

Le défi de la miniaturisation, la réponse des nano-matériaux

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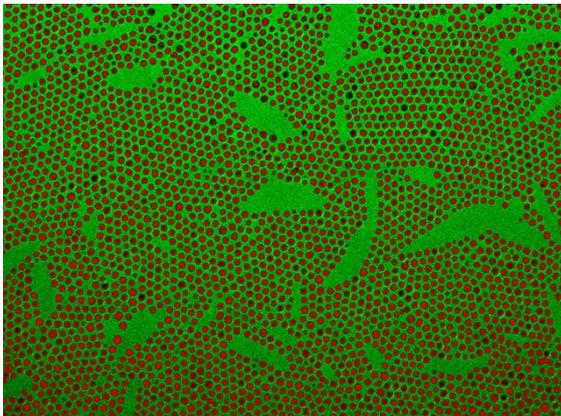
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RESUME

A travers une approche à deux voix, en physique et en chimie, découvrez comment les recherches sur l'élaboration des nanomatériaux, et le contrôle de leur architecture à l'atome près, permettent de proposer des nouvelles voies pour le stockage de l'information et l'affichage haute résolution. Ce propos sera illustré en expliquant le fonctionnement des nouveaux supports magnétiques pour le stockage de l'information haute densité, basé sur l'élaboration de nano-aimants et leur organisation. Nous discuterons enfin des propriétés optiques de nanoparticules d'or qui ouvrent la voie à des nouveaux concepts de pixel pour l'affichage numérique.



Nanocristaux magnétiques de cobalt observés par microscopie électronique à transmission



Solution de nanoparticules d'or de forme sphérique ou allongée. La couleur dépend de la forme à l'échelle nanométrique.

Morphology versus magnetic order in FeRh nanoparticles

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ABSTRACT

The chemically-ordered FeRh alloy undergoes an unusual magnetic phase transition from an antiferromagnetic (AFM) to a ferromagnetic state (FM) at 370K. This transition displays a strong size dependency, as evidenced for instance in ultrafine nanoparticles (NP), [1]. In addition to this size effect, the role of surface termination in the magnetic properties of low-dimensional chemically-ordered magnetic alloys has recently been emphasized in several theoretical studies [2-3]. Besides, NPs of ordered alloys are likely to adopt different morphologies depending on the chemical nature of their exposed surfaces.

Through a combined theoretical and experimental study, we investigated the strong interplay between surface configuration, morphology and magnetic state in magnetic FeRh nanoparticles, [4]. We demonstrate that the surface configuration can stabilize the low temperature ferromagnetic (FM) state in FeRh nanoparticles in the 6–10 nm range.

The nanoparticles were synthesized in an amorphous alumina matrix using UHV magnetron sputtering. We show that they display the most stable configuration for FM nanoparticles, predicted through our first-principles calculations. Their structure, morphology and Rh-(100) surface termination are confirmed by aberration-corrected (scanning) transmission electron microscopy and the FM magnetic state is verified by VSM experiments.

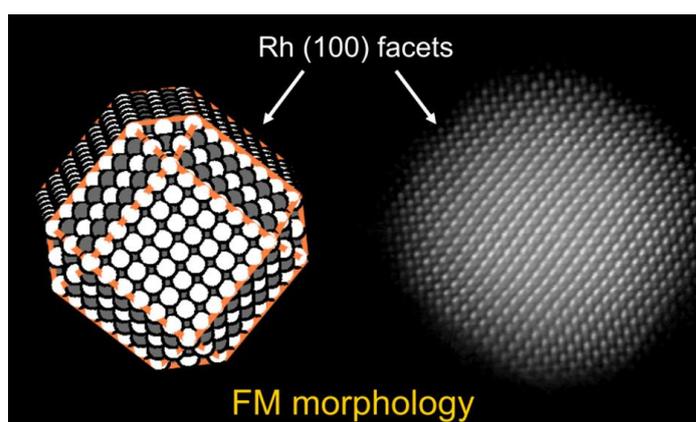


Fig. 1 : Most stable FM morphology in the grown FeRh nanoparticles

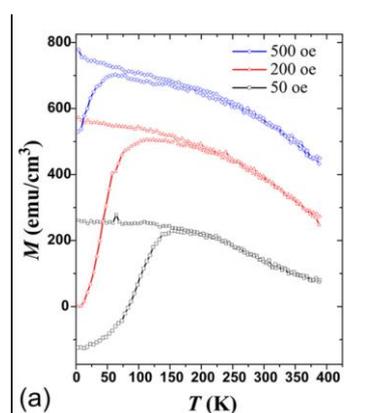


Fig. 2 : Magnetic properties of the FeRh NPs

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Auto-organization and magnetic properties of mass-selected FePt nanoparticles deposited on a moiré pattern.

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ABSTRACT

The FePt alloy, when chemically ordered in the L1₀ phase, is among the magnetic materials displaying the highest magnetic anisotropy constant (K_{eff} around 7 MJ/m³). Therefore, it is a perfect candidate for ultra-high density magnetic storage applications, provided nanoparticles can be prepared in such a high anisotropy phase^[1]. Another requirement for applications, as well as for fundamental studies, is to organize the magnetic nanoparticles in a 2D array. In parallel to investigations on chemically synthesized systems, a great effort is devoted to the bottom-up elaboration of nanomagnet arrays following a physical route.

In this context, one widely used path consists in using template surfaces with specific sites regularly distributed. Such a 2D lattice can be obtained with the moiré phenomenon, which appears when two crystalline structures of slightly different cell parameters are stacked. Thus, a graphene layer epitaxially grown by CVD on a Ir(111) surface displays a 2D spatial modulation corresponding to a hexagonal lattice of 2.5 nm cell parameter^[2]. For the first time, we have obtained promising magnetic properties (huge K_{eff} and spin magnetic moments) of chemically ordered FePt nanoparticles organized on a moiré.

We will first describe the deposition of size selected FePt nanoparticles by Low Energy Cluster Beam Deposition (LECBD) on g/Ir(111). We will discuss the auto-organization of such particles on specific sites of the moiré lattice, as determined by grazing incidence x-ray scattering measurements (GISAXS technique) and x-ray diffraction^[3]. The deposited nanoparticles are sensitive to the moiré pattern and we find that the resulting organization can be preserved up to temperatures around 700°C (figure 1). Quantitative information can be extracted from GISAXS patterns in order to estimate the number of pinned nanoparticles on the surface. Finally, we will report a clear evolution of the magnetic properties of the FePt nanoparticles induced by annealing (phase modification, anisotropy modification, interface effects between FePt and the graphene...) put into evidence by X-ray Magnetic Circular Dichroism (XMCD) measurements (figure 2). The magnetic properties will be compared to those of FePt diluted in an amorphous carbon matrix^[4].

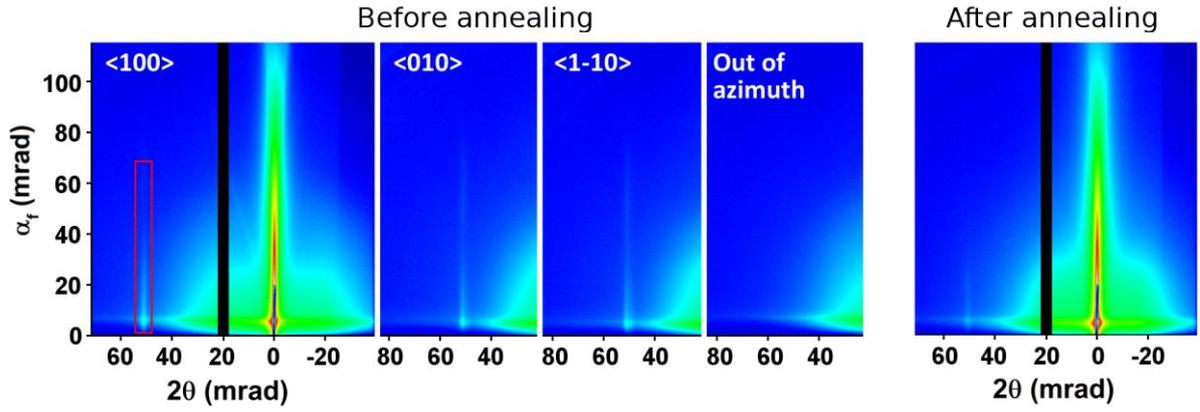


Fig. 1 : Left : GISAXS intensities before annealing along the $\langle 100 \rangle$, $\langle 010 \rangle$ and $\langle 1-10 \rangle$ directions of the hexagonal moiré lattice. The presence of a correlation peak in those directions reflects the hexagonal organization of FePt nanoparticles on the moiré lattice. Out of azimuth, no correlation is visible. Right : GISAXS intensity in the $\langle 100 \rangle$ direction after annealing at 700°C .

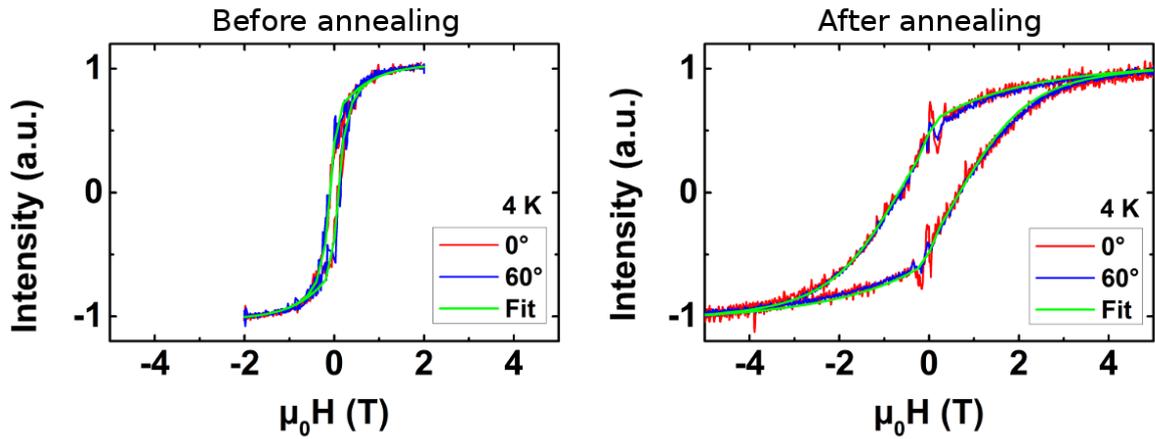


Fig. 2 : Hysteresis loops taken at 4 K for two incidence angles 0° (normal to the surface, in red) and 60° from the normal (in blue), before annealing (left) and after annealing (right). The fits are pictured in green.

