutional neural networks to learn the radial distribution functions of the nanoclusters and distills a low-dimensional chart of the structural landscape (Fig. 1). This strategy is found to give rise to a physically meaningful and differentiable mapping of the atom positions to a low-dimensional manifold in which the main structural motifs are clearly discriminated and meaningfully ordered. Furthermore, unsupervised clustering on the low-dimensional data proved effective at further splitting the motifs into structural subfamilies characterized by very fine and physically relevant differences such as the presence of specific punctual or planar defects or of atoms with particular coordination features. Owing to these peculiarities, the chart also enabled tracking of the complex structural evolution in a reactive trajectory. In addition to visualization and analysis of complex structural landscapes, the presented approach offers a general, low-dimensional set of differentiable variables that has the potential to be used for exploration and enhanced sampling purposes.

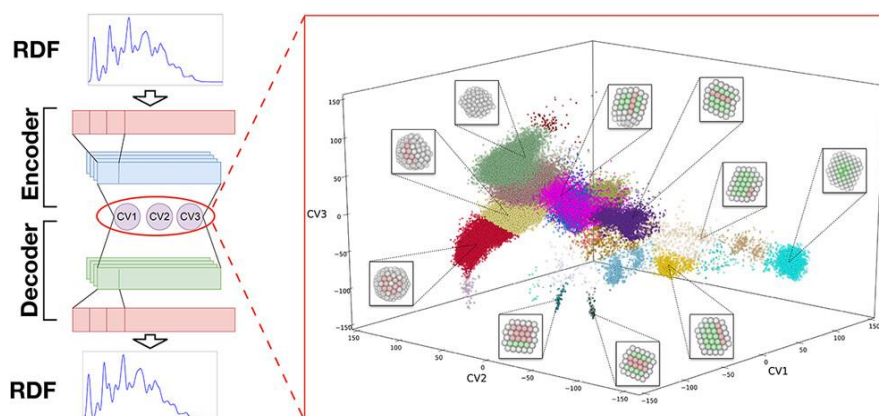


Fig. 1: (left) Convolutional neural network-based autoencoder used to extract a low dimensional representation (CV1, CV2, and CV3) of nanocluster structures. (right) 3D chart showing the various structural families identified for Au₁₄₇.

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Theoretical Investigation of Interband and Plasmonic Excitations in Mono-Metallic In and Bi-Metallic AgIn Nanoclusters

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ABSTRACT

The localized surface-plasmon resonance (LSPR) in the UV range plays a central role in understanding how these materials respond to external electromagnetic perturbations [1]. Nevertheless, the complexity of these materials, which is characterized by their high reactivity, aggregation, and instability, can pose challenges for both their efficient characterization and utilization [2]. In this regard, classical (electrodynamics Mie model) and ab initio simulations offer a powerful framework for exploring the properties of these materials. By evaluating the interplay of size, composition, and environment, which are reflected in spectral features such as the LSPR, these simulations can shed light on the physical-chemical properties of these systems [3].

Current advancements in nanoplasmonics are focused on exploring cost-effective alternatives to traditional plasmonic materials such as silver and gold. In a recent study [2], our collaborators demonstrated the potential of combining noble metals with trivalent metals, such as indium, to achieve a blue shift in the plasmonic feature. This shift is desirable for the development of plasmonics in the UV range. Theoretical simulations are expected to provide further insights into the optical properties of such bimetallic nanoparticles.

In this work, we use the Yabana-Bertsch time-evolution formalism (RT-TD-DFT) implemented in the real-space code Octopus [4] to investigate the electronic structure of model systems comprising mono-metallic In and bi-metallic AgIn nanoparticles with varying sizes and compositions, as well as their optical properties. We are specifically interested in evaluating how shifts in their plasmonic features in the UV region are related to the metallic composition. Our RT-TD-DFT simulations aligns well with experimental observations, demonstrating a blue-shift in plasmon energies upon indium incorporation into Ag clusters.

