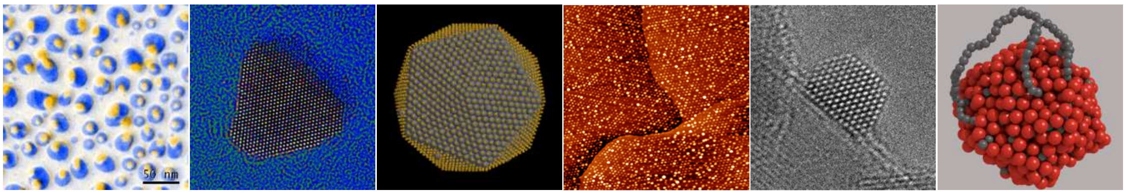
île de Porquerolles **17 – 22 mai 2015**

Réunion Plénière + Réunion Thématique du GdR

« Nanoalliages et Nanohybrides à base de métaux »



GDR CNRS n° 3182

L’ambition du GDR « nanoalliages : synthèse, structure et propriétés » était dans sa version initiale [2008-2011] de comprendre les mécanismes mis en jeu lors de la croissance des nanoparticules bimétalliques, d’étudier leurs propriétés structurales (diagrammes de phases), physiques (magnétiques, optiques) et chimiques (catalytiques) en fonction de leur taille, de leur structure et de leur composition chimique.

Le GDR "Nanoalliages et nanohybrides à base de métaux" a été relancé en 2012 autour de thématiques émergeantes telles que les nanostructures hybrides (métal/oxyde, métal/semi-conducteur ou métal/carbone), les nanofils d’alliages ou encore les systèmes à changement de phase.

Ces thématiques nouvelles destinées à ouvrir la communauté du GDR et à attirer de nouvelles communautés sur ces sujets encore peu développés en France viennent s’ajouter aux thématiques traditionnelles du GDR.

Nous souhaitons ainsi profiter de cette dernière réunion pour renforcer les liens existants et promouvoir de nouvelles collaborations qui nous l'espérons se poursuivront au-delà du GdR.

La réunion est composée :

- d'une réunion plénière où nous souhaitons donner la place à toutes les équipes pour présenter leurs activités ;
- d'une réunion thématique sur la cinétique dans les nanoalliages et nanohybrides.

La stabilité des phases dans les nanoalliages a été au coeur de nombreuses études ces dernières années, tant sur le plan expérimental que théorique. Dépendant de la composition, de la taille et de l’environnement, des comportements s’écartant de ceux observés dans les alliages massifs ont été mis en évidence. En revanche, les mécanismes cinétiques et leurs conséquences demeurent encore peu étudiés au niveau des nanoalliages bien qu’ils représentent un élément essentiel dans l’élaboration et le vieillissement des particules, qu’elles soient élaborées par voie chimique ou physique.

Les mécanismes de diffusion, germination, croissance et coalescence ont été relativement bien étudiés au niveau des systèmes purs mais le passage à des alliages s’avère délicat : ils couplent diffusion sur le substrat, en surface et à l’intérieur des particules et font intervenir plusieurs espèces diffusantes. L’objectif de cette réunion thématique est de faire le point sur les avancées actuelles en terme de compréhension de la cinétique de formation et d’évolution de nanoalliages, à la fois à l’échelle de la particule unique mais également pour des assemblées de particules. Des contributions expérimentales et théoriques sont attendues pour lever un coin du grand voile sur ce domaine.

Organisateurs :

Christine Mottet	**(CINaM, Marseille)**
Christian Ricolleau	**(MPQ, Paris)**
Jérôme Creuze	**(SP2M/ICMMO, Orsay)**
Yann Le Bouar	**(CNRS/ONERA, Châtillon)**

Site web : http://www.cinam.univ-mrs.fr/nanoalliages2015/

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NanoSciences
Provence - Alpes - Côte d'Azur

Programme :

Dimanche 17 mai 2015

17h30	Accueil des participants
18h30	Apéritif
19h15	Dîner

Lundi 18 mai 2015

Session Synthèse et Structure

9h00	Energetics of supported Au-Pd nanoparticles using aberration-corrected TEM, **J. Nelayah**, Matériaux et Phénomènes Quantiques, CNRS / Université Paris Diderot.
9h30	Self-organization of size-selected Fe_xPt_{1-X} clusters deposited on graphene, **L. Bardotti**, Institut Lumière et Matière, CNRS / Université Claude Bernard Lyon 1.
10h00	PDF for structural study of NPs: because XRD doesn't work and TEM is not safe, **P. Lecante**, CEMES, CNRS Toulouse.
10h30	**Pause – café**
11h00	Deposition of Pt Layers on Pd Cubes for Controlled Heterogeneous Catalysis, **A. DeClercq**, CINaM, CNRS / Aix-Marseille Université.
11h30	Covalent Alloys of Transition Metals with Light Elements: Boron and Phosphorus, **S. Carenco**, Chimie de la Matière Condensée, Université Pierre et Marie Curie, Paris.
12h00	**Déjeuner**
16h00	STM and QMD studies of strongly strained Ag Nanodots on Ni(100), **J.-B. Marie**, Matériaux et Phénomènes Quantiques, CNRS / Université Paris Diderot.
16h30	Structure of supported silver nanoparticles on amorphous silica substrate: effect of size, **C. Ngandjong**, ICMN, CNRS / Université d'Orléans.
17h00	**Pause / Posters**
17h30	Size effects in mono- and bi-metallic clusters, **M. Hillenkamp**, Institut Lumière et Matière, CNRS / Université Claude Bernard Lyon 1.
18h00	Quantitative 3D reconstruction of nano-particles based on atom counting in STEM, **F. Moyon**, Groupe de Physique des Matériaux, CNRS / Université de Rouen.
19h15	**Dîner**

Mardi 19 mai 2015

Session Propriétés : Catalyse

9h00 In-situ study of AuCu NanoParticles Epitaxied on TiO_2(110): Synthesis, Structure and Behavior at Low Pressure of Reactant,
Y. Garreau, Synchrotron SOLEIL et MPQ, CNRS / Université Paris Diderot

9h30 Structure and catalytic reactivity of Au-Cu bimetallic nanoparticles,
H. Prunier, MPQ, CNRS / Université Paris Diderot

10h00 Ir-Pd Nanoalloys: Structure, Hydrogen Sorption and Surface Reactivity,
L. Piccolo, IRCELYON, CNRS / Université Claude Bernard Lyon 1

10h30 Pause - Café

11h00 Photocatalytic properties of surface modified TiO_2 with Ni-Au nanoparticles,
A. Luna, Laboratoire de Chimie Physique, CNRS / Université Paris-Sud Orsay

11h30 Synthesis and Characterization of Magnetic $SrFe_{12}O_{19}$ / Fe Nanocomposites,
N. Maât, Groupe de Physique des Matériaux, CNRS / Université et INSA de Rouen

12h00 Déjeuner

Session Propriétés : Optique

16h00 Plasmon Spectroscopy Of Small Bimetallic Cu/Ag and In/Ag Clusters In Relation With Their Structure, **E. Cottancin**, Institut Lumière Matière, CNRS / Université Lyon 1

16h30 Optical Properties of Bi-Metallic Noble-Metal Nanoalloys,
H.-C. Weissker, CINaM, CNRS / Aix Marseille Université

17h00 Pause / Posters

Session Propriétés : Magnétisme

17h30 Magnetic properties of bimetallic nanoparticles elaborated by cluster beam deposition,
V. Dupuis, Institut Lumière Matière, CNRS / Université Claude Bernard Lyon 1

18h00 Structural diameter versus physical diameter in magnetism,
F. Fettar, Institut Néel, CNRS / Université Grenoble Alpes

19h15 Dîner

Mercredi 20 mai 2015

Session Nanohybrides

8h30 Optimized synthesis of FeBi nanoparticles for imaging applications,
C. Amiens, LCC, CNRS / Université de Toulouse

9h00 New Binary Superlattices from Magnetic Nanocrystals and Polyoxometalate Clusters,
R. Breitwieser, MONARIS, CNRS / Université Pierre et Marie Curie Paris

9h30 A surface reaction promotes the formation of bimetallic nanoparticles in ionic liquids,
P.-H. Haumesser, CEA LETI, Université Grenoble Alpes

10h00 Pause - Café

10h30 Synthesis of Air- and Water-Resistant Noble-Metal Coated Cobalt Nanorods,
M. Respaud, LCC, CNRS / Université de Toulouse / INSA

11h30 Size dependent phase diagrams of Nickel-Carbon nanoparticles,
C. Bichara, CINaM, CNRS / Aix Marseille Université

12h00 Déjeuner

Après – midi libre

Jeudi 21 mai 2015

Réunion Thématique : Cinétique

9h00 *Conférence Invitée*:
Simulation of the nucleation and growth of solid-solutions in an aqueous medium,
C. Noguera, INSP, CNRS / Université Pierre et Marie Curie Paris

10h00 Melting, mixing and nucleation at solid/liquid interface in nanometric metallic multilayer,
F. Baras, LICB, CNRS / Université de Bourgogne

10h30 Pause - Café

11h00 *Conférence Invitée*:
Energy landscape approach to kinetics and phase equilibrium in nanoalloys,
F. Calvo, LIPhy, CNRS / Université Joseph Fourier Grenoble

12h00 Déjeuner

16h00 *Conférence Invitée*:
Tuning the Performance and the Stability of Porous Hollow PtNi/C Nanostructures for the Oxygen Reduction Reaction,
F. Maillard, LEPMI, CNRS / Université Grenoble Alpes

17h00 Pause - Posters

17h30 Core-shell and Janus structure formation of Ag-Co/Pt nanoalloys,
P. Andreazza, ICMN, CNRS / Université d'Orléans

18h00 Ageing of out-of-equilibrium bimetallic nanoparticles,
F. Berthier, SP2M/ICMMO, CNRS / Université Paris Sud Orsay

19h15 Dîner

Vendredi 22 mai 2015

Réunion Thématique : Cinétique

9h00 *Conférence Invitée:*
Bimetallic Nanoparticles and Nanostructures Induced by Radiolysis,
H. Remita, Laboratoire de Chimie Physique, CNRS / Université Paris Sud Orsay

10h00 In situ reduction of core-shell Ag@In_2O_3 nanoparticles observed through environmental electronic microscopy,
J. Ramade, ILM, CNRS / Université Claude Bernard Lyon 1

10h30 Pause - Café

11h00 Conclusions

12h00 Déjeuner

Determining the energetics of supported Au-Pd nanoparticles using aberration-corrected TEM

N. T. Nguyen[1], J. Nelayah[1,*], H. Prunier[1], D. Alloyeau[1], G. Wang[1], L. Piccolo[2], P. Afanasiev[2] and C. Ricolleau[1]

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Metallic nanoparticles (NPs) have found applications in a wide variety of fields. While the thermodynamics of NPs is crucial in defining their structure, it can also influence their physical properties such as their catalytic activity [1]. Thus, experimental and theoretical studies of the energetics of metallic NPs are very important for promoting existing applications and developing new ones.

In this contribution, we report on the experimental determination of interface and triple-line energies in supported Au-Pd nanoalloys using transmission electron microscopy (TEM). Au-Pd nanoparticles in the size range of 2 to 5 nm were deposited by pulsed laser ablation on MgO nanocrystals and rutile-TiO_2 nanorods. High-resolution TEM studies showed that the as-grown NPs were fully relaxed face-centered cubic structures with a truncated-octahedral equilibrium shape. Various epitaxial relationships between the truncated octahedra and the oxide supports were identified. With the precise equilibrium morphology of the NPs known, the interface and triple-line energies of the metal/oxide systems were determined by combining particle size measurements in atomically-resolved projected TEM images acquired parallel to the metal-oxide interface and a generalized Wulff-Kaishew construction recently proposed by S. Sivaramakrishnan *et al.* [2]. The latter takes into account the influence of triple-line energy on nanoparticle equilibrium shape. Interface and triple-line energies were investigated as a function of particle composition and epitaxy.

For any given epitaxial relationship, the relative amplitude of the NP truncation at the interface is found to increase linearly with particle size, *i.e.* the bigger the NP, the more it wets the oxide surface. On the rutile support, analysis of Au, Pd, $Au_{38}Pd_{62}$ and $Au_{57}Pd_{43}$ NPs in epitaxial relationship Au-Pd(111)<101>*//Rutile(110)[1-1-1]* shows clearly that the interface and triple-line energies are strongly influenced by particle composition. The value of the interface energy of the bimetallic Au-Pd NPs $\gamma_{i,Au\text{-}Pd}$ is about 1 J m^{-2} which is about two and three times that of the monometallic Pd and Au NPs respectively ($\gamma_{i,Pd} = 0.5 \pm 0.1$ J m^{-2} and $\gamma_{i,Au} = 0.3 \pm 0.2$ J m^{-2}). As for the triple-line energy, it is 0.5 ± 0.1 J m^{-2} for the monometallic nanoparticles. This value is twice the average triple line energy for Au-Pd NPs. On MgO support, where the degree of epitaxy is higher, the interface energy is about 2 J m^{-2} for AuPd stoichiometry.

