

From metastability to equilibrium during the sequential growth in Co-Ag supported clusters

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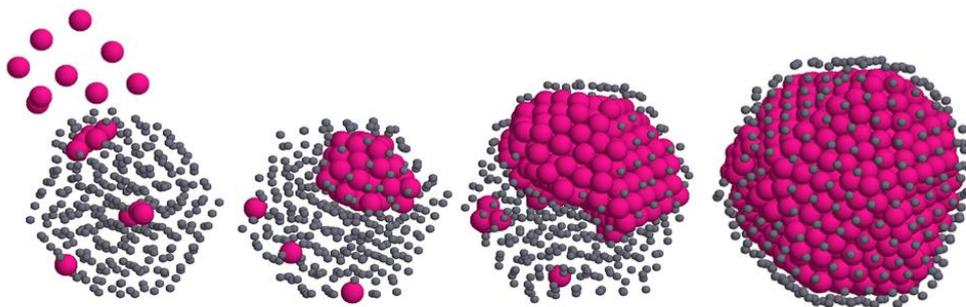
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ABSTRACT

The Co-Ag bimetallic system is a very weakly miscible system in wide ranges of temperature and composition. Since Ag presents lower surface energy and larger size (to minimize elastic energy), a surface segregation of silver is expected at the equilibrium in Ag-based bimetallic alloy surface. To the nanometer scale, the size reduction favors exotic segregation behavior by surface and/or core contraction effects that can be opposed to kinetic trapping effects induced by the growth mode. In our works, atom mobility during the formation of Co-Ag supported nanoalloys were studied through in situ investigations of the structural arrangement evolution. Obtained by sequential atom deposition for each type of atoms (Ag and Co), the different configurations: Co deposition on Ag core and Ag deposition Co core were investigated during the growth.

Firstly, morphological and structural evolutions are followed by in situ and real time wide and small angle X-ray scattering obtained simultaneously in X-ray grazing incidence geometry (GISAXS and GIWAXS) in single or multi-wavelength (anomalous) mode. Secondly, the quantitative structural analysis of experimental data was facilitated and consolidated using Monte Carlo (MC) simulations of Co-Ag nanoalloys in a semi-empirical tight-binding approach. In addition, atomistic simulations of the cluster growth by molecular dynamics (MD) were done to reveal the atom migration leading to phase separation or core-shell formation (Figure). In a metastable deposition mode, i.e. by depositing Co above an Ag core, the configuration is complex: Co atoms incorporate the initial Ag core in sub-layer position leading to janus then core-shell configuration with the Co content. In the more stable reverse deposition mode, unexpected, Ag nucleate in domains on Co core, rather than in shell.



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Molecular Dynamics approach to plasma nanocluster growth and reactivity

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ABSTRACT

Controlling nanocatalyst growth is of paramount importance for improving catalyst size distribution, structure and morphology to achieve high activity and selectivity. Experimentally, Magnetron Sputtering - Gas Aggregation Source is a new tool for designing nano(alloy)catalysts [1] based upon plasma sputtering at high pressure in an inert plasma (Ar) or reactive plasma (Ar with O₂, N₂) which is carrying the grown cluster to a substrate through a nozzle.

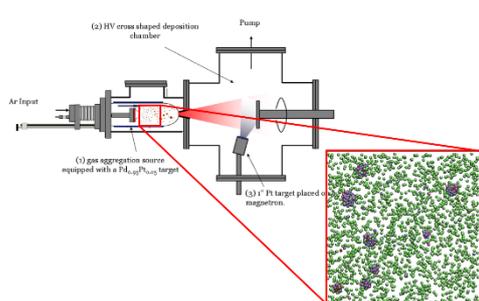


Fig. 1 : Schematics of a plasma condensation source. Inset gives the nanoalloy growth process in the condensation chamber. (after Ref. 1)

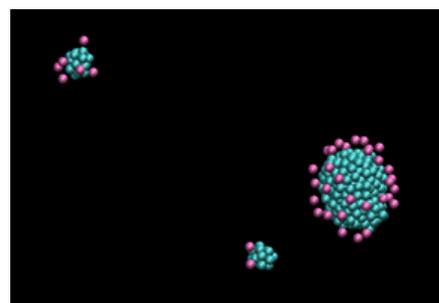


FIG. 2: Example of Pt₉₀Bi₁₀ cluster growth in plasma condensation source. Background Ar gas atoms are removed for clarity.

Initial conditions of MD simulations are selected for matching experimental chemical and physical synthesis by Magnetron Sputtering - Gas Aggregation Source. This takes into account the sputtering properties for determining the initial ratios between sputtered and background gas (reactive or not) atoms. Results concerning the growth of Pt_xNi_yAu_z, Pt_xBi_y (Fig. 2) and Pd_xO_y nanocatalysts under such conditions will be presented. Radial distribution functions and X-Ray Diffraction patterns are systematically computed for enabling direct comparison with experiments.