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Magnetic properties Co_nRh_m alloy clusters

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ABSTRACT

Studying the magnetism of isolated small atomic clusters will allow to bridge between the magnetic behavior of single atoms and larger nanoparticle. High mass resolution Stern–Gerlach deflection experiments on small clusters are of great interest to address fundamental questions about composition, temperature and size dependent magnetism in confined systems. It is, for instance found that the magnetic moments per atom of small cobalt clusters are enhanced compared to the bulk and to nanoparticles,^{1–3} which is related to the reduced coordination number.^{4,5} In the bulk it has been shown that alloying cobalt, with a nonmagnetic 4d metal like rhodium can induce local magnetic moments on the rhodium atoms.⁶ Further, XMCD measurements on cationic cobalt clusters have shown that alloying with rhodium results in enhanced orbital magnetic moments.⁷ Measuring the total magnetic moment for neutral clusters with Stern-Gerlach experiments is therefore important because of their greater similarity with magnetic nanoparticles.

Our recently developed set-up uses a position sensitive detector to accurately and simultaneously measure both the spatial cluster deflection profile and the cluster mass, which is ideal for the study of alloy clusters (fig 1). A velocity scan method has been developed for size-dependent determination of the cluster temperature.

In this contribution, the magnetic deflection of Co_nRh_m ($n=[8-60], m=[0-4]$) clusters will be presented. We found significant enhancements of the magnetic moments of cobalt clusters, by alloying them with rhodium (fig 2). Furthermore the temperature dependent behavior of the clusters will be discussed.

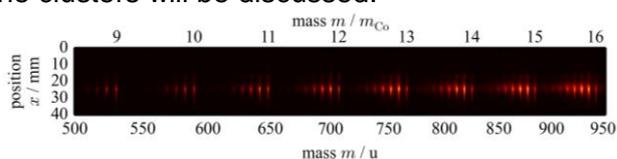


Fig. 1: Example of the combination of mass and position sensitivity in our set-up, for Co_nCr_m clusters. A lighter color corresponds to more particles. Because chromium is lighter than cobalt every replaced atom shifts the peak to the left.

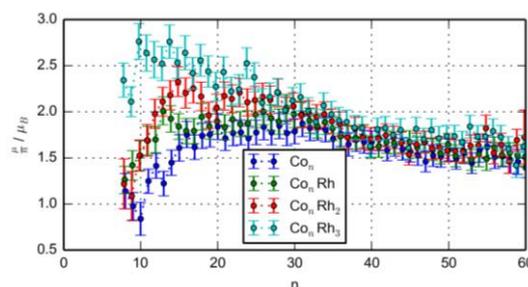


Fig. 2 : Enhanced magnetic moments per atom of neutral Co_n clusters by rhodium addition.

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Vertically-assembled epitaxial magnetic alloy nanowires in SrTiO₃ and CeO₂ matrices

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ABSTRACT

During the last decade, the nanoalloy community has invested significant research effort in the study of self-organization tendencies in low-dimensional bimetallic nanostructures. This has been motivated by fundamental scientific interest, but it has also been driven by the desire to develop efficient synthesis strategies allowing to obtain application-optimized structures. While self-organization can be used to design "free-standing" nanoalloys [1], recent work has shown that bottom-up self-assembly is also a powerful tool for growing novel metal-oxide composite systems [2,3], where the intimate coupling between the embedded nanoalloy and the surrounding matrix gives access to additional degrees of freedom [4].

In this contribution, we present a novel approach aiming at exploiting alloy nanowire-matrix interactions arising from epitaxy for functionality tuning and demonstrate how self-assembly can be used for synthesis of ultrathin bimetallic wires ($d < 5\text{nm}$) vertically embedded in CeO₂ and SrTiO₃ thin films [4]. This allows to generalize planar epitaxy to 3 dimensions and to gain control over the crystallographic orientation of the wires and their strain state.

In the first part of the talk, we focus on perfectly miscible Co-Ni alloys. We present a detailed analysis based on high-resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD) and absorption spectroscopy (XAS) in combination with magnetometry measurements and show how concentration, size and the choice of the oxide matrix impact the magnetic behavior of the system. Based on these results, we demonstrate that strain, resulting from nanoalloy-matrix interactions, is indeed the key parameter which determines the effective anisotropy of the nanoalloy: In ultrathin Co-Ni composite systems, magnetoelastic contributions dominate shape and magnetocrystalline anisotropy. Thus strain engineering can be used to increase the effective anisotropy in Co-rich nanoalloys, achieving high blocking temperatures well above room temperature. In the second part of the presentation, we concentrate on the immiscible bimetallic system Co-Au and show how the use of the same growth technique permits to obtain ultrathin vertically aligned segregated bilayered nanostructures. Despite the small diameter of the wires and the presence of a large metal-oxide heterointerface, phase separation is still effective, which lays the ground for development of self-organized magnetoplasmonic nanocomposite thin-films.

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Tuning the Properties of Bimetallic Nanoparticles by Cluster Beam Deposition

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ABSTRACT

Growth of nanoparticles via cluster beam deposition techniques can lead to structures whose physical and chemical ordering do not have to agree with their equilibrium bulk counterparts [1]. Phenomena such as surface segregation are pronounced due to the nanoparticles' high surface-to-volume ratios, and can have a beneficial or detrimental effect on their properties. For example, NiCr nanoalloys at the magnetic end of their compositional range (ie. 0-15at.% Cr) grown by magnetron sputtering demonstrate counter-intuitive behaviour: full Cr-surface demixing is observed up to ~5at.% Cr [2], whereas above this concentration Cr atoms segregate only partially. This fact has a profound effect on the nanoalloy magnetic properties, due to the competition between ferromagnetic and antiferromagnetic ordering within the clusters. As a result, we were able to readily fine-tune the Curie temperature values of our samples within a wide temperature range, for a variety of applications such as magnetic hyperthermia for cancer treatment [3].



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Development of accurate energy models for magnetic alloys and nanoalloys

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ABSTRACT

Alloys and nanoalloys receive much attention because of their numerous potential applications in various fields like metallurgy, catalysis, magnetism, optics and health [1]. One main scientific challenge is to model their structure and properties as accurately as possible in order to participate to the design of new materials with targeted properties. Computer materials design is indeed a flourishing area with the development of multi-scale simulations. Nevertheless, if the proposed simulations tools are more and more sophisticated, one does not look so much on the side of the energy model (or potential) and its form, while relying on classical semi-empirical models. Energy models would however deserve some improvements by getting closer to the electronic structure. In particular, taking magnetism into account in energy expressions, would be an important step forward for a better description of segregation and ordering phenomena when interested in magnetic materials and (nano)alloys [2, 3, 4]. Based on a recent work on the environment dependence of magnetic moment and atomic level shifts within the tight-binding approximation [5], we present here a methodology to generalize the tight-binding expression of the energy to account for magnetism. This is illustrated in the particular case of CoPt and FeNi alloys, going from perfect pure bulk to alloys and then to alloy surfaces and nanoalloys.

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Modeling of Complex Metal Alloys and Nanoparticles via Multiscale First-Principles Methods

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ABSTRACT

This work is related to DFT based modelling of phase diagrams of complex metal alloys. The thermodynamic phase diagrams serve as road-maps and illustrate the state of a material as a function of temperature, concentrations, components, and pressure. Unfortunately most experimental techniques measure average or macroscopic properties of a material and provide only indirect information regarding the atomistic structure so non-parametric ab initio calculations have been used to supplement the missing points in experimental databases and to guide experimental work to the most interesting areas. In particular, the DFT can provide insight to microscopic features that are manifested as macroscopic properties of a material but the DFT calculations are very time consuming. We have developed a Cluster Expansion (CE) model with heuristic effective cluster interaction selection and Monte Carlo simulations have been used to determine finite temperature configurational phase diagrams for several alloys [1-3]. The modelling of such finite temperature properties provides substantially more information and knowledge than traditional CE studies, which are typically restricted to searching possible ordered ground-state structures at 0 K.

We have recently apply to the same DFT-CE method to nanosize clusters [4]. In the cluster study we have modelled the mixed FeNi clusters and studied the stability if the FCC, BCC and icosahedral cluster with respect of the concentration. .

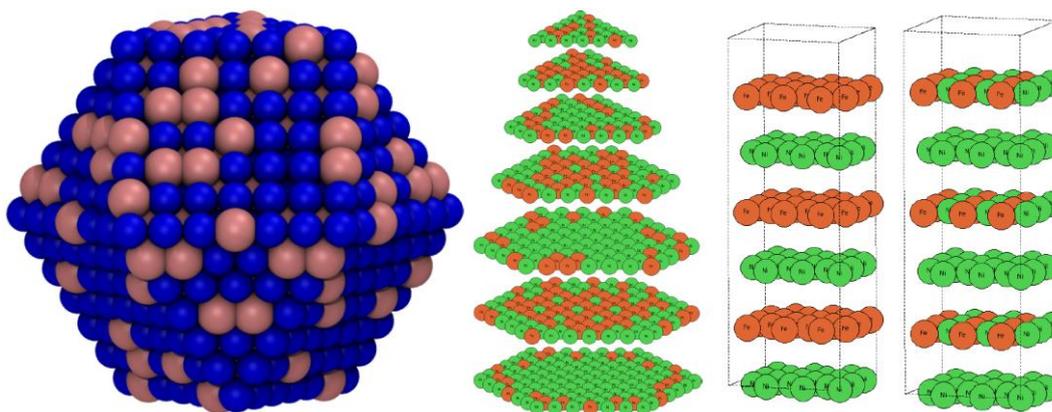


Fig. 1 : Structure of a Fe₃₂₃Ni₆₀₀ cluster .

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Comprehensive Modeling of Cu-Ni Nanophase-Diagrams and Finite-Size Scaling

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ABSTRACT

Studies of chemical-order in Cu-Ni fcc-based nanoalloys consisting of few hundred atoms reported recently about the dominance of asymmetric Janus-like configurations (JA) at low temperatures, transforming at elevated temperatures to random solid-solution-like configurations (RA). The highly efficient statistical-mechanical free-energy concentration expansion method (FCEM [1]), combined with coordination-dependent bond-energy variations (CBEV [2]) based on MEAM elemental surface energies, and coarse-grained hemispherical (CGHS [3]) models, enabled us to explore chemical-order configurations and transitions between them in much larger truncated-octahedron (TO) sizes and over broad ranges of composition and temperature. Namely, this composite analytic methodology makes the construction of detailed nanophase diagrams possible. Depending strongly on size and composition the following new findings regarding low-temperature chemical-order in Cu-Ni TOs can be noted:

- (i) JA configuration is expected to be the most stable for all compositions only in the 201 and 586-atom sizes.
- (ii) For larger TOs (1029 and 4033 atoms) core-shell (CS) configurations prevail only at certain composition ranges around the 50/50 one, the rest being dominated by JA.
- (iii) For even larger TOs (up to ~200,000 atoms) the CS becomes stable over the whole central composition range (having sharp boundaries between 25% and 70% Ni).