References

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2. S. Sivaramakrishnan *et al.*, ***Phys. Rev. B* 82 (13605)**, 195421-195431 (2010).

Self-organization of size-selected Fe_xPt_{1-X} clusters deposited on graphene.

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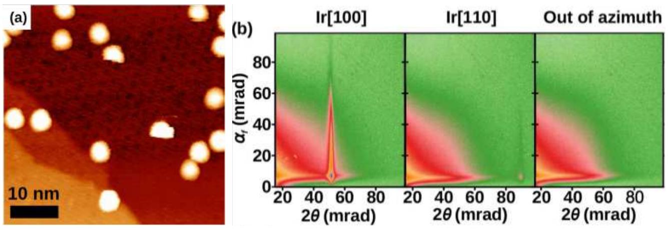
Supported metallic clusters have attracted a lot of interest in the last decades due to the dependence of their physical and chemical properties on their sizes and local environments. Thus, a regular array of mono-dispersed clusters, providing a similar environment to each nanoparticle (NP), can highly facilitate their study or their use for optical, magnetic or catalytic applications. One way to produce such arrays is the deposition or growth of NPs on templates in the form of patterned substrates. Among all possible templates, extensive studies have been performed on graphene epitaxially grown on transition metals. As a matter of fact, moirés corresponding to a regular 2D spatial variation of the corrugation and the electron density in graphene are often present [1]. It has therefore been recently used to organize successfully, by atomic vapour deposition, a large variety of metallic clusters [2]. However, the resulting clusters are usually rather flat, it is impossible to tune independently cluster coverage and sizes and creating array of allow clusters still remains a challenge. The deposition of preformed spherical size-selected clusters appears as an original alternative technique to overcome these limitations.

With this goal, size selected Fe_xPt_{1-x} clusters (1.5 nm in diameter) are deposited on graphene in epitaxy on Ir (111) surfaces for x = 0, 0.5 and 1. By means of complementary techniques (scanning tunnelling microscopy, grazing incidence X ray scattering) (see fig.), the clusters shapes and organization is characterized and the structural evolution during annealing is investigated. We will show that, for all x values, the soft-landed clusters remain quasi-spherical and a large proportion appears to be pinned on specific moiré sites. The quantitative determination of the proportion of organized clusters reveals that the obtained hexagonal array of the almost spherical nanoparticles is stable up to 650 K and even higher when the sample is covered by an amorphous carbon layer.



Typical STM image of Pt clusters deposited at room temperature on graphene (a) and the corresponding GiSAXS patterns (b).

References

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PDF for structural study of NPs: because XRD doesn’t work and TEM is not safe

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ABSTRACT

Elaboration of new metallic nanoparticles tailored for optimal sizes, shapes or properties relies on always more complex syntheses. The end of the story, as reported and illustrated using detailed schemes and clear TEM micrographs of these optimized objects is of course the main point. However, chemists know that, before, numerous trials will provide more questions than answers: NPs are observed (e.g. using TEM), but are they representative of the whole batch [1]? Objects are too small / too much disordered to be safely characterized, are they a milestone on the way or just a dead end [2-3]? Or even worse: can a synthesis produce random results [4]? Access to atomic structure without any assumption is still essential for understanding of the synthesis work, and to correlate to the different properties of interest (e.g. magnetic, catalytic). Of course, TEM is so widespread and relatively easy to apply that not using it should make little sense, but it is by principle a local probe. EXAFS is a very powerful statistic probe but quite “short sighted”, and may never become a routine technique. Classic XRD on small and/or disordered objects just doesn’t work, however PDF analysis is indeed a routine inlab technique which can provide accurate structural parameters on well-defined objects, but also (and maybe more importantly) quickly provide answers about what has to be in a sample, what can be safely excluded and in the worst case help to classify samples from a structuration point of view, in correlation with synthesis parameters. Application of the technique to different systems, always in combination with TEM and sometimes EXAFS will be presented.

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Deposition Of Pt Layers On Pd Cubes For Controlled Heterogeneous Catalysis

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Colloidally prepared nanoparticles provide unique opportunities to be used as model catalysts because of their homogeneous and controlled structure, especially for alloyed NPs.

Pd cubes, primary limited by (100) faces, were synthesised with PVP-I ligands. Then, successive layers of Pt were deposited on the Pd cubes, verified by EDX and HRTEM (Fig.1).

The CO oxidation reaction is one of the most studied and understood reaction and it is therefore an excellent model reaction. We will investigate the catalytic properties for the CO oxidation by gas phase chromatography, for increasing amount of Pt layers. For this study the particles are deposited on SiO_2 and cleaned by UV-ozone. Although the cubic shape of pure Pd is not completely retained, the concave shape, which is limited by high index surfaces, showed already advantages in terms of stability and oxidation resistance [1, 2].

Furthermore, this synthesis could be compared with an in-situ growth study (Fig. 2), showing the growth of the Pt shells directly in HRTEM by the use of a graphene oxide liquid cell, as was already done for spherical alloyed Pt-Pd NPs [3].

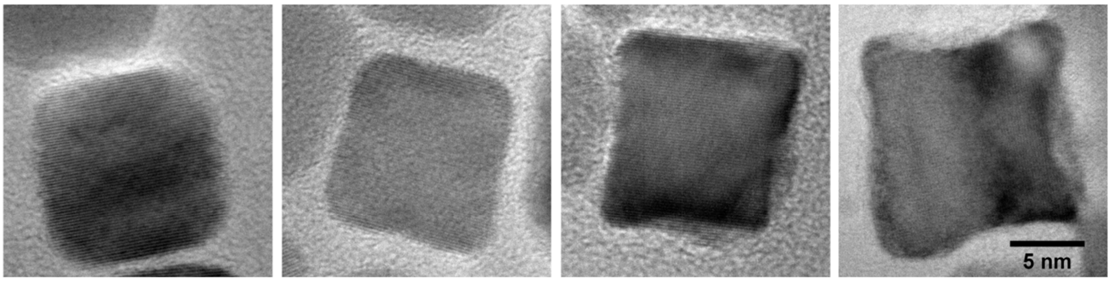

Fig. 1 : Pure Pd cubic NP with successive Pt layers synthesized in a standard reactor (different particles)

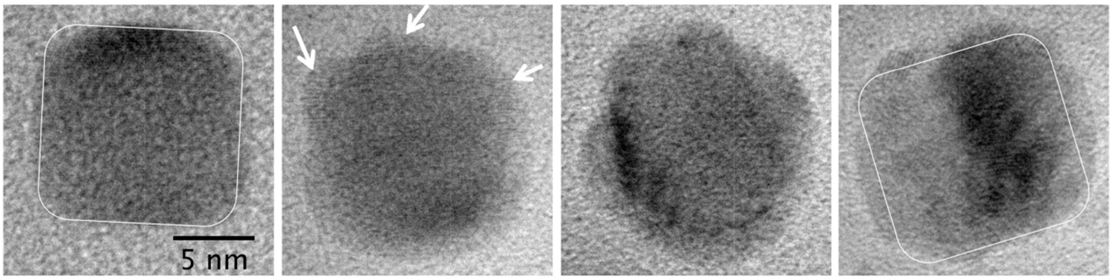

Fig. 2 : Growth of a Pt shell on a Pd cube <u>observed in-situ in a graphene oxide liquid cell</u> (same particle)

ReferenceS

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Covalent Alloys of Transition Metals with Light Elements: Boron and Phosphorus

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Alloyed nanoparticles, containing two or more metals, have proven their relevance for the design of original structure that exhibit unique surface and core configurations. The introduction of lighter elements, namely, boron or phosphorus, can further extend the versatility of these compounds by forming novel covalent structures of controlled size, composition and cristallinity.

Our group has explored within the last few years a variety of synthetic routes to produce such metal phosphide and metal boride nanoparticles, which proved to be versatile in terms of metals (Ni, Co, Hf, Fe, In, Mg, to cite only a few) and in terms of metal-to-light-element ratio. For some transition metals (eg. Ni), the introduction of the lighter element can result in synergistic properties of the surface, such as the ability of reacting with gas or liquids in a catalytic process while retaining the structural integrity. In other cases (Co), synchrotron-based *in situ* monitoring of the particles have instead showed that the covalent alloy may serve as a reservoir providing active metallic clusters when exposed to catalytic conditions.

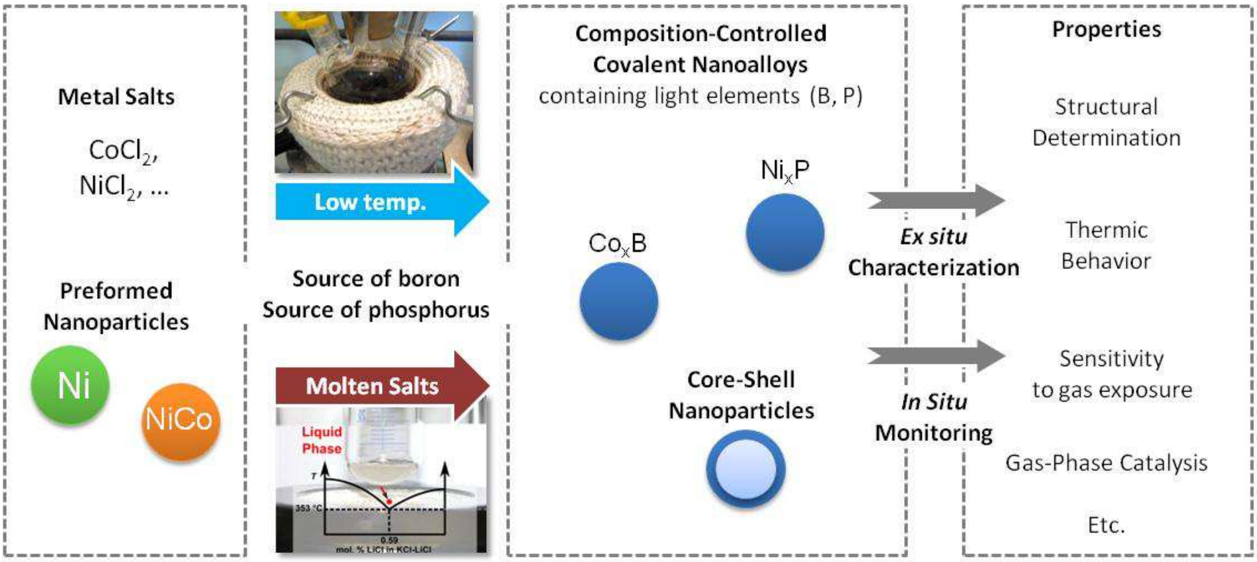

Fig. 3 : Synthetic Routes to Covalent Nano-Alloys Containing Light Elements and their Properties.

References

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STM and QMD studies of strongly strained Ag Nanodots on Ni(100)

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The Ag/Ni system is ideal to study the growth of 2D strained nanoparticles on a metallic surface. Indeed, the large (14%) lattice mismatch between Ag and Ni, their bulk immiscibility, the ratio of their surface free energies and of their cohesive energies forecast that Ag strongly segregates and consequently wets the Ni surface. However, this system displays an unusual behavior still at the core of a controversy [1]: previous studies of Ag/Ni(111) [2] show the coexistence of two different Ag nano-islands : with comparable sizes, both monolayer and bilayer Ag islands are observed. We will present an unpublished work made by Scanning Tunneling Microscopy (STM) and Quenched Molecular Dynamic (QMD) on Ag/Ni(100) in the sub-monolayer regime, which presents many similarities with Ag/Ni(111) or Ag/Cu(100) [3], and comes to bring another light for a better understanding of those systems and more generally on highly strained nano-islands.

After a room temperature deposition, a small amount of Ag atoms is found to be inserted inside the Ni surface. Then a gentle annealing allows Ag islands to grow both **on** and **in** the Ni terraces, leading to the coexistence of two distinct populations of Ag nanoclusters - respectively called on- and in-islands - with very atypical shapes (see Fig. 1).

Both populations are stable and coexist up to 600K, they have the same known c(2x8) (or c(8x2)) superstructure but their shapes are strongly different and there is no evidence of alloying between Ag and Ni. The size and shape evolution of the two populations have been studied by STM in function of Ag coverage up to one monolayer and for different annealing temperatures. The calculation of the step edge energies for in- and on-islands by QMD have shown that an elongated shape for in-islands is energetically more stable than a circular one, with an aspect ratio close to experimental one. The reverse result is obtained for on-islands for which circular shape is expected by calculations and seen by the experiment.

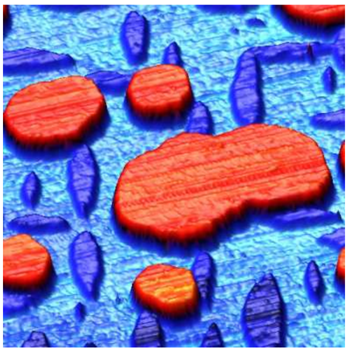

Fig. 4 : STM image (60x60 nm²) of Ag/Ni(100) deposited at room temperature. The two types of islands are pure Ag c(2x8). Elongated blue ones are embedded inside the Ni surface while the red ones are adsorbed on the surface plane.