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Co:FePt nanocomposite magnets prepared combining mass selected cluster beam and e-beam evaporation techniques

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ABSTRACT

Nanocomposite magnets consisting of a fine mixture of a hard magnetic phase and a high saturation magnetization phase are promising systems to overpass performances of the best permanent magnets. Theoretical descriptions of nanocomposite magnets [1] revealed the necessity of confining the soft phase in grains of typically less than 10 nm. Yet standard fabrication processes do not permit to have such a control on the microstructure. In this context nanomaterial-dedicated synthesis could permit to realize model films to experimentally explore fine mechanisms that govern magnet performances in such nanocomposite magnets [2]. Here we report on thorough study of Co:FePt nanocomposite where Co nanoclusters with size of 6 nm constitute the soft magnetic phase which is embedded in L1₀-FePt matrix. Standard structural (e.g. XRD, SEM, TEM) and magnetic (SQUID magnetometry, MFM) characterizations were complemented with X-ray natural linear dichroism (XLD) and X-ray magnetic circular dichroism (XMCD) spectroscopies at the K-edges of Fe and Co. XLD measurements confirmed that Co is embedded in FePt matrix (figure 1(a)).

XMCD measurements in turn show that Co and Fe atoms are ferromagnetically coupled and that the Co:FePt nanocomposite behaves like a single magnetic phase (figure 1(b)).

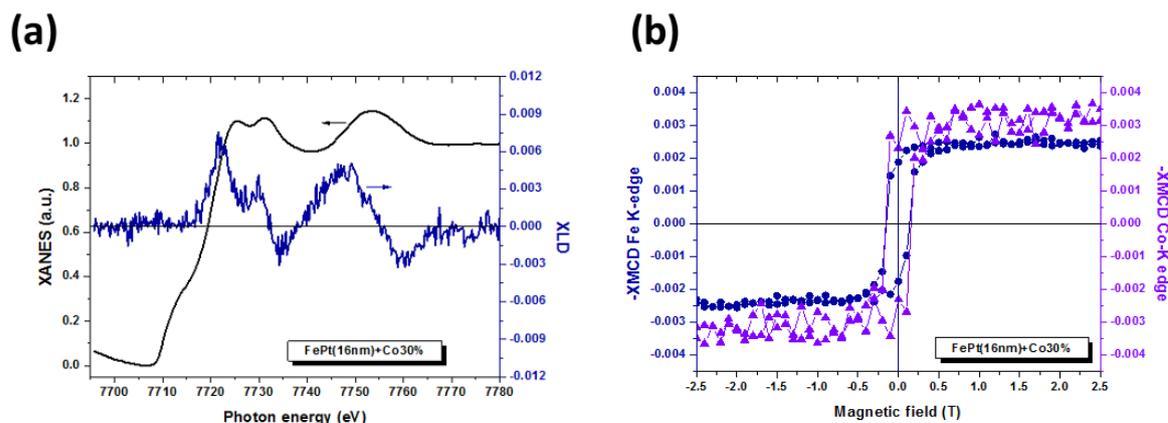


Fig. 1 : X-Ray Linear Dichroism (XLD) after annealing at the Co K-edge displaying the local environment anisotropy of the Co atoms of the embedded clusters which contradicts the as-deposited fcc structure of the Co nanoparticles (a). XMCD hysteresis loops at Fe and Co K-edges showing the simultaneous magnetization reversal of the nanocomposite (b).

Moving And Vibrating: Exploring The Vibrational And Magnetic Properties Of Ni₁₉

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ABSTRACT

Exploring the interplay between atomic vibrations and magnetic properties represents an initial and fundamental step in the rational design of nanostructures for application in spintronic and memory devices [1]. We present accurate *all-electron* density functional calculations performed on Ni₁₉ at *ab initio* level, including several stable isomers and considering perfect and distorted structures. In particular, we report data for Bipyramidal (BIP), double- and distorted double-icosahedral (DIH and dDIH), hexagonal close-packed (HCP) and distorted hexagonal close-packed (dHCP) nanostructures. We found a non-trivial relationship between the relative stability of the nanostructures and the total magnetization for each local minimum, as well as a structure-dependent influence of the total magnetization on the calculated vibrational spectra.

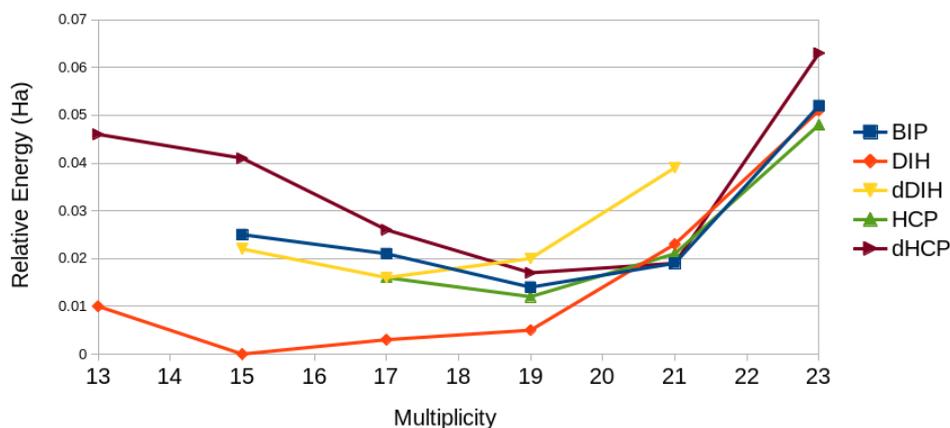


Fig. 1 : Relative stability of structural isomers of Ni₁₉ at different magnetic states.

