

NANOALLOYS

International Research Network

APRIL

14 - 16

IMN 2021 #3

International Meeting on Nanoalloys



Leuven, Belgium

Virtual Conference

Environment and non-equilibrium effects on  
their structures and properties,

Nanoalloy catalysis,

Magnetic and optical properties of nanoalloys

Conference  
book

<https://nanoalloys-irn.cnrs.fr/imn-2021>



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**IMN 2021** is the third International Meeting on Nanoalloys organized by the International Research Network **IRN "Nanoalloys"** (CNRS). It follows IMN 2018 and IMN 2019, which took place at Orléans, France on May 22-25, 2018 and Genova, Italy on June 4-7, 2019, respectively.

The aim of the **IRN "Nanoalloys"** is to share tools and expertise in the field of nanosized alloy particles with bi- or multi-metallic components, including topics as kinetic effects that control the equilibrium and out-of-equilibrium structure, environment effects on the nanoalloy structures, and its impact on cluster's chemophysical properties. The **IRN "Nanoalloys"** reinforces exchanges at European level in the field of alloy nanoparticles, and promotes new collaborations at international level on topics that are at the forefront of research in nanoalloys.

**IMN 2021** brings together experimentalists and theoreticians to foster concerted efforts of experimental and modeling groups. Close collaboration between experimentalists and theoreticians is necessary to investigate nanoalloys at ultimate resolution (structure, property), either statically or dynamically (time-resolved, multiscale) and under environmental conditions. Research in nanoalloys is highly interdisciplinary, comprising chemists, physicists and materials scientists. The plenary IMN meetings are open to a wider community, including groups that are not members of the IRN, both from European and extra-European countries.

**IMN 2021** deals with the properties of nanoalloys and their applications, both from an experimental and modelling point of view, with particular focus on:

- environment and non-equilibrium effects on nanoalloy structures and properties;
- nanoalloy catalysis; and
- magnetic and optical properties of nanoalloys.

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## Wednesday April 14, 2021

- 08:40 Welcome & opening  
*Ewald Janssens (KU Leuven, Belgium)*
- 09:00 Challenges for the nanoalloy mission: predicting the catalytic performance of clusters  
*Richard E. Palmer (Swansea University, UK)*
- 09:25 Equilibrium and kinetic effects in the growth of shape-selected nanoparticles  
*Diana Nelli (Università di Genova, Italy)*
- 09:50 Effective site energies study of driving forces of alloys: from bulk to surfaces  
*Fabienne Berthier (Université Paris-Saclay, France)*
- 10:15 Real-time tracking of optical and structural properties of Ag-based bimetallic nanoparticles  
*Emmanuel Cottancin (Univ. Lyon, France)*
- 10:30 Colloidal synthesis; from bimetallic nanoalloys to high entropy nanoalloys  
*Cora Moreira Da Silva (Laboratoire d'Etude des Microstructures, France)*
- 10:45 Meet-the-speaker session
- 11:15 Core-shell clusters synthesized in helium droplets - structure, phase transitions, and optical resonances  
*Wolfgang E. Ernst (Graz University of Technology, Austria)*
- 11:40 Geometries, stabilities, reactivities, and optical properties of palladium doped gold clusters  
*Piero Ferrari (KU Leuven, Belgium)*
- 11:55 Progress on the role of bismuth as a selectivity modifier in AuPd catalysts  
*Sebastiano Campisi (Università degli Studi di Milano, Italy)*
- 12:10 Accelerating prediction of chemical ordering in nanoalloys: augmented grouping approach  
*Alessandro Fortunelli (Italian National Research Council, Italy)*
- 12:25 Meet-the-speaker session
- 13:00 Break
- 14:00 Networking session
- 14:30 Atomic layer deposition routes to tailor nanoalloys  
*Jolien Dendooven (Ghent University, Belgium)*
- 14:55 Segregation in Au-Cu nanoparticles: a theoretical and experimental approach  
*Grégoire Breyton (Université Paris Diderot, France)*
- 15:20 Palladium-copper nanoalloys and their interaction with hydrogen  
*Estefanía German (University of Valladolid, Spain)*
- 15:35 Comprehensive modeling of Ir subsurface segregation & dimerization in Pd-Ir NPs  
*Micha Polak (Ben Gurion University of the Negev, Israel)*
- 15:50 Meet-the-speaker session
- 16:20 End of scientific session

# Challenges for the nanoalloy mission: predicting the catalytic performance of clusters

Richard E. Palmer\*

*Nanomaterials Lab, College of Engineering, Swansea University, UK*  
*\*r.e.palmer@swansea.ac.uk*

The alloying of one (typically cheaper) metal with another (typically more expensive) metal, in order to maintain or enhance functional performance while reducing the usage of scarce materials, is one of the key drivers for nanoalloy research. Here I will consider three recent examples in which alloying leads, respectively, to enhanced performance, diminished performance or has no effect at all. In each example the results obtained were not predicted in advance. In the first case [1], alloying of Au with Cu to create alloy nanoparticles with a dual target cluster beam source leads to a notably beneficial synergistic effect in the selective catalytic conversion of nitrophenol to aminophenol, a model reaction in the pharmaceutical sector. In the second case [2], doping of MoS<sub>2</sub> clusters, whose efficacy in catalysing the hydrogen evolution reaction (HER) is well established, with Co atoms tends to poison the catalyst – whereas doping with Ni gives a marked enhancement of activity. In the third case [3], the alloying of Cu with Pt (the commercial catalyst for the HER) with Cu, in an effort to reduce the usage of Pt, only serves to dilute the activity; the Cu is a passive bystander. In a fourth and incomplete case [4], alloying Ni with Pt seems at first sight to enhance the HER activity per Pt atom, but further checks are needed. These diverse examples of the benefits, or otherwise, of alloying point to a need for much better predictive understanding of the chemical effects of alloying, including the need to account for the environment(s) to which the clusters are exposed; otherwise we are trapped in case-by-case experimental trials. Probably this goal needs both systematic experimental screening (and characterisation) of nanoalloy performance in reaction conditions and a massive advancement in computational power and methodology.

I will conclude with a brief account of our latest progress in the quest to scale up nanoparticle beam deposition [5], and thus translate the insights into nanoalloy functionality which are needed into high-performance, practical materials.

[1] Rongsheng Cai, Peter R. Ellis, Jinlong Yin, Jian Liu, Christopher M. Brown, Ross Griffin, Guojing Chang, Dongjiang Yang, Jun Ren, Kevin Cooke, Peter T. Bishop, Wolfgang Theis and Richard E. Palmer, *Small* 14, 1703734 (2018).

[2] Jo J.L. Humphrey, Rasmus Kronberg, Rongsheng Cai, Kari Laasonen, Richard E. Palmer, and Andrew J. Wain, *Nanoscale* 12, 4459 (2020).

[3] Maria Chiara Spadaro, Jo J. L. Humphrey, Rongsheng Cai, Lidia Martínez, Sarah J. Haigh, Yves Huttel, Steve J. Spencer, Andrew J. Wain and Richard E. Palmer, *J. Phys. Chem. C* 124 23683 (2020).

[4] Yubiao Niu et al, a collaboration in progress between Swansea, Leuven and NPL.

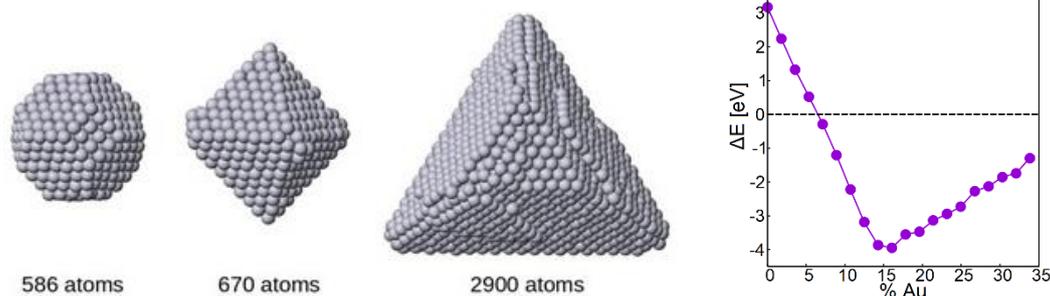
[5] R. Cai, F. Martelli, J Vernieres, S. Albonetti, N. Dimitratos, C. Tizaoui, and R.E. Palmer, *ACS Appl. Mater. Interfaces* 12, 24877 (2020).

# Equilibrium and kinetic effects in the growth of shape-selected nanoparticles

Diana Nelli\*

*Dipartimento di Fisica, Università degli Studi di Genova, Via Dodecaneso 33, 16146, Genova, Italy  
\*nelly@fisica.unige.it*

The properties of nanoparticles are known to strongly depend on their shape. Crystalline and non-crystalline nanoparticles (such as icosahedra and decahedra) can exhibit quite different catalytic and optical properties, and the same applies for crystalline fcc nanoparticles of different shapes. Therefore, producing nanoparticles with controlled geometric structure is extremely important for applications. In this framework, the contribution of numerical simulations is crucial since they allow identify the physical driving forces which address the nanoparticle growth towards a specific structural motif. In general, both equilibrium and out-of-equilibrium kinetic effects can be the cause of such shape-directed growth. Here both possibilities are explored, with the help of two interesting examples of shape-controlled growth in pure and bimetallic nanoparticles. Firstly, we describe the growth of out-of-equilibrium octahedral (Oh) and tetrahedral (Th) Pt nanocrystal in the gas phase [1]. Experimental observations show that the relative abundance of the two geometric structures can be tuned by selecting the average size of the nanoparticles distribution, with Th becoming dominant at larger sizes. The transformation from Oh to Th during the growth is suggested by the experimental data and confirmed by molecular dynamics growth simulations, which reveal the key symmetry-breaking atomic mechanism for this shape transformation. In the second example, the shape of AuPd nanoalloys grown in the gas phase can be changed by tuning their composition [2]. In pure Pd distributions the dominant structures are fcc truncated octahedra (TO), while increasing the Au content there is a transition to icosahedral (Ih) structures in which Au atoms are preferentially placed on the surface. Global optimization searches and free energy calculations confirm that Ih becomes the equilibrium structure for increasing Au content and atomic stress calculations demonstrate that the driving force of this shape change is the more efficient relaxation of anisotropic surface stress in Ih compared to TO.



**Left:** Snapshots of a Pt nanoparticles during a growth simulation, showing the transformation from TO to Oh and then to Th. **Right:** Energy difference between Ih and TO AuPd nanoparticles of size 561 as a function of Au content.

[1] Y. Xia, D. Nelli, R. Ferrando, J. Yuan and Z. Y. Li, submitted.

[2] D. Nelli, C. Roncaglia, R. Ferrando and C. Minnai, submitted.

# Effective site energies study of driving forces of alloys: from bulk to surfaces

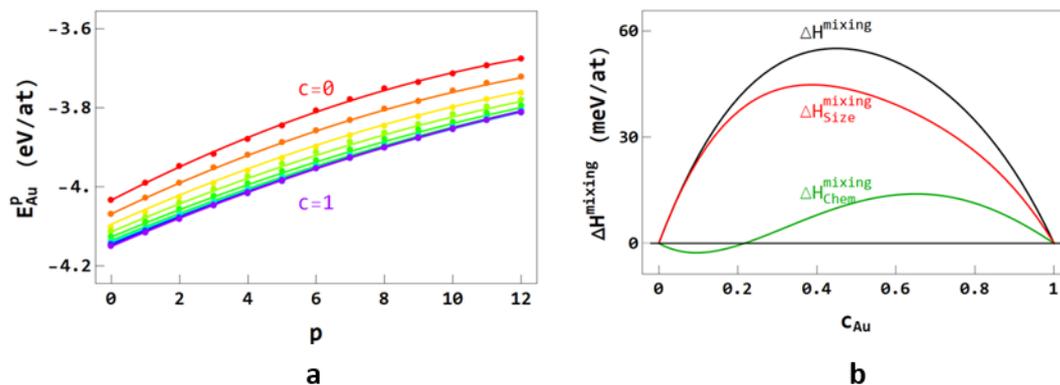
Fabienne Berthier<sup>1</sup>, Bernard Legrand<sup>2</sup>

<sup>1</sup>Université Paris-Saclay, CNRS

<sup>2</sup>Université Paris-Saclay, CEA

The understanding of the driving forces that control the phase diagrams of binary alloys is still very limited, especially in the presence of a strong parametric mismatch between the constituents. We propose a new approach based on the determination of site energies in random solid solutions [1-3]. Thus, the energy of each atom can be obtained after relaxation of the atomic positions and sorted according to the local environment (e.g. according to the number of first neighbors of a given type) and the nominal concentration. This last dependency, which integrates the variation of the lattice parameter as a function of concentration, controls the elastic effect, in other words the size effect, in the presence of a parametric mismatch. When these site energies are accessible, generally from tight binding models, they give access to an analysis of the driving forces governing the thermodynamics of alloys and allow rigid lattice Monte Carlo simulations including the effect of atomic relaxations.

We will first illustrate the potentialities of this approach by considering two alloys with quite similar phase diagrams, Au-Ni and Ag-Cu, whereas the analysis of the driving forces shows a very different origin of the observed miscibility gaps [1]. Then we will compare the bulk and surface driving forces.



(a) Site energy of an atom Au as a function of the number  $p$  of Au neighbors, for different values of the concentration in  $Au_cNi_{1-c}$  alloy. The color scales between red ( $c = 0$ , Ni-pure system) and purple ( $c = 1$ , Au-pure system). The lines are only a guide for the eyes. (b) Evolution as a function of  $c$  of the mixing enthalpy  $\Delta H^{mixing}$  (black line) and of its two contributions  $\Delta H_{Size}^{mixing}$  (red line) and  $\Delta H_{Chem}^{mixing}$  (green line).

[1] F. Berthier, J. Creuze and B. Legrand, Phys. Rev. B 95, 224102 (2017).

[2] F. Berthier and co., Phys. Rev. B 99, 014108 (2019).

[3] F. Berthier and B. Legrand, J. Phys.: Condens. Matter 32, 354001 (2020).

# Real-time tracking of optical and structural properties of Ag-based bimetallic nanoparticles

Emmanuel Cottancin<sup>1,\*</sup>, Elise Camus<sup>1</sup>, Julien Ramade<sup>1</sup>, Marie-Ange Lebeault<sup>1</sup>, Cyril Langlois<sup>2</sup>, Laurent Piccolo<sup>3</sup>, Matthias Hillenkamp<sup>1</sup>, Florent Calvo<sup>3</sup> and Michel Pellarin<sup>1</sup>

<sup>1</sup>Univ. Lyon, Univ. Lyon 1, CNRS, Institut Lumière Matière, UMR 5306, 69622 Villeurbanne, France

<sup>2</sup>Univ. Lyon, INSA-Lyon, MATEIS, Univ. Lyon 1, UMR 5510 CNRS, 69621 Villeurbanne Cedex France

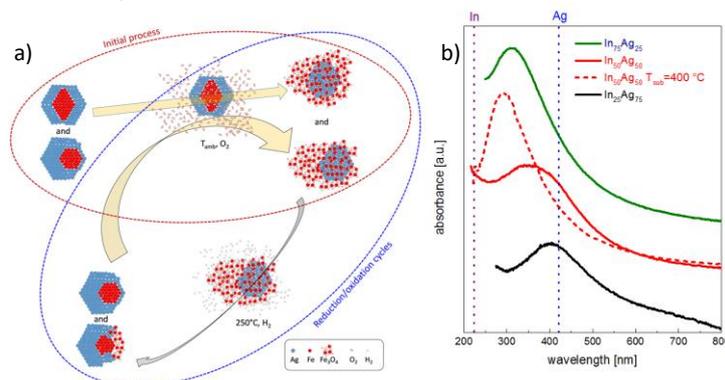
<sup>3</sup>Univ. Lyon, Univ. Lyon 1, IRCELYON – UMR 5256, 69626 Villeurbanne Cedex, France

<sup>4</sup>University Grenoble Alpes and CNRS, LIPHY, F-38000 Grenoble, France

\*emmanuel.cottancin@univ-lyon1.fr

The Localized Surface Plasmon resonance (LSPR) of metallic nanoparticles (NPs) is strongly dependent on their local environment and on their constituent-material dielectric functions. Thus, chemical modifications occurring at their vicinity, or directly within the NPs may be optically monitored. Moreover, Ag-based NPs may display a well-defined LSPR strongly sensitive to small variations of the surrounding. In this respect, Ag-based NPs (produced by laser vaporization) containing another reactive metal have been investigated. The first illustration deals with *iron-silver* NPs investigated through TEM observations, *in situ* optical spectroscopy and Monte Carlo simulations, leading us to conclude that iron and silver initially adopt a segregated configuration with a silver-enriched surface. During oxidation, iron likely diffuses throughout the silver shell, leading to an Ag@Fe<sub>3</sub>O<sub>4</sub> configuration, while an inverse process may occur during annealing under a reducing atmosphere (Figure (a)) [1].

We also performed optical and environmental TEM characterizations on *In-Ag* NPs. Optical spectra (Figure (b)) show LSPRs in the UV range down to 310 nm for as prepared NPs. A NP deposition at elevated temperatures even results in an LSPR <300 nm. Optical and TEM characterizations indicate that *In-Ag* NPs most likely adopt a core-shell structure with a silver-rich alloy core and an indium shell which spontaneously oxidize upon air exposure. The metallic character of the shell can however be recovered by annealing under reducing atmosphere and tracked through LSPR shifts [2]. The restructuring and the reduction of *In-Ag@In<sub>2</sub>O<sub>3</sub>* was also followed in real time by *in situ* HRTEM imaging in the presence of H<sub>2</sub> at high temperature. The resulting NPs after reduction consist of a silver-indium alloy, very stable and remarkably resistant against oxidation [3].



(a) Plausible evolution of the Ag–Fe NP structure under oxidizing and reducing environments. (b) Optical spectroscopy of In<sub>x</sub>Ag<sub>1-x</sub> NPs of varying composition and deposition conditions. The vertical lines show the LSPR wavelengths for pure In and Ag NPs in SiO<sub>2</sub>.

[1] J. Ramade et al., JPCC, 2019. 123(25), p. 15693-15706.

[2] E. Cottancin et al., PCCP, 2014. 16(12), p. 5763-5773.

[3] J. Ramade et al., Nanoscale, 2017. 9(36), p. 13563-13574.

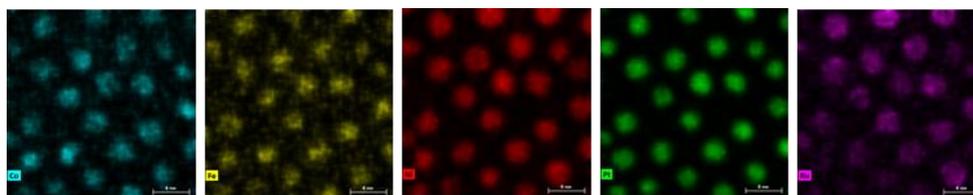
## Colloidal synthesis; from bimetallic nanoalloys to high entropy nanoalloys

Cora Moreira Da Silva<sup>1</sup>, Frédéric Fossard<sup>1</sup>, Armelle Girard<sup>1</sup>, Hakim Amara<sup>1</sup>, Vincent Huc<sup>2</sup>, Annick Loiseau<sup>1</sup>

<sup>1</sup>Laboratoire d'Etude des Microstructures (UMR 104)

<sup>2</sup>Institut de Chimie Moléculaire et des Matériaux d'Orsay, Université Paris Saclay

At the nanometric scale, the synthesis of an alloy (i.e. without phase segregation, whatever the composition) by chemical means remains a very difficult task. In this context, we propose a unique approach based on the colloidal route. This method allows the synthesis of face-centred and monodisperse cubic solid solution nanoparticles with diameters from 5.5 nm to 6.5 nm bimetallic, trimetallic, tetrametallic and pentametallic. Particles are prepared by co-reduction of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pt}^{2+}$  and  $\text{Ru}^{3+}$  precursors. This co-reduction, assisted by temperature, is carried out in the presence of surfactants (oleic acid and oleylamine). This chemical method is based on comparison between precursors' temperatures degradation and above all values of oxidation-reduction potentials of the metal cations used, which imposes different reduction kinetics for each element [1]. High entropy alloys are characterized by the presence of, at least, 5 elements in close equimolar proportion (between 5 and 35%) [2]. The first tests of tetrametallic and pentametallic particles synthesized are close to these criteria. By local chemical analysis we obtain:  $\text{Co}_{19}\text{Fe}_{12}\text{Ni}_{26}\text{Pt}_{43}$  for the tetrametallics. And, for HEA-NPs: Co ( $22 \pm 2$ ) at.%, Fe ( $12 \pm 2$ ) at.%, Ni ( $23 \pm 2$ ) at.%, Pt ( $37 \pm 2$ ) at.% and Ru ( $6 \pm 3$ ) at.% (see Figure). This synthesis route is therefore promising for obtaining HEA-NPs in a relatively simple way.



**HAADF-STEM coupled with EDX analysis images of Co-Fe-Ni-Pt-Ru nanoparticles with Co ( $K\alpha$  line) in blue, Fe ( $K\alpha$  line) in yellow, Ni ( $K\alpha$  line) in red, Pt ( $L\alpha$  line) in green and Ru ( $L\alpha$  line) in dark pink.**

[1] C. Moreira Da Silva et al., *Nanoscale Advances* 2, 3882-3889 (2020).

[2] Y. Yao et al., *Science* 359, 1489-1494 (2018).

# Core-shell clusters synthesized in helium droplets - structure, phase transitions, and optical resonances

Wolfgang E. Ernst, Florian Lackner, and Andreas W. Hauser

*Graz University of Technology, Institute of Experimental Physics, Petersgasse 16, 8010 Graz, Austria*

By doping superfluid droplets of  $10^6$  to  $10^{10}$  helium atoms ( $\text{He}_N$ ) with foreign atoms or molecules, cold complexes of atomic or molecular species are formed that can either be investigated by molecular beam spectroscopic methods or deposited on solid substrates for surface analysis [1]. In this way, large Cu, Ag, Au, Ni, Co, Fe, Pd, Cr, or  $\text{V}_2\text{O}_5$  aggregates of different morphology have been generated and deposited on solid carbon, h-BN, or SiN substrates. Employing different pick-up cells for doping the droplets, core-shell clusters of 3 to 6 nm diameter with one metal surrounding a core of a different species are produced. After surface deposition, the samples are removed and various measurement techniques are applied to characterize the created particles: scanning transmission electron microscopy at atomic resolution, electron tomography [2], temperature dependent STEM and TEM up to 1000 degree C, energy-dispersive x-ray spectroscopy (EDXS), electron energy loss spectroscopy (EELS) and optical absorption [3]. By varying the contents of different metals in core-shell particles, we can tune the plasmon resonance [4]. Special attention is given to the thermal properties of mixed metal clusters and questions about phase changes, alloy formation, and chemical reactivity on the nanoscale [5, 6, 7]. Experimental results are accompanied by theoretical approaches employing computational chemistry, molecular dynamics simulations and He density functional theory [1].

[1] W. E. Ernst and A. W. Hauser, *Phys. Chem. Chem. Phys.* online (2020).

[2] G. Haberfehlner et al., *Nature Communications* 6, 8779-1-6 (2015).

[3] A. Schiffmann et al., *J. Appl. Phys.* 125, 023104-1-8 (2019).

[4] F. Lackner et al., *Eur. Phys. J. D* 73, 104(2019).

[5] M. Lasserus et al., *Nanoscale* 10, 2017-2024 (2018).

[6] M. Schnedlitz et al., *ACS Chemistry of Materials* 30, 1113–1120 (2018).

[7] M. Schnedlitz et al., *J. Phys. Chem. C* 124, 30, 16680–16688 (2020).