References

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Structure of supported silver nanoparticles on amorphous silica substrate: effect of size

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Metallic nanoparticles, especially transition metals, have a number of exciting potential applications in various fields such as optics, catalysis, electronics and magnetism. Size, morphology and structure of these nanoparticles give them remarkable properties that are not found in bulk materials. We are particularly interested in the case of metallic nanoparticles obtained by physical vapor deposition on a substrate interacting weakly such as amorphous silica and carbon. Up to now, theoretical studies and experimental data analysis have neglected the influence of this substrate because of its relatively weak interaction with the deposited metal nanoparticles. However, experimental observations show that there is a truncation effect on the nanoparticles.

The context of this work is the thermodynamics of supported metal nanoparticles using molecular modeling (Monte Carlo and molecular dynamics simulations). Here we are interested in silver nanoparticles (Ag NPs) supported on amorphous silica substrate. The metal-metal interaction is modeled by a tight-binding potential within the second moment approximation (TB-SMA) [1]. The Ag-silica interaction is first described as an average potential coming from all silver atoms in the first atomic layer. The structural stability of supported silver nanoparticles is studied at zero temperature according to the cluster size, structure, aspect ratio and orientation. We propose an estimate of the range of stability of various structures such as Icosahedron (Ih), Decahedron (Dh) and Truncated Octahedron (TOh). Depending on the intensity of the Ag-silica interaction Ih and Dh structures are stabilized at small size, then there is a transition toward the TOh structure with (111) orientation. This transition is shifted toward smaller sizes when the interaction with the support is increased. Finally we apply the Wulff Kaishew theorem to the cluster shapes and for the different orientations to check its validity on small nanoparticles.

We then performed simulations for clusters sizes close to the transitions, by treating the Ag-silica interaction with interatomic potential, to take into account the possible effect of the atomic roughness. The mTTAM potential is used for silica [2] and Lennard-Jones potential adjusted on DFT calculations and experimental results for Ag-silica interaction.

The next step will be to simulate the effects of the temperature on the structure and morphology of Ag NPs in presence of amorphous silica substrate by studying melting and quenching processes.

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Size effects in mono- and bi-metallic clusters

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On this poster we discuss different experimental methods for the fabrication and characterization of small mono- and bi-metallic clusters and nanoparticles. In particular we address the following topics:

- Fabrication of cluster-assembled nanostructures by embedding metal clusters prefabricated in the gas phase in protective matrices: magnetron sputtering/aggregation versus laser vaporization.
- Size effects in the magnetic anisotropy of embedded cobalt nanoparticles: from surface to shape.
- Optical and magnetic properties of bi-metallic Fe_xAu_y and Fe_xAg_y nanoparticles with varying stoichiometry: preliminary results from optical spectroscopy, magnetometry and synchrotron-based XMCD.
- Size effects in the electronic and vibrational relaxation in small silver clusters as evidenced by ultrafast femtosecond spectroscopy: the departure from the scalable size regime.
- Study of size effects in the electronic structure of size-selected very small silver clusters: preliminary results from optical spectroscopy and electron energy loss spectroscopy.

Quantitative 3D reconstruction of nano-particles based on atom counting in STEM

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Mastering the chemical and physical properties of nano-objects in nanomaterials such as nanoparticles is a crucial issue in materials science. These properties are strongly correlated with three dimensional (3D) morphology and composition of nano-objects, which can be accessed by electron tomography. However, although the modern microscopes with aberration correctors allow a spatial resolution below 1 Å, atomic resolution for electron tomography is not obvious. To perform electron tomography and 3D characterization at nanometer scale, high angle annular dark field scanning electron microscopy (HAADF-STEM) is widely used [1,2,3]. Sandra Van Aert et al. [4,5] proposed a statistical approach to determine the number of atom in each column on HAADF-STEM micrography in zone axis. Coupling atom counting along different orientations of a same nano-object, these authors demonstrated the possibility to achieve a 3D reconstruction at atomic scale of nano-particles [6,7]. Based on this statistical method, we developed an original algorithm to reconstruct in 3D at atomic scale one nano-object with only three different orientations. Our 3D reconstruction algorithm was tested with three images from simulations of one nanoparticle under different orientations. As show in figure 1 the accuracy of the 3D reconstruction algorithm is really good.

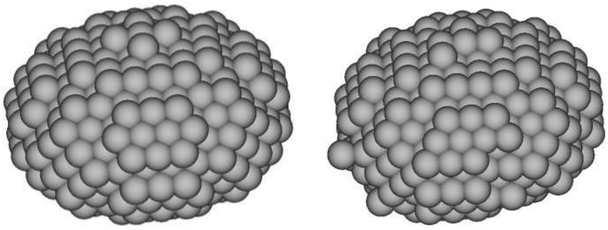

Fig. 1: On the left, nanoparticle made by NanoFabric [8] used for HAADF-STEM simulation, on the right, 3D reconstruction based on three HAADF-STEM image simulations. The 3D reconstruction is very close of the input data.

Thanks to its accuracy this method can be applied for different applications as reconstruction at atomic scale of very small nano-objects or correlative microscopy with atom probe tomography [9].

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In-situ study of AuCu NanoParticles Epitaxied on TiO2(110): Synthesis, Structure and Behavior at Low Pressure of Reactant

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ABSTRACT

Specific properties for applications in electronics, optics, magnetism or catalysis can be achieved using materials based on nanoparticles (NPs). The development and characterization of the bimetallic NPs and the understanding of their physical and chemical properties are thus crucial steps for their technological applications. To improve the catalytic activity of Au-based NPs, a promising method is to use bimetallic NPs that can exploit the synergy between two metals for catalytic reactions. For example, Au-Cu/silica NPs display a better activity for CO oxidation than pure Au or Cu NPs and a better selectivity for preferential oxidation (PROX)[1]. However, the synergies between the two metals and the substrate are not clearly understood.

Scanning tunneling microscopy (STM) and grazing-incidence X-ray diffraction (GIXD) have been used to follow *in situ* the growth and the structure of Au-Cu nanoparticles (NPs) formed on TiO_2(110) by successive metal evaporations [2]. STM observations of the same area of the substrate highlight the strong dependence between the sequence of deposition and the final result. Deposition of Cu first leads to a system where both Au-Cu and pure Au NPs coexist. Deposition of Au first ensures growing mostly bimetallic NPs. GIXD results show that Cu alloys instantaneously with Au NPs at room temperature. Reciprocal space map measurements reveal different epitaxial relationships for crystallized particles and a diffuse ring (see figure) due to the presence of icosahedral NPs that have not specific orientations.

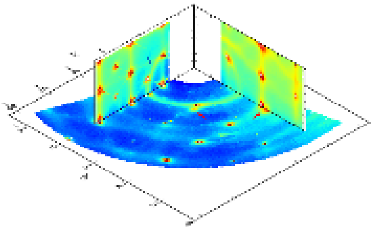

Figure : Reciprocal space maps of AuCu NPs grown on TiO_2(110). Maps are represented in reduced units (h//[001]$_{TiO2}$; k//[1-10]$_{TiO2}$). Intense spots for integer numbers of (hkl) are Bragg peaks coming from the substrate. Red arrows point out the spots related to the NPs that present an epitaxial relationship with the subtract. The blue arrow points out the diffuse sphere due to the non-oriented NPs.

In the presence of oxygen ($PO_2=10^{-7}$ mbar), STM experiments show that Cu NPs of size smaller than 1 nm are unstable [3] but that a small amount of Au (<10%) is enough to ensure their stability. However, GIXD measurements show that the nanoalloys structures are strongly modified during O_2 exposure: the lattice constant of the NPs increases, meaning that Cu segregates at the NPs surface and Au enriches in the core of the NPs. The core-shell configuration obtained is stable at room temperature, even under CO exposure, but annealing above 200°C allows the system to release oxygen and let the Cu diffuse back in the core of the NPs. We also have evidence a reorganization of small non-oriented NPs toward one specific epitaxial relationship in the presence of a $CO+O_2$ gas phase (Ptot < 10 ^{5}mbar).

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Structure and catalytic reactivity of Au-Cu bimetallic nanoparticles

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The Au-Cu system has to be considered as a structural model system, with a particularly rich phase diagram (Fig. 1). This diagram consists in an A1 phase (solid solution with a face-centered cubic structure) and three ordered compounds Au_3Cu, $AuCu_3$ ($L1_2$ phase, ordered cubic structure) and AuCu ($L1_0$ phase, ordered tetragonal structure).

However, the phase diagram, initially set up at the bulk scale could be modified during the reduction of the size process from bulk material to nanoparticles (thermodynamic limit, high surface/volume ratio, confinement effects…). The Au-Cu system also exhibits plasmon resonance properties which can be tuned according to the structure, the composition, the shape and the size of the nanoparticles (NPs). From a catalytic point of view, small gold nanoparticles (<5nm), in spite of a weak stability, present a remarkable catalytic activity at room temperature for the CO oxidation. Coupled to another metal such as copper, they are able to develop synergy effects and can be excellent candidates for some catalytic reactions.

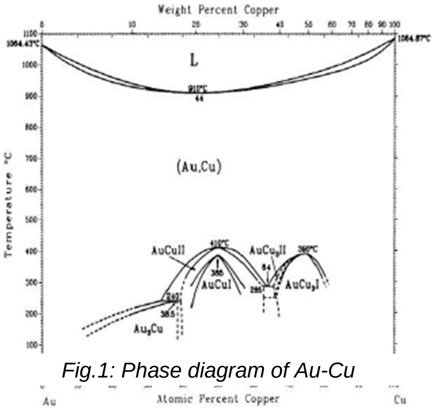

Fig.1: Phase diagram of Au-Cu

This study is based on Au-Cu nanoparticles obtained by two routes of synthesis: a physical one using a pulsed laser deposition [1] and a chemical one using the polyol process [2]. Based on these two methods, greatly diversified Au-Cu nanoparticles with variable size and composition have been synthesized (Fig. 2). These nanoparticles have then been studied thanks to our aberration corrected TEM in order to connect their structural and catalytic properties. We recently equipped this TEM with an environmental device that allows studying nanomaterials in real catalytic conditions (up to 1200°C in temperature and 1bar for gases pressure). Preliminary results have shown that many structural transformations take place on these nanoalloys under oxidation-reduction cycles.

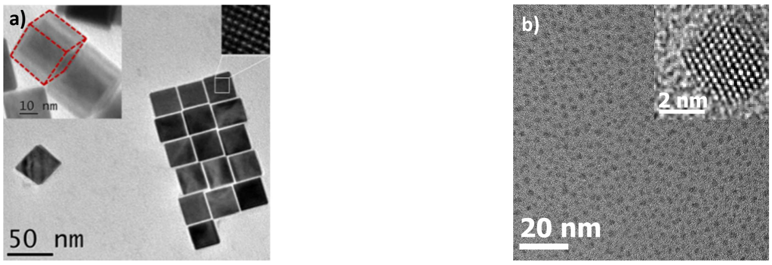

Fig.2: Bright-field images of a) nanocubes (NCs) synthesized by a chemical route, with, in the right insert, high resolution imaging of one NC. In the left insert, edges of a NC have been highlighted with red dotted lines and b) NPs synthesized by pulsed laser deposition and, in insert, high resolution imaging of one NP.

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Ir-Pd Nanoalloys: Structure, Hydrogen Sorption and Surface Reactivity

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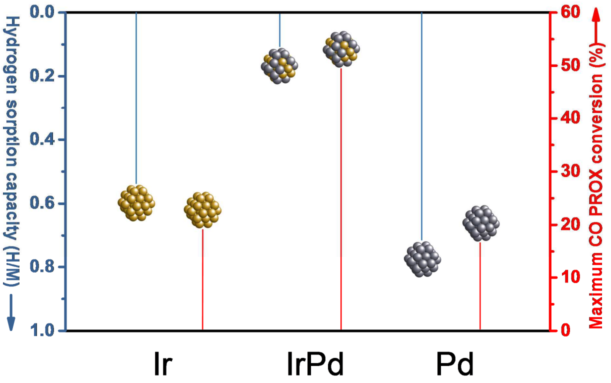
ABSTRACT

The present contribution reports on a collaborative work focused on Ir-Pd nanoalloys through experiments and computational modeling. This bimetallic system, which presents a large miscibility gap in the bulk phase, has been little studied in the past. From the experimental viewpoint, the bimetallic particles were prepared by incipient wetness impregnation of metal-acetylacetonates onto alumina or silica-alumina supports.[1] The bimetallic catalysts and their monometallic counterparts were evaluated for the oxidation of CO and the preferential oxidation of CO in the presence of hydrogen (PROX). Although Pd alone is an excellent CO oxidation catalyst, it is poorly selective to CO$_2$ in PROX. This has been previously ascribed to the formation of Pd hydride, which would favor the (undesirable) oxidation of hydrogen.[2] Ir alone exhibits low performance for both reactions. However, Ir-Pd catalysts appear much more efficient than their Ir and Pd counterparts in PROX (scheme).[3] This synergistic effect has been correlated to Ir-induced inhibition of hydrogen absorption in Pd through nanoalloying.[4] Indeed, the pressure-composition isotherms show a much smaller hydrogen sorption capacity for supported Ir-Pd nanoalloys as compared to Ir and Pd systems (scheme). Moreover, unlike Pd nanoparticles, Ir-Pd nanoalloys do not form a hydride phase. The structure of the bimetallic nanoparticles could not be fully determined experimentally, although TEM-EDX analyses suggest a surface enrichment in Pd.[4] Consistently, computational simulations for small clusters[5] and 2 nm-sized particles[6] predict various chemical configurations mostly driven by a strong surface segregation of Pd, which has profound consequences on surface reactivity.[7]



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Photocatalytic properties of surface modified TiO_2 with Ni-Au nanoparticles.