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Nano-fried-eggs: Structural, Optical and Magnetic Characterization of Physically Prepared Iron-Silver Nanoparticles

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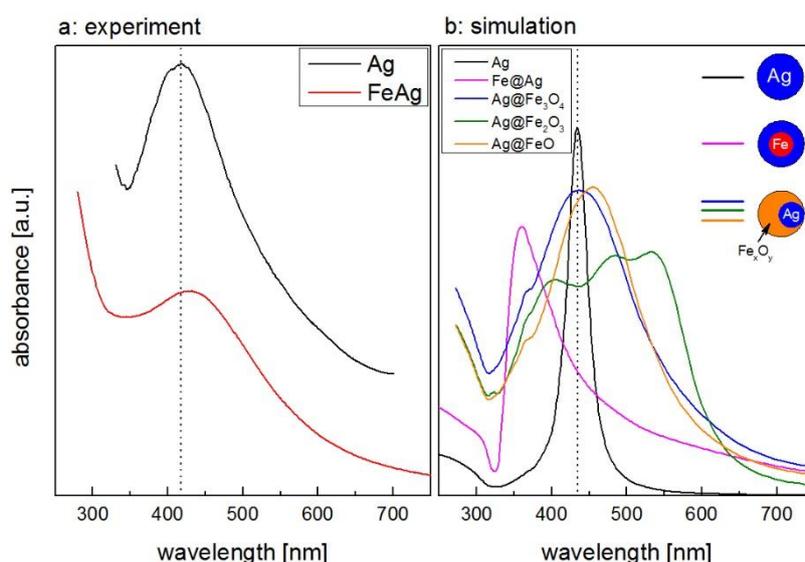
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ABSTRACT

The prospect of combining both magnetic and plasmonic properties in one single nanoparticle promises both valuable insights on the properties of such systems from a fundamental point of view as well as numerous possibilities in technological applications. The combination of two of the most prominent metallic candidates, iron and silver, has, however, presented a lot of experimental difficulties because of their thermodynamic properties impeding miscibility or even coalescence. Here we present the thorough characterization of physically prepared Fe₅₀Ag₅₀ nanoparticles embedded in carbon and silica matrices by electron microscopy, optical spectroscopy, magnetometry and synchrotron-based x-ray spectroscopy. Iron and silver segregate completely into structures resembling fried eggs with a nearly spherical, crystallized silver part surrounded by an amorphous structure of iron carbide or oxide, depending on the environment of the particles. Consequently the particles display both plasmonic absorption corresponding to the silver nanospheres in an oxide environment as well as a reduced but measurable magnetic response. The suitability of such nanoparticles for technological applications is discussed in view of their high chemical reactivity with their environment.



a) Optical absorption spectra of Fe₅₀Ag₅₀ nanoparticles with mean diameter of 4.5 nm and embedded in silica. The surface plasmon absorption peak for pure silver particles of 4.0 nm diameter in silica (black, upper curve) is shown for comparison. b) Simulated absorption spectra for five different compositions and geometries: pure silver, concentric Fe@Ag and eccentric Ag@Fe_xO_y core shell structures.

L₁ core ordering in Pt-Ag nanoalloys from Tight Binding Ising Model

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Pt-Ag alloys present the L₁ ordered phase at low temperature and a miscibility gap between this phase and the A1 solid solution in the silver diluted phase. Moreover, the weak surface energy of silver as compared to platinum leads to a strong silver surface segregation making the chemical ordering in Pt-Ag nanoalloys very interesting and different from the Co-Pt system which has been very much studied [1]. The L₁ ordered phase has been observed experimentally (cf. Poster by J. Pirart) in nanoalloys of 2 to 3 nm elaborated in ultra-vacuum condition and observed by transmission electron microscopy and grazing incidence X-ray diffraction experiments for which model systems are useful to interpret the experimental results.

Therefore we propose a simple Tight-Binding Ising Model (TBIM) fitted to *ab initio* calculations and compared to semi-empirical many-body potential to describe the energetics of Pt-Ag nanoalloys. Using Monte Carlo simulations we determine the equilibrium phases on the whole range of composition and for different sizes, taking into account the temperature effect. We get the surface segregation isotherms for each different surface type of site, as illustrated on Fig. 1, and the core sublattices occupation (Fig. 2) which characterizes the L₁ phase.

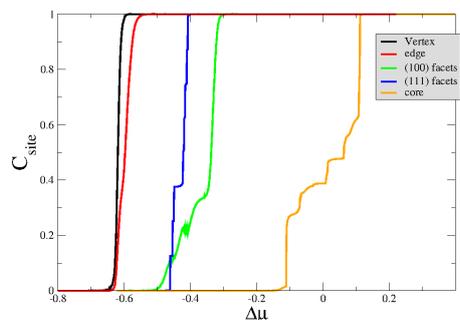


Fig. 1 : Surface sites segregation isotherms at 100K for a truncated octahedron of 1289 atoms

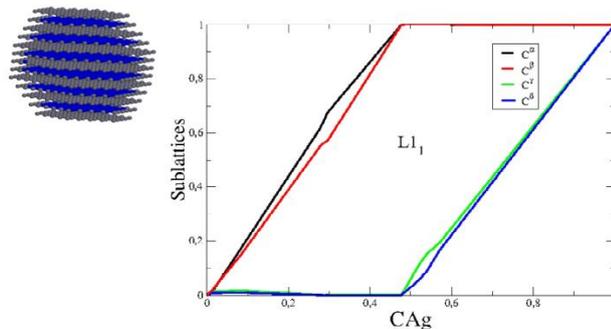


Fig. 2 : Sublattices occupation isotherms at 100K of a truncated octahedron of 1289 atoms as represented in insert for the L₁ ordered structure.