Three types of composition and size-dependent temperature-induced transitions were derived mainly from order-parameter variations: JA to CS, CS to RA, and JA to RA, thus yielding a comprehensive Cu-Ni nanophase diagram.

Plotting the shift in the CS to RA transition temperature vs size for the 50/50 composition revealed finite-size scaling power law with critical exponent > 1 . The deviation from the value reported for surface constrained homogeneous particles ($=1$), is tentatively attributed to the role of the CS inner interface. Scaling-plot extrapolation bridges the critical-temperature gap to even larger Cu-Ni NPs within and well beyond the nanoscale.

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A different balance of power between surface segregation and chemical ordering in Co-Pt and Pt-Ag nanoalloys.

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ABSTRACT

Ordering alloys are interesting systems due to the link between atom arrangement and properties, for instance in the field of catalysis for Pt-based alloys. In fact, Co-Pt system presents higher activity in the electrochemical oxygen reduction reaction than pure Pt [1], whereas Pt-Ag presents skills for plasmonic catalysis [2,3]. According to their bulk phase diagram, these systems are quite different; Co-Pt has three ordered phases ($L1_2$ at Co_3Pt and $CoPt_3$, and $L1_0$ at $CoPt$) while Pt-Ag holds one ($L1_1$ at $PtAg$) which is different from the one observed in Co-Pt. Moreover Silver presents a strong surface segregation tendency in Pt-Ag system whereas neither Co, nor Pt does in Co-Pt. The question arises if bulk ordering remains in nano-sized particles and how surface segregation accommodates chemical ordering. We propose here a theoretical study of surface segregation and chemical ordering.

Extending the study to the whole composition range of the Co-Pt and Pt-Ag alloys, we performed systematic Monte Carlo simulations in semi-grand canonical ensemble with semi-empirical many-body potential within the Second Moment Approximation (SMA) of the density of states which allows atomic relaxations. This potential has been fitted to ab initio calculations within the density functional theory. In the case of Pt-Ag, we use an additional Gaussian term within the SMA potential.

After the bulk phase characterization to check our interatomic potential, we characterized the surface segregation isotherms for Co-Pt semi infinite alloys with the (100), (110) and (111) [4] orientations to be compared to the surface segregation on the nanoparticle facets. We get a purely bidimensional phase $(\sqrt{3} \times \sqrt{3})R30(111)$, which is stable on nanoalloys when (111) facets prevail. The chemical ordering in the core of truncated octahedron clusters up to 3.3 nm can be nicely compared with the bulk phase diagram.

Contrary to the previous system, Pt-Ag presents a rather strong surface segregation which leads to a core-shell structure. Depending to the concentration, this structure can be ordered in the core.

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Tracking the restructuring of oxidized silver-indium nanoparticles under a reducing atmosphere by environmental HRTEM

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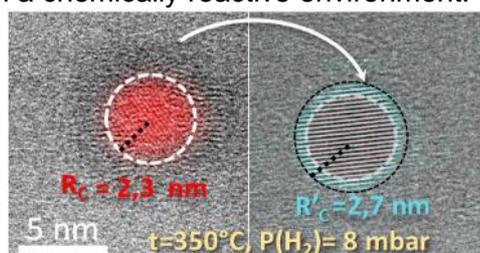
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ABSTRACT

Multimetallic nano-alloys may adopt various structures (alloys, Janus, core-shell...) and display various physicochemical properties evolving under reactive environment. Following and understanding this evolution is therefore crucial for future applications in gas sensing and heterogeneous catalysis. In this context, silver-based bimetallic nanoparticles (NPs) may be of particular interest since their association may result in interesting catalytic and optical properties. Plasmonic sensing is a promising tool to follow the kinetics of reactions at the scale of a large assembly of NPs whereas Environmental Transmission Electron Microscopy (E-TEM) allows the tracking of the structure at the single NP level. In this respect, we performed *ex-situ* optical spectroscopy and E-TEM observations on small bimetallic In-Ag NPs. Firstly, oxidation/reduction cycles were demonstrated through Localized Surface Plasmon Resonance (LSPR) shifts for silica embedded NPs.¹ The Ag-In NPs were then investigated through E-TEM at high resolution.² Indium being strongly sensitive to oxygen, the bimetallic NPs after air transfer adopt a structure consisting of an indium-oxide shell surrounding a silver-rich alloyed core. For large enough hydrogen pressure and temperature, we observed *in operando* the direct reduction of the indium oxide shell along with the growth of the core which gets enriched in indium to form a new alloy extraordinary resistant against oxidation (see figure 1). This study also reveals various domains of stability depending on hydrogen pressure and temperature, the intermediate one corresponding to “Janus” structures. All this work shows the potential of high-resolution E-TEM for unravelling the mechanisms of nanoparticle reorganization in a chemically reactive environment.

Fig. 1 : HRTEM images of In-Ag@In₂O₃ and In-Ag NPs before and after reduction showing evidence of the growth of the core which has been enriched in Indium during the reduction.



Composition-tunable self-organization in $\text{Au}_x\text{Ag}_{1-x}$ phase segregated nanostructures

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ABSTRACT

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

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Monolayer protected nanoalloys: new analysis tools for chiro-optical spectra in the TDDFT framework

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ABSTRACT

The chiro-optical properties of a class of Au/Ag nanoalloys protected by thiols are considered [1], in particular the interplay of plasmonic vs. metal/ligand resonance features. In MPC strong absorption peaks that are related not to a classic metal surface plasmon but rather to an enhancement due to a resonance via electronic conjugation between metallic excitations and molecular-like features due aromatic ligands ("plasmon re-birth") [2] can be predicted. To better understand this phenomenon, we set up a set of analysis tools of the chiro-optical response, featuring Individual Component Mapping of Oscillatory Strength (ICM-OS) and of Rotatory Strength (ICM-RS), Oscillator Strength Density (OSD) and Rotatory Strength Density (RSD) plots, and fragmentation decomposition [3], also exploiting a recently developed efficient TDDFT algorithm [4,5]. OSD/RSD and ICM-OS/RS are complementary tools to visualize and analyze chiro-optical response either in real space (OSD/RSD) or in the conjugate space of molecular orbitals, allowing one to single out the most important contributions in terms of single-particle excitations (ICM), while fragment projection enables one to analyze TDDFT absorption and CD spectra. Through this analysis not only we disentangle plasmonic vs molecular-like contributions to absorption/CD spectra, but we also discover new sources of enhancement or depression of chiro-optical response in medium-size MPC, such as destructive or constructive interference, thus achieving an in-depth understanding which then turns into rationalization and design of chiro-optical plasmonic and molecular-like response of MPC species exhibiting optimal features.

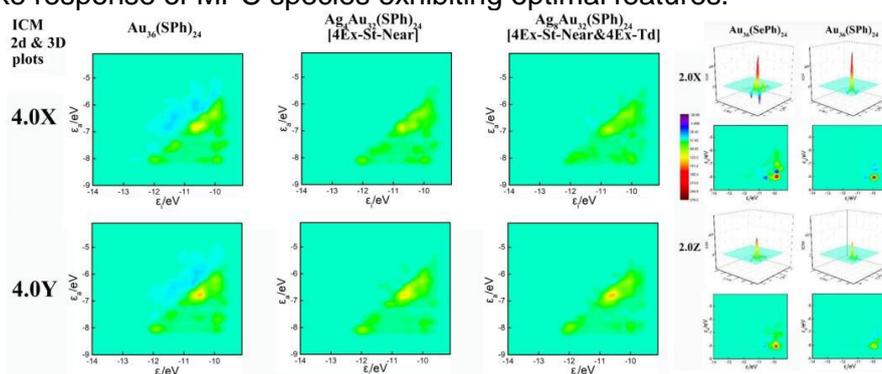


Fig. 1 : 2D (left, middle) and 2D/3D (right) ICM-OS plots of selected MPC.

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Size and Composition Effects on the Surface Energy: Application to Au Segregation in CuAu Nanoparticles

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ABSTRACT

In case of nanoparticles (NPs), a strong size dependent surface energy is expected when the particle diameter is less than a few nanometers. However, its variation with the NPs diameter is not clear since contradictory (experimental and theoretical) results can be found in the literature [1,2].

To address this issue, we perform in this contribution Monte Carlo simulations at atomic-scale employing a tight-binding potential recently developed for Cu-Au alloys. This theoretical approach is supported by *in-situ* transmission electron microscopy to monitor in real time the evaporation of spherical pure liquid NPs and apply the Kelvin model to determine the surface energies [3].

By combining both methods, we unambiguously show that the surface energy of NPs is significantly higher as compared to that of the bulk (see Figure 1a). Moreover, the surface energies of Au being lower than Cu, this leads to Au superficial segregation according to our Monte Carlo simulations (see Figure 1b). Our work thus provides a rational understanding of the key factor that determines the segregation properties of CuAu nanoalloys shedding more light on their chemical reactivities and especially catalytic activities.

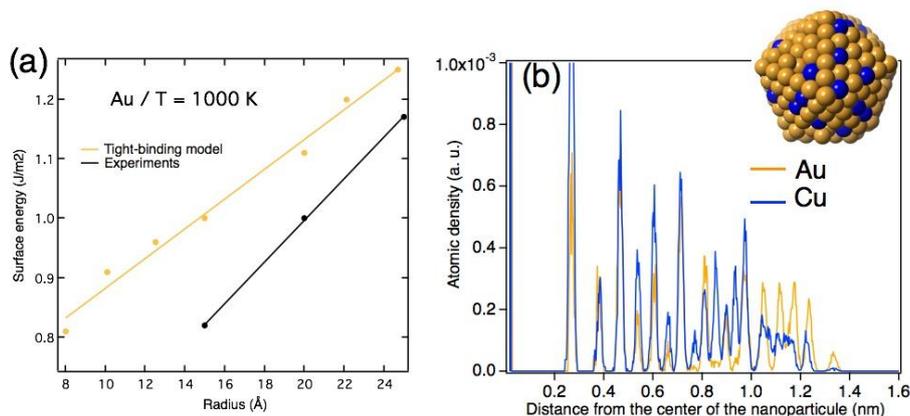


Fig. 1: (a) Size dependent surface energy of Au NPs (experimental vs theory) (b) Equilibrium configuration and concentration profile along the radius of a liquid CuAu NP at 1000 K

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Measuring The Surface Energy Of Bimetallic Nanoparticles Using *In Situ* Heating TEM

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ABSTRACT

Surface energy is an important descriptor of metallic nanoparticles (NPs) as it drives, among others, their nucleation, growth, morphology and reactivity to different environments. Until now, experimental determination of absolute values of surface energy in metallic NPs has been limited to monometallic systems. In this contribution, we present a direct and robust method to experimentally determine the absolute surface energy of bimetallic nanoalloys. Our approach relies on the real-time monitoring of the evaporation of bimetallic NPs in vacuum by *in situ* transmission electron microscopy and the extension of the Kelvin equation to two-component systems. We determined the surface energy of supported Au, Cu and Cu-Au NPs prepared by pulsed laser deposition.