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Hydrogen is considered the clean energy of the future. However the hydrogen production process is still based on fossil raw material, which is an expensive technology and environmental dangerous. The recent growing concern to the global weather changes has encouraged to develop a new green energy sources. Hydrogen production from water using a catalyst and solar energy is an ideal future fuel source. Under that concept Titanium dioxide (TiO_2) modified by metal nanoparticles is a promising strategy[1,2]. Studies performed under UV light had shown good photocatalytic activity using noble metals (Pt, Au, Pd)[3]. On the other hand, recent studies report that TiO_2 modified with transition-metal nanoparticles exhibit a good photocatalytic activity under visible light irradiation[4]. To further explore the potential applications of such materials, metal-semiconductor physical and electronic interactions must be understood.

Here photocatalytic production of hydrogen was studied over a series of TiO_2 modified with Au, Ni, and bimetallic NiAu nanoparticles synthesized by radiolysis, which is a powerful method to synthesize nanoparticles of controlled size, composition and structure.

The optical and the morphological properties of the metal-semiconductor nanoparticles were characterized by UV-Vis reflectance diffuse spectroscopy and High Resolution Transmission Electron Microscopy (HRTEM). The charge-carrier lifetime was measured by Time Resolved Microwave Conductivity (TRMC). Mass spectrometry was used to follow the hydrogen evolution.

Different effects were found depending on the kind of metal, particle size and light illumination. Gold nanoparticles store and shut photogenerated electrons from the TiO_2 to an acceptor in a photocatalytic process increasing the light conversion quantum yield. In the other hand, modification of TiO_2 with Ni nanoparticles induces an increase in the photocatalytic activity under Visible light.

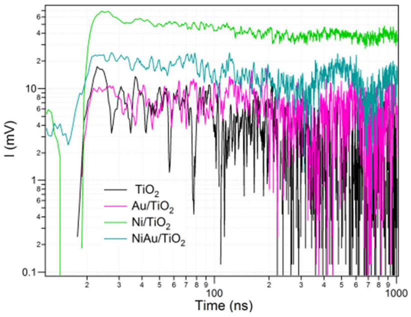

Fig. 1 TRMC transient obtained for the samples studied with λ 460 nm

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Synthesis And Characterization Of Magnetic $SrFe_{12}O_{19}$ / Fe Nanocomposites.

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Rare earth magnetic materials are ubiquitous in our current way of life, and more particularly when they are used as permanent magnets. Due to supplying troubles, toxicity and high cost of these compounds, their replacement by more available and affordable materials is a very current topic.

Designing nanocomposites with high magnetic coupling is currently the subject of numerous investigations, and appears as a very promising way to obtain new permanent magnet materials. With this aim, we have synthesized and investigated strontium hexaferrite-iron nanocomposites.

Iron nanocrystallites are obtained by reduction with sodium borohydride as reducing agent. Dimensions and shape of metallic iron particles have been characterized by Mössbauer spectroscopy and scanning electron microscopy. Iron crystallites appear as filaments linked by one common crystallographic direction, with a dimension of few nanometers.

Synthesis of strontium hexaferrite, with the stoichiometry $SrFe_{12}O_{19}$, has been achieved with a solvothermal process followed by ceramic treatment. By modifying experimental conditions, various shapes and sizes (micronic, sub-micronic and nanometric) are obtained. The first steps of crystallization of strontium hexaferrite have been highlighted.

Nanocomposites have been characterized by X-ray diffraction, electron microscopy (SEM and TEM), and magnetic measurements (VSM and SQUID). The influence of nanostructure on magnetic properties is identified and interpreted. The occurrence of magnetic coupling between iron and strontium hexaferrite particles is discussed.

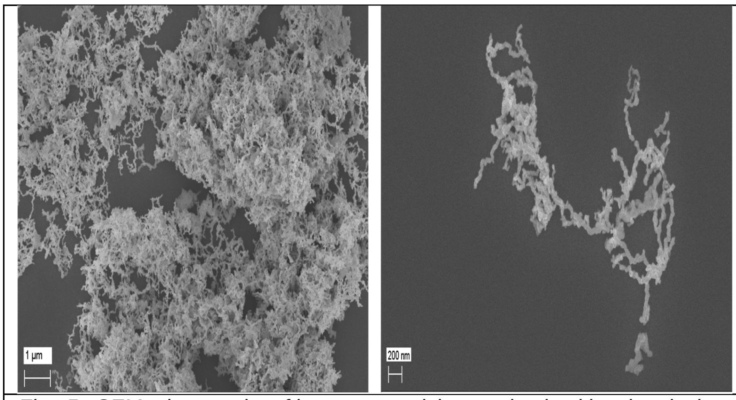

Fig. 5 : SEM micrographs of iron nanoparticles synthesized by chemical reduction.

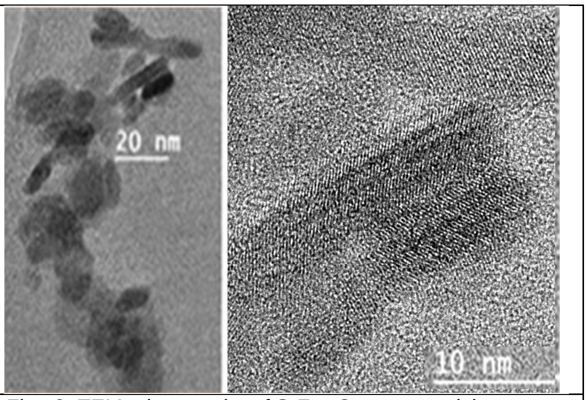

Fig. 2: TEM micrographs of $SrFe_{12}O_{19}$ nanoparticles synthesized by solvothermal process.

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Plasmon Spectroscopy Of Small Bimetallic Cu/Ag And In/Ag Clusters In Relation With Their Structure

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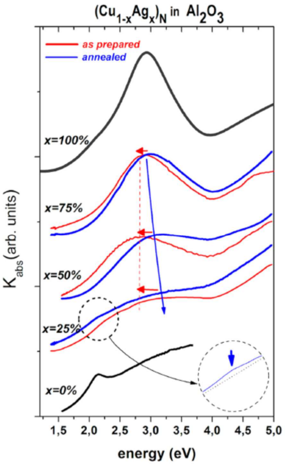
ABSTRACT

The optical properties of small *Cu−Ag* and *In-Ag* bimetallic clusters have been experimentally and theoretically investigated in relation with their chemical structure analyzed by high resolution transmission electron microscopy (*HRTEM*). Clusters of a few nm in diameter are produced by laser vaporization and embedded in silica or alumina. Absorption spectra are dominated by a broad and strong surface plasmon resonance (*SPR*) the features of which are dependent on both the cluster composition and the sample aging. Optical and *HRTEM* measurements combined with theoretical predictions lead us to conclude that these bimetallic clusters are not alloyed at the atomic scale but rather present a segregation of chemical phases. Most likely, they adopt a core−shell configuration (*Cu@Ag* and *Ag@In*). The aging due to oxidation, has also been studied. For the *Cu-Ag* system, the oxidation process is consistent with the formation of a copper oxide layer by dragging out inner copper atoms to the cluster surface [1]. In the case of the *In-Ag* system, an indium oxide shell spontaneously forms around a metallic silver core. The metallic character of indium and copper can nevertheless be recovered by annealing under a reducing atmosphere. These processes are directly mirrored in optical measurements through *SPR* shifts and broadenings that are in agreement with multi-shell Mie theory calculations and FEM (Finite Element Method) simulations [2]. Finally, the latest *HRTEM* analyses on $In_{0.75}$-$Ag_{0.25}$ clusters will be shown: they reveal the presence of indium in a silver-rich core, the stoichiometry and crystalline phase of which depend on the oxidized or reduced character of the clusters.



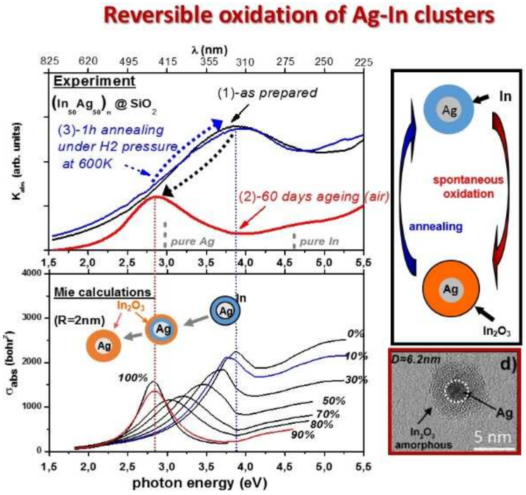


Fig. 6 (left): Optical absorption spectra of $(Cu_{(1-x)}Ag_x)_n$ clusters embedded in Alumina (as prepared and slightly oxidized (red), after annealing under reducing atmosphere (blue)).

Fig. 7 (right) : (top): Experimental absorption spectra of mixed $(In_{0.5}Ag_{0.5})_n$ clusters. (bottom): Calculated Absorption cross-sections for Ag@In clusters for increasing rates of the indium shell oxidation. (right) Scheme of the oxidation–reduction cycle (Ag@In <--> Ag@In_2O_3) and HRTEM image before reduction.

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Optical Properties of Bi-Metallic Noble-Metal Nanoalloys

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ABSTRACT

The Localized Surface-Plasmon Resonance (LSPR) in noble metal nanoclusters led to a large range of applications in biological sensing/detecting technology and other fileds. Its dependence on size, geometry, and environment has been studied by many groups. The effect of composition and configuration on the optical properties of nano-alloys has widely been studied experimentally and theoretically. In particular, full quantum calculations of bi-metallic clusters of up to about 150 noble metal atoms have been performed using time-dependent density-functional theory (TDDFT) for Ag-Au clusters [1,2].

Experimental investigations on Au-Cu clusters of 144 noble-metal atoms have recently revealed that incorporation of Cu gives rise to a LSPR-like peak in the spectra which is absent for both pure Cu and pure Au clusters of the same size [3]. Furthermore, very recently (2015) a theoretical study suggested that Cu induces a plasmonic resonance in bimetallic Au-Cu nanoclusters and compare with the well-studied Au-Ag system [4]. Motivated by these results, we systematically study the effect of alloying on the optical properties of Au-Cu nano-clusters. TDDFT calculations of the optical absorption are performed in the visible and near-UV ranges and discussed in view of the emergence of a plasmon-like resonance.

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Magnetic properties of bimetallic nanoparticles elaborated by cluster beam deposition

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In this paper, we present some specific chemical and magnetic order obtained very recently on characteristic bi-metallic nanoalloys prepared by mass-selected Low Energy Cluster Beam Deposition. We study how the competition between d-atoms hybridization, complex structure, morphology and chemical affinity affects their intrinsic magnetic properties at the nanoscale. The structural and magnetic properties of these nanoalloys were investigating using various experimental techniques that include HRTEM, SQUID magnetormetry, as well as synchrotron techniques such as EXAFS, XMCD and XRD. Depending on the chemical nature of the nanoalloys we observe different magnetic responses compared to their bulk counterparts. In particular, we show how specific relaxation in nanoalloys impacts their magnetic anisotropy; and how finite size effects (size reduction) inversely enhance their magnetic moment [1].

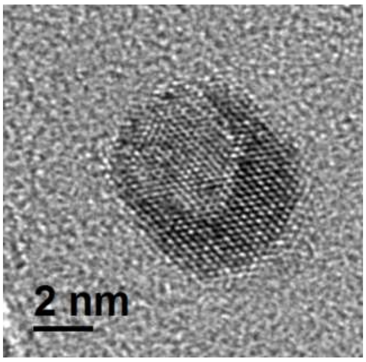

Fig. 8 : HRTEM image of an annealed CoAu nanoparticle (capped with carbon), displaying a core/shell structure with an off-centered Co core surrounded by an Au shell.