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The Contribution of XPS to the Problem of Nucleation-Growth of Nanoparticles: the Case of Cobalt and its Derivatives

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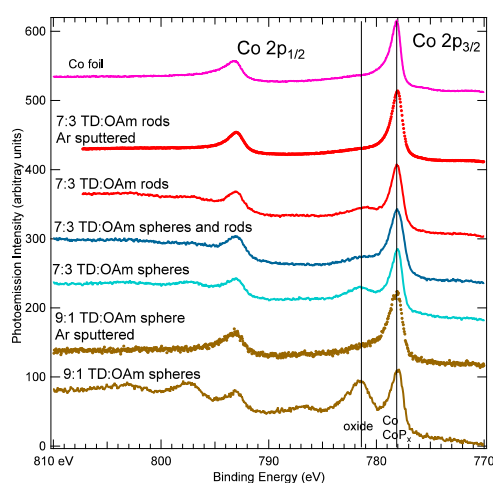
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ABSTRACT

Hcp cobalt nanoparticles have garnered significant scientific interest owing to their catalytic properties and high magnetocrystalline anisotropy, rendering them suitable for the fabrication of magnetic devices. In contrast to other synthesis, such as the reduction of inorganic Co(II) or Co(III) complexes or the decomposition of dicobaltoctacarbonyl molecule, the use of the Co(I)Cl(P(C₆H₅)₃)₃ precursor has emerged as a highly promising procedure to produce nanoparticles with very well controlled shape and size.¹ However, when oleylamine (OAm) is employed as the solvent, the synthesis of Co NPs from Co(I)Cl(Ph₃)₃ (Ph = C₆H₅) becomes



complex due to the occurrence of two distinct time steps associated with equally distinct particle morphologies. Initially, spherical hcp cobalt nanoparticles grow within 1 h at 190 °C followed by their dissolution and the subsequent recrystallization into rod-shaped nanoparticles over an extended period of 10 h. Recently a more profound understanding of the mechanisms underlying nanoparticle formation has been achieved through a series of experimental and theoretical studies lighting on the intricate multifunctional role played by OAm, which is revealed to act as a disproportionation promoter, a surfactant, a source of H₂, an oxidative etching promoter, and ultimately, a templating agent.² A new X-ray Photoelectron spectroscopy, XPS, study illuminates

further insight into the growth mechanism of cobalt nanoparticles.³ It confirms the formation of metallic cobalt and cobalt-nickel by dismutation reaction but provides evidence for the presence of metal phosphidation during the “sphere-to-rod” transition, with an XPS Co/P atomic ratio reaching ~2 for the nanorods only films. Lastly, the novel synthesis produces Co₂P or CoNiP nanorods at a relatively low reaction temperature (~190 °C), compared to the standard process (~330 °C).

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Highly Active Ni–Fe Bi-Metallic Catalysts on DRM and RWGS Reactions

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ABSTRACT

The growth of the population led to the development of industrialization and an increase in energy consumption, respectively. As a result, the amount of carbon dioxide (CO₂) emissions into the atmosphere increases too. The higher air concentration of CO₂ is one of the main factors in the acceleration of the global warming process [1]. Dry reforming of methane (DRM) and reverse water gas shift (RWGS) are interesting methods for CO₂ conversion [2,3].

In this study, Al₂O₃ carrier was prepared by sol-gel method followed by loading of nickel and iron nanoparticles (Ni-Fe NPs). The synthesis of bi-metallic (Ni-Fe) colloidal solutions were prepared by a green synthesis method [4], with the addition of glucose to reduce to metals the corresponding salts (Ni(NO₃)₂, Fe(NO₃)₃) in water. Then, the NH₄OH solution was added dropwise to aqueous solutions of either monometallic or bimetallic Ni and Fe compounds until pH 10 was reached, at room temperature, to obtain a solution with Ni-Fe NPs, respectively. Further, the solution was stirred at 90°C in 2 hours. As a result, working concentrations of Ni and Fe were obtained, at which there was no aggregation of metal particles with subsequent formation of precipitate. The presence of NPs in the solution was confirmed by the Tyndall effect using a red pointer laser. The synthesis of Al₂O₃ is carried out by a simplified method based on sol synthesis by precipitation of Al(NO₃)₃.