The results will be compared to the chemical ordering of the Co-Pt nanoalloys characterized within an equivalent TBIM model but displaying the L₁₀ ordered phase at the equiconcentration and a weaker surface segregation effect [2].

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The Effect of Palladium Doping on the Stability of Gold Clusters

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ABSTRACT

The search for stable cluster species is an important subject in the study of small clusters.^{1,2} Electronic shells emerge due to the quantum confinement of valence electrons that are delocalized over the entire cluster volume. When a cluster has the appropriate number of delocalized electrons, filling the electronic shells leads to an enhanced stability.³ Changes in composition can modify the stability patterns of clusters because it alters the geometry and electronic structure.

Here we analyze the interplay between the electronic structure and the cluster geometry that determines the stability of single palladium doped cationic gold clusters, PdAu_{N-1}^+ ($N=5-20$). For this purpose, photofragmentation experiments are combined with density functional theory calculations (Fig. 1). Palladium doping is found to modify the structure of the gold clusters, in particular altering the 2D to 3D transition size, with direct consequences on the stability of the clusters. It is shown that depending on cluster size, palladium delocalizes one 4d electron, giving an enhanced stability to PdAu_6^+ , or remains with all 4d¹⁰ electrons localized, closing an electronic shell in PdAu_9^+ .

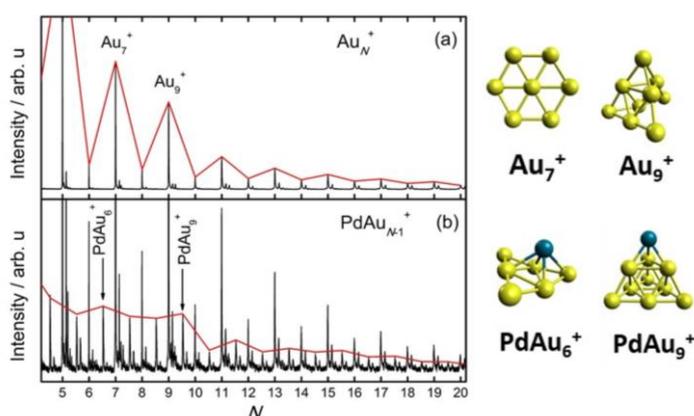


Fig. 1: Left: Mass spectra of Au_N^+ and PdAu_{N-1}^+ clusters after photofragmentation. Right: Ground-state structure of the “magic clusters” Au_7^+ , Au_9^+ , PdAu_6^+ and PdAu_9^+ .

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Size Dependent H₂ Adsorption on Alloy Clusters RhAl_n⁺ (n = 1–12)

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ABSTRACT

Hydrogen (H₂) is an environmentally friendly and highly efficient energy carrier.¹ Aluminum-based alloys are promising H₂ storage materials because of their low weight, high capacity, and low cost.² To model the hydrogenation mechanisms of aluminum-based nanostructured alloys, we have investigated H₂ adsorption on transition metal doped few-atom aluminum clusters.²⁻³ The current contribution deals with H₂ adsorption on rhodium doped aluminum RhAl_n⁺ (n = 1–12) clusters, which is studied by a combination of mass spectrometry, infrared multiple photon dissociation (IRMPD) spectroscopy, and density functional theory (DFT) calculations. It is found that the reactivity of RhAl_n⁺ is strongly size dependent, with the small clusters (n = 1–3) being most reactive. DFT calculations and IRMPD experiments reveal that H₂ adsorbs molecularly on RhAl₂⁺ and RhAl₃⁺, while it prefers dissociative adsorption on other sizes. The correlation of the adsorption energies with electronic properties of the clusters will be discussed. Fig.1 shows the fractions, F(H_{2m}), of RhAl_nH_{2m}⁺ (n = 1–12, m = 1–4) generated from reactions of RhAl_n⁺ with H₂. IRMPD spectra and calculated IR spectra of the lowest-energy isomers for selected RhAl_nH₂⁺ (n = 3 and 8) clusters are shown in Fig.2.

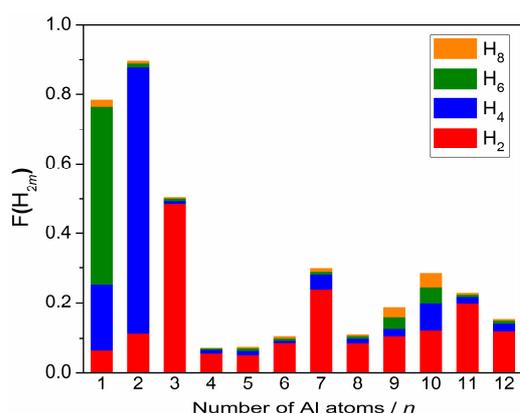


Fig. 1: The fractions of hydrogenated species RhAl_nH_{2m}⁺ (n = 1–12, m = 1–4).