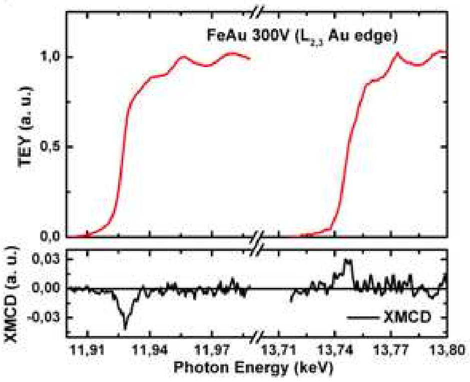

Fig. 9 : Evidence of induced magnetic moment on Au atoms from XMCD measurement at the $L_{2,3}$ Au edge for as-prepared FeAu clusters (around 3 nm in diameter) embedded in amorphous carbon.

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1. PCCP Themed Issue Invitation: Recent advances in the chemical physics of Nanoalloys, Guest edited by: Riccardo Ferrando, Roy L. Johnston and Catherine Louis, in press 2015

Structural diameter versus physical diameter in magnetism

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Nanoparticles are granules with size comprised between 1 and 100 nanometers. The main interest lies on the fact that atoms, localized around the surface in contact with the surrounding matrix, induce new phenomena. This leads to fascinating and surprising discoveries in the fields of biomedical, optical and electronic fields.

From our part, magnetic clusters (Co) sputtered in an insulating layer (Al_2O_3) have been intensively studied for reasons as Coulomb Blockade and discontinuous magnetic tunnel junctions[1]. As a remarkable result, from a set of structural and physical tools, a unique and simple law is found: As shown in Figure 1, the cluster diameter of Co, namely **D**, is linearly dependent of the nominal thickness of Co [**Th(Co)**]. In addition, the deviation of **D** deduced from pure structural technique like Transmission Electronic Microscopy is depending of the used specific technique: see Figure 1. Discussions of both **D~Th(Co)** law and absolute values of **D** will be given in that talk. A comparison with results published in the literature will be also debated.

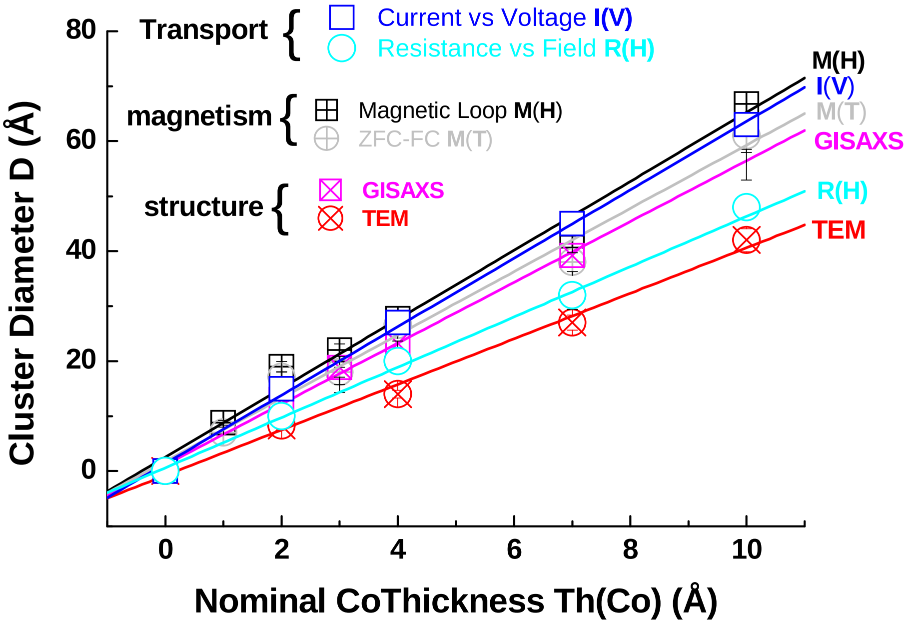

Figure 1 **Cluster diameter D as a function of Co nominal thickness Th(Co) deduced from different techniques: Transmission Electronic Microscopy, Grazing-incidence small-angle X-ray scattering, SQUID (magnetization versus field and temperature) and magnetotransport (current versus voltage and resistance versus field).**

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Optimized synthesis of FeBi nanoparticles for imaging applications

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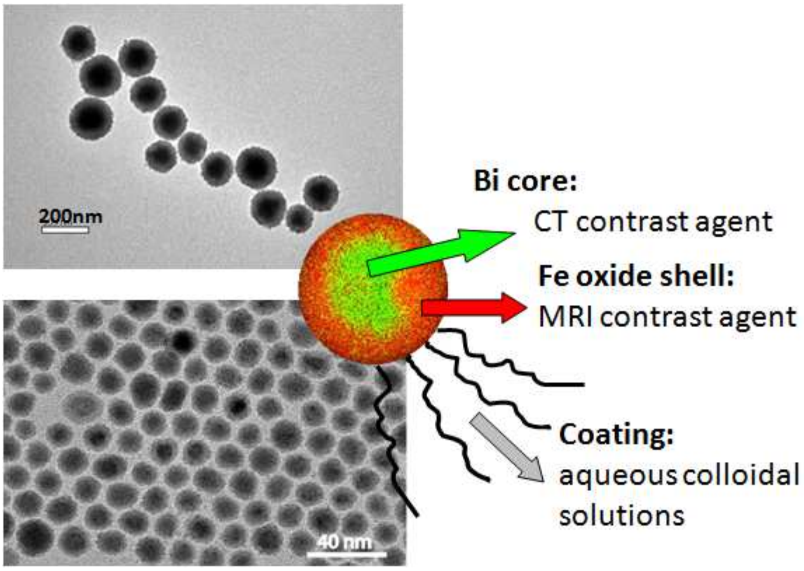
The current trend in biomedical imaging is now focused on the development of dual contrast agents combining two or more functionalities on the same NP.[1] Motivated by this new challenge we developed FeBi NPs as new nanomaterials with potential application as contrast agent for MRI and CT imaging.[2] In addition to the well-known use of iron in the development of MRI contrast agents,[3] we chose Bi as CT imaging agent rather than the more documented gold, because it possesses a larger X-ray attenuation coefficient, has low toxicity and is much less expensive.[4]

The NPs were synthesized using an organometallic approach. They are spherical, and contain a surface enriched in Fe while Bi is mainly located in the core of the NPs. This chemical order maximizes the interaction between the magnetic component and water, and limits the interaction of bismuth with the biological environment. Their growth process will be discussed based on WAXS, TEM, Mossbauer spectroscopy and EXAFS measurements.



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New Binary Superlattices from Magnetic Nanocrystals and Polyoxometalate Clusters

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Controlling the size, shape and elemental compositions of nanoparticles are different ways to get new physical properties in nano-objects assemblies. Recently, a new class of materials has emerged from binary self-assemblies of various nanocrystals (NCs). While most of the NCs-based nanostructures have been extensively studied, here we demonstrate the capability to design a new family of hybrid superlattices comprising of NCs and sub-5nm polyoxometalate (POMs) clusters. POMs are atomically defined anionic oxo-metal molecules formed by the early transition metals in their highest oxidation state. They offer an endless structural diversity and remarkable physical properties (electro- and photo-reduction, magnetism, etc.). The combination of POMs and NCs brings new opportunities to get synergetic effects and/or multi-functional nanomaterials.

In this presentation, we show the successful coassembly of magnetic NCs (γ–Fe_2O_3) and giant Keplerate-type POMs such as $\{Mo_{132}\}$ (*i.e.* $[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$) and $\{Mo_{72}V_{30}\}$ (*i.e.* $[Mo_{72}V_{30}O_{282}(SO_4)_{12}(H_2O)_{56}]^{36-}$). We give evidence that a longer range ordering of NCs is obtained in presence of the molecules for 2D and 3D superlattices. Therefore the fairly uniform geometric environment of the NCs is expected to induce changes in the collective magnetic properties of these assemblies.

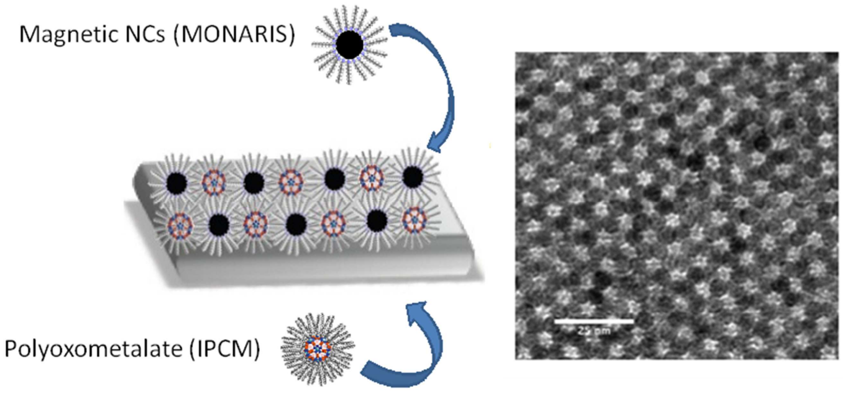

Figure : Illustration and transmission electron microscopy image of a $\{Mo_{132}\}/Fe_2O_3$ self-assembly (scale bar :25 nm).

A surface reaction promotes the formation of bimetallic nanoparticles in ionic liquids

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Unlike traditional solvents, ionic liquids (ILs) can be used to generate metallic NPs in the absence of any additive. Indeed, ILs can dissolve organometallic (OM) precursors, which readily form metallic NPs by decomposition (or reduction) under H_2 [1]. This process provides suspensions of metallic NPs, with accurate size control and high stability [2].

In this work, this approach is extended to binary mixtures of OM precursors. In a first example, the co-decomposition of mesitylcopper (CuMes) and (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium(0) Ru(COD)(COT) in 1-alkyl-3-methylimidazolium bistrifluoromethylsulphonylimide ($C_1C_4ImNTf_2$) is studied [3]. ASAXS measurements (ESRF facility) show that this reaction forms bimetallic NPs with Ru core and Cu shell (Fig. 1). In this case, the reaction between CuMes and surface hydrides on RuNPs has been shown to be key. More recent experiments show that in the case of Ru and Ta, $Np_3Ta{=}CHCMe_3$ also reacts on these hydrides to form Ru core, Ta shell bimetallic NPs (Fig. 2). When trying to react Ru(COD)(COT) on pre-formed TaNPs, two distinct populations are obtained.

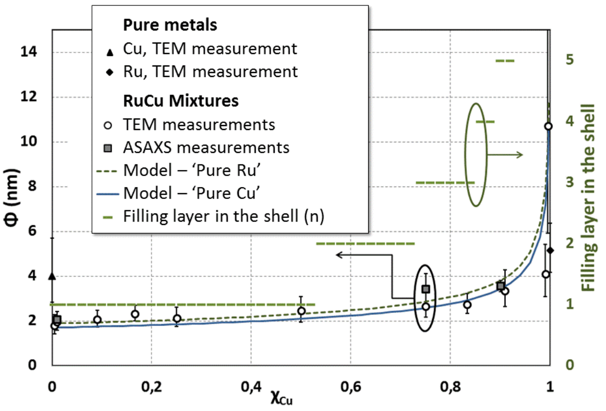

Fig. 10 : Diameter evolution of RuCuNPs with Cu content as measured by TEM and ASAXS, and comparison with a model developed in the present work . Mono- and bimetallic NPs were formed by decomposition of the OM precursors in $C_1C_4ImNTf_2$ for 4 h under 0.9 MPa H_2.

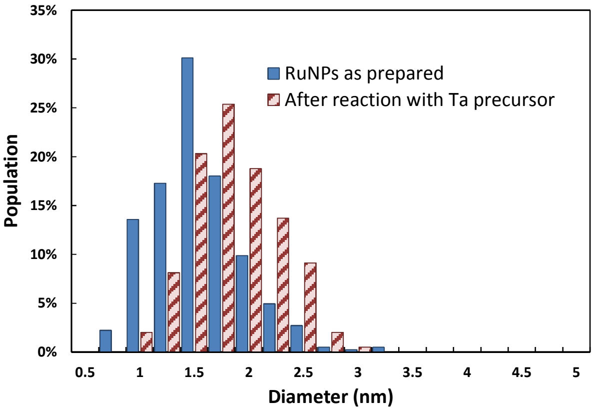

Fig. 11 : Size distribution of RuNPs before and after reaction with Ta precursor under Ar at 100°C for 4 h

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Synthesis of Air- and Water-Resistant Noble-Metal Coated Cobalt Nanorods

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Metallic Co single-crystalline nanorods of *hcp* structure, prepared by the reduction of an coordination Co precursor under hydrogen,[1] exhibit particularly attractive magnetic properties[2] for implementation in domains requiring materials with both high magnetization and high coercivity. They are exellent candidates for applications requiring "hard" magnetic nanoparticles (information storage, permanent magnets), however their use is compromised by their increased sensitivity towards oxygen and water that transforms them to cobalt oxides and/or hydroxides with a concomitant deterioration of their advantageous magnetic properties.

