

NANOALLOYS

International Research Network

JUNE

4-7

IMN 2019 #2

International Meeting on Nanoalloys



Genova
Italy

Structure, Equilibrium and Out-of-equilibrium effects,
Kinetics: Growth and mobility, Environment effects,
Nanoalloy properties and applications

Conference book

Physics Department, Università di Genova

<http://nanoalloys-irn.cnrs.fr/imn-2019/>





<http://nanoalloys-irn.cnrs.fr/nanoalloys-meeting/>

The 2019 International Meeting on Nanoalloys (IMN-2019) is the second plenary meeting organized by the International Research Network IRN "Nanoalloys". It follows IMN-2018, which took place at Orléans on May 22-25, 2018. IMN-2019 will be held in Genova, Italy on June 4-7, 2019.

The main scope of the IRN "Nanoalloys" is to reinforce exchanges at European level in the field of alloy nanoparticles, and to promote new collaborations at international level on the topics that are now at the forefront of research in nanoalloys.

The plenary IMN meetings are, however, open to a wider community, including groups that are not members of the IRN, both from European and extra-European countries.

IMN-2019 brings together experimentalists and theoreticians to foster concerted efforts of experimental and modeling groups. Close collaboration between experimentalists and theoreticians is very often necessary to investigate nanoalloys at ultimate resolution (structure, property), either statically or dynamically (time-resolved, multi-scale) and under environmental conditions. Research in nanoalloys is highly interdisciplinary, comprising chemists, physicists and materials scientists.

Scope :

Nanoalloys are bi- or multi-component metallic nanoparticles. The tremendous growth of interest in nanoalloys comes from the fact that their chemical and physical properties can be tuned by varying the composition and degree of chemical ordering, as well as the size of the nanoparticle. This makes nanoalloys suitable for a wealth of technological applications, such as in data storage and optoelectronic devices, chemical and biological sensors, fuel cells, catalysts, etc., in which nanoalloys can be more efficient or less expensive than single-metal nanoparticles.

Nanoalloys are also quite interesting from the fundamental science point of view, owing to the complexity of their structures and properties and the interplay between them.

The meeting will focus on the following topics:

1- Equilibrium structures: bare and ligand-covered nanoalloys, action of the environment

2- Out-of-equilibrium effects: nucleation, growth, aging in different environments and conditions

3- Applications of nanoalloys to catalysis, magnetism, plasmonics and biomedicine

Conference Chairs

- **Riccardo Ferrando**, Dipartimento di Fisica, Università di Genova, Italy
- **Pascal Andreatza**, ICMN, Interfaces, Confinement, Matériaux et Nanostructures, CNRS, Université d'Orléans, France

Scientific Committee:

Pascal Andreatza (ICMN, Orléans, France)
Magali Benoit (CEMES, Toulouse, France)
Fabienne Berthier (ICMMO, Orsay, France)
Veronique Dupuis (ILM, Lyon, France)
Riccardo Ferrando (Università di Genova, Italy)
Ewald Janssens (KU Leuven, Belgium)
Christine Mottet (CINaM, Marseille, France)
Richard Palmer (Swansea University, UK)
Christophe Petit (MONARIS, Paris, France)
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NANOALLOYS

International Research Network



International Research Network (IRN) / Groupement De Recherches International (GDRI) on Nanoalloys

An IRN is a scientific coordination network gathering French and foreign research teams from European countries around a specific scientific topic. The network is the result of an agreement detailing the scientific content, the composition of the scientific committee and the provisional budget, signed by the authorized representative(s) of the French (CNRS and affiliated universities of research joint units) and the foreign (research organizations or universities) partner institutions.

About the IRN Nanoalloys

Alloy nanoparticles are bi- or multi-component metallic nanoparticles which are often called **Nanoalloys**. As previously said, the tremendous growth of interest in nanoalloys comes from the fact that their chemical and physical properties can be tuned by varying the composition and degree of chemical ordering, as well as the size of the nanoparticle. The properties of nanoalloys can be very different from those of the corresponding bulk alloys and from those of single-metal nanoparticles of the same size. This makes nanoalloys suitable for a wealth of technological applications, as in data storage and optoelectronic devices, in chemical sensors, in fuel cells and as heterogeneous catalysts, in which nanoalloys can be more efficient or less expensive than single-metal catalysts. Nanoalloys are also quite interesting from a basic science point of view owing to the complexity of their structures and properties and the interplay between them. They can be characterized by a new type of phase diagrams, in which a third variable, the nanoparticle size, is added to temperature and composition, which are the conventional variables of bulk phase diagrams.