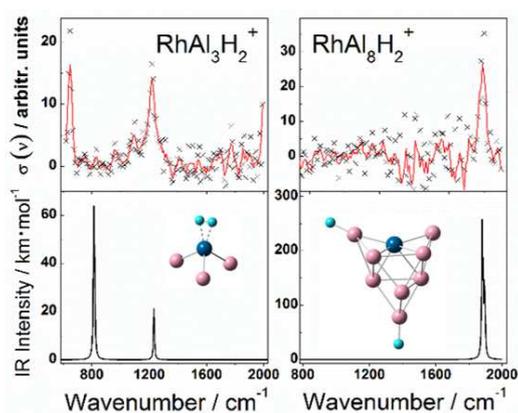


Fig. 2: IRMPD spectra (top) and PBE/SDD&TZVP calculated IR spectra (bottom) for RhAl_{3,8}H₂⁺.

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The Surface stress, phase diagrams of nanoalloys and lead-free solders

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ABSTRACT

In order to synthesize perspective nanomaterials, one needs to study their thermodynamic properties. Namely, it is important to determine the influence of their size on the phase transformations in comparison with the phase diagrams of bulk system. Generally, nanoalloys exhibit a decrease of melting temperature and decrease of temperature of invariant thermodynamic reactions in comparison with their bulk equivalents [1, 2]. We focus on the nanomaterials that can be used as lead-free solders, namely the Ni–Sb–Sn system and the Ni–Bi–In system.

Combining the CALPHAD method [3] with ab initio calculations is a good tool to determine the changes in the transformation temperatures in the nanoalloys. It allows one to calculate the contribution to the total of Gibbs energy of the system due to the surface stress [4-6], which plays important role for nanoparticles. As a first approximation, we employ the model assuming spherical particles. As the Gibbs energy contribution due to the surface stress depends on the size of the nanoparticles, one is able to predict the difference between the thermodynamic behavior of the nanoalloy and the respective bulk material. The surface stress itself [7] can be calculated using the ab initio methods [8]. Recently, we have developed a new approach in determining the surface stress in intermetallic compounds [2]. Since then, the surface stress can be determined for one particular surface plane in the compound.

We have used the FLAPW [9] method as is implemented in the WIEN2k code [10] to determine the surface stress of both elements and intermetallic compounds that exist in the Ni–Sb–Sn system and in the Ni–Bi–In system. We have determined the changes in the temperatures of invariant reactions in dependence of the nanoparticle size for the Ni–Sb–Sn, Ni–Bi and Bi–In nanoalloys.

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Ni_xPt_{1-x} And Co_xMo_y Nanoalloys By Colloidal Synthesis

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Nowadays, Chemical Vapor Deposition (CVD) is the most studied and promising method for single wall carbon nanotubes (SWCNTs) synthesis. This method involves converting gaseous state carbonaceous precursor into a solid material via a nanoparticle (NP) or catalytic film. Nevertheless, this process suffers from a lack of control because the carbon nanotubes growth mechanisms are far from being fully understood¹. One research path focuses on the catalytic NPs role, including the influence of carbon solubility² of nanoalloys such as Ni_xPt_{1-x} on the one hand and the influence of the structure of carbides³ such as Co_xMo_y/Co_xW_y on the other.

In order to gain a control of these NPs structural parameters, we chosen to synthesize various kinds of bimetallic particles using the colloidal route which has demonstrated to be a robust method for preparing monodisperse alloy NPs with size and shape control and homogeneous compositions. The different NPs were fully characterized by transmission electron microscopy (contrast imaging, HAADF^a, EDX^b, electron diffraction). Ni_xPt_{1-x} NPs were synthesized using Platinum(II) acetylacetonate and Nickel(II) acetylacetonate reduced by 1,2-hexadecandiol in organic solvent (dibenzyl ether) with surfactants (oleyamine and oleic acid). Generally, this method leads to core-shell structures NPs⁴ because of the significant difference between Ni²⁺ /Ni (-0.253 V) and Pt²⁺ /Pt (+1.18 V) reduction potentials. Nonetheless, this problem was solved thanks to a rigorous control of the synthesis temperature and we have been able to prepare NPs with uniform composition whatever the Ni concentration (Figure 1). In addition, we have adapted this method to synthesize Co_xMo_y NPs using carbonyls precursors, dicobalt octacarbonyl and molybdenum hexacarbonyl in the same organic media (Figure 2).