# Geometries, stabilities, reactivities, and optical properties of palladium doped gold clusters

Piero Ferrari<sup>1</sup>, Heider A. Abdulhussein<sup>2</sup>, Jan Vanbuel<sup>1</sup>, Laia Delgado-Callico<sup>3</sup>, Andre Fielicke<sup>4</sup>, Roy L. Johnston<sup>2</sup>, Francesca Baletto<sup>3</sup>, Peter Lievens<sup>1</sup>, Joost M. Bakker<sup>5</sup>, Ewald Janssens<sup>1</sup>

<sup>1</sup>Quantum-Solid State Physics, KU Leuven, Belgium

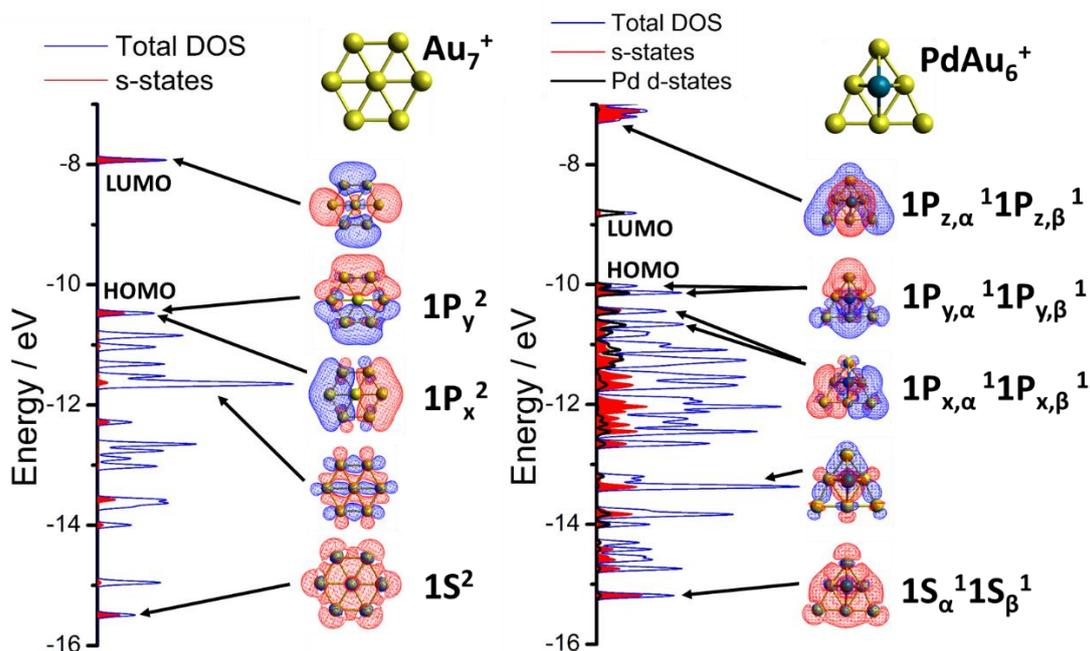
<sup>2</sup>School of Chemistry, University of Birmingham, UK

<sup>3</sup>Department of Physics, King's College London, UK

<sup>4</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

<sup>5</sup>FELIX Laboratory, The Netherlands

The unique characteristics of gold clusters and nanoparticles have received major attention in recent decades. The heavy Au atoms are subject to significant relativistic effects, resulting in a reduced valence s–d energy separation. Therefore, d-electrons are partially involved in most gold cluster properties. Heteroatom doping is known for affecting most chemical and physical properties of clusters [1]. The closed electronic configuration of the Pd atom ( $[\text{Kr}]4d^{10}$ ) makes its interaction with Au ( $[\text{Xe}]4f^{14}5d^{10}6s^1$ ) complicated but interesting. Depending on number of atoms, the Pd dopant can excite one of its d-electrons to a 5s level, making the electronic structure of Pd doped Au clusters very size-dependent and different from that of the pure Au clusters (see Figure). In this contribution, the strong effect of Pd doping on diverse physical and chemical properties of gold clusters cations is discussed, by combining different experimental approaches with density functional theory calculations. In particular, the geometries adopted by the clusters, their size-to-size stabilities [2], their reactivity towards carbon monoxide [3], and their optical absorption properties [4] are discussed in detail.



Comparison of the partial density of states of the clusters  $\text{Au}_7^+$  (left) and  $\text{PdAu}_6^+$  (right).

[1] P. Ferrari, J. Vanbuel, E. Janssens and P. Lievens, *Acc. Chem. Res.* 51, 3174–3182 (2018).

[2] P. Ferrari, H. A. Hussein, C. Heard, J. Vanbuel, R. L. Johnston, P. Lievens and E. Janssens, *Phys. Rev. A* 97, 052508 (2018).

[3] H. A. Hussein, P. Ferrari, J. Vanbuel, C. Heard, A. Fielicke, P. Lievens, E. Janssens and R. L. Johnston, *Nanoscale* 11, 16130–16141 (2019).

[4] V. Kaydashev, P. Ferrari, C. Heard, E. Janssens, R. L. Johnston and P. Lievens, *Part. Part. Syst. Charact.* 33, 364–372 (2016).

## Progress on the role of bismuth as a selectivity modifier in AuPd catalysts

Sebastiano Campisi<sup>1,\*</sup>, Sofia Capelli<sup>1</sup>, Nikolaos Dimitratos<sup>2</sup>, Ellie Dann<sup>3</sup>, Austin Wade<sup>4</sup>, Peter P. Wells<sup>3,5,6</sup> and Alberto Villa<sup>1</sup>

<sup>1</sup>*Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy*

<sup>2</sup>*Dipartimento di Chimica Industriale e dei Materiali, ALMA MATER STUDIORUM Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy*

<sup>3</sup>*School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK.*

<sup>4</sup>*Thermo Fisher Scientific, 5350 NW Dawson Creek Drive, Hillsboro, OR US*

<sup>5</sup>*UK Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Laboratory, Harwell Oxon, Didcot, OX11 0FA, United Kingdom*

<sup>6</sup>*Diamond Light Source Ltd., Harwell Science and Innovation Campus, Chilton, Didcot OX11 0DE, United Kingdom*

\*[sebastiano.campisi@unimi.it](mailto:sebastiano.campisi@unimi.it)

The use of promoters/modifiers is of topical interest in the field of heterogeneous catalysis and gaining insight on the origin of such effects allows to optimize catalyst design and, by implication, the catalytic performances [1-2]. This study aimed to unravel the role of bismuth as modifier of bimetallic well-defined Au-Pd nanoparticles supported on carbon, when used as catalysts for oxidation and hydrogenation reactions.

Cinnamyl alcohol and cinnamaldehyde were selected as model substrates offering the possibility to study the preferential oxidation of the C-OH, C=O, and preferential reduction of C=C, C=O functional groups, respectively. Actually, the presence of small amount of bismuth slightly depressed the catalytic activity but at the same time shifted the selectivity of AuPd nanoalloys in both hydrogenation and oxidation reactions, in agreement with previous reports [3].

The use of a combination of several characterization techniques (transmission electron microscopy, X-rays absorption spectroscopy) helped in determining some structure-activity relationships of trimetallic Au-Pd-Bi catalysts with respect to analogue Au-Pd catalysts. According to the experimental evidence, the modification of activity and selectivity observed for trimetallic AuPdBi catalysts could be ascribed to the presence of highly dispersed bismuth oxide phase in intimate contact with Au and Pd sites. In this view the action of bismuth might be explained in terms of blocking of the most active AuPd sites, resulting in a decrease of activity with simultaneous selectivity enhancement due to the minimization of side reactions.

However, a full understanding of the correlation between the structure of Bi-modified catalysts and the effects on the chemical reactions at their surfaces remains a major challenge. For these reasons further investigation is still required and in this view a perspective regarding more advanced ex situ and in situ technique will be offered.

[1] M. Besson and P. Gallezot, *Catal. Today* 57, 127–141 (2000).

[2] D. Ferri and A. Baiker, *Top. Catal.* 52, 1323–1333 (2009).

[3] N. Cherkasov, A. O. Ibhadon, A. J. McCue, J. A. Anderson and S. K. Johnston, *Appl. Catal. A Gen.* 497, 22–30 (2015).

## Accelerating prediction of chemical ordering in nanoalloys: augmented grouping approach

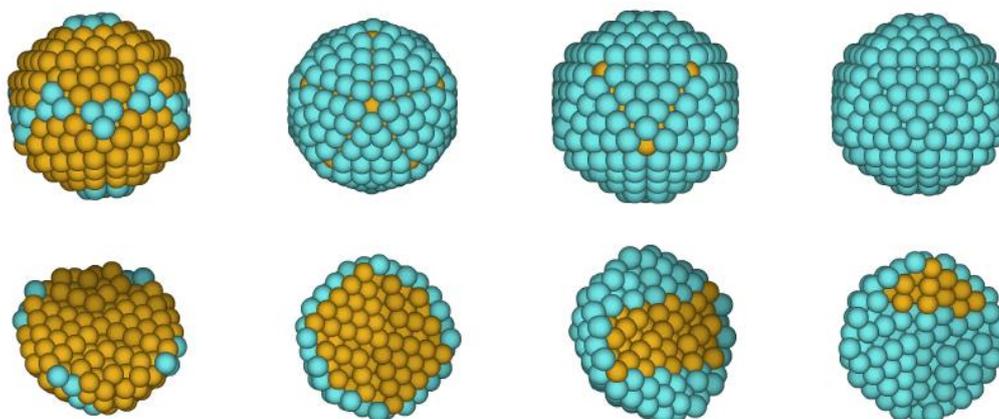
Alessandro Fortunelli<sup>\*</sup>, Giovanni Barcaro, and Davide Fioravanti

CNR-ICCOM & IPCF, via Giuseppe Moruzzi 1, 56124, Pisa, Italy  
<sup>\*</sup>alessandro.fortunelli@cnr.it

Control of structure and chemical ordering is a basic pre-requisite to exploit the many and fascinating properties of metallic nanoalloys. Computational modeling can provide important information in this respect, but its effectiveness is limited by the combinatorial number of possible isomers leading to a computational effort exponentially growing with the size of the nanoalloy. Structural and energetic descriptors are key quantities that can be used as guiding tools to explore/simplify the multi-dimensional PES (Potential Energy Surface) of these complex systems and are at the basis of modern ML (Machine Learning) codes.

In this work we show how the use of descriptors can be synergistically coupled to a Grouping scheme [1], a form of Coarse-Grained approach applied to the chemical ordering PES of nanoalloys, while keeping the full atomistic resolution.

Grouping has already proven to be a powerful tool for a fast and efficient screening of the different possible chemical ordering patterns in a binary alloy exhibiting a high geometrical symmetry. With respect to its first implementation [1], we introduce two important extensions: (i) the possibility of automatically tuning the grouping scheme using completely general structural or energetic descriptors chosen by the user; (ii) the extension of the approach to completely general structure thus not limited to high-symmetry motifs. We will present the application of the code to two prototypical nanoalloy systems: (i) PdPt, as an example of mixing tendency; (ii) AgCu, as an example of segregation tendency. Results (illustrated in the figure) point to new chemical ordering motifs in these systems.



**Evolution of chemical ordering in AgCu nanoalloys of  $\approx 500$  atoms as a function of the composition in anti-Mackay icosahedron**

[1] G. Barcaro, L. Sementa, A. Fortunelli, Phys. Chem. Chem. Phys. 16, 24256 (2014).

## Atomic layer deposition routes to tailor nanoalloys

Jolien Dendooven<sup>1</sup>, Ranjith Ramachandran<sup>1</sup>, Nithin Poonkottil<sup>1</sup>, Eduardo Solano<sup>2</sup>,  
Matthias Filez<sup>1</sup>, Matthias Minjauw<sup>1</sup>, Christophe Detavernier<sup>1</sup>

<sup>1</sup>*Ghent University, Dept. Solid State Sciences, COCOON group, Belgium*

<sup>2</sup>*ALBA Synchrotron Light Source, NCD-SWEET beamline, Spain*

Atomic Layer Deposition (ALD) uses alternate exposures to gas phase reactants to deposit material on a substrate. Because the reactants chemisorb on the surface via self-limiting gas-solid reactions, the amount of material being deposited is controllable at the (sub)monolayer level and is uniform onto 3D surfaces with large surface areas. ALD can be used for the preparation of size- and coverage-controlled noble metal nanoparticles (NPs) [1]. Bimetallic NPs of two noble metals, like Pt-Pd, Pt-Ru and Pd-Ru, can be achieved by leveraging the selective deposition of noble metals onto other noble metals [2]. Extensions of this approach to bimetallic NPs containing non-noble metals are scarce due to the difficulty to deposit non-noble metals in their elemental state. Here, we present two alternative ALD-strategies towards bimetallic NPs containing a non-noble metal next to a noble metal.

A first approach combines ALD with post-deposition annealing [3]. The deposition of an oxide thin film of the desired non-noble metal (e.g.  $\text{In}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{Fe}_2\text{O}_3$ ) is followed by the deposition of the noble metal (e.g. Pt). This bilayer is then subjected to a heat treatment under  $\text{H}_2$  atmosphere, which induces the reduction of the oxide film and subsequent alloying with the noble metal. ALD allows to precisely tune the individual noble metal and non-noble metal oxide layer thicknesses, thus offering excellent control over the composition of the formed bimetallics. In addition, the method enables tuning of the NP size from 1 to 30 nm by changing the total thickness of the bilayer.

A second approach combines ALD of noble metals with post-deposition vapour phase conversion into a bimetallic, without the need for a reduction step at high temperature. More specific, we report the vapour phase conversion of Pt NPs into Pt-Sn bimetallic NPs based on the selective decomposition of tetrakis(dimethylamido)tin, a common Sn ALD precursor, on Pt, which induces a solid-state reaction of metallic Sn with Pt to form nanoalloys at low temperature. The incorporation of Sn in the Pt NPs shows a saturating behavior as a function of the conversion process duration, while the amount of inserted Sn can be controlled via the deposition temperature. It is further shown that the small NP sizes, obtained via Pt ALD, are retained during the conversion process.

[1] Nat. Commun., 2017, 8, 1074.

[2] Nat. Commun., 2014, 5, 3264.

[3] ACS Nano, 2016, 10, 8770.

# Segregation in Au-Cu nanoparticles: a theoretical and experimental approach

Grégoire Breyton<sup>1,2</sup>, Damien Alloyeau<sup>3</sup>, Hakim Amara<sup>2</sup>, Jérôme Creuze<sup>4</sup>, Jaysen Nelayah<sup>3</sup>, Christian Ricolleau<sup>3</sup>, Guillaume Wang<sup>1</sup>

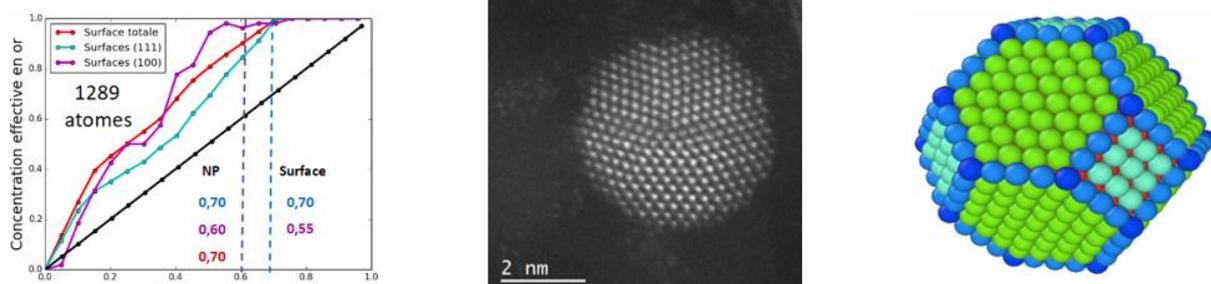
<sup>1</sup>MPQ, Université de Paris, France

<sup>2</sup>LEM, ONERA-CNRS, France

<sup>3</sup>Laboratoire Matériaux et Phénomènes Quantiques, Université de Paris, CNRS, F-75013, Paris

<sup>4</sup>ICMMO, Université Paris Saclay, France

Nanoparticles (NPs) are primarily known for their high surface to volume ratio making them perfect candidate as catalyst for reactivity process. Another attractive aspect of these nano-objects lies in the unexpected reactivity of some materials. For example, gold is known to be inert at bulk scale but very reactive in small sized nanoparticles (< 5 nm) for the CO to CO<sub>2</sub> transformation [1]. Interestingly, this phenomenon is enhanced by alloying gold with copper [2]. However, little is known on the surface structure of the Au-Cu alloy and more precisely of their surface composition which plays a crucial role during reactivity process. In this context, our work aims at characterizing the Au<sub>x</sub>Cu<sub>1-x</sub> nanoparticles structure in order to highlight surface segregations or not by using both a theoretical and experimental approaches. Atomic scale Monte Carlo simulations based on semi-empirical potential [3] have been performed (right figure). A strong segregation of gold over the entire surface is observed whatever the size of octahedron NPs (left figure). Simulations of nanocubes seem to strengthen these results where only (100) facets are present. Experimentally, octahedron NPs and nano-cubes have been synthesized by Pulsed Laser Deposition (PLD) on a substrate of NaCl. This substrate has a cubic structure which favors cubo-octaedron morphologies. Their chemical analysis and structural characterization on an aberration corrected JEOL ARM 200F in TEM and STEM modes are still ongoing (middle figure).



Left: Au segregation on nano-octahedron surface. Middle: HAADF image of Cu<sub>3</sub>Au. Right: Octahedron NP.

[1] Lopez Nuria et al. Journal of Catalysis 223.1 (2004): 232-235.

[2] Liu Xiaoyan et al. Catalysis Today 160.1 (2011): 103-108.

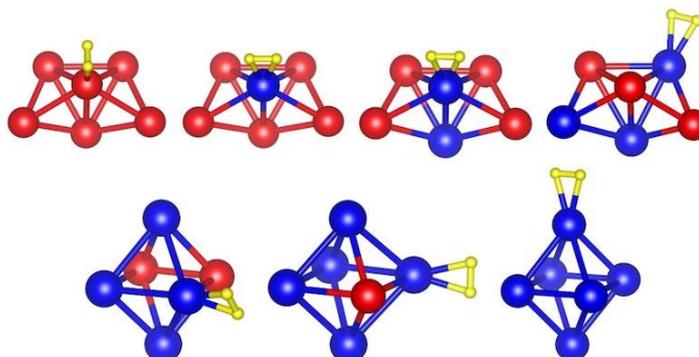
[3] Rosato Vittorio et al. Philosophical Magazine A 59.2 (1989): 321-336.

## Palladium-copper nanoalloys and their interaction with hydrogen

Estefania German, Alfonso Gomez Herranz, Julio A. Alonso, María J. López

*Departamento de Física Teórica, Atómica y Óptica, University of Valladolid, 47011 Valladolid, Spain*

Doping porous carbons with palladium nanoparticles is known to enhance the hydrogen storage capacity of these materials. Alloying palladium with the nonexpensive metal copper will reduce the cost of the nanoparticles. We have studied how alloying with copper affects the hydrogen adsorption properties of  $\text{Cu}_m\text{Pd}_n$  clusters with  $m+n = 6$ , using density functional theory and van der Waals corrections. Formation of  $\text{Cu}_m\text{Pd}_n$  nanoalloys is favorable, a fact consistent with the formation of bulk solid Cu-Pd alloys. Clusters rich in Pd, namely  $\text{Pd}_6$ ,  $\text{CuPd}_5$  and  $\text{Cu}_2\text{Pd}_4$ , preserve the octahedral structure of  $\text{Pd}_6$ . On the Cu rich side, the planar structure of  $\text{Cu}_6$  is not maintained, and  $\text{Cu}_5\text{Pd}$ ,  $\text{Cu}_4\text{Pd}_2$ , and also  $\text{Cu}_3\text{Pd}_3$ , adopt the structure of an incomplete pentagonal bipyramid. Clusters with even number of Cu atoms have zero spin magnetic moment. The magnetic moments of the other clusters are, in general, well localized on the Pd atoms. Molecular adsorption of  $\text{H}_2$  and dissociative chemisorption are both exothermic, and dissociative chemisorption is energetically favorable compared to molecular adsorption. The geometric structures of the  $\text{Cu}_m\text{Pd}_n$  clusters are maintained, in general, after molecular or dissociative adsorption of  $\text{H}_2$ , with very few exceptions. Adsorption binding energies on some alloy nanoclusters rich in Cu are higher than adsorption binding energies on  $\text{Pd}_6$ , so alloying with Cu may become a way to improve hydrogen adsorption in Pd-doped porous carbon materials.



**Lowest energy structures for  $\text{H}_2$  adsorbed on  $\text{Cu}_6$ ,  $\text{Cu}_5\text{Pd}$ ,  $\text{Cu}_4\text{Pd}_2$ ,  $\text{Cu}_3\text{Pd}_3$ ,  $\text{Cu}_2\text{Pd}_4$ ,  $\text{CuPd}_5$  and  $\text{Pd}_6$ . Red and blue spheres represent Cu and Pd atoms, respectively. Small yellow spheres represent H atoms.**

# Comprehensive modeling of Ir subsurface segregation & dimerization in Pd-Ir NPs

Micha Polak<sup>1</sup>, Leonid Rubinovich<sup>2</sup>

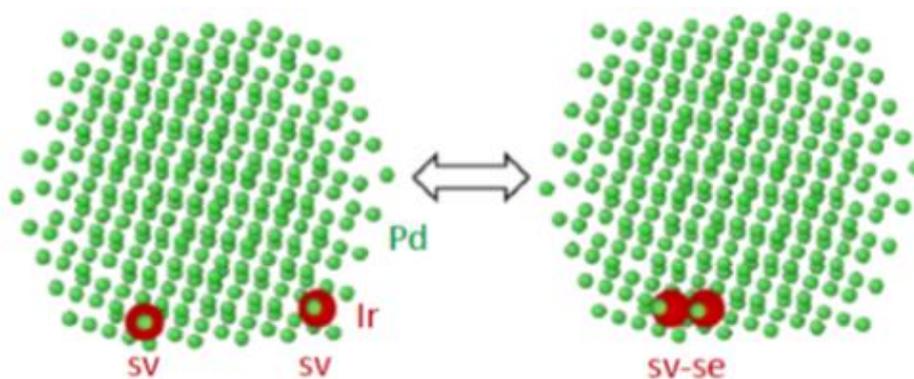
<sup>1</sup>Ben Gurion University of the Negev, Israel

<sup>2</sup>Department of Chemistry, Ben-Gurion University of the Negev

As shown by us some years ago [1], the participation of small numbers of molecules inside a closed reaction space can considerably affect chemical equilibrium. Thus, a significant enhancement of the reaction extent was predicted for exothermic reactions as compared to that of the corresponding macroscopic system (in the thermodynamic limit). Preliminary results of this “NanoConfinement Entropic effect on Chemical Equilibrium” (NCECE), were computed recently for Ir dimerization at certain subsurface sites of dilute Pd-Ir cuboctahedral (CO) nanoparticles (NPs) [2] using the lattice-gas model with elemental coordination-dependent bond-energy variations (CBEV) [3].

The present refined model allows computing Ir dimerization as well as segregation phenomena considering all types of inner core and subsurface sites. The exact statistical-mechanical partition function of the model NPs is computed using MATLAB while considering all possible dimerized and dissociated 2-atomic Ir configurations at the CO lattice (see Figure). Distinct temperature-dependent interplay and competition between the various equilibrated processes are predicted.

The revealed subsurface compositional variations are likely to affect catalytic properties of Pd-Ir nanoparticles, such as those operating in several applications. In this context, reported reactivity modifying ligand effects via hybridization of surface-atom d-states with subsurface atoms are likely to be pertinent.



**Illustration of  $2Ir^{sv} \rightleftharpoons Ir_2^{sv-se}$  equilibrated dimerization at energetically preferred subsurface sites of Pd surface-segregated 561-atom Pd-Ir cuboctahedron, namely at subvertexes (sv) and subedges (se).**

[1] M. Polak and L. Rubinovich, Nano Letters 8, 3543-3547 (2008).

[2] M. Polak M and L. Rubinovich, Int. J. Nanomater. Nanotechnol. Nanomed. 3, 23-26 (2017); L. Rubinovich and M. Polak, Topics in Catalysis 61, 1237-1246 (2018).

[3] L. Rubinovich and M. Polak, Phys. Rev. B 80, 045404 (2009).