The development of a continuous noble metal shell around the cobalt cores would be an ideal solution for rendering the nanorods appropriate for use in an aqueous environment. The growth of a full shell is not straightforward, inhomogeneous deposition of the noble metal on the surface of cobalt results to noble metal decorated nanorods and not to a continuous full shell. However, even small discontinuities are enough for cobalt oxidation to take place in air or in aqueous solutions. Treatment of the Co nanorods with a tin coordination compound prior to noble metal deposition is a key step for the development of a full noble metal shell. Indeed this step allows the formation of shells that are continuous. After noble metal protection, the nanorods are air and water resistant and can be transferred to an aqueous solution and be functionalized by standard antibody immobilization protocols without losing their magnetic properties.

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Size dependent phase diagrams of Nickel-Carbon nanoparticles

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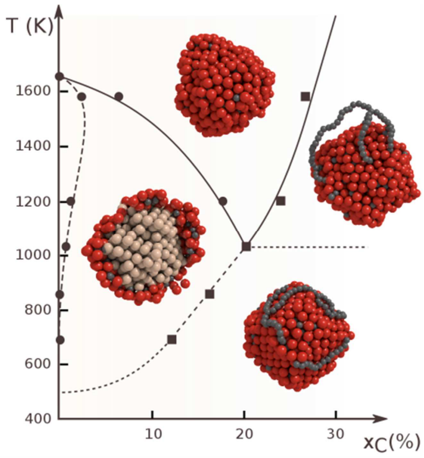
Carbon nanotube synthesis critically depends on the chemical and physical states of the catalyst particle from which they grow. In the typical temperature range (900-1300 K) of SWNT synthesis, pure isolated Ni nanoparticles are solid although atomic diffusion can lead to significant shape changes. Under growth conditions, these nanoparticles are exposed to reactive carbon. Depending on temperature, carbon chemical potential and nanoparticle size, carbon can either stay adsorbed on the surface, or diffuse to subsurface or in the core of the nanoparticle, thereby inducing a partial or complete melting.



On the basis of the tight binding model developed for the Ni-C system coupled with grand canonical Monte Carlo simulations [1], we extend our previous calculations [2, 3] and calculate phase diagrams for Ni-C nanoparticles for sizes ranging from 1 to 3 nm diameter and for face centered cubic and icosahedral structures. As compared to bulk phase diagram, the nanometric size of the nanoparticles used to catalyze SWNT growth induces significant differences. A large liquid shell / crystalline core domain appears instead of the liquid/solid coexistence characteristic of the bulk. Much deeper eutectic points are observed and, for a 3 nm diameter nanoparticle, as shown in the figure, carbon segregation from a mostly solid surface only takes place at temperatures below 850 K, at which SWNT growth is not really efficient.

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Simulation of the nucleation and growth of solid-solutions in an aqueous medium

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ABSTRACT

In the natural environment, crystallization of solid solutions (SS) from aqueous solutions (AS) is an ubiquitous process in which ion partitioning between the aqueous and solid phases yields complex chemical compositions which are very dependent on the conditions of formation (temperature, pressure, and fluid composition). Indeed, very rarely are natural minerals pure phases. We have elaborated a formalism which accounts, at the same time, for nucleation, growth and/or resorption of particles of variable composition (single or double substitution, ideal or non-ideal SS) in an AS. It yields the time evolution of all ion activities in the aqueous medium, together with the particle population characteristics: number, size and composition profile of particles as a function of time and of their time of nucleation. Applications to the precipitation of $(Ba,Sr)CO_3$ and $(Ba,Sr)SO_4$ SS will be presented, highlighting the possibility of engineering the particle characteristics by an adequate choice of initial preparation conditions.

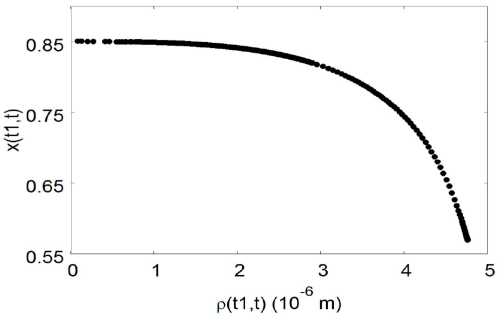

Fig. 1 : Composition profile of an homogeneous $(Ba,Sr)CO_3$ particle

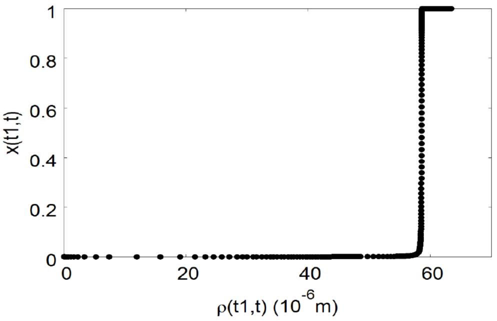

Fig. 2 : Composition profile of a core-shell $(Ba,Sr)SO_4$ particle

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Melting, mixing and nucleation at solid/liquid interface in nanometric metallic multilayer

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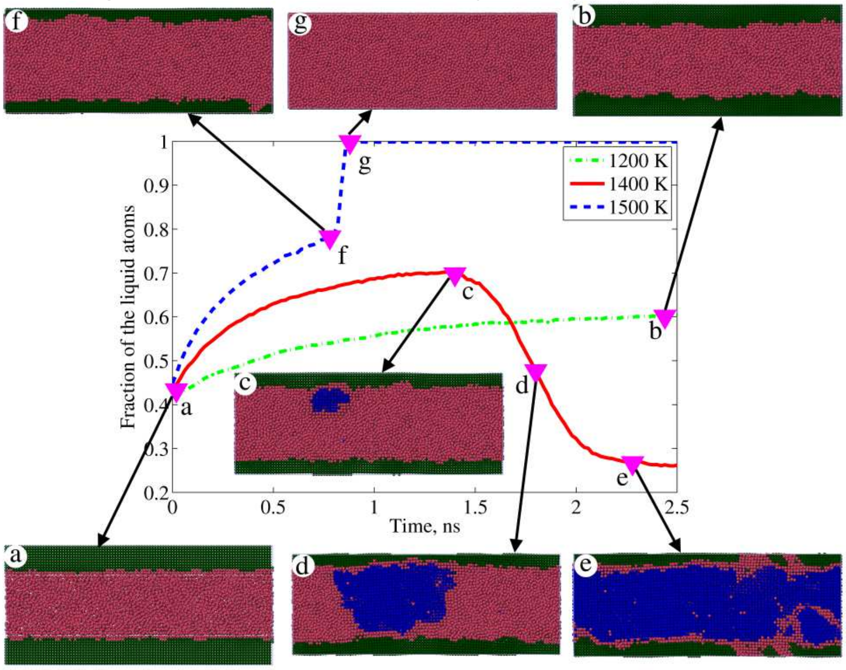
Nanometric metallic multilayers (N2M) are made of thin layers (4-100 nm) of metals deposited alternately. The structure of the N2Ms material is a succession of interfaces separated by a few nanometers. These many areas of contact should promote the mixing between the pure metals and alloying processes. In most cases, it is observed that the ignition temperature of the reaction coincides with the melting temperature of one of the two metals. The mixing is then associated to the dissolution of the solid phase into the liquid one. The Ni-Al reactive foil is chosen as the representative material.

Dissolution process of Ni into liquid Al is studied by means of molecular dynamics simulations, using an embedded-atom method type potential. MD simulations allow describing the elemental mechanisms underlying the dissolution process and prove that the number of Ni dissolved is the key variable to follow the progress of the reaction occurring in NiAl nanofoils. A diffusion-limited dissolution model has also been developed. The model is tractable enough to use simulation data to extract kinetic and thermodynamics parameters such as solubility, melting temperature and diffusion coefficients. The comparison with experimental data is quite satisfactory. The present work allows to assess the predominant role played by diffusion in the kinetic processes at nanoscale in layered systems.



Kinetics and phase transformations at 1200 K, 1400 K and 1500 K. Snapshots of the layered system (initially composed by Ni solid - Al liquid - Ni solid) show the distribution of the atoms according to their structure: fcc in dark green, bcc in blue and liquid in red..

Energy landscape approach to kinetics and phase equilibrium in nanoalloys

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ABSTRACT

Energy landscapes are a powerful concept in chemical and physical sciences able to explain the generic features of structure, equilibrium thermodynamics and global relaxation kinetics. In this contribution we present the general underlying ideas behind this approach and how it can be applied to realistic molecular systems. Two applications of those ideas are presented in relation with nanoalloys described using standard semiempirical potentials. In a first example, the method is applied in the grand-canonical ensemble to predict segregation isotherms in Ag-Pd nanoparticles. Good agreement with conventional Monte Carlo simulations validates the method and reveals off-lattice contributions and the role of vibrations [1].

In our second example we address the structural kinetics of medium-sized Ag-Au and Ag-Ni nanoalloys at selected compositions [2]. The relaxation from a metastable region to the most stable structures can be explored using discrete path-sampling (DPS), a technique which consists of building connected databases of local minima separating two morphologies of interest rather than attempting a direct connection through conventional atomistic simulations. For the highly miscible Ag-Au system, the transformation between core-shell and reverse core-shell structures is found to involve large excursions away from the icosahedral global minimum occuring through elementary mechanisms of surface diffusion and vacancy formation. The immiscible Ag-Ni system, in contrast, naturally forms an asymmetric Ag(shell)Ni(core) structure that requires about 10 eV to extrude the nickel core. The corresponding rearrangement is a long sequence of smooth surface displacements. For both nanoalloys, the predicted rearrangement kinetics obtained using state-to-state transition rates in the harmonic approximation show Arrhenius behaviors.

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Tuning the Performance and the Stability of Porous Hollow PtNi/C Nanostructures for the Oxygen Reduction Reaction

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This paper investigates the potential of porous hollow PtNi/C nanoparticles to electrocatalyze the oxygen reduction reaction (ORR), the key reaction in proton-exchange membrane fuel cells (PEMFCs). Porous hollow PtNi/C nanocatalysts with different Pt-rich shell thicknesses and degree of contraction Pt lattice were synthesized via a method involving galvanic replacement and the nanoscale Kirkendall effect. The most promising electrocatalyst achieved 6-fold and 10-fold enhancement in mass and specific activity for the ORR, respectively over standard solid Pt/C nanocrystallites of the same size. This enhancement was ascribed to (i) their opened porous architecture, (ii) their preferential crystallographic orientation (“ensemble effect”), and (iii) the weakened oxygen binding energy induced by the contracted Pt lattice parameter (“strain effect”). The stability of the hollow nanostructure was investigated by high temperature X-ray diffraction, identical-location transmission electron microscopy, and correlated to changes in catalytic activity.

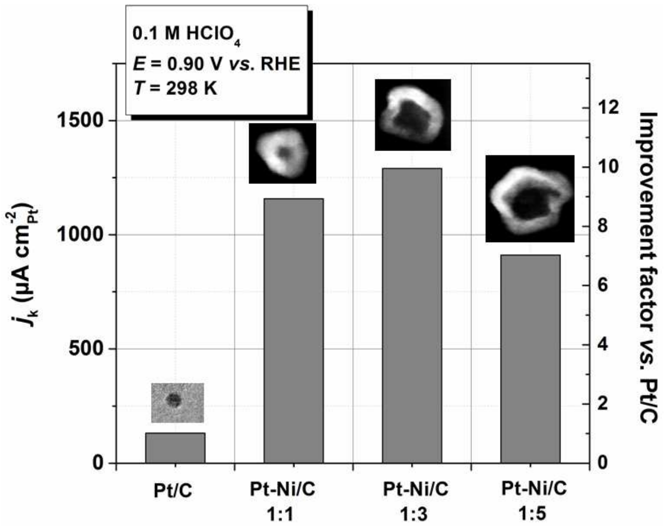

Fig. 12 : Specific activity determined from the steady-state I–E curves at ω = 1600 rpm. O_2-saturated 0.1 M $HClO_4$; potential sweep rate v = 0.005 V s^{-1}; positive-going potential sweep from E = 0.4 to 1.0 V vs RHE; T = 298 ± 1 K. The currents are normalized to the real surface area estimated by CO_{ad} stripping coulometry.

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Core-shell and Janus structure formation of Ag-Co/Pt nanoalloys

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Initially interested by the control of the mixing state (order/disorder) to enhance the properties of nanoalloys, the researchers focused these last years to heterogeneous or hybrid nanoparticles, like core-shell or janus particles (metal-metal or metal-oxide).

The surface composition of an alloy is generally different from that of the bulk. This phenomenon is the so-called surface segregation. In general, we can distinguish three main driving forces in order to predict the nature and the quantity of the segregating species in a binary alloy: the differences in surface energies and radii of the two elements, and their ability to mix in the bulk. In Ag-Co or Ag-Pt systems, we can predict a surface segregation of silver since Ag presents lower surface energy and larger size (to minimize elastic energy). However, while Ag-Co alloys present a large miscibility gap in wide ranges of temperature and concentration as can be seen in the phase diagram [1], the Ag-Pt system exhibits several alloyed phases in addition to a miscibility gap mainly in Pt-rich composition range [2].