DRM and RWGS reactions were carried out in a quartz glass tube (internal diameter= 6 mm). The reaction tube contained a fixed catalyst bed of about 50 mg. X-ray diffraction analysis (XRD) of the catalysts was carried out to determine crystal structure and phase composition using Cu-K α radiation with a wavelength of $\lambda=1.5406$ nm at 40 kV and 15 mA (Rigaku, Miniflex600). Also, the crystallite sizes were estimated using the Scherrer equation [5]. The catalysts were characterized by N₂ physisorption at 77 K (Micromeritics, ASAP 2020 Plus) to calculate the specific surface area using the Brunauer-Emmett-Teller (BET) method. Fourier transform infrared spectroscopy (FTIR) was used to characterize functional groups of catalyst using the DRIFT method (Vertex 70/70, Bruker). Transmission electron micrographs (TEM) of the catalysts were recorded using a JEOL 2100 Plus electron microscope operating at an accelerating voltage of 200 kV. The authors would like to acknowledge the support of the NEST PNRR project and of the Laboratory of advanced electron microscopy – Elemental (<https://elemental.unige.it/>) and of the microscopists L. Negretti and O. Soda.

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Energy Differences between Structural Isomers of Deposited, Size-Selected Au Nanoclusters

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ABSTRACT

The potential energy surface (PES) of a nanoscale system describes the energy in terms of the atomic arrangements. Minima correspond to locally stable atomic structures. Differences in energy between isomers are a critical parameter of the PES. For Au clusters, one typically sees several competing structural isomers, ideal candidates for investigations regarding the PES. A method pioneered by the group provides a rare experimental insight into the PES [1]. The method employs high resolution aberration-corrected STEM imaging of gold nanoclusters at various temperatures, either a snapshot of an ensemble [1] or single cluster video imaging over time [2], with a frame-by-frame comparison to a simulation atlas to identify the cluster structural motif (Fig. 1). The two most prominent isomers are treated as states of a Boltzmann distribution (1), from which the energy difference between the states can be found.

$$\ln\left(\frac{N_{state\ 1}}{N_{state\ 2}}\right) = -\frac{\Delta E}{K_B T} + \frac{\Delta S}{K_B} \quad (1)$$

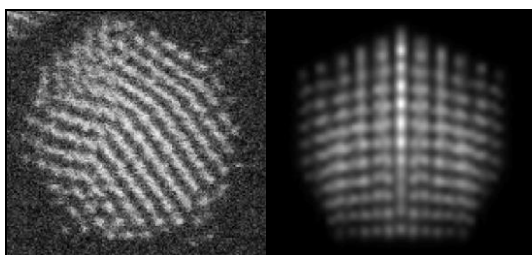


Fig. 20 : HAADF-STEM image of a 441 ± 13 atom Au nanocluster taken at 200°C (Left) and the corresponding simulated Au309 image used to identify its structure as decahedral (dh) rotated to an angle of $\alpha=50^\circ$, $\beta=0^\circ$. (right)

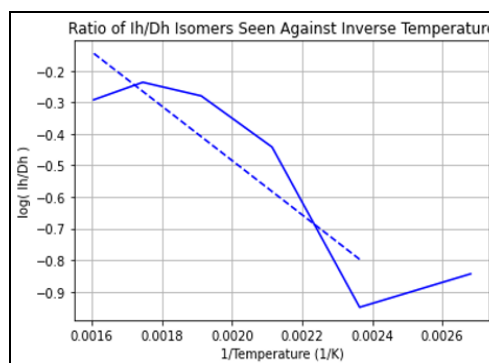


Fig. 21 : Boltzmann plot of isomers of Au441 imaged between 100 and 350°C . Using (1), $\Delta E = 74$ meV.