## Thursday April 15, 2021

- 09:00 Size effect in the stability of PtAg nanoalloys: thermal activation and gas exposure  
*Pascal Andreatza (Université d'Orléans, France)*
- 09:25 Double doping and magnetic properties  
*Francesca Baletto (King's College London, UK)*
- 09:50 Nanocomposite magnet films of FePt integrating Co nanoclusters  
*Damien Le Roy (Université Claude Bernard Lyon 1, France)*
- 10:15 Growth and coalescence in composition tunable PtPd core-shell nanoalloys  
*Chloé Minnai (Okinawa Institute of Science and Technology Graduate University, Japan)*
- 10:30 Catalysis on alloy nanocrystallites and beyond  
*Sergey Kozlov (National University of Singapore, Singapore)*
- 10:45 Meet-the-speaker session
- 11:15 Poster session
- 13:00 Break
- 14:00 Networking session
- 14:30 Surface structure and segregation of nanoalloy catalysts probed by in situ and operando IR  
*Frederic C. Meunier (Université Claude Bernard Lyon 1, France)*
- 14:55 Structure-properties relationship and applications of nonequilibrium magnetic-plasmonic alloy nanoparticles obtained by laser ablation in liquid  
*Vincenzo Amendola (Università degli Studi di Padova, Italy)*
- 15:20 Chemical composition quantification of AgAu bimetallic nanoparticles: evidence of Ag enrichment in the surface  
*Murilo Moreira (Universidade Estadual de Campinas-UNICAMP, Brazil)*
- 15:35 Role of bimetallic Au-Ir subnanometer clusters mediating O<sub>2</sub> adsorption and dissociation on anatase TiO<sub>2</sub>(101)  
*Fernando Buendia-Zamudio (Universidad Nacional Autónoma de México, México)*
- 15:50 Meet-the-speaker session
- 16:20 End of scientific session

# Size effect in the stability of PtAg nanoalloys: thermal activation and gas exposure

P. Andreazza<sup>1,\*</sup>, J. Pirart<sup>1</sup>, M. Haroune<sup>1</sup>, A. Front<sup>2</sup>, D. Rappetti<sup>3</sup>, M. Jankowski<sup>4</sup>, R. Felici<sup>5</sup>, R. Ferrando<sup>3</sup>, C. Mottet<sup>2</sup>, C. Andreazza-Vignolle<sup>1</sup>

<sup>1</sup>Université d'Orléans, CNRS, ICMN UMR7374, 1b rue de la Férellerie, Orléans Cedex 2, France

<sup>2</sup>Aix-Marseille University, CNRS, CINaM, Campus de Luminy, Marseille Cedex 9, France

<sup>3</sup>Physics Department, University of Genoa, Via Dodecaneso, Genoa, Italy

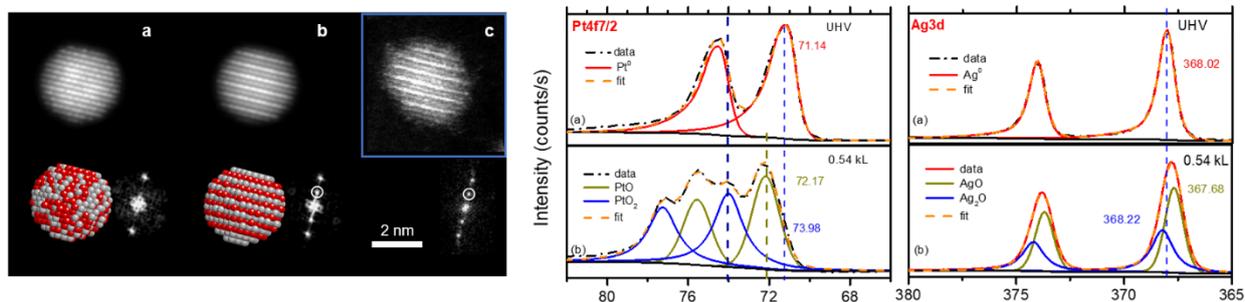
<sup>4</sup>ESRF, Grenoble, France, 5 CNR, Spin Institute, Tor Vergata, Italy

\*pascal.andreazza@univ-orleans.fr

The growth of nanoscale objects on a surface is a growing field of activity in the field of nano-objects. Among the methods, the technique of supported nanoalloy fabrication by condensation of metal atom vapors under ultra-high vacuum makes it possible to control the parameters of temperature and flow of atoms (and therefore of composition and size) in “ultra-clean” environmental conditions. However, these nano-objects are produced out of equilibrium, stabilized by the growth kinetics and/or by the presence of the substrate. They then change over time, with the temperature or their exposure to reactive gases. The morphologies (faceting of nanocrystals, wetting on a substrate), order states (atom arrangement: alloyed, segregated, ordered or disordered) or oxidation are in particular very dependent on the kind of atoms but also on the size of nanoalloys.

Macroscopic Pt-Ag alloy shows an interesting but complex phase diagram [1] especially at low temperature: an ordered alloy  $L1_1$  (alternative planes of Ag and Pt in the [111] direction) is formed only at the equi-stoichiometry of Ag-Pt, and a large miscibility gap outside this composition. At small size, the quasi-equiatomic composition is associated to an alloy phase  $L1_1$  with an important rhomboedral deformation and the Ag surface shell formation. However, an unexpected size behavior is observed which inhibits the  $L1_1$  structure stability as the size increase [2], due to a stress accumulation between the core and the shell increasing in larger objects (above 2.5 nm of domain size).

The coupling of in situ techniques of transmission electron microscopy (HRTEM, HAADF), grazing incidence small and wide angle X-ray scattering (GISAXS, GIWAXS), and X-ray photoelectron spectrometry (XPS) made it possible to follow the evolution of the structure of nanoparticles with the temperature and the mobility of atoms inside the particles and on the surface of the substrate, and upon exposure to a reactive gas such as oxygen or CO.



**STEM HAADF image of disordered a) and ordered  $L1_1$  b-c) PtAg nanoparticle and XPS spectra evolution during atomic O exposure.**

[1] G. L.W.Hart, et al. Acta Materialia 124 (2017) 325.

[2] J. Pirart, A. Front, D. Rappetti, C. Andreazza, P. Andreazza, C. Mottet, R. Ferrando, Nature. Comm. 10 (2019) 198.

## Double doping and magnetic properties

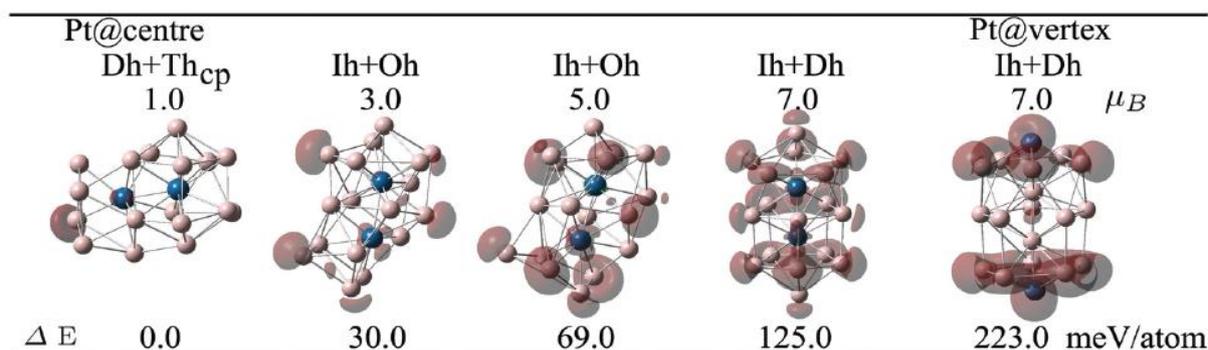
Francesca Baletto<sup>1,\*</sup>, Omar Lopez-Estrada<sup>1,2</sup>, Cono Di Paola<sup>1</sup>

<sup>1</sup>Physics Dept., King's College London, WC2R 2LS, London, UK

<sup>2</sup>Departamento de Física y Química, UNAM, Mexico D.F., Mexico

\*francesca.baletto@kcl.ac.uk

We investigate the effect of double-doping ( $X_2$ ) into a  $M_{19}$  metallic cluster, exhibiting a double-icosahedron. We consider M among common magnetic materials (Fe, Co, Ni, Pt) [1] and Al and a double impurity of Ni and Pt [2]. In CoFe, the most favourable substitutional sites are those which maximise the total magnetic moment of the system: Fe dopants tend to occupy surface sites while Co atoms stay in the inner. For all the other nanoalloys, the doping sites respect a chemical order that leads to a surface energy minimization often followed by a depression of the total magnetization. However, a ferromagnetic order is likely to be observed. Through ab-initio molecular dynamics, we analyse the dynamical behavior of  $Al_{17}X_2$  at finite temperatures. We observe that the 5-fold symmetry axis is usually preserved at 100 K, but a few dynamical structural transformations take place towards three new architectures characterized by a different piling of the pentagon rings around the 5-fold axis. A depletion of the total magnetisation occurs when the surface is delimited by (100) facets, or by distorted (100) facets, associated with the appearance of an antiferromagnetic ordering.



Isomers relaxed at the PBE/SDecp theory level as obtained during BOMD simulations for Pt@centre and Pt@vertex. Total magnetisation (in  $\mu_B$ ), spin densities isosurfaces (isosurface value at  $0.004 \text{ a.u.}^{-3}$ ) and the energy difference (in meV per atom) with respect to the lowest energy isomer listed. Isomer identified on the basis of the subclusters they formed by, Dh is a decahedron of 13 atoms, Ih is an icosahedron of 13 atoms, Oh an octahedron of 6 atoms, and a capped tetrahedron (Th<sub>cp</sub>).

[1] C. Di Paola and F. Baletto, Eur. Phys. J. D (2013) 67: 49.

[2] O. Lopez-Estrada, E. Orgaz and F. Baletto, J. Mater. Chem. C (2020) 8:2533.

# Nanocomposite magnet films of FePt integrating Co nanoclusters

Damien Le Roy<sup>\*</sup>, Charles Paléo, Véronique Dupuis, Clément Albin, Olivier Boisron

*Institut Lumière Matière, Université Claude Bernard Lyon 1, CNRS, Villeurbanne F-69622, France*  
*\*damien.le-roy@univ-lyon1.fr*

Hard magnetic nanocomposites, consisting of a fine mixture between a large magneto crystalline anisotropy phase and a large magnetization phase, are attractive materials for both for integration of hardness-tuned magnets in microsystems and for building next-generation high performance permanent magnets for energy conversion technologies. Theoretical descriptions predicted a potential energy product as high as  $1 \text{ MJ/m}^3$  [1], provided nano-sized softer grains to preserve high enough coercivity. As standard synthesis methods of bulk magnets do not allow such control over the microstructure, model systems in films can give insights about the interplay between the nanoscale microstructure and the magnetic properties [2]. In particular, the degree of interdiffusion at the soft-hard interface is expected to significantly impact the magnetization reversal but is difficult to address experimentally.

To do so, we prepared Co@FePt transition metal-based nanocomposite (NC) films from mass-selected low energy cluster beam deposition technique (MS-LECBD) of Co clusters, in situ embedded in FePt matrix independently produced by alternative electron gun evaporation on the same substrate [3,4]. The Co nanocluster inclusions can be selected in size prior to their deposition, between 1 and 10 nm. The cluster to matrix volume ratio is adjusted controlling the thickness of each Co, Fe, Pt individual layers. We systematically compared the nanoclusters-based film with same stoichiometry and fully alloyed films (NF). Chemical profiles and structure were investigated using polarization-dependent hard x-ray absorption and element-specific spectroscopies (EXAFS, XLD). Transmission electron microscopy (TEM) equipped with energy-dispersive X-ray spectroscopy (EDX) was used to explore the local chemical profile of the composite films. Magnetic properties were characterized in a Superconducting quantum interference device (SQUID) magnetometer together with local and element specific characterizations using circular dichroism (XMCD). We demonstrate the persistence of soft and hard regions and rule out the fully diluted hypothesis. Using a combinatorial approach, we investigated the coercive magnetic field decay when increasing the Co content. Studying these materials in model systems synthesised by nanofabrication routes provides interesting insights in view to develop mass-scale production of such materials.

This work is supported by the ANR collaborative project "SHAMAN" (2018-2021).

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[2] Balasubramanian B. et al, Scientific reports 4, 6265 (2014).

[3] Tournus F. et al, J. Magn. Magn. Mater., vol. 323, p. 1868 (2011).

[4] Paleo C. et al, Phys. Rev. B 102 (22), 224409 (2020).

# Growth and coalescence in composition tunable PtPd core-shell nanoalloys

Chloé Minnai<sup>1,\*</sup>, Diana Nelli<sup>2</sup> and Riccardo Ferrando<sup>2</sup>

<sup>1</sup>*Molecular Cryo-Electron Microscopy Unit, Okinawa Institute of Science and Technology Graduate University, 1919-1 Tancha, Onna-son, Kunigami-gun, Okinawa, Japan 904-0495.*

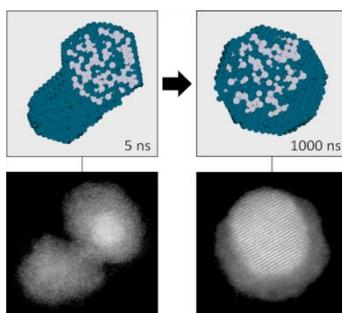
<sup>2</sup>*Dipartimento di Fisica dell'Università di Genova, via Dodecaneso 33, Genova 16146, Italy.*

\**chloe.minnai@oist.jp*

Coalescence is a phenomenon in which two or more nanoparticles merge to form a single larger aggregate. Here Pt-Pd nanoparticles are grown in the gas phase by a magnetron sputtering source and characterized by HRTEM/STEM and EDX techniques for both Pt-rich and Pd-rich compositions of the metallic vapor. The experimental results are rationalized with molecular dynamic growth simulations. Here we present two main results.

(i) This growth procedure can produce in a single step different types of core-shell nanoparticles which present intermixed cores containing both Pt and Pd, and shells made of the majority element, i.e. of (PtPd)@Pt structure for the Pt-rich vapor and (PtPd)@Pd structure for the Pd-rich vapor. Global searches of the optimal chemical ordering show that none of these structures correspond to equilibrium configurations. On the contrary, these core-shell structures are strongly out-of-equilibrium, being the result of kinetic trapping phenomena. This is verified by molecular dynamics growth simulations which can reproduce both the different types of chemical ordering and the variety of geometric shapes found in the experiments [1].

(ii) The degree of coalescence can be tuned from a growth regime in which coalescence is negligible to a regime where the growth outcome is dominated by coalescence events. This transition is achieved by varying both the length of the aggregation zone and the pressure difference between the aggregation and the deposition chamber. In the coalescence-dominated regime, a wide variety of coalescing aggregates is produced. With Molecular-Dynamics simulations we could distinguish four different steps through which coalescence proceeds towards equilibrium. These steps, occurring on a hierarchy of well-separated time scales, consist in: (i) alignment of atomic columns; (ii) alignment of close-packed atomic planes; (iii) equilibration of shape; (iv) equilibration of chemical ordering [2].



**Combined theoretical and experimental investigations of Pt–Pd nanoalloys grown by magnetron sputtering in the gas phase show that the coalescence degree can be controlled and unravel the key atomic-level mechanisms.**

[1] D. Nelli, A. Krishnadas, R. Ferrando and C. Minnai, JPC 124, 14338–14349 (2020).

[2] D. Nelli, M. Cerbelaud, R. Ferrando, C. Minnai. Nanoscale Adv. 3, 836-846 (2021).

# Catalysis on alloy nanocrystallites and beyond

Sergey Kozlov and Uzma Anjum

*National University of Singapore*

Alloying has been one of the most successful strategies for the development of new heterogeneous catalysts. However, the rational design of the nanoalloy catalysts is complicated by the strong dependency of the catalytic activity on the alloy surface composition, which needs to be characterized with atomic resolution. On the other hand, alloy particles in many catalytic applications are crystalline, which simplifies their structural analysis. Whereas 3D characterization of nanoalloy structure remains challenging, the relative arrangement of alloy components within the lattice of such nanocrystallites (i.e. their chemical ordering) can be determined with a high degree of accuracy based on density functional simulations [1]. Once the chemical ordering in alloy nanocrystallite is determined, the catalytic properties of the nanoalloy can be simulated using well-established density functional methods.

In this talk, I will outline recent studies of nanocrystalline alloy catalysts such as Pd-Zn, Cu-Zn, and Ni-Mo [2]. Despite that some of these nanoalloys exhibit core-shell structures and others have both elements present on the surface, all these materials exhibit surface sites with notably diverse reactivities. Moreover, the surface composition of the nanoalloy with a given bulk composition may change with the nanoparticle size, which will affect the properties of the catalyst in a complex manner.

Finally, some alloys may partially oxidize under reaction conditions, which will result in the complete transformation of their catalytic properties. For example, Ni-Mo nanoalloys were shown to develop MoO<sub>x</sub> films on their surface during electrochemical hydrogen evolution reaction. Due to the electron transfer from Ni-Mo alloys, the supported oxide films feature Mo sites in an unusual 3+ charge state. Curiously, the hydrogen evolution activity of Mo<sup>3+</sup> centers is much higher than the activity of pristine Ni-Mo nanoalloy. Thus, nanoalloys may not only be used as promising catalysts but also serve as precursors for the synthesis of complex nanocomposite catalysts with unique properties.

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# Surface structure and segregation of nanoalloy catalysts probed by in situ and operando IR

Frederic C. Meunier\*

Univ Lyon, Université Claude Bernard Lyon, CNRS, IRCELYON, 2 Av. Albert Einstein, 69626  
Villeurbanne, France.

\*fcm@ircelyon.univ-lyon1.fr

Characterizing the surface of supported nanoalloys is not trivial, especially under conditions relevant to catalytic reactions. Examples are given here of reactions involving CO that offer unique opportunities to probe the nanoalloy surface by IR spectroscopy under reaction (*operando*) conditions, in addition to traditional *in situ* studies using CO adsorption.

Alloyed nanoparticles (e.g. Au-Ag, Au-Pt, Pt-Ag, Pt-Sn, Pd-Sn, Pd-Zn, Co-Sn) were supported over standard supports (e.g. silica, alumina, ceria), as well as being embedded inside the mesopores of single-hollow [1] or multi-hollow zeolites [2].

Au, Ag and Au-Ag alloy nanoparticles were embedded in silicalite-1 multi-hollow single crystals [2]. Au and Au-Ag nanoparticles exhibited similar activity for CO oxidation at room temperature. *Operando* diffuse reflectance FT-IR spectroscopy (DRIFTS) revealed the presence of both metals at the surface of the Au-Ag particles, Ag replacing a large fraction of the Au atoms otherwise located at low coordination sites.

The structure of alumina-supported Pt, Au and Au-Pt nanoparticles were investigated by TEM, XRD and CO adsorption monitored by DRIFTS. The DRIFTS interpretation was hampered by the restructuring of Au in the presence of CO, leading to bands similar to those observed on Pt [3]. The kinetics of CO desorption enabled highlighting alloyed phases: Pt-CO were stable at 50°C in He, while CO readily desorbed from Au. Au-Pt samples exhibited complex intermediate behaviors, suggesting surface segregation during the course of desorption.

The formation of intermetallic compounds by combining noble metals such as Pt and Pd with base metals such as Zn and Sn has often been used to modify catalytic properties. The benefits of these alloying in terms of geometric and electronic effects will be discussed for Pd-Sn [4], Pd-Zn [5], Co-Sn [6] and Pt-Sn [7].

Interestingly, several modes of segregation have been observed over Pt-Sn. The oxidation of Sn by O<sub>2</sub> during the preferential oxidation of CO in the presence of large excess of H<sub>2</sub> has been observed, leading to segregated Pt and SnO<sub>x</sub> phases [8]. CO was shown to trigger a similar phase segregation, when dissociating to C and O under specific conditions [9] and also led to surface segregation in Sn-rich samples by pulling more Pt to the surface [10].

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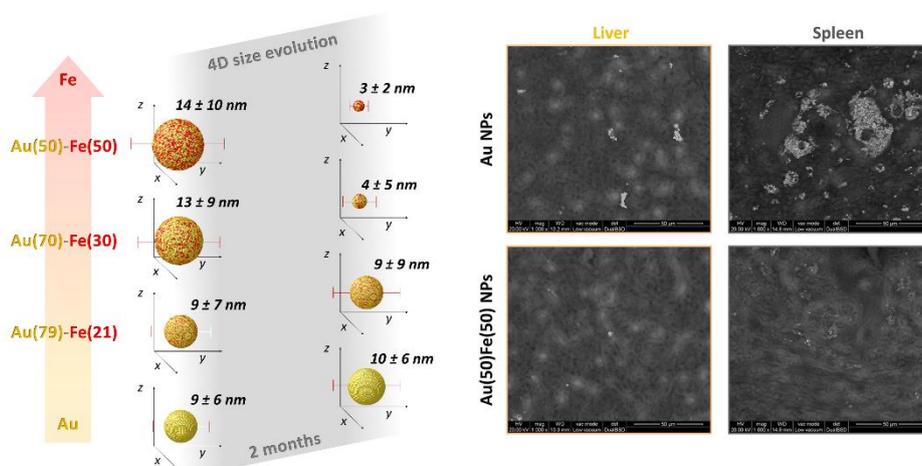
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# Structure-properties relationship and applications of nonequilibrium magnetic-plasmonic alloy nanoparticles obtained by laser ablation in liquid

Vincenzo Amendola\*

Department of Chemical Sciences, University of Padova, via Marzolo 1, 35131, Padova, Italy  
\*vincenzo.amendola@unipd.it

Alloy nanoparticles containing noble and transition metals are appealing for a series of applications and fundamental studies in catalysis, optics and nanomedicine. However, thermodynamics is unfavourable to the largest part of these alloys, which can be realized only by non-equilibrium routes. To this end, we demonstrated that laser ablation in liquid (LAL) is a powerful technique for the synthesis of metal alloys with thermodynamically forbidden composition. The resulting nanoalloys, endowed with both plasmonic and magnetic properties, offered the opportunity to verify the deep modification of the electronic and chemical structure due to alloying, with a strong effect on the localized surface plasmon resonance [1]. Besides, the structural integrity of the nanoalloys in various environments, such as aqueous or physiological solutions, resulted to be dramatically dependent on the composition (see figure). This was exploited in nanomedicine, by obtaining a 4-D multimodal contrast agent with enhanced clearance from the body compared to the corresponding single element nanoparticles [2]. More innovative results and functional optimization are expected by the synergy between LAL synthetic procedures, structural modeling, and experimental verification of functional properties in nonequilibrium nanoalloys.



Sketch of the 4-D size evolution in Au-Fe nanoalloys (left) and clearance of the Au(50)Fe(50) nanoparticles from the liver and spleen of mice after 60 days, compared to pure Au nanoparticles (right).

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# Chemical composition quantification of AgAu bimetallic nanoparticles: evidence of Ag enrichment in the surface

Murilo Moreira<sup>1,2,\*</sup>, Varlei Rodrigues<sup>1</sup>, Matthias Hillenkamp<sup>2</sup> and Daniel Ugarte<sup>1</sup>

<sup>1</sup>*Instituto de Física “Gleb Wataghin”, Universidade Estadual de Campinas-UNICAMP, CEP 13083-859, Campinas - SP, Brazil*

<sup>2</sup>*Institute of Light and Matter, University Lyon, Université Claude Bernard Lyon 1, CNRS, UMR5306, F-69622 Villeurbanne, France*

\**moreiraz@ifi.unicamp.br*

Bimetallic nanoparticles (BNPs) are systems formed by two metals, which can display different types of structures and adopt different morphologies with atomic mixing or segregation. By controlling the size and chemical composition, different physical and chemical properties can be obtained due to quantum and surface-induced phenomena. Thus, it is of interest to establish reliable methods for the characterization of not only the size and crystalline structure but also the chemical composition of small alloy NPs (sub-10 nm), if possible on the single particle level. Here we demonstrate the quantitative chemical characterization of benchmark Ag/Au BNPs using Energy-dispersive X-ray Spectroscopy (EDS) combined with Scanning Transmission Electron Microscope (STEM).