In this study, we have investigated the atom arrangement in Ag-based nanoparticles NPs (Ag-Co and Ag-Pt) obtained by atom codeposition and by sequentially atom deposition versus the temperature and their stability after thermal treatment (annealing). Firstly, morphological and structural evolutions are followed by in situ and real time wide and small X-ray scattering obtained simultaneously in X-ray grazing incidence geometry [3,4] on the UHV setup of SIXS beamline (core-shell formation and phase separation). 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 core-shell or janus configuration depending on the initial core size and the composition evolution. The quantitative structural analysis are facilitated and consolidated using Monte Carlo (MC) simulations of Co-Ag nanoalloys in a semi-empirical tight-binding approach [4]. Preliminary results show that AgPt NPs prepared by sequential depositions (Pt then Ag) exhibit a metal mixing tendency with a strain relaxation causes by Ag deposition. For the simultaneous deposition mode, the nanoparticle structure is strained as Pt pure NPs.

Secondly, combined chemically selective results obtained by anomalous grazing incidence X-ray scattering [5] (AGISAXS/AGIWAXS) and high resolution electron microscopy /High-angle annular dark-field imaging will be presented on the annealing effects.

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Ageing of out-of-equilibrium bimetallic nanoparticles

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ABSTRACT

For an alloy, it is often possible to observe different configurations depending on the experimental process [1]. The non-equilibrium configurations should evolve towards the thermodynamically stable configuration for sufficient long time. When the physical properties of metastable nanostructures are interesting for technological applications the question of their life-time is of great interest.

In this study 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 [2]. We consider a cuboctahedron nanoparticle of 309 atoms (Cubo_5). Energetic parameters of the rigid lattice pair interaction energy model are fitted to represent the Cu-Ag system characterized by a strong tendency to phase separate and the tendency of Ag atoms to segregate at the surface.

Starting from an initial configuration with a random distribution of the two species, the nanoparticle passes through a metastable onion-like configuration on its way to its equilibrium core-shell structure at low temperature (see fig. 1). The analysis of the MFA-SK fluxes between the different sites during the kinetics emphasizes the role of the edges of the inner shells in the kinetic pathways leading to the dissolution of the onion-like structure.

We present the main features of the ageing kinetics starting from other metastable nanostructures such as reverse core-shell and Janus configurations. To conclude on this part, we briefly discuss the following point: are the present results specific to the case of nanoalloys or are they also observable in infinite or semi-infinite alloys ?

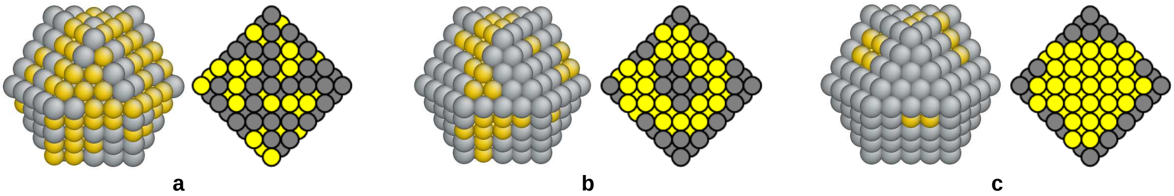

Fig. 13 : Snapshot of the Initial configuration (a), of the metastable onion-like configuration (b) and of the equilibrium core-shell configuration (c) in KMC simulation of the cuboctahedron of order 5 (309 atoms) at T=300 K and c=0.52. Left: view of the surface, Right : cross section. Cu atoms are in yellow and Ag atoms in grey.

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Bimetallic Nanoparticles and Nanostructures Induced by Radiolysis

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Synthesis of nanoparticles with well-controlled size and shape is often critical for their performances especially in catalysis or electro-catalysis. Therefore a lot of research is being carried out to develop synthetic approaches to achieve control over the composition, structure, size and shape of the nanostructures.

Radiolysis is a powerful method to synthesize metal nanoparticles (NPs) of controlled size and shape, and in particular bimetallic NPs of controlled structure (core/shell or alloys) and composition in solutions or in heterogeneous media. The hydrated electrons and the reducing radicals produced during radiolysis of the solvent induce homogeneous reduction in the water phase. Compared to chemical reducing processes that follow a diffusion front, radiolysis presents the advantage of inducing a homogeneous nucleation and growth in the bulk. We have shown that the structures of bimetallic nanoparticles (Ag-Au, Au-Pd, Au-Pd…)(core/shell nanoparticles or alloys) can be controlled by controlling the dose rate, which fixes the reduction kinetics.[1-2]

Hexagonal mesophases have been used as nanoreactors to synthesize nanostructured materials. Different 1D, 2D or 3D metal nanostructures have synthesized by radiolytic reduction of metallic salts confined in the water phase. Our templating approach allows synthesis of bimetallic nanoballs of tunable three-dimensional porosity and composition.[3-4] These nanostructures might find applications in catalysis, electrocatalysis and sensing.

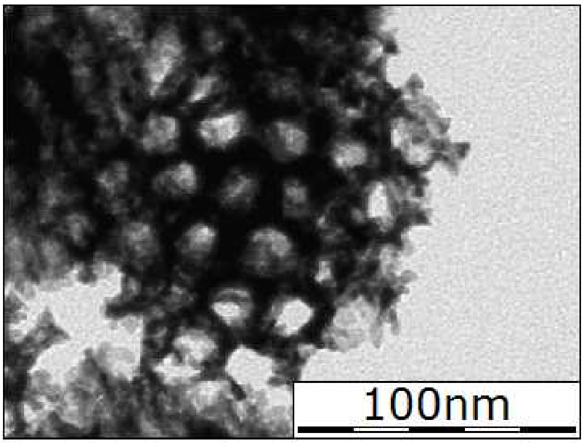

Fig. 14 : *Porous Pt-Pd nanoball induced in mesophases by radiolysis.*

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In situ reduction of core-shell $Ag@In_2O_3$ nanoparticles observed through environmental electronic microscopy

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The structure of bimetallic catalysts, in the form of alloyed or segregated nanoparticles (NPs) may evolve, depending on the environmental conditions (atmosphere, temperature, pressure) of the catalytic reactions. This may induce modifications of both their catalytic (activity, selectivity, stability) and optical (localized surface plasmon resonance, LSPR) properties. Hence, optical and structural characterizations of these NPs have to be performed under controlled environment, close to the chemical reaction conditions.

For the first time, the *in situ* reduction of $Ag@In_2O_3$ NPs performed in an environmental transmission electronic microscope (ETEM) has been observed under the presence of H_2. This work follows a previous study [1] showing the reversibility of the oxidation and reduction process, directly mirrored in optical measurements through SPR shifts and broadening. Here the aim is to follow structural modifications at the unique NP scale during the reduction process.

Size-selected Ag/In clusters of controlled composition have been synthesized in high vacuum by laser vaporization. After exposure to ambient air, a dielectric indium oxide shell is formed around the silver core and the initial system is thus an $Ag@In_2O_3$ structure.

Inside the ETEM, the NPs were exposed to various temperature and H_2 pressure, with a protocol consisting in rising the H_2 pressure from 1 mbar to 12 mbar at different temperature stages (ambient temperature to 500 °C). Several structural modifications have been tracked in real time, such as the transition from a core/shell to a Janus structure. The shell reduction was accompanied by the core enlargement (fig 1). This resulted from partial indium incorporation into the silver core, as confirmed by a "post-mortem" EDX analysis showing the presence of indium in the NPs.

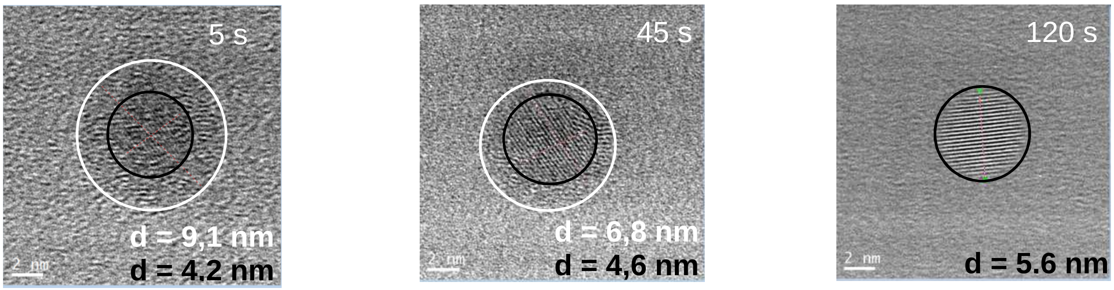

Figure 1: Evolution of the core and shell diameters of an Ag/In_2O_3 nanoparticle at 350 °C and 8 mbar H_2 pressure.

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POSTERS

New trends in nanoparticles shape optimization: application to the Fe-Au system

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ABSTRACT

Mastering the synthesis of isolated core-shell nanocrystals having a thermally stable designed morphology is one of the main challenges to be faced for opening the route to new applications of multi-functional nanoparticles (NP). The core-shell chemical distribution allows preserving the respective properties of the core and the shell while favoring interactions between them. The control of the morphology is important because the nature of the exposed facets conditions the surface electronic and crystallographic structures, modifying numerous properties of the NPs.

In this work we focus on the Fe-Au system. Interestingly, these two metals present a large miscibility gap and the low surface energy of Au, compared to that of iron, promotes a core-shell chemical distribution, with a Fe (magnetic) core and an Au (biocompatible) shell. Our objective is to favor the growth of a given Au facet by varying i) the Au and Fe volumes, ii) the deposition conditions and iii) the deposition temperature and post-deposition annealing. In parallel, DFT calculations are performed to evaluate the evolution of the adsorption energy of small organic molecules (CO, H2O, HCOOH …) as a function of the number of gold layer (shell thickness) deposited on the iron core.

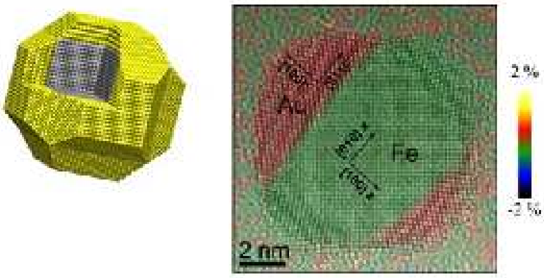

Figure 1. Model of the grown Fe@Au NPs and HREM micrograph of an NP superimposed to its GPA analysis along the z direction.

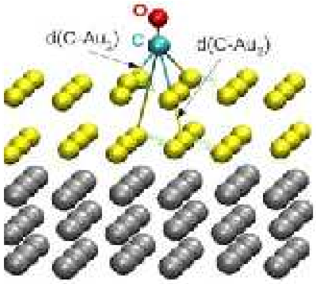

Figure 2. CO molecule adsorbed on 2 Au MLs epitaxially grown of Fe (001).

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Ordering and surface segregation in Pd-Au nanoparticles : from surface alloys to nanoalloys

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The study of chemical ordering and surface segregation effects in nanoalloys is crucial in the characterization of their properties and applications. Pd-Au catalysts are very efficient for various reactions, in particular in the CO oxydation [1]. Experimental studies started to elaborate and characterize Pd-Au nanoparticles in *ultra vacuum* under the form of regular arrays of bimetallic clusters by vapor deposition on nanostructured substrate observed by STM [2] or by pulsed laser deposition and HRTEM observations [3]. These systems have the particularity to form ordered compounds in bulk alloy but the question arises if the ordering remains in nano-sized particles and how surface segregation accommodates core ordering. We propose here a theoretical study of surface segregation and chemical ordering.

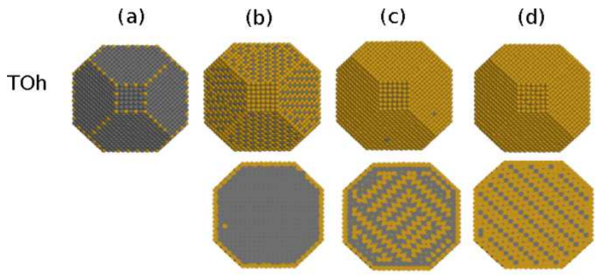

Fig. 1 : Snapshots of the chemical configurations at 100 K of the TOh nanoalloys of $Pd_{1-c}Au_c$ as referred in the Fig.2. Au atoms are represented in yellow and Pd atoms in grey [4].

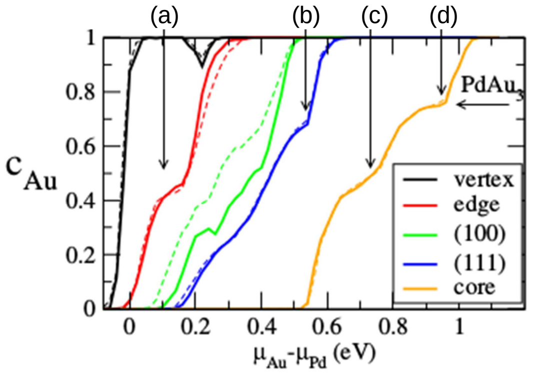

Fig. 2 : Isotherms at 100 K for the TOh_{8678} of $Pd_{1-c}Au_c$ nanoalloys giving the concentrations on each type of sites as a function of the difference in chemical potential μ_{Au}-μ_{Pd} [4].