Figures 1a-b show the evolution of an assembly of Cu₅₀Au₅₀ NPs during *in situ* heating at 700°C. By adjusting the particle size evolution of individual NPs with a generalized Kelvin law [1], the surface energy of the NPs could be extracted (Figure 1c). The determination of the absolute values of the surface energy of the monometallic and bimetallic NPs suggests that the surface energy for liquid Cu-Au nanoalloy follows a Vegard's law-like behaviour (inset of Figure 1c). These experimental observations are confirmed by Monte Carlo simulations which bring additional insights into the structural stability and thermodynamic properties of Cu-Au NPs at high temperatures.

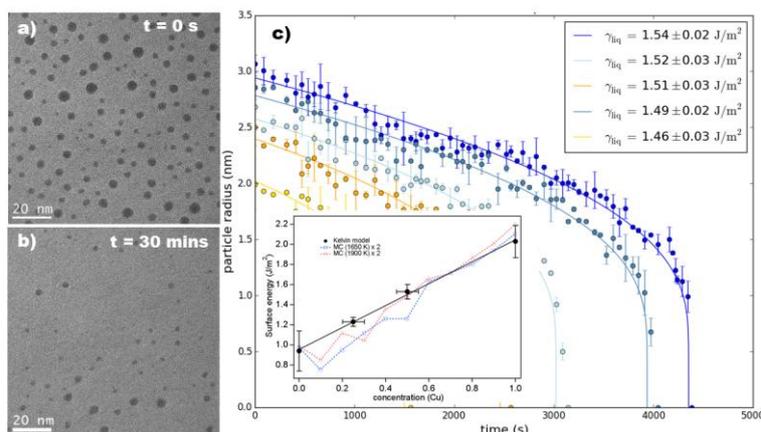


Fig. 1 : (a) and (b) TEM images showing the evaporation of Cu₅₀Au₅₀ NPs at 700 °C. (c) Variation of the radii of six CuAu NPs with time. Insets: corresponding extracted surface energies and variation of the surface energy of Cu_(1-x)Au_x systems, blue/red lines are Monte Carlo simulations, the full black line is a linear fit of experimental data.

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Reduced sintering of mass-selected Au clusters on SiO₂ by alloying with Ti

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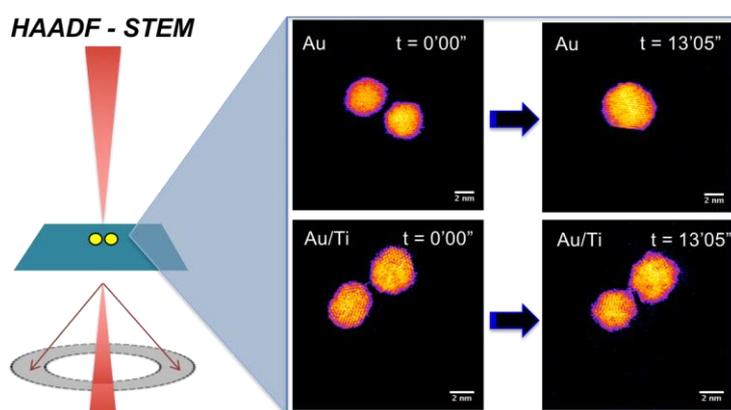
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ABSTRACT

Au nanoparticles represent the most remarkable example of a size effect in heterogeneous catalysis. However, a major issue hindering the use of Au nanoparticles in technological applications is their rapid sintering. We explore the potential of stabilizing Au nanoclusters on SiO₂ by alloying them with a reactive metal, Ti. Mass-selected Au/Ti clusters (400,000 amu) and Au₂₀₅₇ clusters (405,229 amu) were produced with a magnetron sputtering, gas condensation cluster beam source in conjunction with a lateral time-of-flight mass filter, deposited onto planar silica supports and characterised by XPS and LEIS. The sintering dynamics of mass-selected Au and Au/Ti alloy nanoclusters were investigated in real space and real time with atomic resolution aberration-corrected HAADF-STEM imaging, supported by model DFT calculations. A strong anchoring effect was revealed in the case of the Au/Ti clusters, because of a much increased local interaction with the support, by a factor 5x in the theoretical simulations. This interaction strongly inhibits sintering, especially when the clusters are separated by more than ~0.6 nm. Heating the clusters at 100°C for 1 hour in a mixture of O₂ and CO, to simulate CO oxidation conditions, led to some segregation in the Au/Ti clusters. However, in line with the model computational results, Au atoms were still present on the surface. Thus size-selected nanoalloy Au/Ti clusters deposited on oxide supports appear to be promising candidates for sustainable gold-based nanocatalysis.



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Morphology of faceted Fe@Au nanoparticles: A combined experimental and theoretical study

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ABSTRACT

Controlling the synthesis and the final morphology of bimetallic nanoparticles is a current major challenge in order to meet the ever-growing need for nanotechnologies. The presence of two metals combined with size effects favors both new original properties, absent in single metals, and especially multifunctionality. Among the different possible chemical orderings, core-shell configurations allow preserving the properties of each metal while favoring the interaction between them. In addition, core-shell NPs can provide a powerful way for stabilizing specific surface facets with higher efficiency, e.g. for catalysis or molecule binding. However, these developments require that structure and morphology of core-shell NPs be rationalized to become predictable.

Here we focus on core-shell Fe@Au nanoparticles. In this configuration the biocompatible gold shell protects the toxic iron-core from oxidation while preserving its magnetic properties. Furthermore, the gold shell facilitates the anchoring of specific molecules, which makes Fe@Au a suitable candidate for medical applications in hyperthermia or drug delivery.

Recently, Fe@Au core-shell nanoparticles in the 5-15 nm range displaying an original polyhedral morphology were successfully synthesized through a physical route in a UHV device [1]. In the present work the combined effects of temperature and of the amount of deposited metal on the nanoparticle size and morphology are investigated both experimentally and theoretically. Advanced TEM-based techniques (HREM, STEM-HAADF, EDX) down to the atomic scale were used to analyze the grown nanoparticles. Parallel tempering Monte Carlo simulations using a dedicated semi-empirical EAM potential [2] were performed in order to search for the equilibrium morphologies of the core@shell NPs as a function of temperature, at fixed shell thicknesses.

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Synthesis of size tunable Au@Ag core-shell nanoparticles : optical and vibrational properties

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ABSTRACT

The bimetallic system offers a large variety of new properties, potentially extending the already numerous applications of metallic nanoparticles. In particular, the core-shell nanoparticles have properties, which are tunable in function principally of the two metals chosen, the size of the core and the thickness of the shell.

Au@Ag nanoparticles are synthesized through the stepwise Ag reduction on preformed Au NPs through organometallic route¹. The final size of the core-shell NPs and therefore their optical properties can be modulated at least from 5 to 11 nm by either tuning the Ag shell thickness or changing the size of the Au core. The core-shell structure was confirmed by STEM-HAADF and EELS (Figure 1a). The acoustic vibrational modes of Au@Ag NPs were characterized by low-frequency Raman spectroscopy (Figure 1b). The measured wavenumbers of quadrupolar modes are in good agreement with those calculated using an elastic sphere with a core-shell structure². These results highlight a core-shell coupling in Au@Ag bimetallic nanoparticles. By using UV-Vis spectroscopy, the NP localized surface plasmon resonance (LSPR) was investigated. The measured absorption spectra are in good agreement with those calculated using the discrete dipole approximation (DDA) method. In both cases, when the silver thickness is increased, a blue shift of the LSPR is observed (see Figure 1c-d).

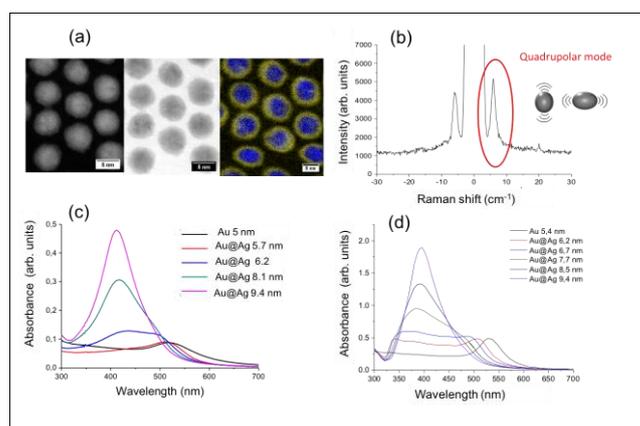


Figure 1. (a) On the left, HAADF dark and bright field images of Au@Ag NPs of 6.7 nm and on the right, the corresponding EELS cartography (silver appears in yellow color and gold in blue color). (b) low-frequency Raman spectrum of Au@Ag core-shell NPs of 6.7 nm. (c) and (d) Absorption spectra of Au@Ag NPs with different silver thicknesses experimental and calculated using the DDA method respectively.

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Singular morphological and structural evolution of Ag-Pt nanoalloys under oxygen exposure

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ABSTRACT

Bimetallic nanoparticles (NPs) are widely studied in terms of their size dependent thermodynamic properties. Indeed, the nanosize can induce drastic changes of physico-chemical properties or enhance them compared to their bulk counterparts. These particular properties clearly depend on the NPs' structure and the chemical arrangement within the NPs. Therefore, following the nanoscale atomic arrangement at equilibrium and during phase transition due to the temperature or environment is essential but very complex. In fact, nanoalloys such as Ag-X (X = Pt, Cu, Ni, Pd, Au) exhibit partial or complete superficial segregation of Ag at the NP's surface [1]–[5]. Nevertheless, the question still remains: is it only due to nanosize effect or also to kinetic effects (kinetic trapping during the growth) and/or environment effect (gas exposure)?

The case of Ag-Pt bimetallic alloy is of an especial interest because this system exhibits a large miscibility gap in bulk but being still able to form the equicomposition Pt₅₀Ag₅₀ ordered alloy (L1₁ structure) at temperature below 750°C [6], [7]. At the nanoscale, the composition's range of existence of the L1₁ ordered phase seems to be enlarge thanks to the Ag surface segregation and the strain state of the NPs [8]. Ag-Pt nanoalloys are very interesting in terms of carbon monoxide oxidation: Pt sites can chemisorb CO and Ag sites activate O₂ by dissociating it [9].