In this study, we have generated surfactant-free NPs in the range of 3-9 nm in diameter by means of a gas aggregation source using a cylindrical magnetron [1]. The NP chemical composition is defined by an appropriate choice of the axial sputtering target formed by twisted metallic wires. Three samples of AgAu BNPs were prepared and about 50 NPs of each sample measured individually. The average Au concentration values were  $(76 \pm 3) \%$ ,  $(54 \pm 4) \%$ , and  $(49 \pm 2) \%$ . In particular, we have optimized experimental conditions to improve quantitative chemical results; composition ratios were calculated using the traditional Cliff-Lorimer method. The EDS image-spectra were treated using semi-automatic image processing and noise reduction approaches such as principal component analysis (PCA) [2].

Preliminary results suggest a size-dependent composition variation with Au depletion for particles smaller than 4 nm. Additionally, retrieving NP information from selected pixels from the core and the surface independently, Ag enrichment in the surface is evidenced. This silver segregation to the surface can be attributed to differences in surface energy [3] or to the higher reactivity towards oxygen [4]. These results thus demonstrate the possibility of quantifying the chemical composition of small bimetallic nanoparticles on the single particle level and open the way for further studies concerning segregation effects or chemical reactivity.

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## Role of bimetallic Au-Ir subnanometer clusters mediating O<sub>2</sub> adsorption and dissociation on anatase TiO<sub>2</sub>(101)

Fernando Buendia-Zamudio<sup>1</sup>, Lauro Oliver Paz-Borbón<sup>2</sup>, Jorge Fabila<sup>1</sup> and Dario Romero<sup>1</sup>

<sup>1</sup>*Institute of Physics, UNAM*

<sup>2</sup>*Universidad Nacional Autónoma de México*

A comprehensive, computational study on the oxygen molecule (O<sub>2</sub>) activation and dissociation on bimetallic Au-Ir subnanometer clusters supported on TiO<sub>2</sub>(101) - up to 5 atoms in size - is performed. A global optimization DFT-based Basin Hopping algorithm is used to determine putative global minima (GM) configurations of both mono- and bimetallic clusters supported on the metal oxide surface, for all sizes and compositions. Our results indicate a strong cluster-oxide interaction for mono-metallic Ir clusters, with calculated adsorption energy (E<sub>ads</sub>) values ranging from 2.53 up to 4.66 eV. Similar values are calculated for bimetallic Au-Ir clusters (2.35 up to 4.71 eV). However, weaker E<sub>ads</sub> values are calculated for Au clusters (ranging from 0.44 up to 1.36 eV). The inclusion of advanced vdW corrections - via the Tkatchenko-Scheffler method with an iterative Hirshfeld approach - systematically increase the calculated E<sub>ads</sub> values. As a general trend, we demonstrate that for supported Au-Ir clusters on TiO<sub>2</sub>(101), those Ir atoms preferentially occupy cluster-oxide interface positions while acting as anchor sites for the Au atoms. The overall geometric arrangements of the putative global minima configurations define O<sub>2</sub> adsorption and dissociation, particularly involving the mono-metallic Au<sub>5</sub>, Ir<sub>5</sub>, as well as the bimetallic Au<sub>2</sub>Ir<sub>3</sub> and Au<sub>3</sub>Ir<sub>2</sub> supported clusters. Spontaneous O<sub>2</sub> dissociation is observed on both Ir<sub>5</sub> and on the Ir-metallic part of Au<sub>3</sub>Ir<sub>2</sub> and Au<sub>2</sub>Ir<sub>3</sub> supported clusters. This is in sharp contrast with supported Au<sub>5</sub>, where a large activation energy is needed (1.90 eV). Interestingly, for Au<sub>5</sub> we observe that molecular O<sub>2</sub> adsorption is favorable at the cluster/oxide interface, followed by a smaller dissociation barrier (0.71 eV). From a single-cluster catalysis (SCC) point of view, our results have strong implications in the ongoing understanding of oxide supported bimetallic, while providing useful insights for the continuous in-silico design of novel sub-nanometer catalysts.

## Friday April 16, 2021

- 09:00 Nano-objects: growth mechanisms and electronic properties  
*Magali Benoit (Center for Materials Elaboration and Structural Studies, Toulouse, France)*
- 09:25 Design of methanol oxidation catalysts based on gas-phase (bi)metallic clusters  
*Didier Grandjean (KU Leuven, Belgium)*
- 09:50 Morphological transition of spherical (bi-)metallic nanoparticles to nanorods  
*Arthur Moisset (Sorbonne Université, France)*
- 10:15 Combining numerical and experimental approaches to study the substrate effect on the structure and the aspect ratio of supported metallic NPs: system Ag/Pt on silica  
*Fatima Ait Hellal (Université d'Orléans, France)*
- 10:30 Nanoalloying Pt with Ge to obtain highly selective catalysts  
*Elisa Jimenez-Izal (Euskal Herriko Unibertsitatea UPV/EHU & Donostia International Physics Center, Spain)*
- 10:45 Meet-the-speaker session
- 11:15 Surface modification of photocatalysts with bimetallic nanoparticles for water treatment and hydrogen generation  
*Hynd Remita (Université Paris-Saclay, France)*
- 11:40 Role of conjugation in ligand-metal interaction in nanoalloys or clusters and limits of simplified ligand modeling  
*Hans-Christian Weissker (Aix-Marseille Université, France)*
- 11:55 Epitaxial growth of a gold shell on intermetallic FeRh nanocrystals for biomedical applications  
*Patrizio Benzo (CEMES-CNRS and Université de Toulouse, France)*
- 12:10 How doping modifies NO adsorption onto group IX transition metal clusters  
*Joost Bakker (Radboud University, The Netherlands)*
- 12:25 Meet-the-speaker session
- 13:00 Closing
- 13:30 End of scientific session
- 14:30 Round-table IRN members
- 16:00 End of round-table IRN members

# Nano-objects: growth mechanisms and electronic properties

Magali Benoit<sup>1</sup>, Julien Lam<sup>1</sup>, Florent Calvo<sup>2</sup>, Ségolène Combettes<sup>1</sup>, Patrizio Benzo<sup>1</sup>, Nathalie Tarrat<sup>1</sup>, Anne Ponchet<sup>1</sup>, Marie-José Casanove<sup>1</sup>, Joël Puibasset<sup>3</sup>, Hilal Balout<sup>1</sup>

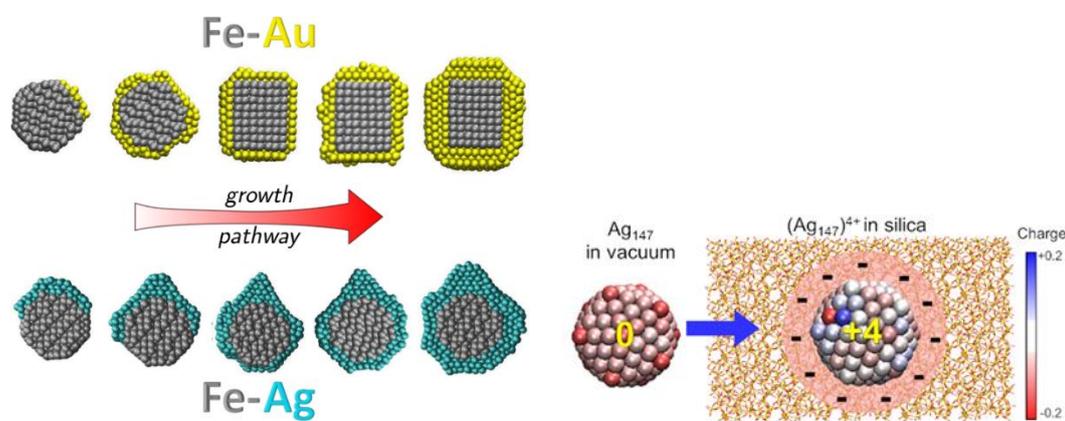
<sup>1</sup>CEMES-CNRS, France

<sup>2</sup>LiPhy - Université de Grenoble, France

<sup>3</sup>ICMN Université Orléans, France

The Surface, Interface and Nano-object (SINanO) group at CEMES (Toulouse) conducts a multidisciplinary research (physics, chemistry, biology) devoted to the growth and the study of the structural, physical and chemical properties of i) surfaces and interfaces, ii) nano-objects and iii) their interactions with atoms or molecules (adsorption, self-organization, ligand-driven growth and functionalization). Our research is fundamental, but often addresses functional devices or materials that aim to become functional, such as lasers, devices for spintronics or nanoparticles for hyperthermia or antibiotic therapy, for example. An originality of the SINanO group is to combine experimental and theoretical approaches on a large number of topics.

In this context, I will present two examples of recent investigations conducted in our group. The first one concerns the Fe@Au and Fe@Ag core-shell nanoparticles for which we propose a model explaining their evolving morphologies during growth [1,2,3]. I will show how the combination of theory, multi-scale simulations and experiments can help understanding the atomistic mechanisms at play in the formation and morphologies of these nano-objects. The second one deals with the electronic depletion undergone by Ag nanoparticles when they are embedded in a silica matrix [4,5].



**Left: evolution of the morphology of Fe@Au(Ag) nanoparticles as a function of Au(Ag) shell volume. Right: Charge variation of Ag<sub>147</sub> due to the surrounding silica matrix.**

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# Design of methanol oxidation catalysts based on gas-phase (bi)metallic clusters

Didier Grandjean\*

*Quantum Solid-State Physics, Department of Physics and Astronomy, KU Leuven, Celestijnenlaan 200D, Leuven 3001, Belgium*

*\*didier.grandjean@kuleuven.be*

We present an original approach to design methanol oxidation (electro)catalysts based on the production of well-defined gas-phase mono- and bi-metallic clusters by Cluster Beam deposition (CBD) characterized by a combination of High-Angle Annular Dark Field - Scanning Transition Electron Microscopy (HAADF-STEM), X-ray Photoelectron Spectroscopy (XPS) and X-ray Absorption Fine Structure (EXAFS) spectroscopy, assisted by Density Functional Theory (DFT) modeling.

Size-selected Au clusters dispersed on a conducting fluorine-doped tin oxide (FTO) show a strong enhancement in mass activity for the methanol electro-oxidation due to a high density of exposed under-coordinated Au atoms at the surface of the faceted Au NCs [1]. In AuAg bimetallic clusters a composition-tunable chemical arrangement showing an inversion of chemical ordering by going from Au-rich to Ag-rich compositions with the minority element always occupying the nanoparticle core is rationalized in terms of a four-step growth process of a general character [2]. Finally PtNi bimetallic clusters on inert flat oxides whose atomic architecture results from a similar growth model as in the AuAg system, present a low temperature methanol dehydrogenation catalytic activity attributed to the formation of a skin of Pt atoms with d-band centres downshifted by subsurface Ni atoms that weakens the CO interaction [3]. These results highlight the benefits of using CBD-based approach in fine-tuning material properties on the nanoscale and designing high-performance catalysts.

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# Morphological transition of spherical (bi-)metallic nanoparticles to nanorods

Arthur Moisset<sup>1</sup>, Alexandre Sodreau<sup>2</sup>, Anthony Vivien<sup>1,2</sup>, Caroline Salzemann<sup>1</sup>, Pascal Andreazza<sup>3</sup>, Suzanne Giorgio<sup>4</sup>, Marc Petit<sup>2</sup> and Christophe Petit<sup>1</sup>

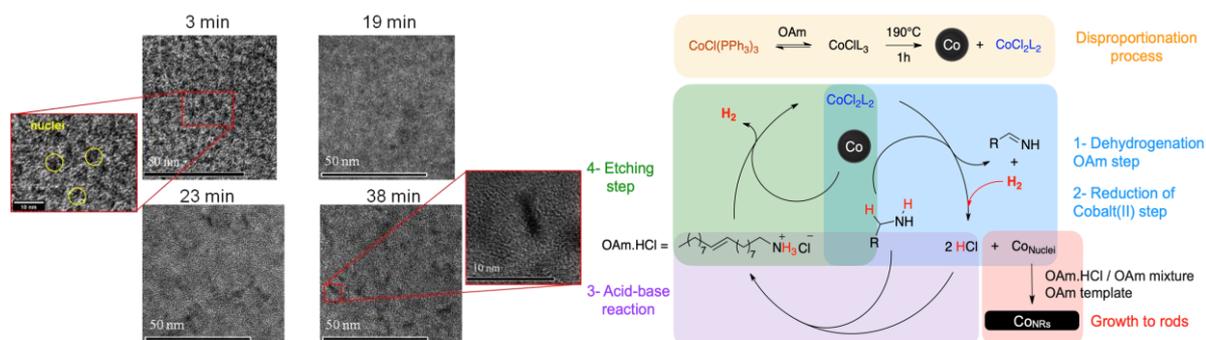
<sup>1</sup>Sorbonne Université, CNRS, MONARIS, UMR 8233, 75005 Paris, France

<sup>2</sup>Sorbonne Université, CNRS, Institut Parisien de Chimie moléculaire, UMR 8232, 75005 Paris, France

<sup>3</sup>Université d'Orléans, CNRS, Interfaces Confinement Matériaux et Nanostructures, UMR 7374, 45100 Orléans, France

<sup>4</sup>Université d'Aix-Marseille, CINAM, Centre Interdisciplinaire de Nanoscience de Marseille, UMR 7325, 13288 Marseille, France

Understanding of cobalt nanorods (Co NRs) formation still remains challenging it comes to enhancing their anisotropic properties applicable in magnetic [1] or catalytic areas [2]. Herein, a morphological transition is observed from spherical cobalt nanoparticles (NPs) to Co NRs overtime (9h) on a mixture of  $[\text{CoCl}(\text{PPh}_3)_3]$  and oleylamine (OAm). As was previously described spherical Co NPs were synthesized *via* a disproportionation process [3,4]. Based on *in-situ* (Environnemental – Transmission Electronic Microscopy; E-TEM, left figure) and *pseudo in-situ* (TEM and Small Angle X-Ray Scattering; SAXS) observations, two steps of this unique mechanism have been characterized with first the dissolution of the spheres and then the regrowth in rods' shape in presence of an OAm template. Further ex-situ experiments show that these steps are the result of interdependent reactions occurring between Co NPs, cobalt (II) and OAm. The latter, plays numerous roles in this synthesis: surfactant, disproportionation promoter, hydrogen source allowing the reduction of cobalt (II) complexes, its ammonium salt derivative is involved in oxidative etching of Co NPs and it promotes the anisotropic growth in NRs (right figure). These coupling actions of reduction and etching generate two cobalt reservoirs of nuclei under thermodynamic conditions. The same shape transformation was observed for other metals (nickel) and nanoalloys (cobalt-nickel). We believed this mechanism could also be applied to them. During this talk, I will present this original morphological transition.



Left: E-TEM images of the nanospheres dissolution and the formation *in-situ* of the cobalt.

Right: Proposal mechanism for the morphological transition from Co NPs to Co NRs.

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# Combining numerical and experimental approaches to study the substrate effect on the structure and the aspect ratio of supported metallic NPs: system Ag/Pt on silica

Fatima Ait Hellal<sup>\*</sup>, Caroline Andreatza-Vignolle, Pascal Andreatza and Joël Puibasset

*Interfaces, Confinement, Matériaux et Nanostructures, UMR 7374, CNRS, Université d'Orléans, 1b rue de la Férollerie, 45071 Orléans cedex 02, France*

*\*Fatima.ait-hellal@cnrs-orleans.fr*

Nanoparticles (NPs) have different properties in comparison to the bulk due to size reduction, which makes them very interesting for several applications. Metallic nanoparticles are elaborated by many routes including chemical (in solution) or physical (under UHV, reactive or inert gas) methods and sometimes are deposited on substrates with which they interact. Their stability, their structure and their evolution then depend on the support's nature. This is typically the case of crystalline supports (like MgO), where the NP's shape is strongly influenced by the substrate. Otherwise, one may want to minimize this effect by using substrates with weak interaction which is the case of amorphous silica [1,2] or amorphous carbon [3]. However, in this case, the interaction has been proven to be non-negligible and may modify the morphology.

We focus our interest on supported silver and platinum nanoparticles, and molecular simulation is a powerful tool for the comprehension of the interaction nature between the NPs and these supports. The metal-metal interaction and the interaction between silica species are well known in literature. In our work, we used the tight binding semi-empirical potential within the second moment approximation (TB-SMA) and the mTTAM potential, respectively, to describe them. But, the metal-substrate interaction is not yet completely understood. We propose to describe it based on Lennard Jones potential. The objective of this study is to determine the metal-silica interaction parameters based on experimental wetting angles results. Ag and Pt NPs are deposited on various silica substrates by atomic evaporation under ultra-high vacuum conditions. Combined TEM and X-ray scattering analysis give information regarding the morphologies and structures of the supported Ag and Pt nanoparticles, in particular their aspect ratios which allow us to find the adhesion energies. The L-J parameters are found to be  $\epsilon$  (Ag-O) = 0.080 eV and  $\epsilon$  (Ag-Si) = 0.013 eV for Ag-SiO<sub>2</sub> and  $\epsilon$  (Pt-O) = 0.11eV and  $\epsilon$  (Pt-Si) = 0.018 eV for Pt-SiO<sub>2</sub>. The giving metal-substrate interactions permit to investigate on the stability of supported AgPt alloys.

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# Nanoalloying Pt with Ge to obtain highly selective catalysts

Elisa Jimenez-Izal<sup>1,2,\*</sup>, Andoni Ugartemendia<sup>1</sup>, Jose M. Mercero<sup>1</sup>

<sup>1</sup>*Polimero eta Material Aurreratuak: Fisika, Kimika eta Teknologia, Kimika Fakultatea, Euskal Herriko Unibertsitatea UPV/EHU & Donostia International Physics Center (DIPC) PK 1072, 20080 Donostia, Euskadi, Spain*

<sup>2</sup>*IKERBASQUE, Basque Foundation for Science, Bilbao 48009, Euskadi, Spain*

\**elisa.jimenez@ehu.eus*

With increasing environmental concerns worldwide as well as the scarcity and cost of noble metals, the use of nanocatalysts is a novel way to exploit resources more efficiently and minimize waste. They are also good models to look for catalysts with optimized properties. In this talk we will explore gas-phase and MgO supported size-selected Pt clusters, and propose Ge as an alloying agent to boost their catalytic performance. On the one hand, the archetypal reaction of alkane dehydrogenation will be considered, due to the high relevance of light olefins as building blocks in the chemical industry [1]. Platinum is not only the most active pure metal for the C-H bond cleavage, but it also exhibits a low reactivity toward C-C bond cleavage. However, it binds alkenes too strongly, promoting further dehydrogenation. As a consequence, coke deposits are built on the surface of the catalyst, deactivating it. Selectivity control is key to prolong the lifetime of Pt. On the other hand, CO poisoning will be tackled. This is a severe problem affecting the Pt catalysts in diverse applications, such as the hydrogen Fuel Cells, FCs. In FCs H<sub>2</sub> is oxidized at the anode, that consists of Pt nanoparticles deposited on a carbon substrate. Such a catalyst is highly susceptible to deactivation via CO poisoning [2]. In this talk we show how nanoalloying Pt with Ge could give rise to more selective catalysts towards both coke formation and CO poisoning, thus leading to more resistant and durable catalysts [3,4]. Finally, we will emphasize that the activity, selectivity, and poisoning of supported cluster catalysts are all ensemble-effects, and cannot be properly described on the basis of just one cluster structure, which has been the prevalent theoretical approach.

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# Surface modification of photocatalysts with bimetallic nanoparticles for water treatment and hydrogen generation

Hynd Remita<sup>1,\*</sup>, Xiaojiao Yuan<sup>1</sup>, Maria G. Mendez Medrano<sup>1,2</sup>, Daniel Bahena<sup>3</sup>, José Luis Rodríguez López<sup>2</sup>, Christophe Colbeau Justin<sup>1</sup>

<sup>1</sup>*Institut de Chimie Physique, UMR 8000 CNRS, Université Paris-Saclay, 91405 Orsay France*

<sup>2</sup>*Advanced Materials Department, IPICYT, 78216 San Luis Potosí, SLP, Mexico*

<sup>3</sup>*Centro de Investigación y de Estudios Avanzados, IPN, 107360, D.F., Mexico*

\**hynd.remita@universite-paris-saclay.fr*

Development of efficient photocatalysts under solar light for water and air treatment and solar fuel production is a main challenge to solve energy and environment issues. TiO<sub>2</sub> is a very efficient photocatalyst due to its photocatalytic activity, high photochemical stability and low cost. The limitation in TiO<sub>2</sub> application results from low quantum yield due to fast charge carriers (electron/hole e<sup>-</sup>/h<sup>+</sup>) recombination and its activation only under UV irradiation because of the value of its band gap. Its surface modification with metal nanoparticles (NPs) can lead to enhancement of the photo-conversion quantum yield and may allow the extension of the light absorption of wide band-gap semiconductors to the visible light [1-4]. In particular, plasmonic photocatalysts have appeared as a very promising way to induce a photocatalytic activity of TiO<sub>2</sub> in the visible range [1]. On another hand, conjugated polymer (CP) nanostructures emerge as a new class of photocatalysts, which are very active under visible light [5].

TiO<sub>2</sub> and CP photocatalysts were surface-modified with mono- and bi-metallic nanoparticles induced by radiolysis [1-6]. Time Resolved Microwave Conductivity (TRMC) is a very powerful technique to study charge-carrier dynamics and to understand the effect of semiconductor modification on their photocatalytic activity. Modification of TiO<sub>2</sub> or CP nanostructures with bimetallic nanoparticles can lead to much higher photocatalytic activity than their monometallic counterparts, and synergistic effects can be obtained with nanoalloys. Some results on modification of semiconductors (titania and CPs) with bimetallic NPs for water treatment and hydrogen generation will be presented and discussed [2,3,4,6].

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# Role of conjugation in ligand-metal interaction in nanoalloys or clusters and limits of simplified ligand modeling

Hans-Christian Weissker\*

*Aix-Marseille Univ., CNRS, CINAM, Marseille, France  
European Theoretical Spectroscopy Facility ([www.etsf.eu](http://www.etsf.eu))  
\*weissker@cinam.univ-mrs.fr*

To understand the effects of alloying on the properties of nanoalloys, they have to be studied separately from other influences like surface structure, shape, etc. For wet-chemically produced clusters, in particular, the interaction between the ligands and the metal core needs to be well described.

The modeling of the electronic and optical properties of nanoalloys and metal clusters has traditionally relied on simplification of the ligands, as for instance truncation and subsequent replacement by methyl groups or saturation by hydrogen atoms. Very similar spectra obtained for the prototypical Au<sub>144</sub> cluster compound with different ligands seemed to suggest that the nature of the ligands does not play an important role [1,2]. However, the effect of such truncation has been rarely studied systematically. In addition, in experiments it is difficult to compare like systems with different ligand types.

In my talk, I discuss the limits of ligand truncation and eventual problems arising from it using recent examples [3]. I will then make use of the recently determined experimental structure of the Au<sub>144</sub> cluster compound(s) which turned out to have identical core structure in spite of their very different ligands [4]. Using induced densities from real-time TDDFT calculations [5], I demonstrate that the conjugation between aromatic ligand rings and the metal core plays a primordial role for the optical properties and, in turn, determines the feasibility of ligand-truncation.

[1] H.-Ch. Weissker, H. Barron Escobar, V. D. Thanthirige, K. Kwak, D. Lee, G. Ramakrishna, R.L. Whetten, and X. Lopez-Lozano, *Nat. Commun.* 5, 3785 (2014).

[2] H.-Ch. Weissker, O. Lopez-Acevedo, R.L. Whetten, and Xochitl Lopez-Lozano, *J. Phys. Chem. C*, 119, 11250-11259, (2015).

[3] R. Sinha-Roy, R. L. Whetten and X. López-Lozano, P. García González, and H.-Ch. Weissker, *J. Phys. Chem. C* 121, 5753 (2017).

[4] R.L. Whetten, H.-Ch. Weissker, J. Jesús Pelayo, S.M. Mullins, X. López-Lozano, and I.L. Garzón, *Acc. Chem. Res.* 52, 34-43 (2019).