Extending the study to the whole composition range of the $Pd_{1-c}Au_c$ alloys, we performed systematic Monte Carlo simulations in semi-grand canonical ensemble with semi-empirical many-body potential fitted to *ab initio* calculations within the density functional theory. We characterized the segregation isotherms for Pd-Au bulk on the whole range of compositions and for different temperatures in order to draw bulk phase diagrams. Then the truncated octahedron (TOh) cluster of 8678 atoms is studied as illustrated in figures above. Its chemical structure is compared in its core with the bulk phase diagram and in its facets with the (111) and (100) infinite surfaces segregation isotherms.

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Finite Size Effect in Chemical Bonding of diluted Pd in gold nanoparticles

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In surface science approach extended crystal surfaces are widely used as models of the facets and the defects of nanoparticle catalysts. However the existence of finite-size effects challenges this approach to the understanding of heterogeneous catalysis. For instance, many previous studies have shown that the catalytic activity of gold nanoparticles is dependent on the cluster size [1,2]. Size effect has been demonstrated to be important in a variety of catalytic systems involving transition metals [3-4].

In contrast with monometallic catalysts, finite size effects in chemical bonding of nanoalloys are still unknown. In this work [5], the size-dependent of a variety of AuPd nanoalloy structures were investigated by mean of first principles calculations. The variation in C-O adsorption energies, C-O vibration frequencies ($\nu_{C\text{-}O}$) and Pd d-bond centers (ε_d) on a series of Au_{n-1}-Pd_1 nanoparticles (with n varies from 13 to 147) and on two semi-finite surfaces were calculated as a function of cluster size. The results show that the adsorbate-induced perturbation is extremely local and it only concerns the isolated Pd interacting with the gas molecule. Hence, except for 13 atom cluster (Figure 1), in which molecular behaviour is predominant, no finite-size effects are observed for surface Pd atom substituted in AuPd nanoalloys above 38 atoms.

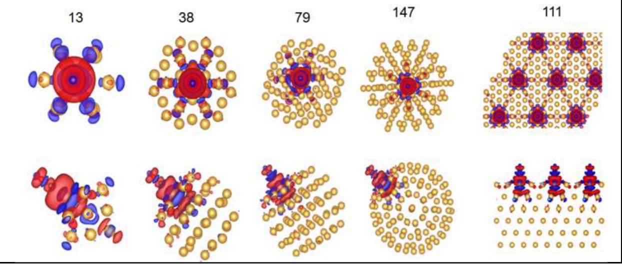

Figure 1.; Charge density difference ($\rho_{cluster+C\text{-}O} - \rho_{cluster} - \rho_{C\text{-}O}$) plots (top and side views) for Pd at facet site of AuPd clusters TOh38, TOh79, Ih147 and AuPd(111) surface. The plot for CO13 (Pd in vertex) is reported for comparison. Blue (red) contours signify areas of accumulated (depleted) electron density. The plotted contours are chosen to be (0.02e/A^3).

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Enhanced Photoactivity of Ag-Cu/TiO_2 Under UV and Visible Light

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Ag, Cu and bimetallic Ag-Cu nanoparticles were synthesized on the surface of commercial TiO_2 compounds (P25) by radiolytic reduction [1]. The as-prepared photocatalyts were characterized by High Angle Annular Dark Field (HAADF) Scanning Transmission Electron Microscopy (STEM), Energy-Dispersive X-ray Spectroscopy (EDS), and Diffuse Reflectance Spectroscopy (DRS). Their electronic properties have been studied by Time Resolved Microwave Conductivity (TRMC) to follow the charge-carrier dynamics [2]. The photocatalytic properties of the modified TiO_2 were studied for phenol photodegradation and for acetic acid oxidation in aqueous suspensions under UV and visible irradiation. The modification with the metal nanoparticles induces an increase in the photocatalytic activity under both UV and visible light [3]. TRMC measurements show that the TiO_2 modification with Ag, Cu and Ag-Cu nanoparticles plays a role in charge-carrier separations increasing the activity under UV-light. Indeed, the metal nanoparticles act as a sink for electrons, decreasing the charge-carrier recombination. The TRMC signals show also that electrons are injected from the metal nanoparticles in the conduction band of TiO_2. Copper is able to activate TiO_2 in a wider range of wavelengths under visible light irradiation, compared to the activation achieved by the presence of silver. Action spectra correlate with absorption spectra for irradiation wavelengths in the range of 350-470 nm proving that decomposition of acetic acid is carried out by the photocatalytic mechanism [4].

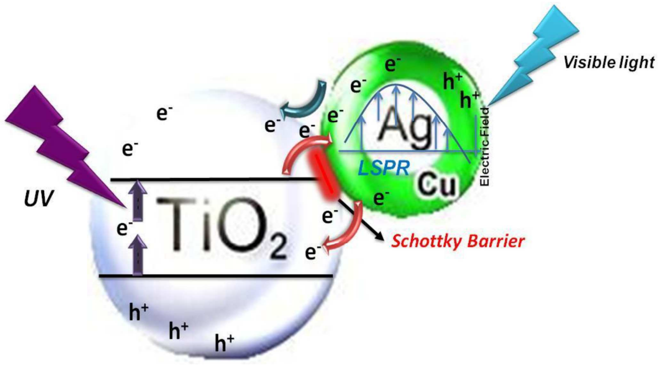

Fig 1. Proposed mechanism for UV and visible light with metal NPs supported on a semiconductor material

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Au-Pd nanoparticles deposited by pulsed laser ablation on titania nanorods: An investigation of their structural and catalytic properties

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In recent years, the new chemical and physical properties that derived from the synergistic effects of mixing gold and palladium atoms have been of great interest to many catalytic reactions. While significant progress has been made in the synthesis of monometallic nanoparticles (NPs) with well-defined composition, structure, size, and morphology, more accurate control over nucleation and particle growth stages is required to achieve the rational design of supported bimetallic nanocrystals. Recently, it has been shown that pulsed laser ablation (PLD) is a versatile method for the synthesis of supported Au-Pd NPs with a high control in particle size, composition, crystal structure and surface density[1].

In this contribution, we report on the synthesis, structural characterization and catalytic properties of Au-Pd NPs deposited by PLD on rutile titania nanorods. Rod-like rutile titania nanocrystals with narrow size distribution were prepared using a two-step hydrothermal procedure developed by Li and Afanasiev [2]. The TiO_2 nanorods preferentially expose (110) facets. Bimetallic Au-Pd nanoalloys with well-controlled composition were grown on the nanorods by alternate ablation of two monometallic ultrapure Au and Pd targets in an ultrahigh-vacuum chamber. During particle nucleation and growth, the nanorods were heated at a temperature of 300°C. The nominal thickness of metal deposited was 1 nm and the alternate ablation approach enabled any composition of nanoalloys to be precisely obtained. In this work, a series of Au-Pd NPs with Au, Pd, $Au_{38}Pd_{62}$ and $Au_{57}Pd_{43}$ stoichiometries were synthesized.

Transmission electron microscopy imaging of the as-synthesized samples showed the formation of well-separated NPs with a size distribution between 2 and 8 nm. As a result of the poor epitaxy between the metallic NPs and their support, most NPs displayed droplet-like morphology with ill-defined crystalline structure. Wherever a higher degree of epitaxy prevailed, Au-Pd NPs in the shape of truncated octahedron and having a completely disordered (random alloy) fcc structure were formed. Various epitaxial relationships were identified between the nanoparticles and the titania support, with the two dominant previously unreported relationships being Au-Pd(111)<101>*//Rutile(110)[1-1-1]* and Au-Pd(100)<101>*//Rutile(110)[1-10]*.

The catalytic properties of the PLD-synthesized Au-Pd NPs were investigated in the selective hydrogenation of 1,3-butadiene into butenes and the oxidation of carbon monoxide to carbon dioxide to highlight the influence of particle composition on catalytic performances. The results of these studies will be presented and discussed.

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Bimetallic CoAg nano-particles structure study for magneto-plasmonic properties

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ABSTRACT

Bimetallic nanoparticles (1-5 nm diameter) formed by a noble metal and a ferromagnetic transition metal open the way to a coupling between plasmonic and magnetic properties. Because these nanoparticles are sensitive to magnetic fields and could have a strong absorbtion behaviour in visible spectrum, it is interesting to consider interactions between both effects.

The TEM study of these CoAg nano-clusters enables to better understand, thanks to their crystalline structure, geometry properties and stoichiometry, their plasmonic absorbtion and magnetic anisotropy.

Similar studies have been performed for CoAu clusters [1] which have revealed core/shell (Co/Au) structures. Different results have been obtained by investigations on CoAg.

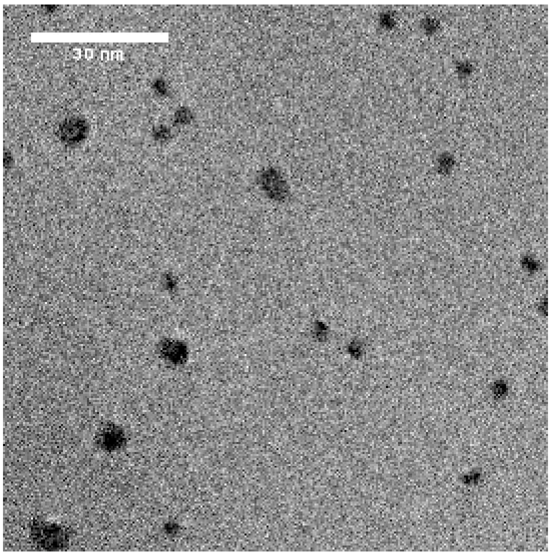

Fig. 1 . TEM image of Co(50)Ag(50) of 2 different sizes of nanoclusters

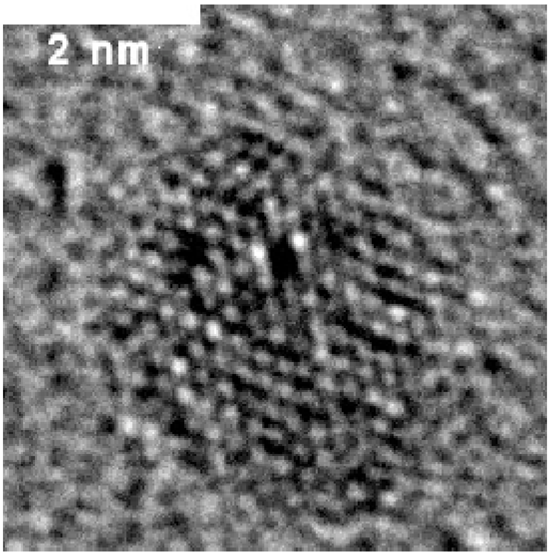

Fig. 2 . HRTEM of a Co(50)Ag(50) nanocluster

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Nom	Prénom	Organisme	Ville
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NGANDJONG	Alain Cabrel	ICMN	Orléans
NOGUERA	Claudine	INSP	Paris
PICCOLO	Laurent	IRCELYON	Lyon
PRUNIER	Hélène	MPQ	Paris
RAMADE	Julien	ILM	Lyon
RESPAUD	Marc	LCC	Toulouse
REMITA	Hynd	Lab. de Chimie Physique	Orsay
RICOLLEAU	Christian	MPQ	Paris
SANTINI	Catherine	UMR CNRS 5265 C2P2	Lyon
WEISSKER	Hans-Christian	CINaM	Marseille

Réunion Plénière et Thématique « Nanoalliages et Nanohybrides 2015 »

île de Porquerolles, du 17 au 22 mai 2015

	Dimanche 17	Lundi 18	Mardi 19	Mercredi 20	Jeudi 21	Vendredi 22
08h30				Amiens		
09h00		Nelayah	Garreau	Breitwieser	Noguera (invitée)	Remita (invitée)
09h30		Bardotti	Prunier	Haumesser		
10h00		Lecante	Piccolo	Pause/Poster	Baras	Ramade
10h30		Pause / Posters	Pause /Posters	Respaud	Pause / Posters	Pause
11h00		DeClercq	Luna-Barron		Calvo (invité)	Conclusions
11h30		Carenco	Maât	Bichara		
12h00		Déjeuner	Déjeuner	Déjeuner	Déjeuner	Déjeuner
16h00		Marie	Cottancin		Maillard (invité)	
16h30		Ngandjong	Weissker			
17h00		Pause / Posters	Pause / Posters		Pause / Posters	
17h30	Accueil	Hillenkamp	Dupuis		Andreazza	
18h00	Apéritif	Moyon	Fettar		Berthier	
19h15	Dîner	Dîner	Dîner	Dîner	Dîner	

Synthèse / Structure   Propriétés   Nanohybrides   Cinétique