Our objective is to study structural phase transition of Ag-Pt NPs as a function of size, temperature and oxygen exposure. Ag, Pt and Ag-Pt NPs have been prepared by atomic vapor deposition using two separate sources under ultra-high vacuum (UHV) on the synchrotron radiation beamline. In order to compare the thermodynamic behavior between monometallic and bimetallic NPs, in situ grazing incidence small and wide angle X-ray scattering (respectively GISAXS and GIWAXS) have been performed during oxidation and reduction cycles. During these cycles, a singular NPs' diffusion on the amorphous carbon substrate is observed and depends clearly on the atoms' nature and the size of the NPs. It also exhibits several phase transitions and structural reorganization between an oxidized state and a reduced state for Ag, Pt and Ag-Pt NPs with a complete reversibility between these two states.

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***In-situ* E-TEM Study Of TiO₂-supported Copper-gold Nanocatalysts Under O₂ And H₂ Atmospheres**

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ABSTRACT

Supported bimetallic copper-gold nanoparticles (NPs) are of interest to heterogeneous catalysis as they often perform better than their monometallic counterparts in many oxidizing and reducing reactions [1]. If the effects of the metal alloying on the catalytic performances of Cu-Au NPs are undeniable, the origin of these effects is still largely unknown. This stems from the lack of direct observations of the NPs in their reaction environments, *i.e.*, at high temperature and high pressure. In this contribution, we present *in situ* gas TEM studies of the morphological and chemical transformations of TiO₂-supported Au, and Cu-Au nanoparticles under O₂ and H₂ atmospheres as a function of gas pressure and temperature, using windowed-cell environmental transmission electron microscope.

Figure 1a) compares STEM-HAADF images of Au/TiO₂ NPs under 1 atm of H₂ at 400  C and 100  C. At 400  C, the equilibrium shape (ES) of the NPs are mainly of truncated octahedral type. As the temperature is lowered to 100  C, no change in ES is observed. In comparison, AuCu₃/TiO₂ NPs under the same gas environment present different ES at 400  C and 100  C. A rounding of particle shape is observed as temperature is decreased (Figure 1b). The distinct morphological transformation of Au and AuCu₃ NPs is attributed to their different H₂ adsorption properties. Our TEM observations implies that H₂ is weakly adsorbed on Au and thus, their stable ES under reducing environment. Addition of Cu to Au activates H₂ adsorption. As H₂ is adsorbed on AuCu₃ NPs, they develop, in addition to (111) and (100) facets, high index ones which leads to rounded NPs. Under O₂, the adsorption of molecular species is activated on both Au and AuCu₃ NPs. Additionally, the bimetallic NPs show high resistance to oxidation.

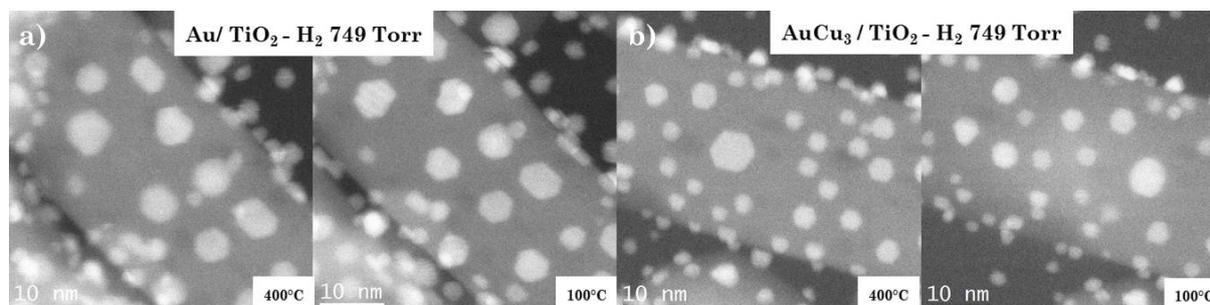


Fig. 1 : STEM-HAADF images showing the shape evolution of TiO₂ supported Au a) and AuCu₃ b) nanoparticles at 400  C and 100  C under one atmosphere of H₂.

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Growth of Palladium Nanoclusters by Gas Aggregation Source: Role of O₂ Addition

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ABSTRACT

Our interest in the growth of Palladium nanoclusters (NCs) is due to their outstanding performance as catalyst for the electro-oxidation of small organic molecules [1, 2]. Palladium NCs can be produced by magnetron sputtering Gas Aggregation Source (GAS) [3] though it is still a challenge to enhance the deposition rate. Interestingly, reactive gas addition (O₂ or N₂) can increase the deposition rate of different metals by promoting a reactive cluster formation, however, NCs chemical composition strongly varies, besides there is a lack of information about their nanostructure [4]. The aim of this work is to study the role of oxygen in the Pd nanoclusters formation, size, deposition rate and nanostructure.

When adding O₂, we observe a characteristic transition zone (TZ) from a clean to a poisoned Pd target surface [5]. Due to the relatively high pressure in the GAS (about 40 Pa), the TZ starts at an oxygen flow rate as low as 0.030 sccm. O₂ addition affects the NC size distribution and the proportion of negatively charged NCs. Deposition rate reaches a maximum value at the end of the TZ with an enhancement of approx. four times its value without oxygen. Grazing incidence X-ray (GIXD) on NCs confirms the FCC structure of the Pd while HRTEM micrographs gives detailed information about their crystal quality. Addition of oxygen beyond the TZ leads to the formation of an "amorphous" phase of PdO. At higher oxygen flow rates, it is possible to observe by HRTEM micrographs the presence of crystalline PdO nanoclusters. Molecular dynamics simulations were performed in order to elucidate the role of the oxygen during NC growth.

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Effect of redox treatments on the structure evolution of γ - Al_2O_3 supported bimetallic noble metal-copper nanocrystal catalysts

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ABSTRACT

As monometallic catalysts, also bimetallic nanocrystal (NCs) can suffer sintering and/or be re-dispersed in certain conditions and gas atmosphere. Reactants induced Ostwald ripening and particle disintegration is a function of three main interactions: adsorbate-metal, metal-support and metal-metal.¹ Notably, in the case of bimetallic systems, the two NCs components will be characterized by different interactions with the adsorbate and with the support, and the presence of the second metal will alter these interactions as well.^{2, 3} To understand and prevent/favor these transformations, two types of Cu-based bimetallic alloyed NCs, namely PtCu and PdCu (Fig. 1a), were synthesized by means of colloidal synthesis methods. The two families were characterized by the same NC size of about 5 nm, the same atomic ratio between Cu and the noble metal of 50/50, and were deposited on the same γ - Al_2O_3 support. These catalysts were treated under high temperature oxidizing and reducing atmospheres and the samples were characterized ex-situ after each treatment. Complete dealloy between the noble metal and the Cu occurred after the oxidizing treatment, with the formation of a $\text{Cu}_x\text{Pd}_{1-x}\text{O}$ solid solution for PdCu NCs. Metallic Pt NCs were formed from PtCu ones, while no crystalline phase associated to Cu was detected. Electron microscopy analysis and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) data confirmed the formation of PdCu mixed oxide (Fig. 1b,c), with Cu and Pd localized in the same regions of the alumina support. On the opposite, the same techniques highlighted how the Pt remained localized in well-defined NCs, while the Cu was instead spread all over the alumina support in the form of oxidized Cu species/clusters. Reducing the catalyst largely restored the PdCu alloy NCs, and partially also the PtCu ones, highlighting how the Cu could migrate back to the Pt NCs. Among the other techniques, *in situ* X-ray absorption spectroscopy analyses are ongoing to characterize the evolution of the chemical states and compositions after and during the two treatments.

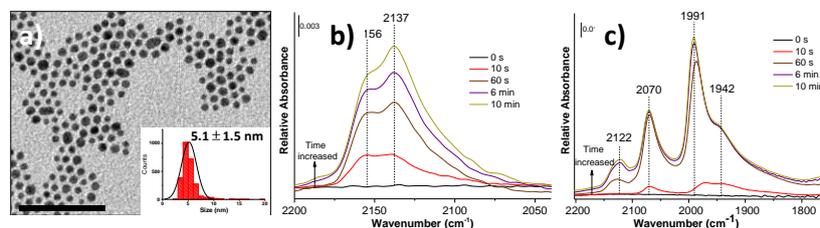


Fig. 1 : BF-TEM image of the as-prepared (a) PdCu NCs with the corresponding size distribution histogram, DRIFTS spectra in the carbonyl region recorded during the adsorption of CO at room temperature on PdCu/ Al_2O_3 catalyst after (b) oxidizing and (c) reducing pre-treatments.

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Catalytic Properties of Alloyed Metal (Ultra)NanoStructures

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ABSTRACT

We will discuss our studies on heterogeneous catalysis by subnanometer – or ultra-nano (i.e. containing up to 10-20 metal atoms) – alloyed metal clusters, with specific attention to the use of quantum mechanical (QM) approaches and modeling of realistic conditions and environment. Supported ultra-nano clusters represent a class of materials which can exhibit superior catalytic properties with respect to traditional systems in addition to optimizing atom-economy efficiency [1]. Alloying opens a wide scope for catalytic tuning in this field, but only few examples have been thoroughly investigated to date. Using a Reactive Global Optimization (RGO) approach as a computational technique able to explore the reactive phase space of these systems in the presence of reactant molecules [2], we will show how the application of systematic sampling under realistic conditions naturally leads to the concept of ligand/cluster/support catalytic complex. The simultaneous presence on the metal catalyst of chemical species at various stages of the reaction and the strong influence of the support translates in fact into the formation *in-situ* and under reaction conditions of a ligand/cluster/support complex aggregate, which acts as the real catalytically active species. Then, to predict reaction rates which can be compared with experiment, QM predictions of individual local minimum structures and interconversion barriers must be coupled with kinetic Monte Carlo algorithms.

We will present applications of this approach to the oxidation reaction of CO to CO₂ catalyzed by (Ag-Au)₃/MgO(100) and Ag₉Pt₂₋₃/a-Al₂O₃ systems, including detailed comparison with experiment [3].

Finally, realistic modeling must take into account the degrees of freedom associated with the support. Specifically, we will demonstrate the crucial importance of an amorphous oxide support for stabilizing and promoting the cluster catalytic activity, and we will propose structural models derived from first-principles simulations for ultrathin (≈ 0.7 nm-thick) amorphous alumina with 3 different hydroxylation degrees, thus corresponding to three different operando (temperature, humidity) conditions.