[5] R. Sinha-Roy, P. Garcia-Gonzalez, X. Lopez Lozano, R.L. Whetten, and H.-Ch. Weissker, *J. Chem. Theory Comput.* 14, 6417-6426 (2018).

# Epitaxial growth of a gold shell on intermetallic FeRh nanocrystals for biomedical applications

Patrizio Benzo<sup>1,\*</sup>, Ségolène Combettes<sup>1</sup>, Magali Benoit<sup>1</sup>, Teresa Hungria<sup>2</sup>, Cécile Garcia<sup>1</sup>, Sophie Barre<sup>1</sup>, Béatrice Pecassou<sup>1</sup>, Marie-José Casanove<sup>1</sup>

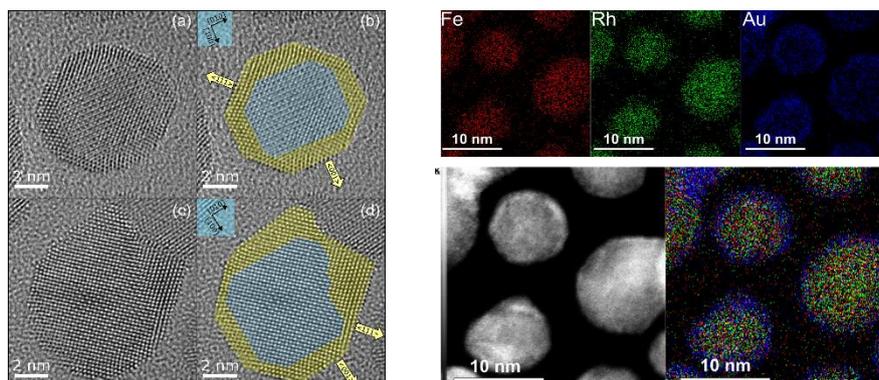
<sup>1</sup>CEMES-CNRS and Université de Toulouse, 29 rue J. Marvig, 31055 Toulouse, France

<sup>2</sup>Centre Raimond Castaing, Université de Toulouse, 3 rue Caroline Aigle, F-31400 Toulouse, France

\*patrizio.benzo@cemes.fr

In contrast with bimetallics, multimetallic nanoparticles (NPs) can combine different chemical orders in the same NP, which favors an enhanced tuning of their properties. Thus, taking advantage of our experience in the development of FeRh and Fe@Au NPs,[1,2] we focused on the synthesis of trimetallic (Fe, Rh, Au) nanocrystals with controlled composition and chemical distribution. Indeed, owing to its remarkable properties and in particular to its first-order magnetic transition at a physiologically relevant temperature ( $\sim 310\text{K}$ ), intermetallic FeRh has a great potential for biomedical applications (contrast agent for MRI, drug delivery...). As for pure iron, its coverage by a biocompatible gold shell remains desirable.

First FeRh nanocrystals, 8.5 nm of mean diameter, were formed according to a Volmer–Weber growth mode, using a physical vapor deposition route. The growth conditions were tuned so as to achieve the atomic scale chemical order displayed by the intermetallic B2-FeRh phase. Then the gold layer was deposited at a lower temperature [3]. We will detail the main features of the grown trimetallic NPs, with a particular focus on the epitaxial growth of the Au shell over the B2-FeRh core exposed facets, and their interest for the applications.



**Left (a–d) HREM images (greyscale and artificially colored) of FeRh @ Au NPs: (top) with regular shape; (bottom) with off-centered core.**

**Right: EDS analysis of the chemical distribution of the different elements. (Top) Elemental maps of Fe, Rh, and Au; (bottom) HAADF-STEM image and corresponding chemical map emphasizing the FeRh-core@Au-shell distribution.**

[1] P. Benzo, S. Combettes, B. Pecassou, N. Combe, M. Benoit, M. Respaud, and M. J. Casanove, *Phys. Rev. Mat.* 3, 096001 (2019).

[2] M. Liu, P. Benzo, H. Tang, M. Castiella, B. Warot-Fonrose, N. Tarrat, C. Gatel, M. Respaud, J. Morillo and M. J. Casanove, *EPL*, 116, 27006 (2016).

[3] P. Benzo, S. Combettes, C. Garcia, T. Hungria, B. Pecassou and M. J. Casanove, *Cryst. Growth Des.* 20, 4144-4149 (2020).

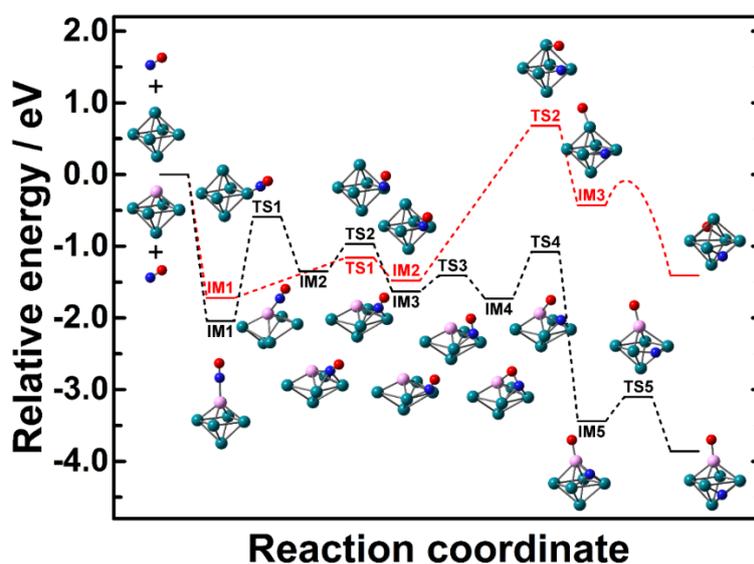
## How doping modifies NO adsorption onto group IX transition metal clusters

Joost Bakker<sup>1</sup>, Olga Lushchikova<sup>1</sup>, Ken Miyajima<sup>2</sup>, S Kudoh<sup>2</sup>, Y Zhang<sup>2</sup>, Masato Yamaguchi<sup>2</sup>, Toshiyaka Nagata<sup>2</sup>, Fumitaka Mafuné<sup>2</sup>

<sup>1</sup>Radboud University, The Netherlands

<sup>2</sup>The University of Tokyo, Japan

Rhodium and Iridium are group 9 elements that can both catalytically reduce NO to N<sub>2</sub> and O<sub>2</sub>, and are therefore widely used in three-way catalytic converters. Since the rate-limiting step for NO reduction is the dissociative adsorption of NO, it is of great interest to understand this adsorption mechanism on a detailed level. For this, we study the adsorption of NO molecules onto clusters of these materials, using mass-selective FEL-based IR action spectroscopy. We show how doping of the materials used reveals that the oxophilicity of the cluster is the key characteristic that drives dissociation.



**Poster session**  
**Thursday April 15, 2021**  
**11:15 – 13:00**

- P 1  $\eta$ -carbides nanoparticles catalysts synthesis for SWCNTs growth  
*Thomas Blin (ICMMO)*
- P 2 Study of the optical and structural properties of AgAl and AuAl nanoalloys  
*E. Camus (CNRS, France)*
- P 3 DFT global optimization for Au-Pd monometallic and bimetallic clusters supported on TiO<sub>2</sub>(110), using a Basin-hopping algorithm  
*Jonathan Casildo Luque Ceballos (Universidad Nacional Autónoma de México)*
- P 4 Strain hardening induced by uniaxial compression on Au@Pd nanocubes  
*Juan Andres de la Rosa Abad (Universidad Nacional de Cordoba, Argentina)*
- P 5 A universal signature in the melting of metallic nanoparticles  
*Lia Delgado-Callico (King's College London, UK)*
- P 6 Au-modified Pd nanoalloy catalyst exhibits improved activity and stability for NO direct decomposition  
*T. Elgayyar (CNRS, France)*
- P 7 Structure, energetics, and thermal behavior of bimetallic Re-Pt clusters  
*Luis E. Gálvez-González (Universidad de Sonora, México)*
- P 8 Dynamical properties of zeolite-encapsulated sub-nanometre metal particles  
*Christopher Heard (Charles University in Prague, Czech Republic)*
- P 9 Size and Surface/Interface effects on the magnetic behavior of B<sub>2</sub>-like supported FeRh nanoclusters  
*Guillermo Herrera (CNRS, France)*
- P 10 Effect of nafion content and hydration level on the electrochemical area of Pt nanocatalyst  
*Juan Jiménez García (Universidad Nacional de Cordoba, Argentina)*
- P 11 Numerical study of hetero-adsorption and diffusion on (100) and (110) surfaces of Cu, Ag and Au  
*E. El Koraychy (University of Genoa, Italy & Hassan II University of Casablanca, Morocco)*
- P 12 Out of equilibrium polymorph selection in nanoparticle freezing  
*Julien Lam (CNRS, France)*

(Poster session continued)

- P 13 Elucidating elementary steps of CO<sub>2</sub> hydrogenation over copper clusters with IR spectroscopy  
*O.V. Lushchikova (Radboud University, The Netherlands)*
- P 14 DFT simulations of CO adsorption and oxidation at pure and doped small Pt clusters  
*Luis M. Molina (Universidad de Valladolid, Spain)*
- P 15 Surfactants' influence on the lattice parameter of colloidally synthesized nanoparticles  
*Cora Moreira Da Silva (Laboratoire d'Etude des Microstructures, France)*
- P 16 Evidence of structural modifications of Au-Cu nanoalloys during butadiene selective hydrogenation via ex situ and in situ STEM  
*Abdallah Nassereddine (Université de Paris, France)*
- P 17 Supported FeNi nanocatalysts: an organometallic route for a diversity of systems  
*François Robert (CNRS, France)*
- P 18 Regression and clustering algorithms for AgCu nanoalloys: from energy predictions to structure recognition  
*Cesare Roncaglia (Università di Genova, Italy)*
- P 19 Size effects on the shell arrangement in core@shell nanoalloys  
*Manoj Settem (Indian Institute of Technology Madras, India)*
- P 20 Structural transitions in Au nanoclusters  
*Manoj Settem (Sapienza University of Rome, Italy)*
- P 21 Hydrogen-driven surface segregation in Pd-alloys  
*Pernilla Tanner (Chalmers University of Technology, Sweden)*
- P 22 Mitigating CO poisoning by modifying the Ge concentration in novel PtGe catalysts  
*Andoni Ugartemendia (Euskal Herriko Unibertsitatea (UPV/EHU) & Donostia International Physics Center (DIPC), Spain)*
- P 23 IR structural characterization of cluster-molecule reaction products as catalytic model systems  
*Frank J. Wensink (Radboud University, The Netherlands)*
- P 24 Molecular dynamics simulation of surface oxidation of Pd  
*Ying Wu (Northwestern Polytechnical University, China)*
- P 25 O<sub>2</sub> activation by AuAg clusters on a defective (100)MgO surface  
*Carlos Vital (Universidad Nacional Autónoma de México, Mexico)*

## $\eta$ -carbides nanoparticles catalysts synthesis for SWCNTs growth

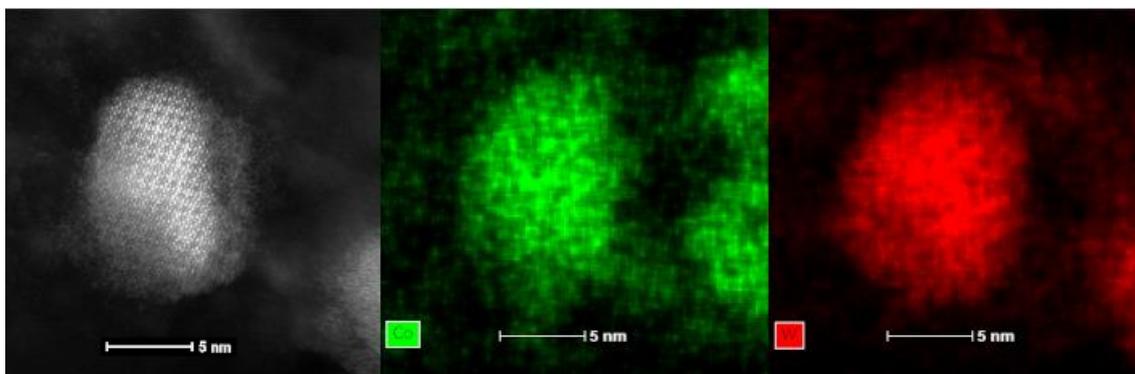
Thomas Blin<sup>1</sup>, Frédéric Fossard<sup>2</sup>, Jean-Sébastien Mérot<sup>3</sup>, Vincent Huc<sup>1</sup>, Armelle Girard<sup>3</sup>, Laure Catala<sup>1</sup>, Annick Loiseau<sup>2</sup>

<sup>1</sup>ICMMO, Institut de Chimie Moléculaire et des Matériaux d'Orsay, Université Paris Saclay

<sup>2</sup>Laboratoire d'Etude des Microstructures

<sup>3</sup>LEM, UMR 104 CNRS-ONERA

Single Walled Carbon Nanotubes (SWCNT) would be an excellent alternative to the silicon technologies in computer and would increase the calculation power [1]. The major issue is 99% semiconductor nanotubes is necessary for this technology to work. This selectivity is yet far to be achieved during the synthesis also inspiring, progress has recently been made using metallic carbides [2]. To go further, we are using carbides bimetallic nanoparticles catalysts, called  $\eta$ -carbides. Indeed, recently Hua An et al. [2] managed to realize a selective (12, 6) SWCNT growth, with a 1,26 nm diameter, by using Co<sub>6</sub>W<sub>6</sub>C as a catalyst. The purpose of the current study is finding a pathway towards the synthesis of  $\eta$ -carbides nanoparticles. To obtain these catalysts, octacyanomethylates-based networks are used as precursors, their general chemical formula estimate is Cs<sub>2</sub>M<sub>7</sub>[M'(CN)<sub>8</sub>]<sub>4</sub>·6H<sub>2</sub>O with (M= Co or Ni and M'=Mo or W). The metals M and M' are linked by CN bound in a 3D network. The precursors turn into catalyst nanoparticles after a thermal treatment. The treatment consists of an annealing at 800°C and under inert atmosphere. We have observed two cases of thermal decomposition. In the first case, a mixture of metallic and carbide nanoparticles is observed (ex: Co and Mo<sub>2</sub>C). In the second case, nanoparticles are found to be the Co<sub>3</sub>W<sub>3</sub>C bimetallic carbide (see Figure) as determined from combined analyses using TEM structure imaging, EDX analysis and DRX diffraction.



**Left: HAADF STEM image of a Co<sub>3</sub>W<sub>3</sub>C nanoparticle obtain by thermal treatment. Middle and right: EDX analysis of this nanoparticle.**

[1] Hills, G., Lau, C., Wright, A. et al. Modern microprocessor built from complementary carbon nanotube transistors. Nature 572, 595–602 (2019).

[2] Hua An, Akihito Kumamoto, Rong Xiang, Taiki Inoue, Keigo Otsuka, et al. Sci. Adv. (2019).

# Study of the optical and structural properties of AgAl and AuAl nanoalloys

E. Camus<sup>1,\*</sup>, M. Pellarin<sup>1</sup>, N. Blanchard<sup>1</sup>, C. Langlois<sup>2</sup>, L. Roiban<sup>2</sup>, M. Hillenkamp<sup>1</sup>, P. Andreatza<sup>3</sup>, and E. Cottancin<sup>1</sup>

<sup>1</sup>Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, 69622 Villeurbanne, France

<sup>2</sup>INSA-Lyon, MATEIS, Université Claude Bernard Lyon 1, CNRS, 69621 Villeurbanne, France

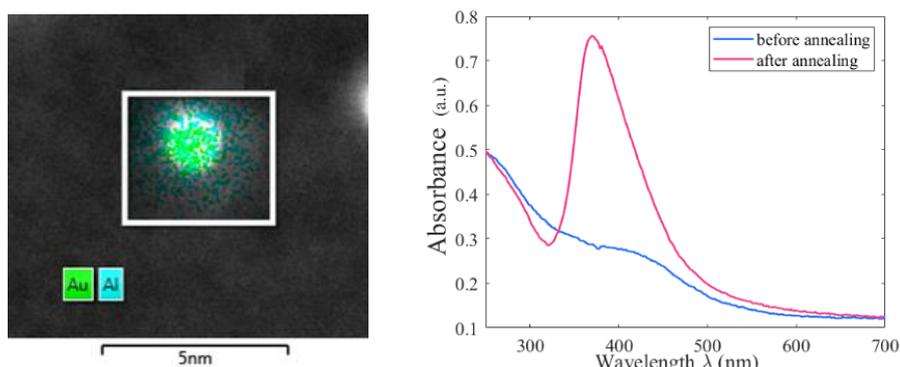
<sup>3</sup>Université d'Orléans, CNRS, ICMN, 45071 Orléans, France

\*elise.camus@univ-lyon1.fr

Bimetallic nanoalloys are of great interest in plasmonics because their optical absorption is dominated by a Localized Surface Plasmon Resonance (LSPR) that not only depends on their size, shape and environment, but also on their composition and chemical order (segregation versus homogeneous alloying). As a consequence, their optical properties can be modified through the structural and chemical transformations that may occur if the nanoalloys are interacting with a reactive environment.

In this context, we previously investigated the optical and structural properties of In-Ag nanoparticles (NPs) for which LSPRs in the UV range and a silver-rich alloyed phase quite stable regarding oxidation were observed [1,2]. Pure NPs made of aluminium, a cheaper and more abundant trivalent metal than indium, also exhibit a pronounced LSPR in the UV range but are strongly sensitive to oxidation. Thus, Ag-Al and Au-Al NPs, produced by laser vaporization, were investigated for various compositions, in order to verify if a phase, stable against oxidation, could exist as it does for the In-Ag system.

For the Ag-Al system, the absorbance spectra measured after annealing at 500°C exhibit LSPR at higher energies as compared to pure silver NPs, suggesting that metallic aluminium is present in the NPs. Moreover, for all the Ag/Al studied ratios, the LSPR is broadened and red-shifted after aging, showing that the NPs are sensitive to oxidation. Such measurements are in progress with Au-Al NPs. In parallel, (HR-)TEM observations and EDX analysis give preliminary information on the structure of the NPs. For the Au-Al system, they seem to reveal a core@shell structure with an Au-rich core and an AlO<sub>x</sub> shell. In the near future, GISAXS and GIWAXS measurements will complete the study for both kinds of nanoalloys.



Left: EDX map on a single Au<sub>33</sub>Al<sub>66</sub> NP. Right: Absorbance spectra of Ag<sub>75</sub>Al<sub>25</sub> NPs embedded in silica,  $\phi = 3.8$  nm, before and after an annealing (500°C).

[1] E. Cottancin et al., PCCP, 2014, 16(12): p. 5763-5773.

[2] J. Ramade et al., Nanoscale, 2017, 9(36): p. 13563-13574.

# DFT global optimization for Au-Pd monometallic and bimetallic clusters supported on TiO<sub>2</sub>(110), using a Basin-hopping algorithm

Jonathan Casildo Luque Ceballos, Lauro Oliver Paz-Borbón

*Universidad Nacional Autónoma de México*

In the modern nanoscience, the global optimizations plays a crucial part in materials design, since the materials properties can be tailored to improve them for future applications [1]. The huge interest for metal oxide-supported clusters is since the combination of a metal clusters with an oxide surface trends to improve the catalytic activity of the system, as there is a strong evidences that the active sites in several catalytic processes are located exactly on the cluster/oxide interface [2, 3]. To the best of our knowledge, there are no systematic studies reported in the literature involving bimetallic, subnanometer AuPd cluster adsorption on rutile TiO<sub>2</sub>(110).

Because of this, we performed an extensive DFT-based Basin Hopping global optimization study to find the most stable bimetallic Au-Pd clusters supported on the TiO<sub>2</sub>(110) oxide surface, involving up to 5 atoms in size for all compositions. Our Basin Hopping algorithm is coupled to Quantum Espresso [4]. We implemented the DFT+U approach with a U=3.0 eV for the Ti atoms, using a (4x2) rutile TiO<sub>2</sub> (110) surface consisting of 192 atoms, involving 12 atomic layers; where only the bottom layers were fixed during structural optimizations. Ultrasoft pseudopotentials are used to describe Ti, O, Au, Pd atoms, along with the dipole correction to avoid spurious interactions between neighboring images. We quantify how strong the metal clusters interact with the TiO<sub>2</sub> (rutile) surface via calculated adsorption energies. Our DFT+U results indicate that, in most cases, a 3D growth is observed for both monometallic and bimetallic clusters. Quantification of charger transfer effects and intrinsic electronic structure (PDOS) using a Bader analysis will be further discussed.

[1] Marc Jäger, Rolf Schäfer, Roy Johnston, *Nanoscale*, 2019, 11, 9042-9052.

[2] Sergio Tosoni, Gianfranco Pacchioni, *Chem. Cat. Chem*, 2019, 11(1), 73-89.

[3] Julien Engel, Samantha Francis, Alberto Roldan, *Phys. Chem. Chem. Phys.*, 2019, 21, 19011-19025.

[4] Lauro Oliver Paz-Borbón, et al., *Phys. Chem. Chem. Phys.*, 2019, 21, 15286.

## Strain hardening induced by uniaxial compression on Au@Pd nanocubes

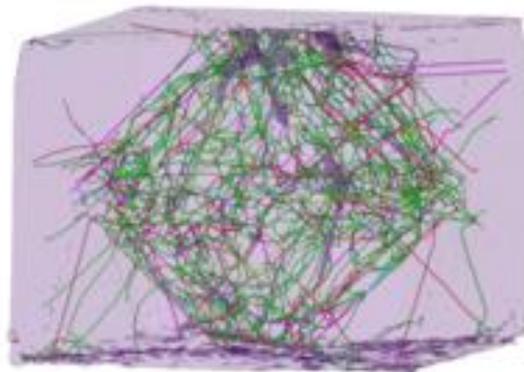
Juan Andres de la Rosa Abad<sup>1</sup>, Eduardo Bringa<sup>2</sup>, German Soldano<sup>1</sup>, Sergio Mejía Rosales<sup>3</sup>, Marcelo Mariscal<sup>1</sup>

<sup>1</sup>Universidad Nacional de Córdoba, Argentina

<sup>2</sup>Universidad de Mendoza, Argentina

<sup>3</sup>Universidad Autónoma de Nuevo León, México

In this work we investigate the mechanical response Pd nanocubes and Au@Pd core-shell of nanoparticles 30 nm size subjected to compression by an external indenter. In pristine Pd nanocubes, stacking faults across the whole cube were observed. In contrast, for the Au@Pd core-shell nanocubes, such structural failures were blocked by the Au-Pd interface, and partial dislocations are always around the interface during all the nanoindentation (see Figure). We observed that the Poisson's ratio is a good predictive of the elastic-plastic region in the pristine Pd nanoparticle. In contrast, the Au@Pd nanocube shows a different Poisson's ratio profile reaching a constant value after 10 % compression. The mechanical properties of the Au@Pd nanocube are diminished by the gold core, compared with the Pd nanocube. A little strain hardening is observed in the Au@Pd nanocube.