For size selected Au441, assembled from size 147, we find mainly Dh and lh isomers. The energy difference was $\Delta E_{lh-Dh} = 74$ meV (Fig 2). For Au clusters with ~ 4000 atoms, an energy difference of $\Delta E_{Dh-FCC} = 149.0$ meV was found. Further examples will be discussed but these show the power of the variable-temperature single cluster video imaging method.

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Cross-Coupling Of Pd-Cyclometallated Complexes on Ag(110)

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ABSTRACT

Pd-cyclometallated compounds may be relevant for catalytic purposes, but very little is known about their interactions with metal substrates. Indeed, the few studies present in literature mainly focus on Ir(III)- and Pt(II)-containing complexes, of interest as light emitters [1,2].

Here we report on the interaction of the Pd-cyclometallated compound $C_{22}H_{14}Br_2N_2Pd_2Cl_2$, possibly relevant for catalytic applications, with Ag(110) [3-5]. The system is investigated by scanning tunnelling microscopy and X-ray photoemission spectroscopy, while the initial and final configurations observed are validated by ab-initio calculations. The molecules dissociate upon interaction with the surface; depending on experimental conditions, different self-assembled structures form and different cross coupling reactions between the organic fragments occur (see Fig. 1).

These results demonstrate a rich chemistry at the base of the cyclometallate-metal interaction, that significantly modifies the nature of the compounds, and we envisage the possibility to tune the final product of cross-coupling reactions by selecting the suitable preparation protocol.

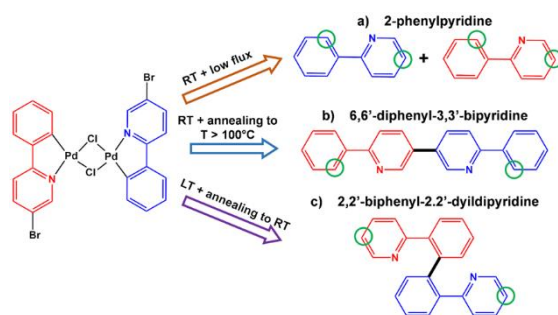


Fig. 1 : Scheme of the reaction products obtained after depositing the $C_{22}H_{14}Br_2N_2Pd_2Cl_2$ cyclometallate on Ag(110) in ultra high vacuum: a) RT deposition at low flux [3]; b) RT deposition + annealing [4]; c) LT deposition + annealing to RT [5]. The molecular species obtained are stabilized by the Ag substrate through the saturation of the C dangling bonds with Ag surface atoms. Here we have virtually substituted Ag atoms with H atoms in the position highlighted by small green circles.

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Presenting Pt-Mn Catalyst for Methanol Aqueous-Phase Reforming and a CSCP Approach for Catalytic Processes: Theoretical Studies