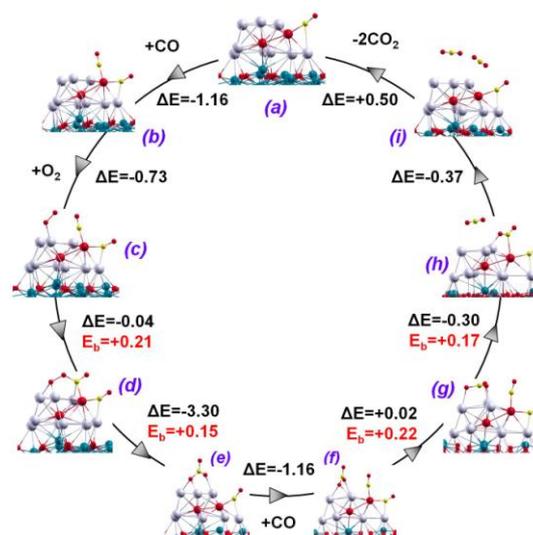


Fig. 1 : CO_x catalytic cycle over Ag₉Pt₂/a-Al₂O₃

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Supported Co-Re Nanoparticles As Efficient Catalysts For Hydrogenation Reaction

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ABSTRACT

With the aim of replacing costly and rare noble metals, this is the first time, to our knowledge, that the potentiality of supported bimetallic Co-Re catalysts is presented for the selective hydrogenation of citral into unsaturated alcohols (valuable intermediates widely used in perfumes, pharmaceuticals, pesticides and foods). Co-Re catalysts with various x wt% Re contents were prepared by co-impregnation (CI), successive impregnation (SI) and surface redox reaction (SRR) methods [1] by using TiO₂ as support, and CoCl₂ and NH₄ReO₄ as precursor salts. They were characterized by complementary physico-chemical techniques such as X-Ray Diffraction (XRD), Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), H₂-Temperature Programmed Reduction (H₂-TPR), as well as a gas phase probe reaction.

The presence of a bimetallic interaction in the nanoparticles was highlighted for both SI and SRR preparation methods, but with discrepancies on the final oxidation state of the Re species. With the increase of Re loading deposited by SI, the reduction degree of Re gradually decreases (Fig. 1A). This phenomenon can be explained by the fact that some Re species are away from Co at high rhenium loadings.

Compared to Co and Re nanoparticles isolated from each other, the bimetallic Co-Re particles induce a synergetic effect on both the activity and selectivity during citral hydrogenation (Fig. 1B). It can be attributed to the likely presence of a binary alloy, even if the latter is difficult to highlight on heterogeneous catalysts with very low metal charges dispersed on the support.

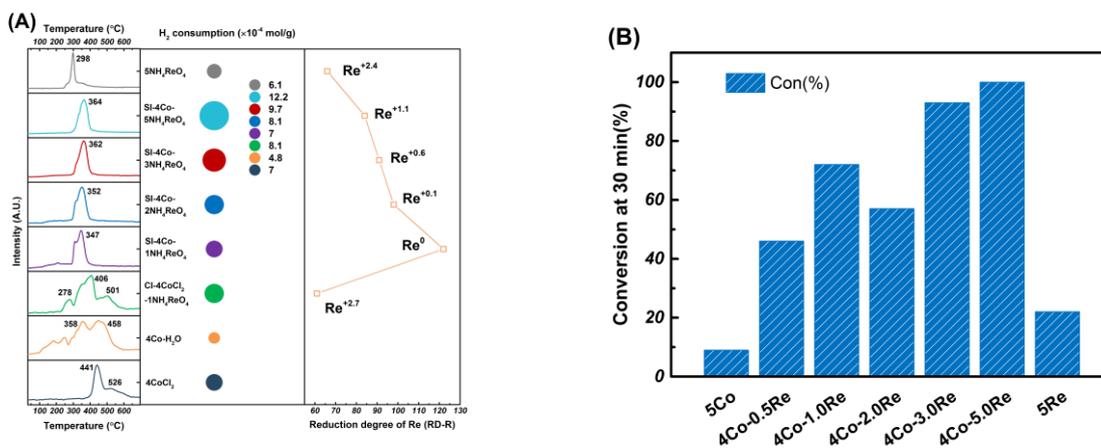


Fig. 1. (A) H₂-TPR results for SI-4Co-xNH₄ReO₄/TiO₂ and (B) citral hydrogenation results over SI-4Co-xRe/TiO₂

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Computational Study of Free And Oxide-Supported Au-Rh And Pd-Ir Nanocatalysts

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ABSTRACT

As most chemical reactions happen on surfaces, nanoparticles are ideal for heterogeneous catalysis due to their optimal surface to volume ratio. Alloying two metals can furthermore improve catalytic performance by increasing selectivity, activity or resistance to poisoning due to electronic or geometric effects. Tuning nanoalloy morphology may even enhance catalytic properties by controlling reactivity and/or selectivity. The properties of nanoparticles are also under the influence of a substrate in real world applications. Hence, an accurate description of nanocluster-support interaction is important in nanoalloy catalysis applications and can be achieved by atomistic modelling based on first principle electronic structure calculations.

We will present recent studies of fcc-Au-Rh [1-4] and Pd-Ir [5,6] nanoalloys supported on TiO₂(110). In experimental studies, TiO₂ has been used as a substrate because it has well defined single phase nanorods (which are suitable for structural analysis) and it is a reducible oxide (which can act as an oxygen reservoir and enhance the catalytic activity) [1]. We have studied the relative stabilities of different chemical ordering arrangements of the Au-Rh and Pd-Ir nanoalloys, for a range of compositions [2,5], and how these are influenced by the TiO₂ substrate [4,6]. The effect of chemical ordering and the substrate on the strength of adsorption of small adsorbates such as H₂, O₂ and CO will be discussed [3,4].

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Nanogenomics: Encoding The Catalytic Activity Via Site Description

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ABSTRACT

Nanogenomics allows to encode the catalytic activity of nanostructures only accounting for the geometrical genome of nanostructure, which is defined as the full list of different types of sites, where chemical reactions might occur, and related occurrence. We have developed a generic scheme to calculate the genome for various nanostructures and monodisperse samples, and to retune information over the catalytic activity at finite temperatures. Further, we are going to show how the same scheme can be used as a lattice for a kinetic Monte Carlo approach and we will use it to estimate the water production for MgO-supported PtNi nanoparticles.[1]

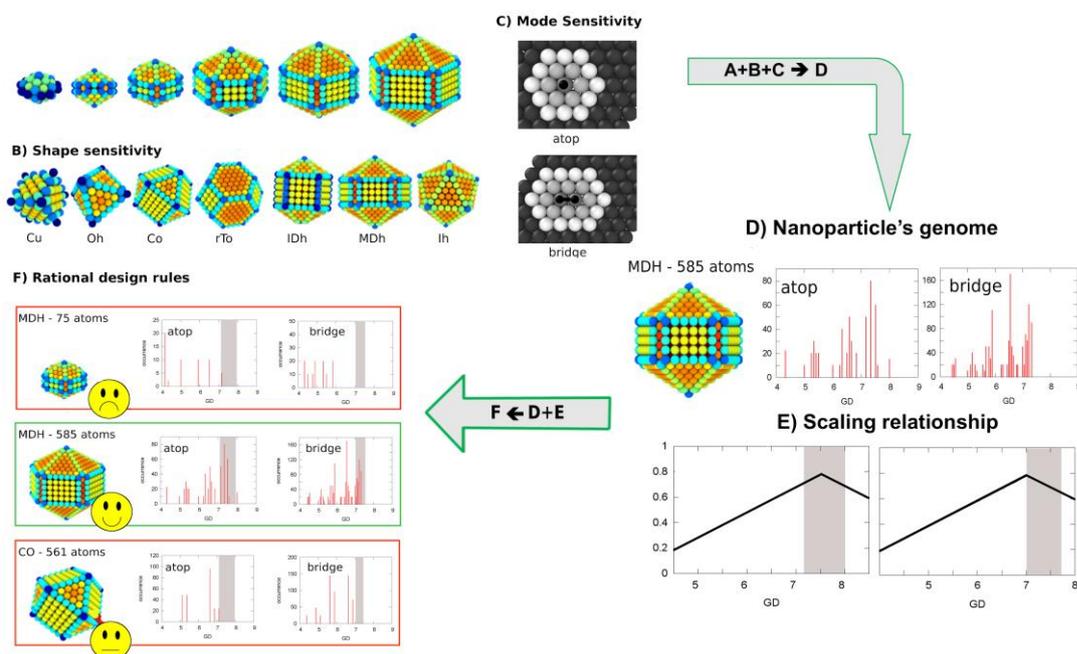


Fig. 1 : Nanocatalysts' design route

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Designing alloy nanoparticles: from precise production to catalysis testing

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ABSTRACT

Bimetallic clusters offer the opportunity to generate new chemical and electronic properties that are different from the parent metals, and thus achieve catalytic performance with enhanced selectivity, activity and stability. With this aim, coupled with a desire to reduce the usage of critical metals, such as Pt¹, Pt-Cu bimetallic clusters have been produced via gas phase, ligand-free synthesis: specifically, using the Multiple Ion Cluster Source (MICS) recently developed in Madrid². The conventional magnetron-based cluster source is based on the sputtering of a single pure or alloy target under vacuum conditions, followed by aggregation of the atoms in the gas phase via 3-body collisions including the condensation gas (the coolant). In the MICS the single magnetron is replaced with three independent magnetrons, allowing the production of a wide range of alloy clusters. The advantage of this source is the possibility to control both the cluster's composition and atomic structure, by changing the mutual magnetron positions as well as the sputtering rates of the elemental targets employed. In the present work we deposited binary Pt-Cu clusters with the same size and composition, but different atomic structures: alloy, core@shell and shell@core, in order to investigate the effect of the nanostructure on both gas-phase and electro catalytic performance. Such structure-activity relationships can now be exploited via a new kind of nanoalloy source developed at Swansea (the Matrix Assembly Cluster Source), which enables scale-up of the cluster production rate towards the gram scale³.