Partial dislocations at the final state of the Au@Pd indented nanocube

# A universal signature in the melting of metallic nanoparticles

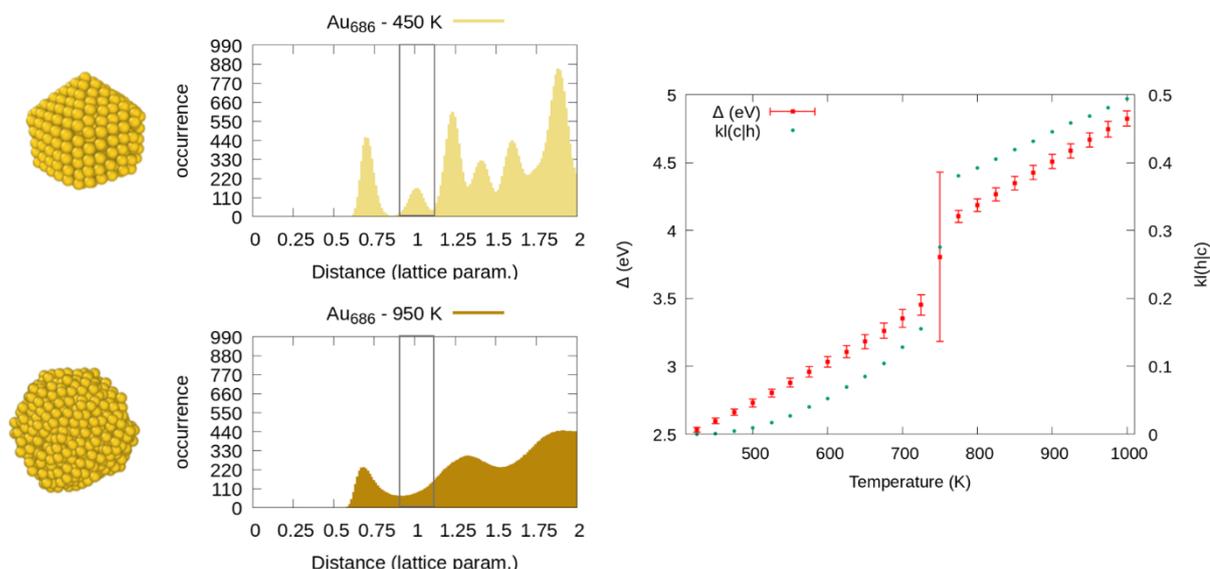
Laia Delgado-Callico<sup>1</sup>, Kevin Rossi<sup>2</sup>, Francesca Baletto<sup>1</sup>

<sup>1</sup>Department of Physics, King's College London, UK

<sup>2</sup>Ecole Polytechnique Fédérale de Lausanne, Switzerland

Predicting when phase changes occur in nanoparticles is fundamental for designing the next generation of devices suitable for catalysis, biomedicine, optics, chemical sensing, and electronic circuits. Nevertheless, a standard definition for melting of nanoparticles is still missing and estimating the melting temperature is challenging. We analyse the solid–liquid change of several late-transition metals nanoparticles, i.e. Ni, Cu, Pd, Ag, Au, and Pt, through classical molecular dynamics. We consider various initial shapes from 146 to 976 atoms, corresponding to the 1.5–4.1 nm size range, placing the nanoparticles in either a vacuum or embedded in a homogeneous environment, simulated by an implicit force-field.

We discover a universal signature in the distribution of the atomic-pair distances that distinguishes the melting transition of monometallic nanoparticles. Regardless of the material, its initial shape, size, and environment, the second peak in the pair-distance distribution function disappears when the nanoparticle melts. As the pair-distance distribution is a measurable quantity, the proposed criterion holds for both numerical and experimental investigations. Therefore, opening new experimental routes alternative to calorimetry to measure the phase change temperature. This criterion is particularly advantageous for systems whose heat capacity vs. temperature curves are of difficult interpretation, as it is the case of nanoparticles embedded in a strongly interacting environment.



The left panel displays the average pair-distance distribution function of gold at two temperatures: cold (solid) at the top and hot (melted) at the bottom, with a representation of the structure at each temperature. The second peak and its disappearance are signaled by the black box. The right panel reports its caloric curve (red) and cross-entropy  $KL(h|c)$  (green) temperature dependence.

# Au-modified Pd nanoalloy catalyst exhibits improved activity and stability for NO direct decomposition

T. Elgayyar<sup>1</sup>, J. Schnee<sup>2</sup>, A. Tuel<sup>1</sup>, L. Burel<sup>1</sup>, F. Bosselet<sup>1</sup>, Y. Schuurman<sup>1</sup>, F.C. Meunier<sup>1,\*</sup>, L. Delannoy<sup>2</sup> and C. Thomas<sup>2</sup>

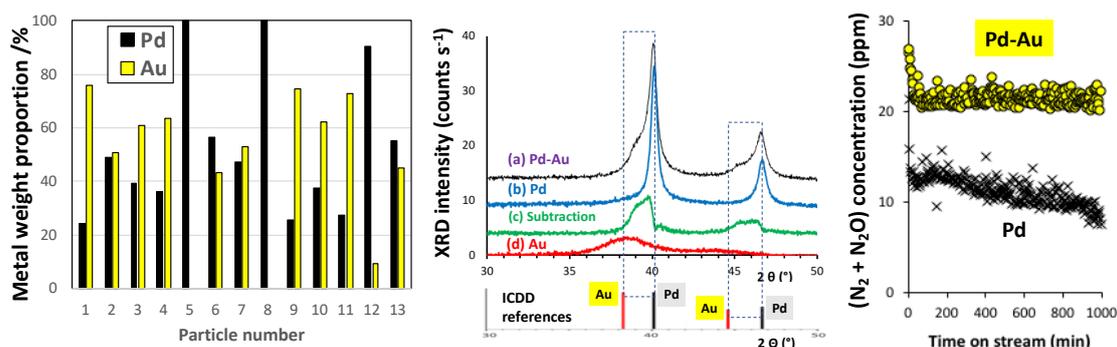
<sup>1</sup>Univ Lyon, Université Claude Bernard Lyon, CNRS, IRCELYON, 2 Av. Albert Einstein, 69626 Villeurbanne, France

<sup>2</sup>Sorbonne Université, CNRS, Laboratoire de Réactivité de Surface (LRS), F-75005 Paris, France  
\*fcm@ircelyon.univ-lyon1.fr

A better technology for the control of NO<sub>x</sub> emissions from combustion processes is desirable, particularly one not requiring the use of reducing agents. NO<sub>x</sub> direct decomposition remains a challenge, even over noble metal-based catalysts, because of the poisoning of the metal surface by oxygen. Au is inactive for NO direct decomposition, but is one of the metals most resistant against oxidation. The objective of this work was to assess whether or not it was possible to obtain active and stable activity for NO direct decomposition by combining inert Au with an active metal such as Pd, which is known to deactivate.

Silica-supported Pd, Au and Pd-Au nanoparticles (between 3 and 8 nm in size, TEM not shown) were prepared using earlier recipes. TEM-EDX analyses (Left figure) realized over 13 nanoparticles of the Pd-Au sample showed that most of those contained both metals, though their composition was inhomogeneous. *In situ* XRD analyses carried out at various temperatures under H<sub>2</sub> evidenced the formation of Pd-Au alloyed phases, with lattice parameters comprised between those of pure Au and pure Pd (Middle figure). Alloyed phases were also present and stable under air at 500 °C, though Pd content decreased (not shown).

The direct decomposition of NO to N<sub>2</sub> and N<sub>2</sub>O was studied. Au/SiO<sub>2</sub> appeared inactive (not shown). Interestingly, the Pd-Au was more active than the parent Pd sample (Right figure). The Pd-Au also exhibited a stable activity with time, in contrast to the parent Pd material. Detailed product analyses (not shown) showed that O release was higher for the Pd-Au catalyst, confirming that Au prevented Pd deactivation by facilitating O desorption.



Left: Proportion (in wt.%) of Pd and Au measured by TEM-EDX of over 13 nanoparticles present in the bimetallic sample. Middle: *In situ* X-ray diffraction patterns of the SiO<sub>2</sub>-supported (a) Pd-Au, (b) Pd and (d) Au collected in air after oxidation at 500 °C and reduction in H<sub>2</sub> at 450 °C. The pattern (c) corresponds to the subtraction (a) – 0.9 x (b) and represents the pattern associated with alloyed nanoparticles. The bottom lines are the positions related to pure Au (PDF-00-001-1172, in red) and pure Pd (PDF-00-046-1043, in black). Right Concentration in ppm of (N<sub>2</sub> + N<sub>2</sub>O) recorded over the Pd/SiO<sub>2</sub> and Pd-Au/SiO<sub>2</sub> samples. Reaction temperature: 450 °C. Feed: 500 ppm NO in He.

## Structure, energetics, and thermal behavior of bimetallic Re-Pt clusters

Luis E. Gálvez-González<sup>1</sup>, Alvaro Posada-Amarillas<sup>2</sup> and Lauro Oliver Paz-Borbón<sup>3,\*</sup>

<sup>1</sup>*Programa de Doctorado en Ciencias (Física), División de Ciencias Exactas y Naturales, Universidad de Sonora, Blvd. Luis Encinas y Rosales, 83000, Hermosillo, Sonora, México*

<sup>2</sup>*Departamento de Investigación en Física, Universidad de Sonora, Blvd. Luis Encinas y Rosales, 83000 Hermosillo, Sonora, México*

<sup>3</sup>*Instituto de Física, Universidad Nacional Autónoma de México, Apdo. Postal 20-364, 01000 Ciudad de México, México*

\*oliver\_paz@fisica.unam.mx

Bimetallic Re-Pt is a widely used catalyst in petroleum-reforming to obtain high-octane gasoline, but experimental and theoretical information of such system at the sub-nanometer scale of this system - namely as cluster aggregates - is currently lacking. Thus, in this work we performed a Density Functional Theory (DFT) based global optimization study to determine the physicochemical properties of the most stable Re-Pt gas-phase clusters up to 6 atoms, for all compositions. Our results indicate that in those putative global minima (GM) geometries, Re atoms tend to aggregate while most Pt atoms remain separated from each other. This is even observed in Pt-rich clusters an indication of the strength of the Re-Re and Re-Pt bonds over pure Pt-Pt ones -due to a strong, directional hybridization of the Re half-filled  $5d$  and the nearly full Pt  $5d$  states. We observe that doping monometallic Pt clusters even with a single Re atom increases their binding energy values and widens the bimetallic cluster HOMO-LUMO gap.

As catalysis occur at elevated temperatures, we explore the concept of cluster fluxionality for Re-Pt minima in terms of the calculated isomer occupation probability,  $P(T)$ . This allow us to quantify the abundance of GM and low-energy isomer configurations as a function of temperature. This is done at size 5 atoms due to the wide isomer observed variety. Our calculations indicate that for pure  $\text{Re}_5$ , the  $P(T)$  of the GM configuration substantially decreases after 750 K. Respectively, for  $\text{Re}_4\text{Pt}_1$ , the GM is the dominant structure up to nearly 700 K, when the second-energy isomer becomes the stable one. Although no ordering changes are seen for  $\text{Re}_3\text{Pt}_2$ ,  $\text{Re}_2\text{Pt}_3$  and  $\text{Re}_1\text{Pt}_4$ , we do observe a structural transition—between the GM and the second isomer—for pure  $\text{Pt}_5$  above 1000 K. We expect that this type of combined *first-principles* analysis add to the overall, continuous understanding of the stability and energetics of ultra-fine and highly-dispersed Re-Pt petroleum-reforming catalysts and the scarce available information on this particular bimetallic system.

# Dynamical properties of zeolite-encapsulated sub-nanometre metal particles

Christopher Heard, Andreas Erlebach, Dianwei Hou, Lukas Grajciar

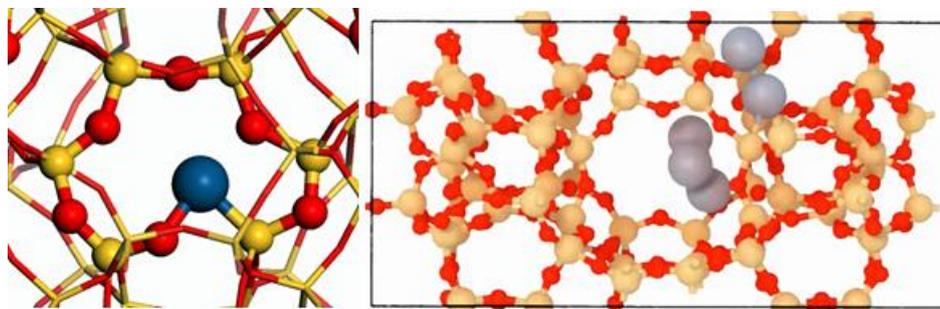
*Department of Physical and Macromolecular Chemistry, Charles University in Prague, Czech Republic*

Catalytic (sub)nanometre metal particles are inherently non-equilibrium systems, whose physico-chemical properties are governed by a balance of environmental factors, including temperature, presence of adsorbates and support interactions [1]. In our work, we aim to unravel the dynamical properties of catalytically relevant zeolite-encapsulated Pt particles at the atomic scale. To do this, we have developed a holistic computational approach that encompasses ab initio global optimisation, kinetic Monte Carlo and dynamical simulations that employ novel neural network potentials.

We find that Pt exhibits a surprisingly high resistance to migration within the zeolite pore, due to unusual, locally defective binding modes. Framework heteroatom substituents are found to enhance sintering resistance by dramatically increasing inter-cage migration barriers, which are dependent on the Si:Al ratio [2]. Conversely, reducing adsorbates are found to dramatically reduce sintering resistance, due to electronic effects which promote migration and increase volatility.

The development of reactive machine learning methods [3] allows us to investigate the kinetics of cluster diffusion and ascertain sintering mechanisms and growth rates of metal clusters, along with the topological factors which affect them.

In this presentation, we will highlight our recent findings on Pt clusters encapsulated within industrially important zeolite frameworks and outline the future directions of our work.



**Left: The globally optimal configuration of a Pt atom encapsulated into siliceous zeolite LTA. Right: Snapshot of a molecular dynamics simulation of metal cluster growth in zeolite MWW with a neural network potential.**

[1] M. Moliner, J.E. Gabay, C.E. Kliewer, R.T. Carr, J. Guzman, G.L. Casty, P. Serna, A. Corma, *J. Am. Chem. Soc.* 138, (2016), 15743.

[2] D. Hou, L. Grajciar, P. Nachtigall, C.J. Heard, *ACS Catal.* 10, (2020), 11057.

[3] A. Erlebach, P. Nachtigall, L. Grajciar, (Arxiv) [arxiv.org/abs/2102.12404](https://arxiv.org/abs/2102.12404).

## Size and Surface/Interface effects on the magnetic behavior of B2-like supported FeRh nanoclusters

Guillermo Herrera<sup>1</sup>, Guillermo Herrera<sup>1</sup>, Adela Reyes Contreras<sup>2</sup>, Ingrid Cañero Infante<sup>3</sup>, Edwige Otero<sup>4</sup>, Philippe Ohresser<sup>4</sup>, Bertrand Vilquin<sup>3</sup>, Pedro Rojo-Romero<sup>3</sup>, Xiaorong Weng<sup>5</sup>, Lucio Martinelli<sup>5</sup>, Gilles Renaud<sup>5</sup>, Damien Le Roy<sup>1</sup>, Florent Tournus<sup>1</sup>, Alexandre Tamion<sup>1</sup>, Véronique Dupuis<sup>1</sup>

<sup>1</sup>Institut Lumière Matière, UMR 5306, Université Lyon 1-CNRS, Université de Lyon, France

<sup>2</sup>Faculty of Sciences, Universidad Autónoma del Estado de México, Toluca, México

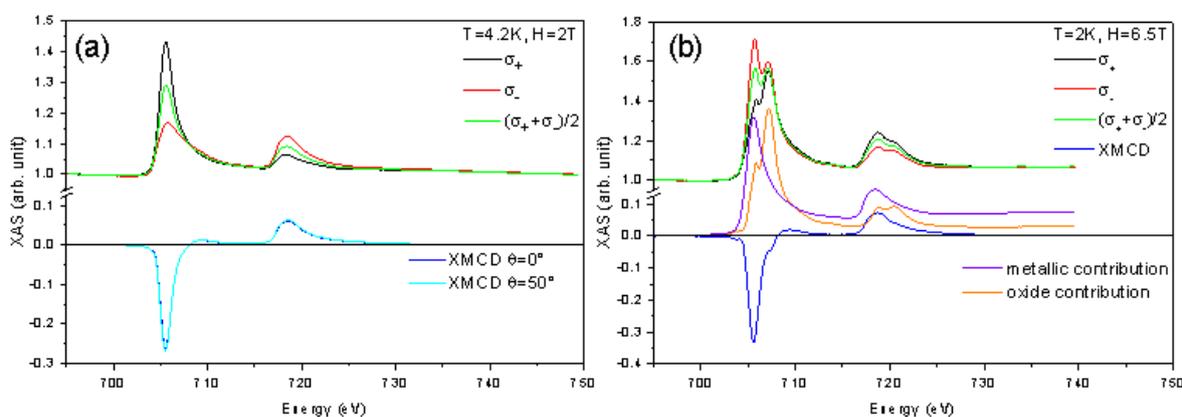
<sup>3</sup>Institut des Nanotechnologies de Lyon, CNRS UMR 5270 ECL INSA UCBL CPE, France

<sup>4</sup>Synchrotron SOLEIL, L'Orme des Merisiers, F-91192 Gif-sur-Yvette, France

<sup>5</sup>Université Grenoble Alpes, CEA, INAC, MEM, F-38000 Grenoble, France

FeRh CsCl-type (B2) phase presents an antiferromagnetic to ferromagnetic transition around 370 K. We have shown that mass-selected FeRh clusters smaller than 5 nm diluted in a carbon matrix can reach the B2 phase after annealing with the persistence of high magnetization down to 3 K [1,2].

We have prepared FeRh nanoclusters up to 7 nm using Mass Selection Low Energy Cluster Beam Deposition on BaTiO<sub>3</sub> (001) (ferroelectric) and SrTiO<sub>3</sub> (001) (paraelectric) surfaces, and embedded in a carbon matrix. Investigations on as grown and annealed samples using High-Resolution Transmission Electron Microscopy, magnetometry, grazing incidence diffraction and small-angle scattering and X-Ray Magnetic Circular Dichroism (XMCD) spectroscopy (Fig. 1) allow us to present a complete overview of the epitaxial, electronic and chemical effects on the magnetic properties of our samples in the framework of new nanomultiferroic systems based on combining magnetic nanoclusters and ferroelectric thin films.



Fe L<sub>2,3</sub> XAS and XMCD spectra for annealed FeRh nanoclusters of 7 nm over carbon matrix (a) and on BTO (b)

The authors would like to acknowledge the support from IRN Nanoalloys (CNRS) and the collaborative project VOLCONANO ANR-19-CE09-0023 project which include the (G.H.) PhD grant in progress.

[1] A. Hillion et al., Phys. Rev. Lett. 110 (2013) 087207.

[2] V. Dupuis et al. Beilstein J. Nanotechnol. 7 (2016) 1850.

[3] B. Wague et al., Journal of Modern Physics 11, 509-516 (2020).

## Effect of nafion content and hydration level on the electrochemical area of Pt nanocatalyst

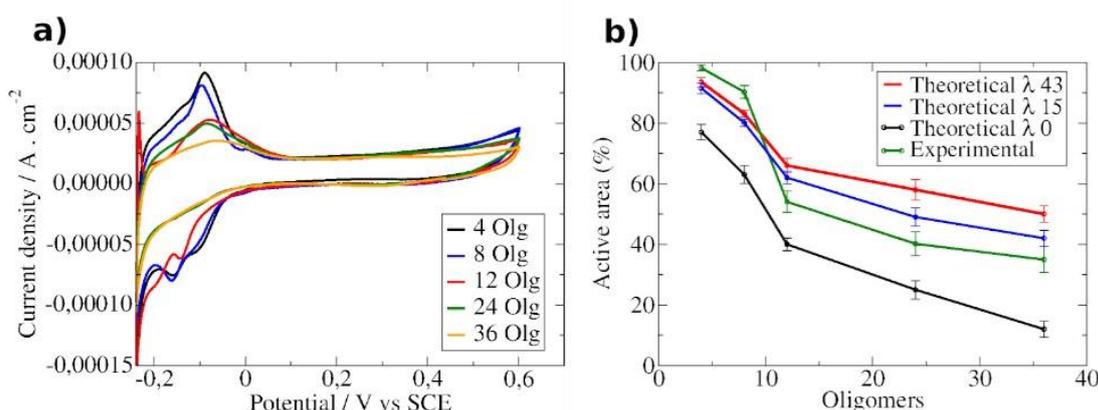
Juan Jiménez García<sup>1</sup>, Jimena Olmos-Asar<sup>1</sup>, Esteban Franceschini<sup>2</sup>, Marcelo Mariscal<sup>1</sup>

<sup>1</sup>Universidad Nacional de Cordoba, Departamento de Química Teórica y Computacional, Facultad de Ciencias Químicas, Argentina

<sup>2</sup>Universidad Nacional de Cordoba, Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Argentina

In the last decades, polymeric membrane-based fuel cells (PEMFC) have been extensively studied. However, despite a great scientific effort, there are still some aspects of fuel cell operation that are difficult to access from an experimental point of view, as is the case of the three-phase zone. In this zone, the membrane (commonly Nafion) is interacting with the supported nanocatalysts on which the catalytic activity of the system depends. In this work we use molecular dynamics studies and electrochemical experiments on a Nafion/Pt/C system to evaluate different factors such as Nafion content, hydration level, temperature and the different sizes and structures of the metallic NPs that can be found in the PEMFC. Our aim is to find the appropriate conditions to maximize the electrochemically active area of the Pt/C catalysts, optimizing their use. All these factors are fundamental in the characterization of the electrochemically exposed area of the metallic NPs.

The results obtained reveal (see figure) that at high Nafion contents, the catalyst utilization is affected due to the strong interaction between the sulfonic groups of Nafion and the surface of the Pt NPs. On the other hand, when the hydration level of the system decreases, the sulfonic groups have a higher occupation in the NP surface, covering the active area with hydrophobic Nafion chains and increasing the inactive area. These and other effects found in this work allow us to know at an atomistic level how the utilization of the catalyst is affected, which is an important step to establish the relationship between several factors and the effectiveness and durability of the PEMFC system.



a) Cyclic voltammograms measured (5 mV.s<sup>-1</sup>) in H<sub>2</sub>SO<sub>4</sub> for different contents of Nafion. b) Comparison between theoretical and experimental measures of the catalyst utilization (in percentages) for different contents of Nafion and hydration levels (λ).

# Numerical study of hetero-adsorption and diffusion on (100) and (110) surfaces of Cu, Ag and Au

E. El Koraychy<sup>1,2\*</sup>

<sup>1</sup>*Physics Department, University of Genoa, via Dodecaneso 33, 16146 Genoa, Italy*

<sup>2</sup>*Physic Department, Faculty of Science Ben M'sik, Hassan II University of Casablanca, B.P. 7955, Casablanca, Morocco*

*\*elkoraychy@fisica.unige.it*

Diffusion in solids is fundamental in the art and science of materials and an important topic of solid-state physics, physical metallurgy, and materials science. A deeper knowledge about diffusion requires information on the positions of atoms and how they move in solids. In our work, the diffusion on metallic surfaces is studied using Molecular Dynamics simulations combined with Embedded Atom Method potential. Static activation energies governing various diffusion processes (jumps and exchanges) are calculated by quenched MD. Dynamic activation energies are calculated at high temperature from the Arrhenius plots of different diffusion mechanisms and compared to static barriers. Our numerical results reveal that the jump process requires very high activation energy compared to the exchange process either on the terrace or near the defects.

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[2] E. El koraychy, K. Sbiaai, M. Mazroui, R. Ferrando, Y. Boughaleb, Chem. Phy. Lett. 669, 150-155 (2017).