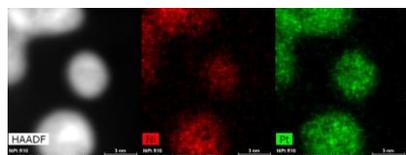


Fig. 1 : HAADF-STEM^c uniform Ni₃Pt NPs contrast is confirmed by Ni map (red) and Pt map (green) recorded using EDX analysis on a FEI-TITAN G2

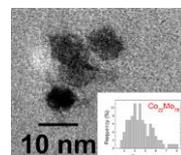


Fig. 2 : TEM image of Co₂₂Mo₇₈ NPs and their diameter distribution in inset

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^a High-Angle Annular Dark-Field imaging

^b Energy-Dispersive X-ray spectroscopy

^c Scanning Transmission Electron Microscope

Structural Transformations In AuCo Nanoalloys Studied By Molecular Dynamics

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ABSTRACT

Structural transformations in AuCo nanoalloys of various sizes and compositions are studied using Molecular Dynamics (MD) simulations [1]. First, the transformation between randomly intermixed configurations and core-shell chemical ordering Co@Au is studied. Randomly intermixed configuration is relevant because it can be the initial configuration obtained in gas-phase growth experiments. This transformation presents a three-shell intermediate metastable configuration Au@Co@Au [2], which may have a long lifetime, depending on temperature. The first part of the transformation (from intermixed to three-shell) is very fast, so it is studied using standard MD techniques and analysed step by step. The second transition (from three-shell to core-shell) is much slower and at room temperature needs to be studied by accelerated MD methods, such as Metadynamics [3]. Second, the transformation from reverse core-shell Au@Co to Co@Au is studied by Metadynamics at room temperature.



Fig. 1: From Au@Co@Au to Co@Au

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Sputtering Deposition Of Nanoparticles Onto Liquid Substrates: State Of The Art

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ABSTRACT

This state-of-the-art introduces a very interesting method to generate stable metal nanoparticles using the sputter vacuum deposition technique onto liquid substrates. This innovative method takes advantages of the extremely low vapor pressure of liquid (such as ionic liquid, vegetable oil, silicon oils, ...) so that the preparation of nanoparticles can be carried out at low pressure or under high vacuum conditions. The size of the nanoparticles can be tuned by the surface composition of the liquid substrate and by varying the operation parameters like temperature of the liquid and the voltage applied on the sputtering cathode. Indeed, metal nanoparticles with small size (~2.5 nm) and narrow size distribution have been prepared by this technique^{1,2}. Recently, few papers deal with the synthesis of alloy nanoparticles using this technique. Alloy nanoparticles dispersed in a liquid medium can be produced via a chemical reaction induced by sputter of metal into liquid³ or sputtering of an alloy target or a bimetallic target with an alternative configuration². By using this last method, the alloy composition can be easily control through the independent control of sputter parameters for each metal target.

Plasma sputtering deposition onto solid support is known to be an efficient method for producing Pt catalytic nanoparticles used in proton exchange membrane fuel cell (PEMFC). However, the sputtering onto solid support make the control of the nanoparticles properties rather difficult. In order to optimize the morphology of the Pt based catalyst toward the oxygen reduction reaction (occurring in fuel cell), we propose to use this innovative technique using low pressure magnetron sputtering and liquid support. Pt/C ink is then prepared by mixing the liquid containing the catalyst and carbon powder in order to prepare PEMFC electrodes and evaluate the electrocatalytic activity of this Pt based catalyst.

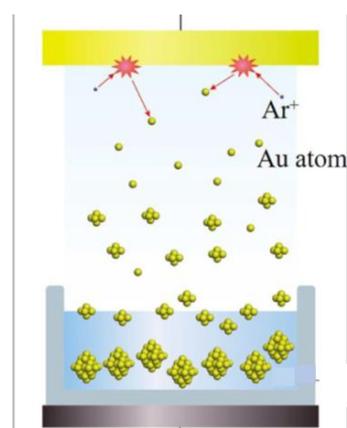


Figure 2 : schematic illustration of the matrix-sputtering method¹

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Sensitivity of Plasmonic Bimetallic Clusters to Oxidation: Optical Properties and Chemical Structure

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ABSTRACT

Silver containing bimetallic clusters (X-Ag) of a few nm in diameter are produced in the gas phase by laser vaporization and embedded in silica or alumina films. Their optical absorption spectra are dominated by a strong and broad surface plasmon resonance (SPR) sustained by silver. The SPR is sensitive to the spatial arrangement of metallic species (alloying, segregation...). The chemical structure can then be probed or at least speculated from an analysis of the SPR in relation with theoretical simulations. However, these samples are subjected to aging and especially oxidation because of the residual permeability of the dielectric matrix and the unavoidable contact of clusters with the ambient atmosphere. This results in changes in their chemical structure and modification of their SPR (spectral shift and damping).

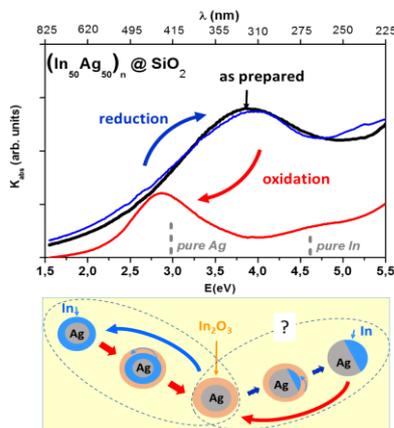


Fig. 1: (up): optical absorption spectra of $(In_{50}Ag_{50})_n$ clusters embedded in a silicon dioxide matrix (black curve: as prepared, red curve: after ageing in air, blue curve: after annealing (600°C) under a reducing N_2+H_2 environment (down): possible mechanisms involved in oxidation-reduction cycles under the assumption of a chemical phase segregation.