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Multiscale Structure Reconstruction (MSR) Model for Predicting the Shape Evolution of Metallic Nanoparticles under Reaction Conditions: from Monometallic to Nanoalloy

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ABSTRACT

Metal nanoparticles (NPs) have attracted intensive attention in nanoscience and nanotechnology due to their unique physical and chemical properties, which are mainly determined by their sizes and shapes. In recent years, many in-situ experimental observations have shown that metal nanoparticles could change their shapes and structures dramatically and reversibly under reactive gas conditions. However, owing to the difficulties in obtaining 3-D in-situ high-resolution characterizations and the lack of effective theoretical models, the precise prediction of shape evolution is still a challenging and demanding task. In our recent works we developed a multiscale structure reconstruction (MSR) model to quantitatively predict the equilibrium geometries of metal nanoparticles at different temperatures and gas pressures and to simulate the shape evolution changes under reaction conditions [1-2]. This MSR model was also extended to take into account the interaction between the metal nanoparticle and the oxide support as well as in presence of gas mixture. In this talk I will present results on the shape evolution of Au/Cu/Pt/Pd/Rh [1-4] nanoparticles under reaction conditions and I will show how this model perfectly reproduces the experimental results and explains some intriguing phenomena, as the CO induced break-up of Pt surfaces [5]. Based on this DFT-based MSR model, and DFT-based Ising model [6] the study of the shape evolution of nanoalloys under reaction conditions is ongoing. This work offers possibilities for obtaining atomic-scale structures and insights beyond the experimental limits.

Radiolytic Synthesis of Gold-Silver Bimetallic Nanoparticles Stabilized by Calix[8]arenes

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ABSTRACT

Among the numerous methods available to synthesize metallic nanoparticles, radiolysis is a powerful one to produce nanoparticles of controlled size and shape in solutions and heterogeneous media. No chemical reactants are needed as the reducing species (solvated electron, radicals) are generated from the solvent by the ionizing radiation [1].

The ligands, polymers or supports used to stabilize the nanoparticles play also an important role for further applications. Lately, calixarenes, cyclo-oligomers formed via a phenol-formaldehyde condensation appear very attractive ligands for several applications [2] such as catalysis or sensors due to their chemical versatility, host-guest properties and surface accessibility [3].

We present here that the simultaneous radiolytic reduction of silver and gold metallic salts in the presence of calix[8]arenes in ethanol solution gives small alloyed spherical nanoparticles with sizes around 3.5 nm, but with an inhomogeneous structure (Fig. 1 left). In order to get a better control of the structure and composition, polymetallic complexes based on calix[8]arenes and Ag^I and Au^I ions have been synthesized. Their reduction leads to the formation of homogeneously alloyed bimetallic clusters (Fig. 1 right)

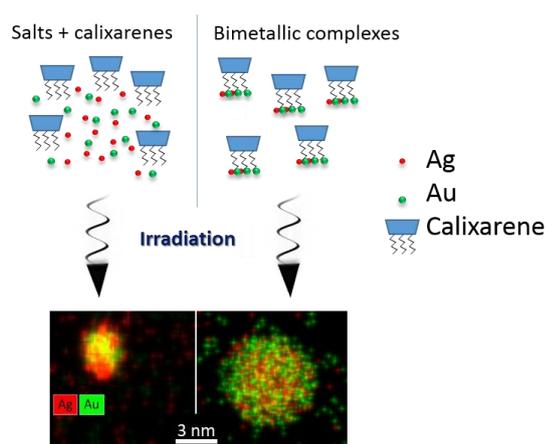


Fig. 1 : EDX-STEM maps of gold-silver bimetallic nanoparticles synthesized in ethanol solution by radiolytic reduction of (left) metallic salts in the presence of calixarenes or (right) polymetallic calixarene complexes

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Nanofabrication and Nanostructuring: When Ionic Liquids Meet Applications

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ABSTRACT

Ionic liquids offer unique opportunities for the (electro)chemical synthesis of metals. Due to their wide electrochemical window and ability to stabilise small nanoparticles (NPs), they are well suited to the chemical synthesis of a variety of metallic NPs.[1,2] A novel example is the elaboration of suspensions of CoNPs in $C_1C_4ImNTf_2$ that could be used as ferrofluids.[3]

More recently, this approach was extended into a versatile route to generate bimetallic NPs in ILs. Interestingly enough, surface hydrides present on at least one of the two metals were shown to promote the formation of bimetallic core-shell NPs, even in the case of non-miscible metals, e.g. Cu@Ru.[4] Recent results will be presented on the tentative synthesis of MnCuNPs (Fig. 1) as precursors of metallic thin films for the fabrication of interconnect structures such as through silicon vias.

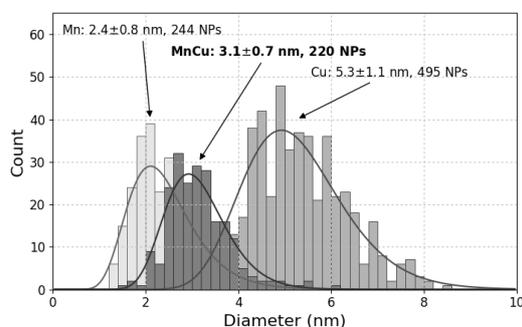


Fig. 1 : Compared size distributions of Cu, Mn and Mn-CuNPs formed in $C_1C_4ImNTf_2$ under 0.9 MPa H_2 at 100°C during 4 h.

Another extension of this approach is the supported synthesis of metallic NPs for several technological applications. CuNPs could be successfully deposited throughout a several- μ m thick layer of mesoporous Si used in integrated gas chromatography devices, showing the ability of ILs to penetrate such substrates.[5] In this contribution, the synthesis of Pt and CoPt catalysts on carbon substrates in suspension in an IL will be investigated to produce catalytic inks for the fabrication of fuel cell electrodes.

Finally, future extensions of this strategy will be discussed, including on-going process developments towards industrial scale manufacturing of such suspensions.

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Metal Nanoalloy Synthesis By Solvothermal Hot Injection Technique

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ABSTRACT

The synthesis of nanoalloys is one integral part of nanoscience and development of efficient preparative methods is a challenging task due to their chemical, phase, and morphological variability.

Nanoparticles of metal alloys exhibit many interesting properties, such as depression of melting point, plasmon resonance, catalytic activity and magnetic properties. Nanoalloys can be prepared by many approaches, but the solvothermal synthesis, specifically in oleylamine is highly advantageous. Hot injection technique should ensure homogeneous conditions for nanoparticle nucleation and growth.

AgNi and AgCu nanoparticles were synthesized by injection of metal precursors oleylamine solution to a mixture of oleylamine and octadecene at 230 °C. After 10 minutes, the reaction mixture was cooled down to room temperature in a water bath. Nanoparticles were isolated, purified, dispersed in hexane and characterized.

Size, shape, morphology, elemental distribution, optical and magnetic properties were described by using various techniques. Core/shell structure of AgNi, importance of used precursors to final morphology of AgCu and simple technique for Janus or solid solution synthesis were demonstrated.

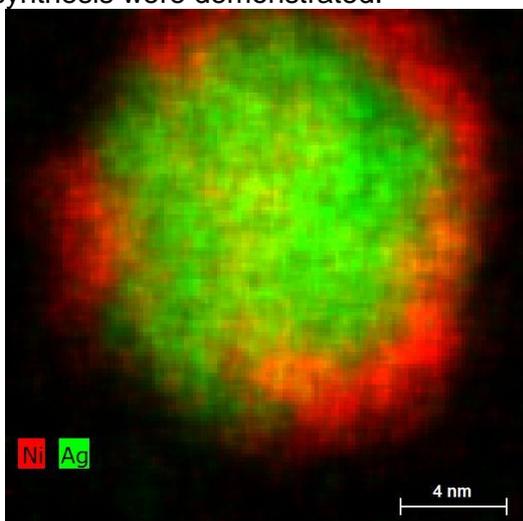


Fig. 1 : STEM-EDS of AgNi – core/shell structure

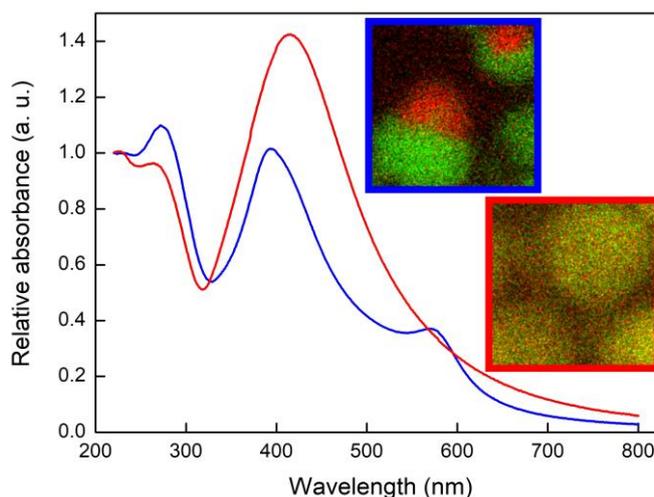


Fig. 2 : Morphology and optical properties of AgCu

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Study of Pt-Co interaction in bimetallic supported catalysts

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ABSTRACT

Platinum (Pt) is a noble metal widely used in catalytic hydrogenation reactions but also rare and expensive, meaning that it is necessary to replace it partially or totally by non-noble metal as cobalt (Co). As alternative, we developed Pt-Co bimetallic catalysts with the goal to decrease the amount of platinum while maintaining same catalytic performances. These catalysts supported on alumina were prepared by two methods of synthesis. The first one consists of co-impregnating (COI) of Pt and Co precursor salts on the support and the second one of controlling the deposition of the platinum on the surface of cobalt supported on alumina via redox reaction route (RO) in aqueous phase. These catalysts have been characterized by ICP, H₂-chemisorption, TPR, XRD, TEM-EDX, XPS and EXAFS. For both systems, the results have shown the presence of nanoalloy with significant bimetallic interactions, leading to the improvement of the reducibility of the cobalt due to the presence of platinum [1-3].

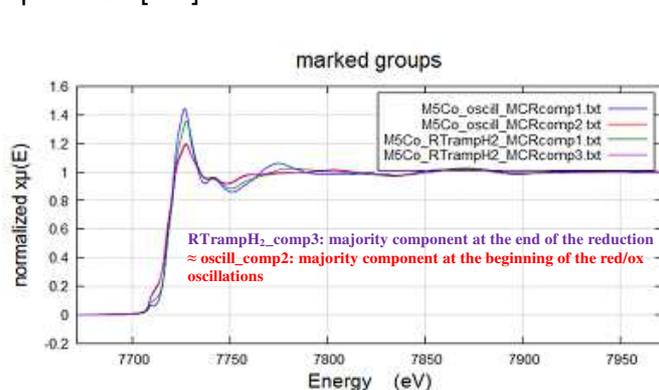


Fig. 1: XAS spectra of the main components displayed by Pt-Co RO catalyst according to gaseous treatment (K edge Co): green and violet lines are the two main components obtained during the reduction phase, blue and red lines are the main component obtained during red/ox oscillations.