# Out of equilibrium polymorph selection in nanoparticle freezing

Julien Lam<sup>1</sup>, Jonathan Amodeo<sup>2</sup>, Fabio Pietrucci<sup>3</sup>

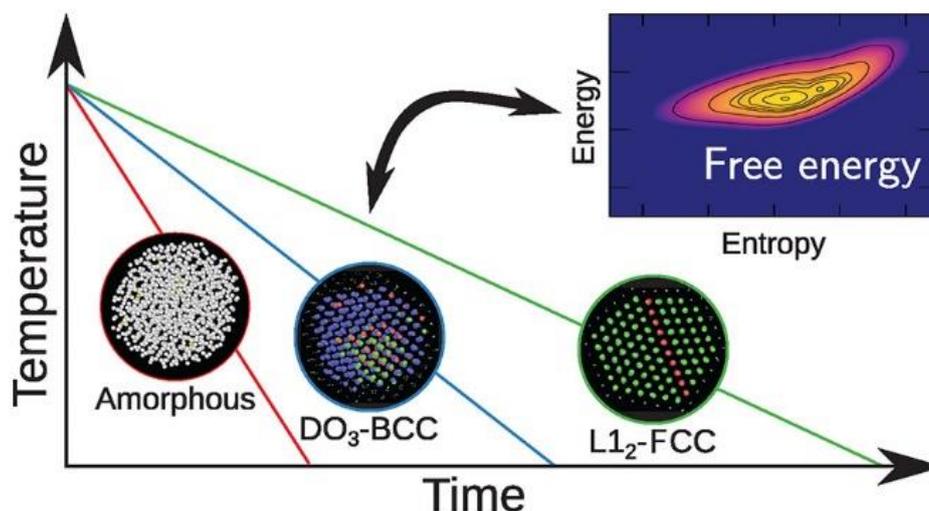
<sup>1</sup>CEMES, CNRS and Université de Toulouse, 29 rue Jeanne Marvig, 31055 Toulouse Cedex, France

<sup>2</sup>Université de Lyon, INSA-Lyon, MATEIS, UMR 5510 CNRS, 69621 Villeurbanne, France

<sup>3</sup>Sorbonne Université, CNRS UMR 7590, IMPMC, 75005 Paris, France

Methods for synthesizing nanoparticles often involve out-of-equilibrium processes which may lead to the formation of metastable structures. However, in this context, the underlying processes including nucleation and growth that bring the raw materials into nanoparticles remain difficult to approach from the experimental point of view.

In this work, we perform freezing simulations of liquid nanodroplets and observe the out-of-equilibrium formation of nanocrystals as the temperature is decreased. We especially focus on the intricate role of the cooling rate as it is pivotal in driving the processes from a thermodynamical to a kinetical pathway. Working on the example of Ni<sub>3</sub>Al nanoparticles, quick and long cooling rates lead to the formation of respectively amorphous and the bulk most stable structure. More importantly, we predict that intermediate values of the cooling rate are able to stabilize a novel structure. In order to understand the nucleation processes, free energy calculations are performed using state-of-the-art collective variables that help navigating in this rich structural landscape. Our results show that while being unstable at room temperature, this novel structure becomes free energetically stable at the crystallization temperature thus unlocking an alternative nucleation pathway.



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## Elucidating elementary steps of CO<sub>2</sub> hydrogenation over copper clusters with IR spectroscopy

O.V. Lushchikova<sup>1,\*</sup>, M. Szalay<sup>2</sup>, T.Höltzl<sup>2</sup>, H. Tahmasbi<sup>3</sup>, J. Meyer<sup>3</sup> and J.M. Bakker<sup>1</sup>

<sup>1</sup>Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7, 6525 ED Nijmegen, The Netherlands

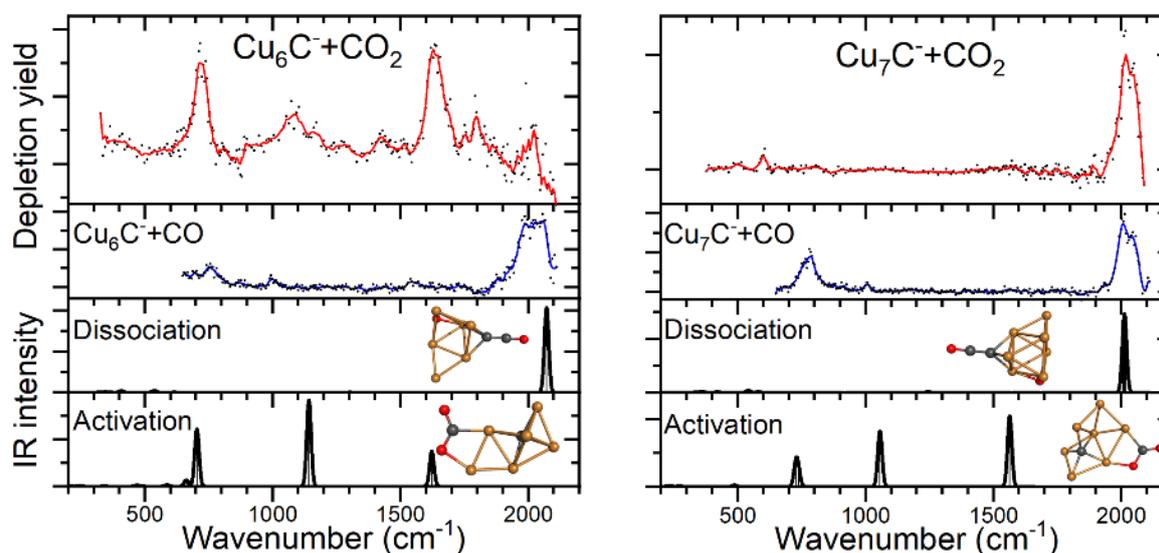
<sup>2</sup>Furukawa Electric Institute of Technology, Késmárk utca 28/A, 1158 Budapest Hungary

<sup>3</sup>Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, Einsteinweg 55 2333 CC Leiden, The Netherlands

\*olga.lushchikova@ru.nl

The catalytic recycling of CO<sub>2</sub> to liquid fuels, such as methanol, may help to control the atmospheric CO<sub>2</sub> content. Methanol can be produced by the hydrogenation of CO<sub>2</sub>. Although this reaction is thermodynamically favorable, the strong C-O and H-H bonds require the use of a catalyst to initiate the reaction. Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts have been the industrial standard, where recently nm-sized Cu particles have been identified as the active sites. A molecular-level understanding of the elementary steps of CO<sub>2</sub> hydrogenation is required for the rational design of an improved catalyst.

To get this knowledge, we study the interaction of CO<sub>2</sub> and H<sub>2</sub> with copper clusters as well-defined model systems with many under-coordinated adsorption sites. The structure of the formed complexes is investigated by a combination of infrared photodissociation spectroscopy and density functional theory calculations. We here present IR spectra of cationic Cu clusters reacted with H<sub>2</sub> and CO<sub>2</sub> individually, and with both together. We find evidence for H<sub>2</sub> dissociation, but CO<sub>2</sub> remains unactivated. In contrast, anionic Cu<sub>n</sub>C<sup>-</sup> show size-selective activation and dissociation of CO<sub>2</sub>.



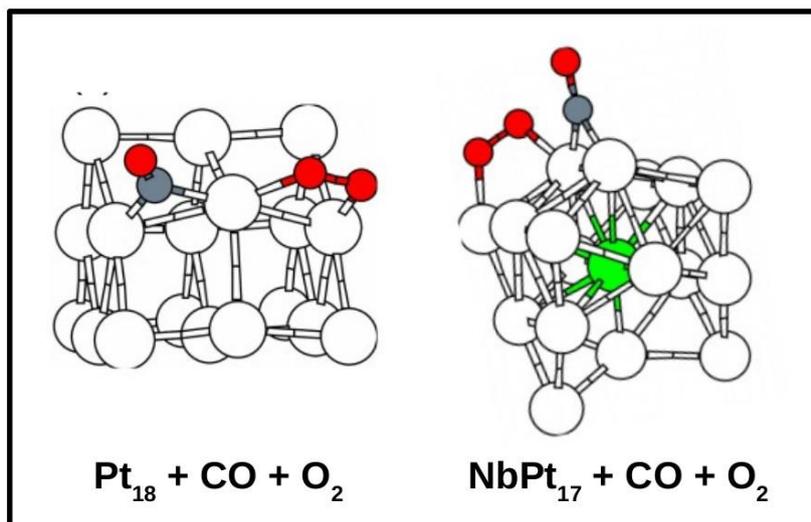
The IRMPD spectrum (red) of Cu<sub>6</sub>C<sup>-</sup>+ CO<sub>2</sub> in the left column compared to the reference IRMPD spectrum (blue) of Cu<sub>6</sub>C<sup>-</sup>+ CO and calculated spectra (black). The right column illustrates the same graphs for complexes with Cu<sub>7</sub>C<sup>-</sup>.

## DFT simulations of CO adsorption and oxidation at pure and doped small Pt clusters

Luis M. Molina<sup>\*</sup>, Lope Domínguez, Carlos Arranz and Julio A. Alonso

*Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid, Spain*  
<sup>\*</sup>*lmolina@fta.uva.es*

The interaction of carbon monoxide (CO) and pure and doped platinum clusters has been studied by ab-initio DFT simulations. These clusters are promising catalysts for a number of interesting reactions, involving CO adsorption and its interaction with oxygen and other coadsorbates. In this communication, we will first focus on the effect that cluster size and dopant type have on the reactivity of the cluster towards bonding of CO. We will report the results of a systematic study of CO bonded to small Pt<sub>N</sub> and XPt<sub>N</sub> clusters (X=Zr, Mo, Nb). The interaction between the 5s molecular orbital of CO and the Pt d states presents interesting variations with cluster size. Also, we analyzed the strong modifications induced by CO on the spin state of these clusters (with sizable magnetic moments). Finally, we have also studied the complete CO oxidation reaction  $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$  on a specially unreactive Pt<sub>18</sub> cluster, either pure or doped with a Nb impurity. The presence of Nb does not only changes the structure and properties of the pure Pt cluster, but also results in sizable changes to the way it binds CO or O<sub>2</sub> adsorbates.



Equilibrium structures of CO and O<sub>2</sub> coadsorbed to Pt<sub>18</sub> and NbPt<sub>17</sub> clusters

## Surfactants' influence on the lattice parameter of colloiddally synthesized nanoparticles

Cora Moreira Da Silva<sup>1</sup>, Armelle Girard<sup>1</sup>, Diana Drago<sup>2</sup>, Yann Le Bouar<sup>1</sup>, Vincent Huc<sup>2</sup>, Annick Loiseau<sup>1</sup>

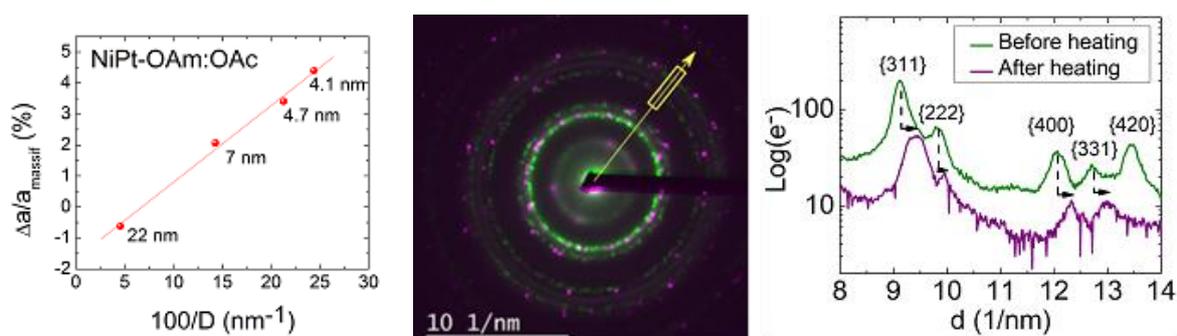
<sup>1</sup>Laboratoire d'Etude des Microstructures, France

<sup>2</sup>Institut de Chimie Moléculaire et des Matériaux d'Orsay - Paris Saclay, France

The presence of surfactants during colloidal synthesis is a key element of the process. Nevertheless, their influence on nanoparticles at atomic and crystallographic scale still unresolved from an experimental or theoretical point of view. Lattice parameters variations studies were done by electron diffraction on various nanoalloys (diameter around 5 nm), in particular on Ni-Pt nanoparticles encapsulated in oleylamine and oleic acid as surfactants. A lattice parameter expansion around 4 - 5 % is observed [1], whereas a contraction should occur with the nanometric effects [2]. After ruling out the hypotheses of particle oxidation by EDX and atoms' insertion other than Ni and Pt into the primitive cell by XPS, Ni<sub>56</sub>Pt<sub>44</sub> and pure nickel nanoparticles were analyzed with a Vermaak model [3]. We applied this model to several nanoparticles, with several sizes. The study shows that this phenomenon was due to a surface effect (Left figure). A surface tensile force is present on the surface of the nanoparticles. In order to confirm this surfactants effect, nanoparticles were heated in a microscope and their lattice parameters were monitored in situ by electron diffraction. A contraction of the lattice parameter was observed during the thermal degradation of the surfactants (Middle and right figure).

Pure nickel nanoparticles coated by hexanethiol have also been studied with the same process and a "compressive force" on the nanoparticles' surface has been measured.

These results show that the influence of surfactants can no longer be neglected, in particular their charge transfer effect, which seems to be at the origin of these forces on the particle surface.



**Left: Relative variation of lattice parameter (%) as function of particle diameter (nm<sup>-1</sup>). Middle: intensity profiles of electron diffraction peaks before heating (green line) and after heating (purple line) showing the peak shift. Right: superimposition of electron diffraction before heating (in green) and after heating (in purple), showing lattice contraction.**

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# Evidence of structural modifications of Au-Cu nanoalloys during butadiene selective hydrogenation via ex situ and in situ STEM

Abdallah Nassereddine<sup>1</sup>, Christian Ricolleau<sup>1</sup>, Catherine Louis<sup>2</sup>, Laurent Delannoy<sup>2</sup>, Damien Alloyeau<sup>1</sup>, Jaysen Nelayah<sup>1</sup>

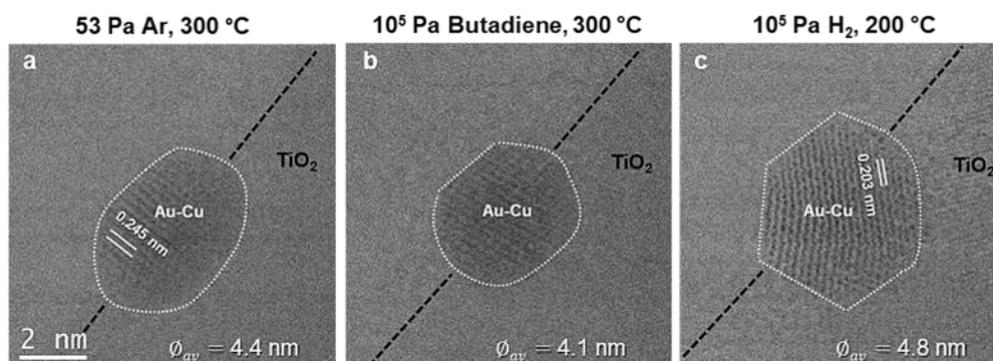
<sup>1</sup>Laboratoire Matériaux et Phénomènes Quantiques, Université de Paris, CNRS, 75013, Paris, France

<sup>2</sup>Laboratoire de Réactivité de Surface, Sorbonne Université, CNRS, 75005, Paris, France

The effects of metal alloy on the catalytic performance of Au-Cu bimetallic nanoparticles (BIM NPs) in selective hydrogenation of butadiene are undeniable. However, the origin of these effects is still largely unknown due to the lack of direct observations of BIM NPs under the reaction conditions [1]. In this contribution, we will first compare the catalytic performances of BIM NPs with different nominal compositions AuCu, Au<sub>3</sub>Cu and AuCu<sub>3</sub> and then address their structural dependent catalytic performances by ex situ and in situ atomic scale scanning TEM.

Au-Cu BIM NPs were prepared on anatase NPs by deposition-precipitation with urea followed by hydrogen activation at 300 °C [2]. Laboratory testing of the BIM catalysts in the selective hydrogenation of butadiene show that they exhibit intermediate activities between that of monometallic copper and gold ones. In addition, the catalytic stability with time of reaction of BIM catalysts increases with nominal gold content. Ex situ STEM imaging shows that while the BIM NPs have mainly FCC structures before reaction, there is a decrease in the average particle size coupled with a stabilization of highly disordered non-FCC structures after reaction. In addition, single particle X-ray spectroscopy analyses show that gas and temperature conditions induce composition redistribution during reaction.

In situ STEM studies in gas environment mimicking laboratory catalyst test conditions bring some insights under H<sub>2</sub> and butadiene and thermally induced structural transformations (see figure). In this poster, we will highlight the first results of these in situ studies.



In situ bright field-STEM images of the same AuCu NP under (a) 53 Pa Argon and (b) butadiene and (c) hydrogen at near atmospheric pressure, showing gas-dependent particle size ( $\phi_{av}$ ), shape and structure.

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[2] Delannoy et al., Physical chemistry Chemical Physics, 16.48 (2014): 26514-26527.

## Supported FeNi nanocatalysts: an organometallic route for a diversity of systems

François Robert<sup>1, \*</sup>, Pierre Lecante<sup>3</sup>, Vincent Collière<sup>1,2</sup>, Achraf Sadier<sup>4</sup>, Robert Wojcieszak<sup>4</sup>, Jean-Sébastien Girardon<sup>4</sup>, Éric Marceau<sup>4</sup>, Catherine Amiens<sup>1,2</sup> and Karine Philippot<sup>1,2</sup>

<sup>1</sup>CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP 44099, F- 31077 Toulouse Cedex 4, France

<sup>2</sup>Université de Toulouse, UPS, INPT, F-31077 Toulouse Cedex 4, France

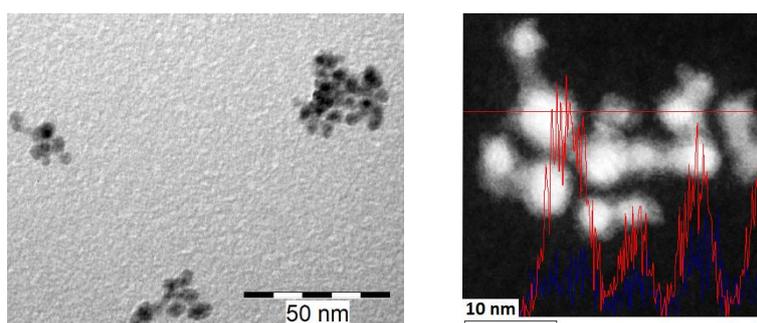
<sup>3</sup>CNRS, CEMES (Centre d'Elaboration des Matériaux et d'Etudes Structurales), 29 Rue Jeanne Marvig, BP 4347, F-31055 Toulouse Cedex 4, France

<sup>4</sup>Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, 42, rue Paul Duez, 59000 Lille, France

\*francois.robert@lcc-toulouse.fr

This project falls within an environmental approach where the purpose is to replace the noble metals by tunable and low-cost substitutes in supported nanocatalysts used by the food-processing industry for the hydrogenation of sugars into polyols [1]. We focus on the development of scalable synthesis routes towards bimetallic Fe-based supported nanoparticles (NPs) [2], and more precisely FeNi NPs with a special interest in the distribution of each element inside the nanoparticles, and its possible influence on their catalytic properties.

In order to tailor the structure and chemical order of the nanoparticles, an organometallic approach is chosen. It involves a controlled decomposition of organometallic and/or metal-organic complexes and a stabilization of the nanoparticles by organic ligands [3]. From the hydrogenation of  $[\text{Ni}(\text{COD})_2]$  and two different Fe complexes:  $\{\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2\}_2$  and  $[\text{Fe}(\text{NPh}_2)_2]_2$ , at 150°C under 3 bar of  $\text{H}_2$ , nanoparticles of three compositions were synthesized ( $\text{Fe}_9\text{Ni}_1$ ,  $\text{Fe}_1\text{Ni}_1$ ,  $\text{Fe}_1\text{Ni}_2$ ) and fully characterized (ICP-AES analysis, TEM, EDX, WAXS, EXAFS, and Squid measurements). Depending on the Fe precursor used in the synthesis, different systems were identified: a core-shell organization with preferential location of Ni in the core and Fe at the surface (see figure), and an alloy FeNi arrangement. These NPs deposited on silica have been successfully tested in the hydrogenation of xylose to xylitol, with core-shell system of global composition  $\text{Fe}_1\text{Ni}_2$  giving the highest activity.



**NPs  $\text{Fe}_1\text{Ni}_2$  analyzed by TEM in low resolution (left) and by ARM (right) in STEM and EDX mode (red line; Fe = blue, Ni = red).**

[1] G. Chieffi, C. Giordano, M. Antonietti and D. Esposito, *J. Mater. Chem. A*, 2, 11591-11596 (2014).

[2] D. Shi, R. Wojcieszak, S. Paul, and E. Marceau, *Catalysts* 9, 451-479 (2019).

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

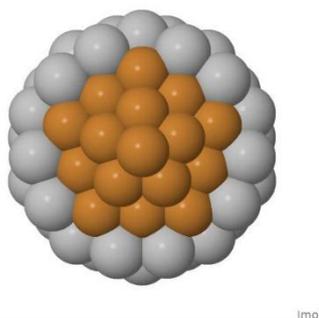
Cesare Roncaglia<sup>1,\*</sup> and Riccardo Ferrando<sup>2</sup>

<sup>1</sup>*Dipartimento di Fisica dell'Università di Genova, via Dodecaneso 33, Genova 16146, Italy*

<sup>2</sup>*Dipartimento di Fisica dell'Università di Genova and CNR-IMEM, via Dodecaneso 33, Genova 16146, Italy*

*\*roncaglia@fisica.unige.it*

Machine learning landed rather recently in the field of nanoparticles, showing its abilities to perform complex task such as force field reconstruction and acceleration of energy landscape exploration [1]. Applications of these tools are indeed of some interest whenever physically meaningful models are not available. Given the strong support of basin hopping global optimizations [2], we implemented for this purpose a Support Vector Regressor (SVR) to successfully predict the mixing energy of AgCu nanoalloys, a quantity nowadays unknown in its functional form. Moreover, with the help of unsupervised learning algorithms and of Common Neighbor Analysis (CNA), we showed that these techniques produce a physically meaningful classification of such nanoalloys in different structural families.



**AgCu nanoparticle with 45 silver atoms and 55 copper atoms**

[1] Claudio Zeni, Kevin Rossi, Aldo Glielmo & Francesca Baletto, On machine learning force fields for metallic nanoparticles, *Advances in Physics*: X, 4:1 (2019).

[2] G Rossi and R Ferrando, *J. Phys.: Condens. Matter* 21 084208 (2009).

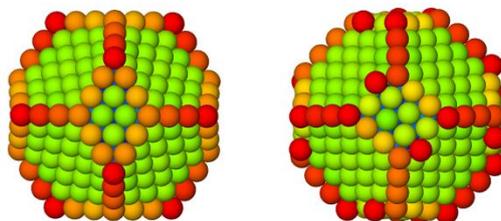
# Size effects on the shell arrangement in core@shell nanoalloys

Manoj Settem, Anand Kanjarla

Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras,  
Chennai, Tamil Nadu, India – 600 036

Core@shell nanoalloys are an important class of materials with excellent catalytic, optical, and magnetic properties. It is essential to understand the structure of the core@shell nanoalloys which influences their stability and properties. In this work, we study the structure of the shell (with single-atom thickness) in lattice mismatched systems, specifically Cu-Ag, as a function of size. In the case of octahedral motif, at very small sizes ( $< 2$  nm), three distinct shell arrangements have been considered [1]. Among them, structures where the  $\{100\}$  facets have a *pseudo hexagonal* arrangement (see figure) are favored energetically. With increase in size, the shell structure changes such that the  $\{111\}$  planes on the surface have hexagonal close packed (hcp) stacking. As a result of the *hcp* stacking, the stability of octahedral motifs increases and they compete with the icosahedral motifs.

At larger sizes, the shell adopts a mixed stacking (*fcc + hcp*) similar to the bulk interfaces between lattice mismatched metals. The following sequence of structures can be expected as a function of increasing size:  $Ih$  (hcp)  $\rightarrow$   $Ih$  (mix)  $\rightarrow$   $Dh$  (mix) +  $Oh$  (mix)  $\rightarrow$   $Oh$  (mix) where  $Ih$ ,  $Dh$ ,  $Oh$  refer to icosahedron, decahedron, octahedron and hcp, mix refer to the hcp stacking and the mixed stacking. In the case of Cu@Ag nanoalloys with mixed stacking at large sizes, the  $\{100\}$  facets of the Ag shell adopt a pseudo hexagonal arrangement where the alternate atomic rows shuffle in the opposite  $<110>$  directions [2]. The pseudo hexagonal surfaces exhibit lower atomic pressures compared to the regular  $\{111\}$  surfaces which could be potentially exploited for catalysis. These pseudo hexagonal surfaces are stable only above a critical size which would depend on the lattice mismatch.