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ABSTRACT

Catalytic conversion of oxygenated hydrocarbons via aqueous-phase reforming (APR) is a catalytic technology potentially useful to reduce and transform biowaste in industrial plants into more valuable products as hydrogen which is a clean energy carrier. Bimetallic alloys have been increasingly studied for energy applications, especially for hydrogen production due to their favorable chemical/physical properties. Bimetallic Pt-Mn catalysts have been experimentally reported as efficient catalysts in APR with a high hydrogen production rate and selectivity. Herein, we applied periodic density functional theory (DFT) calculations to extensively investigate the energetics of methanol-APR on Pt and Pt-Mn catalysts to understand their catalytic behavior. We found that successive hydrogen abstraction from adsorbed CH₃OH species generates hydrogen atoms which are strongly bound on the Pt(111) surface, resulting in hydrogen poisoning of the surface. The reaction mechanism of CH₃OH-APR under high coverage of hydrogen was then investigated, as corresponding to the proper resting-state conditions. Water dissociation to OH+H on high-H-coverage Pt(111) is the rate determining step for CH₃OH-APR with an energy barrier for the given step of 0.86 eV (and an overall energy barrier of 0.96 eV). The presence of Mn in Pt-Mn alloys at Pt₂Mn composition promotes the H₂O dissociation step reducing the activation barrier to 0.64 eV. Additionally, Mn atoms alleviate the interaction between hydrogen and Pt surface atoms, thus preventing hydrogen poisoning issues and promoting hydrogen evaluation in APR process. Next, we extend/extrapolate knowledge from one catalyst to a “conformally similar” catalyst by obtaining a database of structures from the investigation of CH₃OH-APR on a worked-out system (in our case, the Pt catalyst) to accelerate constructing the potential energy surface (PES) for the CH₃OH-APR reaction on different metal systems exploiting techniques of Modified Atomic Cluster Expansion (MACE) machine learning interatomic potentials. We present here an original approach (that we name Conformal Sampling of Catalytic Processes, CSCP), to accelerate and achieve an accurate and thorough sampling of novel systems by exporting information from existing data on a worked-out case. We use methanol decomposition (of interest in the field of hydrogen production and storage) as a test catalytic reaction. Starting from worked-out Pt-based systems, we show that after only two iterations of active-learning CSCP is able to provide reaction energy diagrams for a set of 7 diverse systems (Pd, Ni, Au, Ag, Cu, Co, Fe) leading to DFT-accuracy-level predictions. The CSCP approach thus offers itself as an operative tool to fully take advantage of accumulated information to achieve high-throughput sampling of catalytic processes.

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Decahedral Shaped Nanoparticles

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ABSTRACT

It is well known that Gold and other metals nanoparticles can often assume a decahedron (Dh) shape [1,2]. This structure cannot be completely closed using only five regular tetrahedra from a Face Centered Cubic (FCC) lattice. Although the tetrahedra might come to forming a closed shape, some distortion is required to achieve that. That distortion results in a Body-Centered Tetragonal (BCT) overall lattice. Multimetallic nanoparticles are expected to experience additional strain due to differences in the atomic radii of their constituent components. In this presentation we discuss nanoalloys of AuPdCuCo (or Ni). We analyse large nanoparticles as a model for High Entropy Alloys (HEA) which are some of the most important materials in modern metallurgy [3-5]. We found that the nanoalloys have also a fivefold decahedral structure with regular or irregular shape. We analyse the structure of the multimetallic Dh nanoalloys using atomically resolved Scanning/Transmission Electron Microscopy (S/TEM). Energy Dispersive X-Ray Spectroscopy (EDS) mapping and diffraction methods. We were able to map the strain and the changes on the crystal structure. This analysis also revealed that the nanoparticle's shape corresponds to a rather flattened decahedron, like a "pancake." We perform molecular dynamics calculations of the structure of Dh nanoparticles. These calculations reveal the shape and strain distribution of the nanoparticles and allow us to predict some of their mechanical properties.

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Interfacial Engineering Enables Polyaniline-Decorated Bismuth Sulfide Nanorods towards Fast UV-Vis Photodetector