To address this issue, we have developed an experimental approach that consists in combining optical spectroscopy and high resolution transmission electron microscopy both carried out under controlled gaseous environment and temperature. We present here these set-ups as well as selected results obtained on *Fe-Ag*, *Cu-Ag* and *In-Ag* [1] bimetallic clusters.

In particular, we will show how structural and chemical changes upon oxidation and reduction processes observed in environmental electron microscopy (ETEM) can be correlated to the spectral modifications induced on the cluster SPR under similar conditions thanks to numerical simulations of their optical response.

Nanosized range of chemical order in weakly miscible Ag-Pt alloys

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ABSTRACT

The nanoalloys' structural properties are highly complex and very interesting because of their size-dependent evolution. Indeed, metal nanoalloys have different chemical and physical properties compared to their bulk matter counterpart, due to the size reduction. In particular, Pt-Ag nanoalloys have been widely studied due to their promising catalytic properties [1].

Macroscopic study of Pt-Ag alloy shows an interesting but complex phase diagram [2], [3] especially at low temperature: an ordered alloy is formed only at the equi-stoichiometry of Ag-Pt, and a quasi-complete immiscibility for the rich-Pt side compared to a partial immiscibility for an important Ag concentration.

Concerning Pt-Ag nanoalloys, the size reduction can modify the ordered alloys stability, or induce segregation between the two elements to create particles whose structure could be core-shell, janus-like... Three principal forces allow to predict the nanostructure (alloy, segregation, etc...): the size and surface energy difference between the two elements and also their ability to mix in the bulk. For Pt-Ag nanoparticles, Monte Carlo simulations [4], [5], taking into account these three forces, predict a core(Pt)-shell(Ag) segregation in competition with an alloying effect depending on the composition. The aim is to experimentally determine, depending on the composition, the consequences of surface effects: does the surface segregation of silver dominate over the effects of alloying, even ordering?

In this study Pt-Ag nanoalloys were prepared by atomic evaporation using two separate sources operating simultaneously under ultra-high vacuum conditions. Structural study shows a disordered/ordered phase transition depending on the annealing temperature and the composition. For the quasi-equiatom composition an alloy phase L1₁ (alternative planes of Ag and Pt in the [111] direction) with an important rhomboedral deformation is observed in a specific arrangement, in agreement with our DFT calculations.

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Stability of Silver Nanoparticles on Silica Supports

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ABSTRACT

Properties of nanosized systems (nanoparticles) are known to differ from bulk ones. Moreover, experimental and simulation data show that the support used to produce these nanoparticles, despite weakly interacting like amorphous silica, may have a non-negligible effect, in particular on the morphology and structure of the nanoparticle [1,2]. We are thus interested in the prediction of the relative stability of the various structures a supported nanoparticle can adopt. The support will be varied, in particular its surface nature and roughness.

Considering the typical dimensions of the system (few nanometers), a molecular approach based on effective potentials will be considered. The metal-metal interaction is modeled by a tight-binding semi-empirical potential within the second moment approximation (TB-SMA), the interactions between atoms constituting silica are described by the mTTAM potential, and the metal-silica interaction is based on a Lennard Jones potential, with parameters adjusted on experimental and Density Functional Theory calculations.

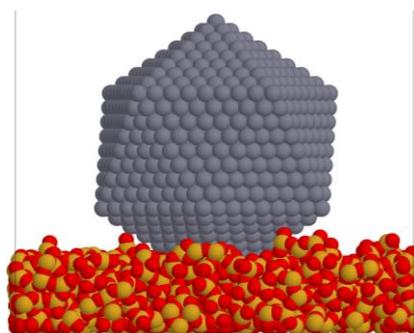


Fig. : Silver icosahedron on rough silica support.

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Chemical Ordering Optimization In AuAg Nanoclusters By Basin Hopping-DFT

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ABSTRACT

We perform a DFT global optimization of chemical ordering of AgAu nanoclusters using a basin hopping (BH) algorithm. Calculations are made using the PBE¹ exchange-correlation functional. We study two different clusters, 55-atom icosahedra and 38-atom truncated octahedra (TO), at various compositions.

We find some non trivial behaviour in the optimal positioning of gold atoms which tend preferentially to occupy surface sites. In the silver rich TO we find that for $N_{Au} \leq 2$ the gold atoms are placed inside the cluster in the optimal configuration. When $N_{Au} \geq 3$ some gold atoms appears in surface sites even though there are 6 internal sites. Then, for a wide range of compositions we find that only 2 gold atoms occupy internal sites. In 55-atom icosahedra gold atoms tend to occupy low coordination sites and then developing dimers and then wire-like patterns^{2,3} (see Fig. 2).