**Two distinct types of pseudo hexagonal rearrangement of the surface  $\{100\}$  facets.**

[1] E. Panizon and R. Ferrando, *Nanoscale* 8, 15911-15919 (2016).

[2] P. T. Sprunger, E. Lægsgaard, and F. Besenbacher, *Phys. Rev. B* 54, 8163- 8171 (1996).

## Structural transitions in Au nanoclusters

Manoj Settem<sup>1</sup>, Alberto Giacomello<sup>1</sup>, Riccardo Ferrando<sup>2</sup>

<sup>1</sup>*Department of Mechanical and Aerospace Engineering, Sapienza University of Rome, Italy*

<sup>2</sup>*Department of Physics, University of Genoa, Italy*

Gold nanoclusters have been studied extensively compared to the other metallic clusters owing to a wide variety of structures that have been predicted theoretically. Although there are a lot of studies which have focused on Au nanoclusters, the understanding of structural transitions is far from complete. In this work, we study the structural transitions in Au nanoclusters using Parallel Tempering Molecular Dynamics (PTMD) which allows us to sample configurations efficiently. Specifically, we focus on Au<sub>147</sub> nanoclusters. Although 147 is a geometric “magic” number corresponding to a Mackay Icosahedron, decahedral and octahedral structures are predicted to be lower in energy compared to icosahedral structures. Different structural motifs are used as the initial structures for the PTMD simulations. We compare and analyze the structures obtained at various temperatures.

# Hydrogen-driven surface segregation in Pd-alloys

Pernilla Tanner\* and Paul Erhart

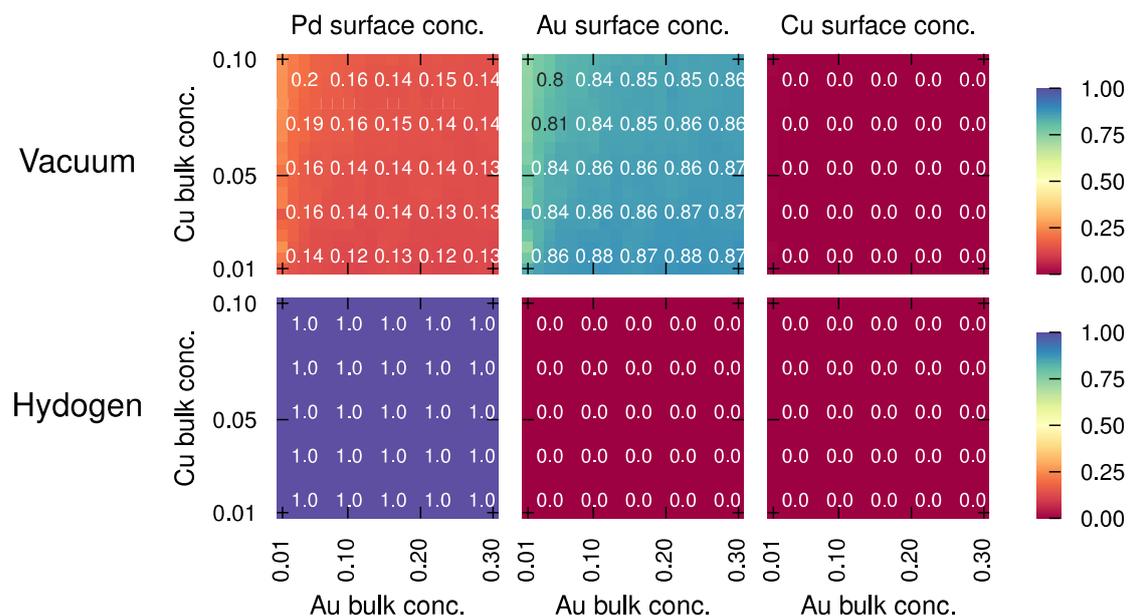
Chalmers University of Technology, Department of Physics, S-412 96 Gothenburg, Sweden

\*tannerp@chalmers.se

The safe widespread application of hydrogen-based fuels requires hydrogen sensors that are long-term stable, inexpensive and specific with a short response time. In this regard, optical sensing based on nanostructured Pd-alloys has shown great potential, but challenges remain, in particular with regard to the surface composition under operation. While the latter is crucial for long-term functionality and stability, it is experimentally very challenging to obtain accurate atomic-scale information.

Here, we therefore scrutinize the behavior of three particularly relevant surface alloys AuPd, CuPd and AuCuPd in vacuum and in the presence of adsorbed hydrogen. To this end, we employ alloy cluster expansions trained using density functional theory calculations. To overcome the symmetry reduction implicit to surface systems, we exploit local symmetries, which enables us to achieve accurate and reliable models at a modest computational cost.

We observe segregation of primarily Au in vacuum and Pd in the presence of adsorbed H. In addition, we find that surface segregation often induces oscillations in composition as well as intricate correlation of the atomic configuration between the surface layers, which demonstrates the importance of atomic-scale studies to fully understand the segregation behavior.



Surface composition of AuCuPd in vacuum and in the presence of adsorbed H.

## Mitigating CO poisoning by modifying the Ge concentration in novel PtGe catalysts

Andoni Ugartemendia<sup>1,\*</sup>, Abel de Cózar<sup>1,2</sup>, Jose M. Mercero<sup>1</sup>, Elisa Jimenez-Izal<sup>1,2</sup>

<sup>1</sup>*Polimero eta Material Aurreratuak: Fisika, Kimika eta Teknologia, Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU) & Donostia International Physics Center (DIPC) PK 1072, 20080 Donostia, Euskadi, Spain*

<sup>2</sup>*IKERBASQUE, Basque Foundation for Science, 48009 Bilbao, Euskadi, Spain*

\*augartemendia003@ehu.eus

The energy overconsumption of non-renewable energy sources and their limited supplies pose one of the major global concerns. Many efforts have been put through in the development of more sustainable and environmentally friendly energy sources. Fuel cells stand as one of the most promising alternatives. Unfortunately, before such technology can be commercialized several issues have to be addressed. Undoubtedly, CO poisoning stands as one of the major drawbacks. The high activity of the platinum group metal (PGM) catalysts favours the formation of a CO layer, hindering any reaction and thus leading to a loss in the power density [1,2]. A very promising route to tackle CO poisoning is alloying PGM clusters with a second much cheaper element [3]. In this vein, in our previous work [4] it was shown that singly doped Pt<sub>n-1</sub>Ge<sup>+</sup> clusters reduce the affinity to CO. Herein, as a continuation of our previous work we aim to test the effect of Ge concentration on CO poisoning. Density functional theory (DFT) calculations were performed on small size Pt clusters in gas phase, alloyed with different amounts of Ge. The potential energy surface (PES) was sampled concisely by means of Bond Length Distribution Algorithm (BLDA) based global minima search techniques [5]. It was found that the concentration of Ge was a key factor to tune the catalytic properties. Clusters of equal Pt and Ge concentration presented the weakest affinity towards CO. The underlying reason was mainly electronic. The effective mixing between Pt and Ge reduces the d orbitals available to interact with the 2π\* orbital of CO. Besides, as Ge concentration increases, more charge is accumulated in Pt and the Pauli repulsion between the cluster and CO increases. Furthermore, the catalytic activity of the nanoalloys was tested towards the dissociation of H<sub>2</sub>. The results revealed that the catalytic activity is not lost upon alloying. We believe that the remarkable properties of Ge found in this work could help mitigate a long standing problem in fuel cell technology.

[1] X. Cheng, et al., J. Power Sources 165, 739-756 (2007).

[2] J. Baschuk, X. Li, Int. J. Energy Res. 25, 695-713 (2001).

[3] S. Ehteshamia, S. Chan, Electrochim. Acta 93, 334-345 (2013).

[4] A. Ugartemendia, K. Peeters, P. Ferrari, A de Cózar, J.M. Mercero, E. Janssens, E. Jimenez-Izal, submitted.

[5] H. Zhai, A.N. Alexandrova, J. Chem. Theory Comput. 12, 6213-6226 (2016).

# IR structural characterization of cluster-molecule reaction products as catalytic model systems

Frank J. Wensink<sup>1</sup>, Maximilian G. Münst<sup>2</sup>, Jakob Heller<sup>2</sup>, Christian van der Linde<sup>2</sup>,  
Martin K. Beyer<sup>2</sup>, Joost M. Bakker<sup>1,\*</sup>

<sup>1</sup>Radboud University, FELIX Laboratory, Toernooiveld 7, 6525ED Nijmegen, The Netherlands

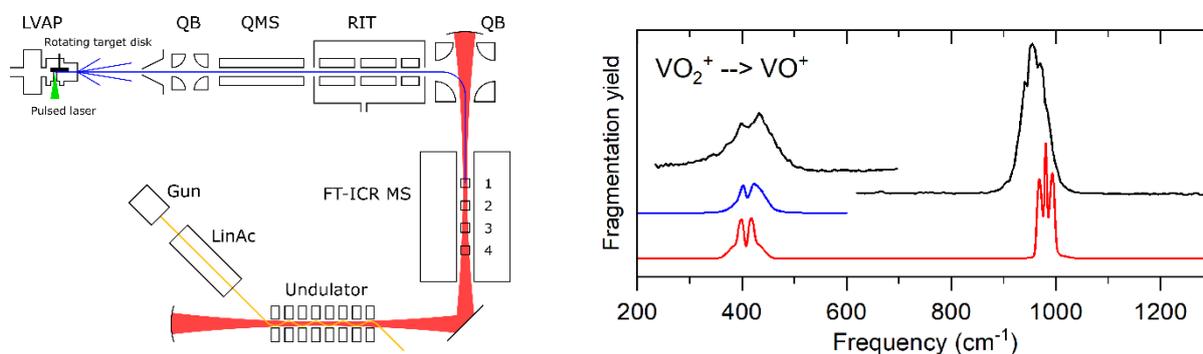
<sup>2</sup>Universität Innsbruck, Institut für Ionenphysik und Angewandte Physik, Technikerstraße 25, 6020  
Innsbruck, Austria

\*j.bakker@ru.nl

In heterogeneous catalysis, the mechanism of reactions over transition metal catalysts is often only poorly understood. To get insight in fundamental chemical interactions with transition metals at the highest level of detail, we study the interaction between isolated metal ions and clusters of pure and mixed elemental composition with simple molecules such as oxygen, methane, hydrogen and methanol.

For this, we generate metal ions and clusters using laser vaporization, and react them with gaseous molecules of interest in a radio-frequency ion trap. After the reaction, we analyze the formed products by a combination of mass-spectrometry and IR spectroscopy. Spectra are recorded using FELICE, the Free Electron Laser for Intra-Cavity Experiments. By comparison with density functional theory calculations, we can elucidate on product structures and reconstruct the reaction pathways.

Here, we present the direct IR characterization of strongly bound  $\text{MO}_2^+$  (M=V, Nb, Ta) [1] and  $\text{MCH}_2^+$  (M=Pt, Rh) species by the intra-cavity laser FELICE.



**Left: Schematic of the experimental instrument, with at its heart the reactive ion trap (RIT) and the FT-ICR mass spectrometer, where ions are irradiated by infrared light. Right: The experimental spectrum of  $\text{VO}_2^+$  in black, and calculated spectra including rotational contours in red and blue.**

[1] F. J. Wensink, M. G. Münst, J. Heller, M. Ončák, J. M. Bakker and C. van der Linde, J. Chem. Phys. 153, 171101 (2020).

# Molecular dynamics simulation of surface oxidation of Pd

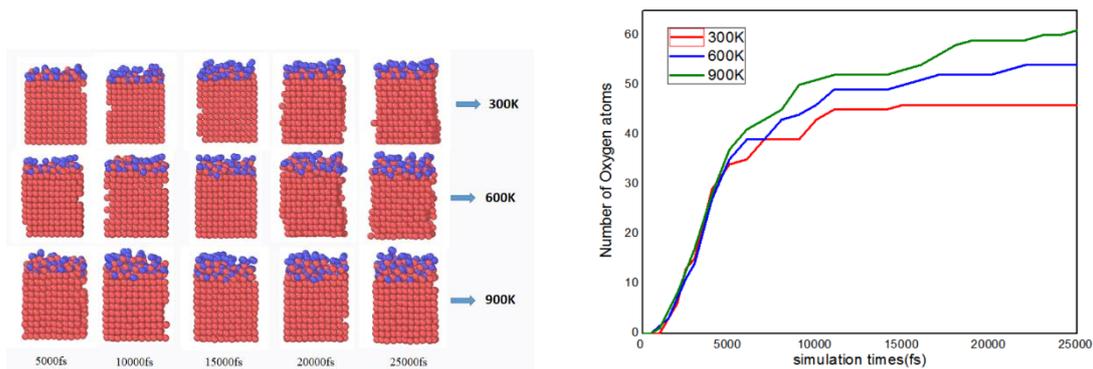
Ying Wu<sup>1, 2</sup> and Fuyi Chen<sup>1, 2,\*</sup>

<sup>1</sup>State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China

<sup>2</sup>School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, 710072, China

\*fuyichen@nwpu.edu.cn

In recent years, direct formate fuel cell (DFFC) has attracted more and more attention as promising green energy. Pd is recognized as an anode catalyst for formic acid fuel cells due to its abundant reserves and excellent catalytic performance. However, Pd nanoparticles still have some disadvantages, such as easy agglomeration and poor electrochemical stability, doping and alloying of Pd is an effective way to solve these problems, such as PdAg nanoalloy. Most materials will be oxidized when exposed to air, which has a great impact on the structure and properties of materials. Molecular dynamics (MD) simulation of the metal oxidation process is an effective way to understand the mechanism and influencing factors of metal oxidation. In the molecular dynamics simulation of Pd oxidation process at different temperatures, we found that the oxidation rate of Pd is fast at the initial stage of oxidation, and the oxidation rate gradually slows down with the progress of the oxidation process until the oxidation tends to saturation, and temperature has no obvious effect on the oxidation rate of Pd. In addition, the oxidation process of Pd is not carried out layer by layer. When the surface atoms are not saturated, the oxygen atoms have already entered the subsurface.



Left: Molecular dynamics simulation of surface oxidation of Pd at 300K, 600k and 900K.

Right: Variation of oxygen uptake with time during Pd surface oxidation at 300K, 600k and 900K.

## **O<sub>2</sub> activation by AuAg clusters on a defective (100)MgO surface**

Carlos Vital

*Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apdo. 70-360, C. P. 04510, Coyoacán, Ciudad de México, Mexico*

In the present work, we discuss the electronic properties of supported dispersed bimetallic clusters with respect to their size, geometry, and Au<sub>n</sub>/Ag<sub>m</sub> (n + m = 6) composition. We have studied with supercell-density functional theory calculations the role of the charge transfer from the MgO defective support toward the cluster in the activation of O<sub>2</sub> by Au<sub>n</sub>Ag<sub>m</sub> clusters. We first considered gas-phase clusters with different atomic compositions; then, we deposited all of them on a pristine (100)MgO surface and finally on a more realistic (100)MgO F-center. We performed a global and unrestricted search of the (cluster + surface) geometry. The Mexican enhanced genetic algorithm has been used to exhaustively explore the potential energy surface. Our results show that O<sub>2</sub> activation depends on the Au<sub>n</sub>/Ag<sub>m</sub> ratio. It has been found that both metals involved play different and important roles toward (a) the actual O<sub>2</sub> dissociation and (b) weakening of the oxygen-cluster bond, which, in turn, may promote the possibility of a catalytic process to take place, such as the oxidation process of CO and NO<sub>x</sub> among others.

[1] J. Chem. Phys. 152, 024303 (2020).



## List of participants

<b>Name</b>	<b>First Name</b>	<b>Affiliation</b>	<b>Country</b>
Ait Hellal	Fatima	Université d'Orléans	France
Alonso	Julio A.	University of Valladolid	Spain
Amanova	Aisara	Université Paris Saclay	France
Amara	Hakim	Laboratoire d'Etudes des Microstructures	France
Amendola	Vincenzo	University of Padova	Italy
Amiens	Catherine	Université Paul Sabatier	France
Andreazza	Caroline	Université d'Orléans	France
Andreazza	Pascal	Université d'Orléans	France
Anjum	Uzma	National University of Singapore	Singapore
Anzaldo Grundler	Alina Tlaneci	Universidad Nacional Autónoma de México	Mexico
Arslan	Haydar	Zonguldak Bulen Ecevit University	Turkey
Bakker	Joost	Radboud University	Netherlands
Baletto	Francesca	King's College London	United Kingdom
Beltran	Marcela	Universidad Nacional Autónoma de México	Mexico
Benoit	Magali	CEMES-CNRS	France
Benzo	Patrizio	CEMES-CNRS	France
Berthier	Fabienne	CNRS, Université Paris-Saclay	France
Blin	Thomas	Université Paris Saclay	France
Breyton	Grégoire	University of Paris	France
Buendia-Zamudio	Fernando	Universidad Nacional Autónoma de México	Mexico
Campisi	Sebastiano	Università degli Studi di Milano	Italy
Camus	Elise	Université Lyon 1, Institut Lumière Matière	France
Casanove	Marie-José	CEMES-CNRS	France
Chen	Fuyi	Northwestern Polytechnical University	China
Cheng	Daojian	Beijing University of Chemical Technology	China
Chinnappa	Vana	KU Leuven	Belgium
Cottancin	Emmanuel	Université Lyon 1, Institut Lumière Matière	France
De Knijf	Kobe	KU Leuven	Belgium
de la Rosa Abad	Juan	Universidad Nacional de Córdoba	Spain
Delgado-Callico	Laia	King's College London	United Kingdom
Dendooven	Jolien	Ghent University	Belgium
Dupuis	Veronique	Université Lyon 1, Institut Lumière Matière	France
El Koraychy	El Yakout	Università degli Studi di Genova	Italy
Elgayyar	Taha	Université Lyon 1, IRCELYON, CNRS	France
Ernst	Wolfgang E.	Graz University of Technology	Austria
Ferrando	Riccardo	Università degli Studi di Genova	Italy
Ferrari	Piero	KU Leuven	Belgium
Fortunelli	Alessandro	CNR-ICCOM	Italy
Front	Alexis	LEM-CNRS	France
Galloni	Melissa Greta	Università degli Studi di Milano	Italy
Gálvez-González	Luis E.	Universidad de Sonora	Mexico
German	Estefania	Universidad de Valladolid	Spain
Girard	Armelle	Université Paris Saclay	France
Grandjean	Didier	KU Leuven	Belgium
Haroune	Moussa	Université d'Orléans	France
Hasan	Sara	University of Lahore	Pakistan
Heard	Christopher	Charles University in Prague	Czech Republic
Herrera	Guillermo	Université Lyon 1, Institut Lumière Matière	France
Janczak-Rusch	Jolanta	Empa, Swiss Federal Laboratories for Materials Science and Technology	Switzerland
Janssens	Ewald	KU Leuven	Belgium
Jimenez	Juan	Universidad Nacional de Córdoba	Spain

Jimenez-Izal	Elisa	Euskal Herriko Unibertsitatea & Donostia International Physics Center	Spain
Kaw	Kevin Anthony	KU Leuven	Belgium
Khanna	Vaibhav	University of Oxford	United Kingdom
Kozlov	Sergey	National University of Singapore	Saudi Arabia
Lam	Julien	CEMES-CNRS	France
Le Roy	Damien	Université Lyon 1, Institut Lumière Matière	France
Liao	Ting-Wei	National Central University	Taiwan
Libeert	Guillaume	KU Leuven	Belgium
Liu	Lifeng	Int. Iberian Nanotechnology Laboratory	Portugal
Lopez	Maria J.	Universidad de Valladolid	Spain
Luque-Ceballos	Jonathan	Universidad Nacional Autónoma de México	Mexico
Lushchikova	Olga	Radboud University	Netherlands
Marceau	Eric	Université de Lille	France
Martinez Moreira	Murilo Henrique	Université Claude Bernard Lyon 1	France
Mendez Medrano	Ana Andrea	San Luis Potosí Institute of Scientific Research and Technology	Mexico
Meunier	Frederic	Université Lyon 1, IRCELYON, CNRS	France
Minnai	Chloé	Okinawa Institute of Science	Japan
Moisset	Arthur	Sorbone University - CNRS, MONARIS	France
Molina	Luis M.	Universidad de Valladolid	Spain
Moreira Da Silva	Cora	Université Paris Saclay, ONERA - CNRS	France
Mottet	Christine	Aix Marseille Université, CINaM - CNRS	France
Nassereddine	Abdallah	Université de Paris	France
Nelli	Diana	University of Genoa	Italy
Nguyen	Thi Hong Trang	KU Leuven	Belgium
Palmer	Richard E.	Swansea University	United Kingdom
Petit	Christophe	Sorbone University, MONARIS - CNRS	France
Pierron-Bohnes	Veronique	Université de Strasbourg, IPCMS	France
Polak	Micha	Ben Gurion University	Israel
Prabhu	Nikhil	KU Leuven	Belgium
Puibasset	Joël	Université d'Orléans, CNRS - ICMN	France
Rahm	Magnus	Chalmers University of Technology	Sweden
Remita	Hynd	CNRS-Université Paris-Saclay	France
Ricolleau	Christian	Univ. of Paris, Laboratory Materials and Quantum Phenomena	France
Robert	François	Lab. de Chimie de Coordination, Toulouse, CNRS	France
Roncaglia	Cesare	Università degli Studi di Genova	Italy
Settem	Manoj	Sapienza University of Rome	Italy
Tanner	Pernilla	Chalmers University of Technology	Sweden
Ugartemendia Biurrun	Andoni	University of the Basque Country	Spain
Umair Hassan	Muhammad	University of Sargodha	Pakistan
van der Tol	Johan	KU Leuven	Belgium
Vital	Carlos	Universidad Nacional Autónoma de México	Mexico
Weissker	Hans-Christian	CINaM Marseille	France
Wensink	Frank	Radboud University	Netherlands
Wu	Ying	Northwestern Polytechnical University	China
You	Zhi	Yanshan University	China

	Wednesday April 14	Thursday April 15	Friday April 16
8:40	Opening		
9:00	Richard Palmer (Swansae University)	Pascal Andrezza (Université d'Orléans)	Magali Benoit (CEMES)
9:25	Diana Nelli (Universita di Genova)	Francesca Baletto (King's College London)	Didier Grandjean (KU Leuven)
9:50	Fabienne Berthier (Université Paris-Saclay)	Damien Le Roy (Université Claude Bernard Lyon 1)	Arthur Moisset (Sorbonne Université)
10:15	Emmanuel Cottancin (Université Lyon 1)	Chloé Minnai (OIST Okinawa)	Fatima Ait Hellal (Université d'Orléans)
10:30	Cora Moreira Da Silva (Lab. d'Etude Microstruct.)	Sergey Kozlov (National University of Singapore)	Elisa Jimenez-Izal (Euskal Herriko Unibertsitatea)
10:45	Meet-the-speaker session	Meet-the-speaker session	Meet-the-speaker session
11:15	Wolfgang Ernst (Graz University of Technology)		Hynd Remita (Université Paris-Saclay)
11:40	Piero Ferrari (KU Leuven)		Hans-Christian Weissker (Aix-Marseille Université)
11:55	Sebastiano Campisi (Uni. degli Studi di Milano)	Poster session	Patrizio Benzo (Université de Toulouse)
12:10	Alessandro Fortunelli (CNR-ICCOM Pisa)		Joost Bakker (Radboud University)
12:25	Meet-the-speaker session		Meet-the-speaker session
13:00	Break	Break	Closing
14:00	Networking session	Networking session	
14:30	Jolien Dendooven (Ghent University)	Frédéric Meunier (Université Claude Bernard Lyon 1)	
14:55	Grégoire Breyton (Université Paris Diderot)	Vincenzo Amendola (University of Padova)	
15:20	Estefania German (University of Valladolid)	Murilo Moreira (UNICAMP Campinas)	
15:35	Micha Polak (Ben Gurion University of the Negev)	Fernando Buendia-Zamudio (UNAM, México)	
15:50	Meet-the-speaker session	Meet-the-speaker session	
16:20			Round-table IRN members