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ABSTRACT

Herein, we reported photoelectric measurements of the polyaniline decorated with bismuth sulfide (Bi₂S₃/PANI) nanohybrid based metal-semiconductor-metal (MSM) device in the broad electromagnetic (EM) spectrum from ultraviolet (UV) to visible (Vis) range. Bi₂S₃ nanorods decorated with π -conjugated polymer PANI were utilized as photodetection devices with a wide range of applications in imaging and communication. In such a novel structure, the fast electron transfer at the interface of Bi₂S₃ and PANI occurs, which enhances the performance of the photodetectors. Current-voltage (*I*-*V*) characteristics of the Bi₂S₃/PANI nanohybrid MSM photodetector device show good ohmic nature. This photodetector device offers the highest external quantum efficiency (EQE), 10⁴%, in the UV and visible regions. It also shows the greatest detectivity of the order 10¹⁴ Jones. The photoresponsivity of the Bi₂S₃/PANI nanohybrid photodetector device shows 270 mA W⁻¹ in the UV region and 1270 mA W⁻¹ in the visible region at only 1 V with the minimum optical signal of 50 μ W cm⁻². The highest photoresponsivity of the Bi₂S₃/PANI nanohybrid photodetector offers 26,760 mA W⁻¹ and 13,250 mA W⁻¹ for the UV and visible spectra, respectively. The higher values of the LDR are 64.31 dB and 58.21 dB in the UV and visible regions, respectively, at 100 V with the lowest illumination intensity. The minimum value of NEP found in the order of 10⁻⁹ W, which is the lowest value, suggests that the nanohybrid material is perfect for low-intensity photon signals. This work provides a simple and effective method for preparing MSM photodetector technology, which exhibits a magnificent performance in the UV-to-Vis region.

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Structure of Cantor and Noble Metal High-Entropy Alloy Nanoparticles Produced by Laser Ablation in Liquid

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ABSTRACT

High-entropy alloy (HEA) nanoparticles (NPs) represent a relatively new class of nanomaterials composed of at least five elements at a near-equimolar ratio. The tunability of used elements and atomic ratios is limitless, which offers multiple opportunities for nanomaterial design, e.g. the tuning of surface potentials in electrocatalysis.[1] The synthesis of HEA NP by Laser Ablation in Liquid (LAL) is a promising scalable method previously utilized for the generation of Cantor Alloy (CrMnFeCoNi) NP with fcc-structures and homogeneous elemental distributions [2]. However, the stability of the internal phase structure of HEA NPs against an excess of individual elements is underexplored.

In this work, we investigate to which extent the crystal structure and elemental distribution of Cantor Alloy and noble metal (NM) CuPdAgPtAu HEA NP synthesized by LAL change when the individual elements Mn, Cr (Cantor), and Ag, Cu, Pt (NM) are enriched up to 50 at% in the corresponding alloy NPs. The colloidal HEA NPs were synthesized by LAL using picosecond and nanosecond pulse durations. SAED/XRD and TEM/EDX provided structural information and elemental distribution in the particles. Homogeneous elemental distributions were primarily retained in all samples even upon element enrichment. Furthermore, we identified a pulse duration effect: crystalline fcc Cantor alloy NPs were generated when picosecond pulses were used, while nanosecond pulsed LAL yielded amorphous NPs (Fig. 1).

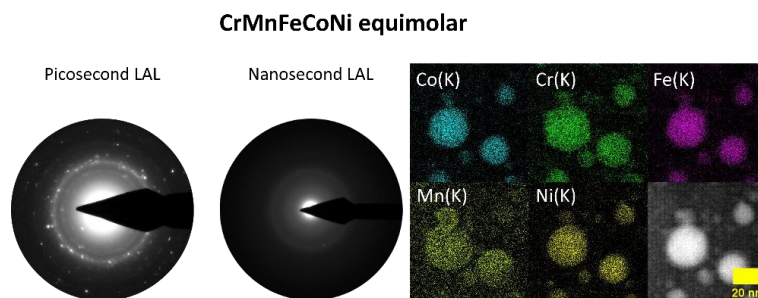


Fig. 2 : Exemplary structural information of equimolar Cantor HEA NP, displaying the effect of pulse durations on crystal structure from SAED (left) and elemental distribution in individual particles from EDX mappings (right).