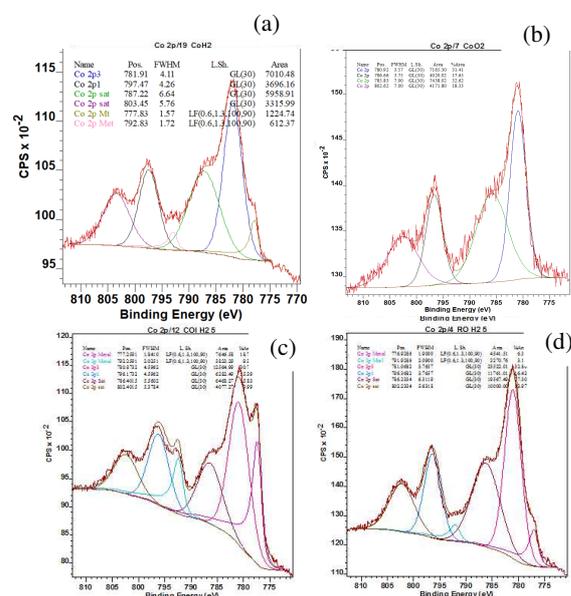


Fig. 2: XPS spectra for Co 2p region of Co catalyst ((a) reduced, (b) oxidized) and Pt-Co bimetallic catalysts ((c) COI and (d) RO).

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CO₂ Adsorption on Gas-Phase 4-atom Cu-Pt Clusters: A DFT Study

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ABSTRACT

A systematic computational study of CO₂ adsorption on gas-phase Cu_{4-x}Pt_x (x = 0-4) clusters is presented. An exhaustive potential energy surface exploration is initially performed out using our recent Density Functional Theory Basin-Hopping global optimization implementation [1]. Ground-state and low-lying energy isomers are identified for Cu_{4-x}Pt_x clusters. Secondly, a CO₂ molecule adsorption process is analyzed on the ground-state Cu_{4-x}Pt_x configurations, as a function of cluster composition. Our results show that the gas-phase linear CO₂ molecule is deformed upon adsorption, with its bend angle varying from about 134° to 145°. Cu_{4-x}Pt_x cluster geometries remain unchanged after CO₂ adsorption, with the exception of Cu₃Pt₁ and Pt₄ clusters. For these particular cases, a structural conversion between the ground-state geometry and the corresponding first isomer configurations is found to be assisted by the CO₂ adsorption. For all clusters, the energy barriers between the ground-state and first isomer structures are explored.

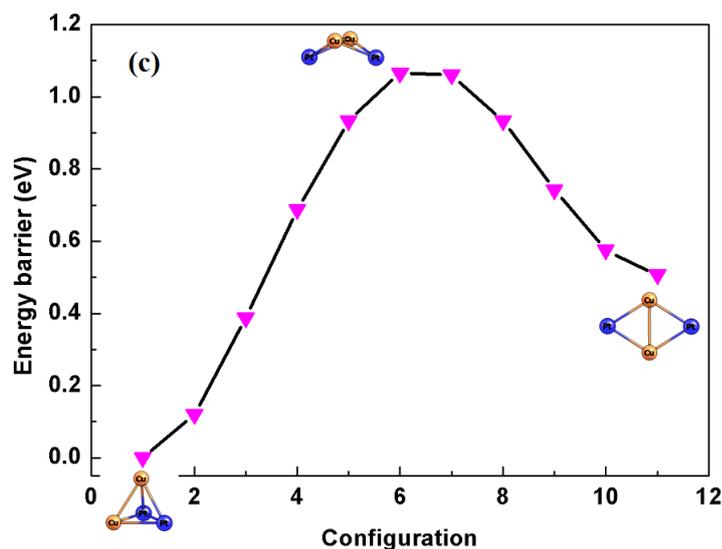


Fig. 1 : Calculated energy barrier between ground-state and first isomer for Cu₂Pt₂ cluster.

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What is hidden behind phase diagrams and ageing kinetics of nanoalloys ?

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ABSTRACT

The aim of this talk is to illustrate the methodology developed by the team to get phase diagrams of nanoalloys and to follow the kinetics from out-equilibrium states toward equilibrium configurations.

First we show that a phase diagram of nanoalloys consists in a set of phase diagrams related to the various classes of surface sites or to the internal layers. For example, for the Wulff polyhedron of 405 atoms (PW405) in the Cu-Ag system characterized by a large difference in atomic radii between the components and a tendency to phase separation, we distinguish three phase diagrams : the (100) facets diagram, the (111) facets diagram and the phase diagram for the layers of the core [1]. The analysis of the Monte Carlo simulations within an effective lattice formalism and a mean-field approximation is very powerful to show that each of these diagrams is linked to very different physical phenomena.

Then we explore the time evolution of non-equilibrium bimetallic nanoparticles toward equilibrium configurations using both Kinetics Monte Carlo (KMC) simulations and a kinetic mean-field description which provides the time evolution of the concentration for *each site* called MFA-SK approach (Mean-Field Approximation, Site Kinetics), based on the same atomic model. We show that the MFA-SK approach allows us to analyze the kinetics of the dissolution of the onion-like structure and to identify the main paths of the kinetic process [2].

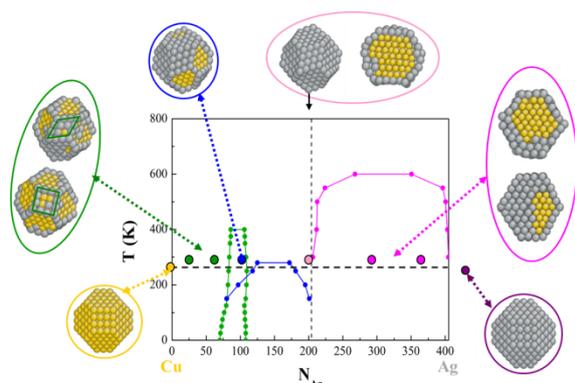


Fig. 1 : Phase diagram CuAg of a PW405 nanoparticle.

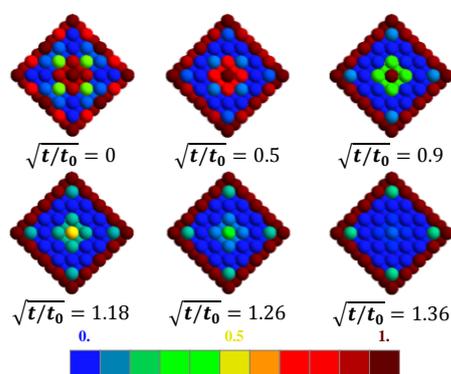


Fig. 2 : Time evolution of a Cubo5 CuAg nanoparticle

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Structural Stability of Bimetallic Pd_xPt_{55-x} and Trimetallic Pd_xPt_{55-x}Au₉₂ Nanoalloys

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ABSTRACT

In recent years, binary and ternary metal nanoalloys take much attention due to the applications in fields such as catalysis, solid-state physics, chemical-physics, biomedicine and optics[1-3]. Varying the type of metals, cluster size and composition is a useful way to design the specific nanomaterials which has the tailored properties for processes catalytically controlled. In this study, the structures of 55-atom Pd-Pt binary nanoalloys and 147-atom Pd-Pt-Au ternary nanoalloys are investigated by means of computer simulations. We found that the most stable composition is Pd₃₇Pt₁₈ for 55-atom binary nanoalloys and Pd₃₀Pt₂₅Au₉₂ for 147-atom ternary nanoalloys from excess energy graphs (Figure 1). The orientations of Pd and Pt atoms differ for both binary and ternary case.

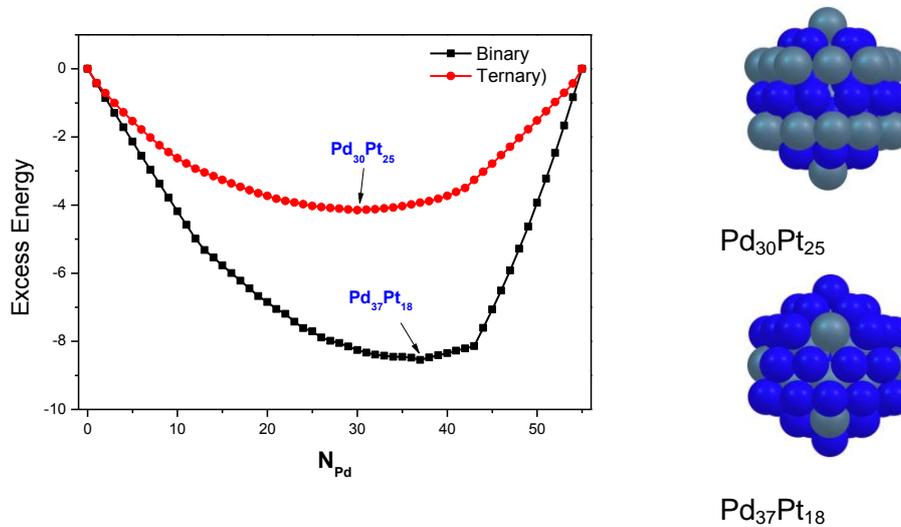


Fig. 1 : Excess energy graphs of binary Pd-Pt and ternary Pd-Pt-Au nanoalloys and the most stable compositions.

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Equilibrium Structures Of Nanoalloys Determined By Computational Methods

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ABSTRACT

The equilibrium structures of nanoalloys are determined computationally by a combination of methods comprising global optimization searches by atomistic force fields, density-functional theory calculations, Monte Carlo and molecular dynamics simulations. Weakly miscible systems, such as AgCu, AgNi [1,2] and AuCo [2] are treated first, with the aim of deriving general trends in size- and composition-dependent structural transformations. Then, systems with tendency to intermixing are considered, such as AuCu [4] and AgPd [5], showing a complex interplay between intermixing and surface segregation.

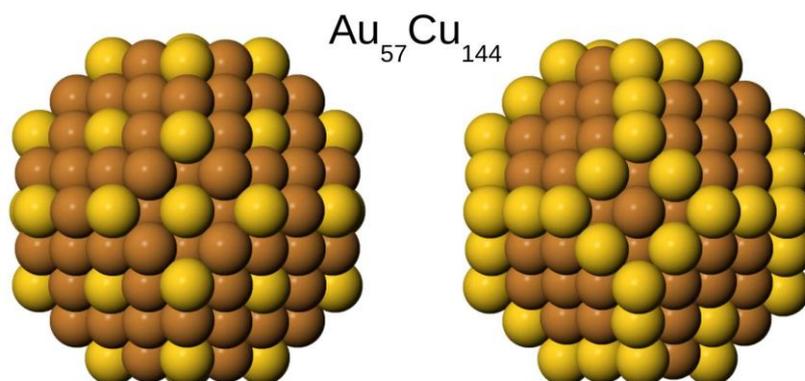


Fig. 1 L_{12} structure and optimized structure of $Au_{57}Cu_{144}$

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