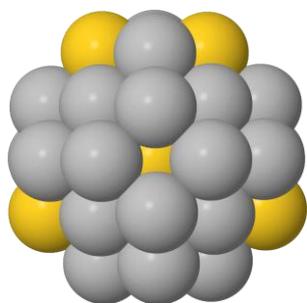


Fig. 1 : Best minimum for Au_6Ag_{32}

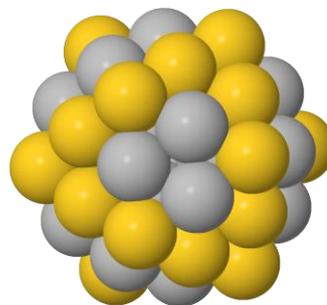


Fig. 2 : One of the best minima for $Au_{24}Ag_{31}$

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MD Simulations of Au Cluster Coalescence

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ABSTRACT

The coalescence of small clusters into larger ones is a relevant step of many cluster formation pathways, e.g. those taking place in ultra-high vacuum cluster sources¹, those resulting from the diffusion of small clusters on inert substrates², or those due to external stimuli such as TEM irradiation³. Coalescence is influenced by the cluster composition, size and original structure. Temperature plays a role as well: coalescence may involve solid-solid transitions or solid-liquid-solid transitions, a picture that is complicated by the fact that the original clusters and the coalesced one may have significantly different melting temperatures. Here, we use MD simulations to investigate the coalescence of Au clusters in vacuum. The final cluster structures have 200-300 atoms and result from the coalescence of clusters with a size of 50-150 atoms. In this size range, three different structural motifs (icosahedral (Ih) decahedral (Dh) and fcc) are in close competition. We observe that the coalescence between two Ih structures, or between an Ih and a Dh, often results in the formation of a Dh cluster. When an Ih cluster coalesces with an fcc one, instead, the fcc motif prevails.

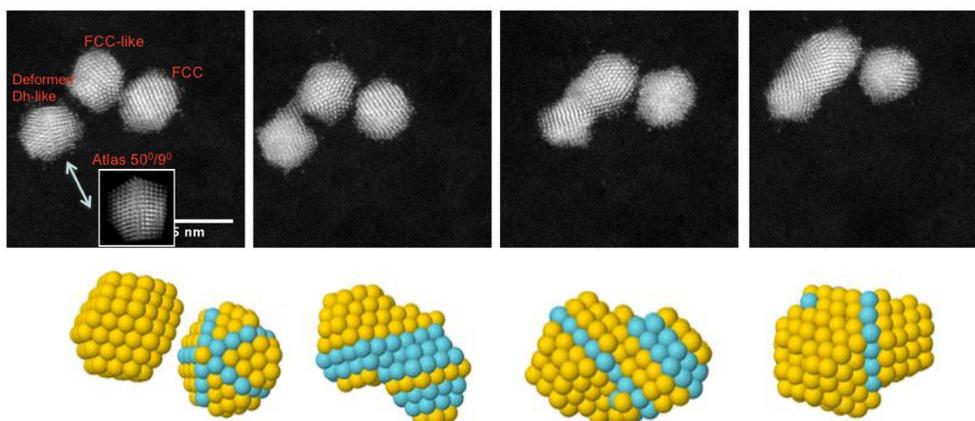


Fig. 1 : Top: High-Angle Annular Dark Field (HAADF) images of Au₉₂₃ clusters coalescing on an amorphous carbon substrate (R.E. Palmer). The initial cluster structures are Dh-like and fcc. Bottom: the simulation of the coalescence between a truncated octahedron (fcc) and a Dh of size 162 and 147, respectively. Blue atoms sit on dislocation planes.

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Polypyrrole nanostructures for water depollution and hydrogen generation

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ABSTRACT

Conjugated polymer nanostructures (CPNs) emerge as a new class of photocatalysts for organic pollutant degradation under UV and visible light. Polypyrrole (PPy), as a conjugated polymer, exhibits a wide range of applications¹⁻⁴. We present here the first illustration of employing pure PPy nanostructures as a very efficient photocatalysts for water depollution. PPy nanostructures were either synthesized in soft templates (formed by hexagonal mesophases) by chemical polymerization (PPy-NS-c) or obtained by radiolysis (PPy-NS-γ). Bulk PPy was synthesized without any template via chemical oxidation (PPy-bulk) as bulk. Among these three samples, PPy-NS-c shows the best photocatalytic activity under UV light, while PPy-NS-γ exhibits the highest activity for phenol degradation under visible light. These samples have been characterized by different techniques: SEM, TEM, FTIR, UV-Vis spectroscopy, wettability...

Hydrogen production from water by photocatalysis offers a promising way to solve environment and energy issues. We modified PPy nanostructures with cocatalysts based on monometallic Pt, Ni and Co and bimetallic PtNi and CoNi nanoparticles for H₂ production. The modified PPy nanostructures give also promising results for hydrogen generation under ultraviolet light. The effect of the nature of the metal precursors and their loading were studied.

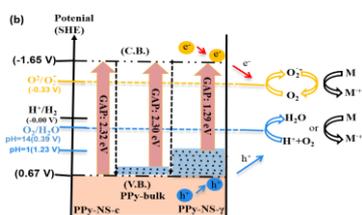


Figure 1. possible photocatalytic mechanism of PPy-NSs

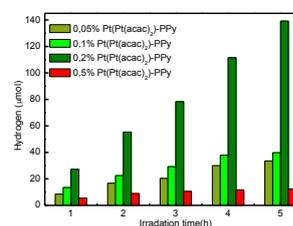


Figure 2. Hydrogen generation of Pt/PPy

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