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Investigation of Size Dependence for the Properties of NiCoRh Nanoalloys

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ABSTRACT

Multimetallic nanoalloys have been widely studied in recent years for their surprisingly different properties from their bulk counterpart [1]. A main application of nanoalloys is their use as heterogeneous catalysts since the catalytic activity may be modified and fine tuned by alloying [2]. The transition and noble metal nanoalloys of the 3d (Fe, Co, Ni, Cu) and 4d (Rh, Pd, Ag) metals have increasing interest especially in their use as catalysts [3].

In this study, the properties of NiCoRh nanoalloys are investigated by a combination of empirical potentials (EP) and DFT approaches. A systematic search is performed for nanoalloys of sizes 38 and 55. The optimization searches are performed by using Basin-hopping Monte Carlo method within Gupta potential. The lowest energy structures optimized by EP are subjected to DFT reoptimization. Also, the relationship between size, structural geometry, pressure and magnetic properties is investigated.

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Preferential Orientations of FeRh Nanomagnets Deposited on a BaTiO₃ Epitaxial Thin Film

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ABSTRACT

Inspired by epitaxial FeRh film studies on perovskite oxide [1], and motivated by the possibility to obtain hybrid multiferroic nanosystemsthis study, we have deposited size-selected FeRh clusters (diameter around 4 nm), at low energy and under ultra-high vacuum conditions, on a thin layer of BaTiO₃ (BTO) epitaxially grown on SrTiO₃ (STO). Using synchrotron radiation in grazing incidence configuration, we have observed the chemical ordering of FeRh nanoparticles into the B2 phase upon annealing. In addition, the orientation dependence of x-ray diffraction FeRh peaks indicates that particles, despite their random deposition, are finally adopting preferential orientations, reflecting an atomic coherence with the BTO surface [2]. In addition to the usual epitaxy relationship met for thin films, a novel orientation is observed (corresponding to a 45° in-plane rotation). These results show how cluster deposition offers an alternative approach to usual bottom-up growth methods and open the way to a possible control of FeRh nanomagnet properties taking advantage of the interfacial coupling with a substrate. Additional measurements reveal the similar behavior on crystalline STO substrate, with other specific favorable coincidences between FeRh and STO. Besides, as for previous FeRh NPs embedded in carbon matrix [3], no metamagnetic (AFM-FM) phase transition has been observed from XMCD measurements.

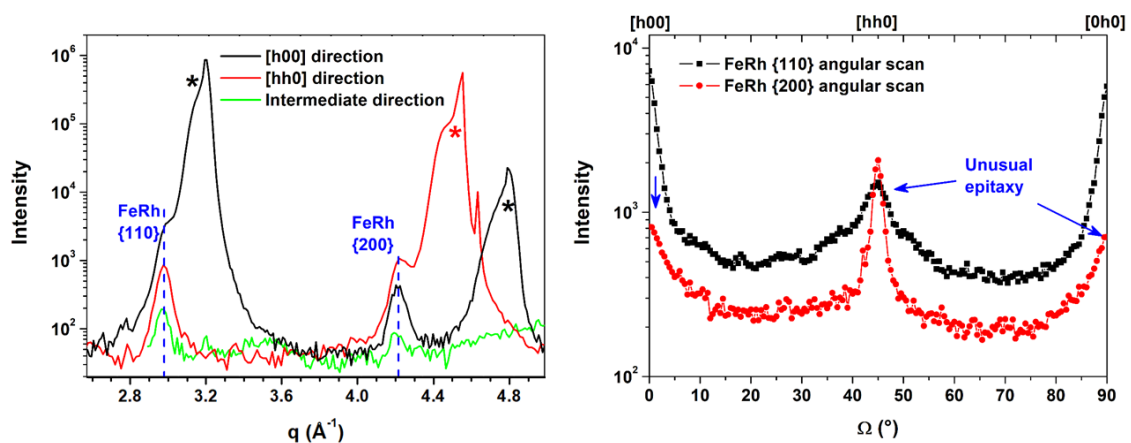


Fig. 22 : Grazing incidence XRD signal showing a strong dependence of FeRh peaks upon the orientation on the surface.

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Characterization of Stoichiometrically Different BFO Thin Films for Photoanodes

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ABSTRACT

Most of the photoanodes (PA) constituted by ternary metal oxides (TMOs) present a scant efficiency ascribed to the low charge transfer [1,2] and to the high recombination rate of charge carriers, quantified by K_{inj} and K_{rec} , respectively [3]. Currently, the PA synthesis methods hinder a comprehensive investigation of the correlation among the different TMO phases, morphology and stoichiometries with the charge transport properties (deduced from the reaction kinetics constants), in particular for grain sizes below 50 nm. In this work, different bismuth ferrite oxide (BFO) thin films were studied as PA for water splitting reaction, varying the concentrations and distributions of iron and bismuth within the PA. The samples were prepared using Supersonic Cluster Beam Deposition (SCBD) and thermal evaporation followed by a thermal annealing at 500°C for 2 hours.

Despite their different stoichiometry, with Fe atomic concentration ranging from 6% to 60% for different samples, X-ray diffraction (XRD) shows the presence of almost pure $Bi_{24}Fe_2O_{39}$ crystals of approximately 30 nm in size for all films. Transmission electron microscopy (TEM) analysis revealed that excess iron forms an amorphous/nanocrystalline matrix surrounding Bi and with Fe_2O_3 crystallites around 3-5 nm. The reaction kinetics constants (K_{inj} for the injection process and K_{rec} for the recombination process) were determined by intensity modulated photocurrent spectroscopy (IMPS). PA with small amount of iron exhibited surface states and charge accumulation on the surface revealing a small K_{inj} . Furthermore, their absorbance peaks appear in UV region, limiting the PA's performance. An increased amount of iron mitigated these phenomena by increasing the system's K_{inj} more than tenfold for the sample with highest Fe concentration and shifting the band gap in the visible region from 2.57 eV to 1.97 eV. However, the presence of Fe_2O_3 nanocrystallites also led to a higher charge recombination, consequently reducing the effective photocurrent output.

These findings suggest that optimizing the iron content in BFO thin films could significantly enhance their performance as photoanodes, paving the way for more efficient solar water splitting devices.

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Support-Induced Strain Engineering of the Chemical Ordering in Anchored Ni-Pt Nanoalloys

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ABSTRACT

For nanoalloys of multi-metallic components, chemical ordering is a key feature to be investigated, since it determines their physical and chemical properties and resultant potential applications (e.g., catalysis, sensing, etc.). To date, numerous theoretical works have inspected the pattern of chemical ordering of nanoalloys, but mostly with the implicit assumption of a vacuum environment. However, insights into the structure of supported alloy nanoparticles and their interaction with the substrate are also of particular value, especially with a view to said applications.

When an alloy nanoparticle is anchored onto a specific substrate, a portion of it (all of it, if small enough) may become epitaxially aligned with the substrate, which might occur even if the lattice mismatch between the contacted surface of the nanoparticle and the substrate is significant. [1,2] This inspired the investigation of a usually neglected tuneable parameter, that is the strain that can be induced *via* stretching or compressing the support. In our current work, we constructed a group of truncated octahedral Ni-Pt alloy nanoparticles of different sizes and compositions and investigated their relaxation under various straining conditions using a combination of MD and MC methods. Our simulation results demonstrated that, by exerting a continuous sequence of strains, the segregation behaviour of specific metal components might be tuned, thus presenting new patterns of chemical ordering.

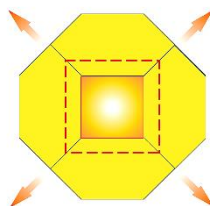


Fig. 1: A schematic illustration of the model nanoparticle (a bottom viewpoint of truncated octahedron), of which the bottom layer is under strain. The red dash line depicts the contour of the expanded layer. The substrate is implied based on this bottom viewpoint.

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