Research in nanometer-size multicomponent metallic nano-objects, "Nanoalloys" is highly interdisciplinary. In fact, the scientific community working in this field comprises chemists, physicists and materials scientists. International collaborations at the European level are very often necessary to develop innovative research approaches, which very often require the close collaboration between experimental and theory/simulation groups. For such a rapidly growing and interdisciplinary field, networking initiatives are therefore of vital importance.

The aim of the Nanoalloys International Research Network is to share complementary tools and expertise developed by French and foreign colleagues in the field of nano-sized alloy particles with bi- or multi- metallic components. This network is dedicated to promote new hot topics, such as kinetic effects which control the equilibrium and out-of-equilibrium structure, environment effects on the nanoalloy structures and its impact on cluster's chemophysical properties.

Network Coordination

Coordinator: **Pascal Andreazza**, ICMN, Interfaces, Confinement, Matériaux et Nanostructures, CNRS, Université d'Orléans, France

Vice coordinator: **Riccardo Ferrando**, Department of Physics, Università di Genova, Italy

An "Executive Committee" and a "Scientific Committee" manage the following network activities on proposition by the Coordinators:

- the organisation of conferences, lectures, seminars, symposiums, study days, theme-based workshops or any other type of meeting dealing with the scientific theme;
- facilitate and encourage exchange of information and documentation on the scientific theme;
- identify common research projects relating to the scientific theme;
- coordinate replies to invitations to tender for supporting research and technological development;
- encourage permanent training initiatives and promote pedagogical operations.

Themes:

1. Equilibrium properties: structure and environment effects

- 1.1. Size-dependent nanoalloy phase diagrams and transitions
- 1.2. Effects of the environment (supports, matrix confinement, organic ligands, liquid environments, gas adsorption)
- 1.3. Strain engineering in binary and ternary nanoalloys

2. Out-of-equilibrium effects: kinetic, mobility, environment

- 2.1. Growth Kinetics
- 2.2. Ageing : from metastable initial state to equilibrium
- 2.3. Collective effects in assemblies of nanoalloys

3. Nanoalloy properties and their relationship with structure and environment

- 3.1. Catalytic properties: pressure gap, surface segregation, stability and chemical reactivity
- 3.2. Magnetic properties: morphologies, strain and coupling nanocomposites to improve magnetic moment and anisotropy
- 3.3. Optical properties: effect of the matrix, or ligands, morphologies and coupling in nanohybrids to tailor plasmonic properties

Website: <http://nanoalloys-irn.cnrs.fr/>



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Program

Tuesday, June 4

15h00 – 18h00 An Introduction To Metal Nanoparticles And Nanoalloys

15:00 – 15:40 **Riccardo Ferrando**

Università di Genova, Italy

Tutorial 1: Structures Of Metal Nanoparticles And Nanoalloys

15:40 – 16:20 **Richard E. Palmer**

University of Swansea, UK

Tutorial 2: Nanoparticle Nucleation And Growth

16:30 – 17:10 **Christian Ricolleau**

Université Paris 7 Denis Diderot, France

Tutorial 3: Understanding Nanoalloy Properties Through New Generation Aberration-corrected Electron Microscopy

17:10 – 17:50 **Emmanuel Cottancin**

Université Claude Bernard Lyon, France

Tutorial 4: Plasmonic Properties Of Nanoalloys In Relation With Their Chemical Structure

18h00 – 19h30 Welcome Party and Conference Registration

Wednesday, June 5

Session 1 **Chair: Riccardo Ferrando and Pascal Andreezza**

8h30 – 9h10 *Registration*

9h10 – 9h30 *Opening*

9h30 – 9h50 *IRN activity presentation*

9h50 – 10h10 Atomic Ordering In Large Bimetallic Particles From
O1 DFT+Topological Calculations
Konstantin Neyman, Universitat de Barcelona, Spain

10h10 – 10h30 Site-specific Wetting Of Iron Nanocubes By Gold Atoms In Gas-
O2 phase Synthesis
Junlei Zhao, University of Helsinki, Finland

10h30 – 11h00 *Coffee Break*

Session 2 **Chair: Francesco Bisio**

11h00 – 11h20 Shell Thickness Induced Core Transformation In Core(Fe)-
O3 shell(Au) Magnetic Nanoparticles
Marie-José Casanove, Université de Toulouse, France

11h20 – 11h40 Magnetic Properties Of Ferromagnetic/antiferromagnetic Metallic
O4 Nanocomposites: Influence Of Alloying At The Interface
Davide Peddis, Università di Genova, Italy

11h40 – 12h00 Magnetoplasmonic Nanoalloys
O5 **Alessio Gabbani, Università di Pisa, Italy**

12h00 – 12h20 Fcc-Co Clusters In L₁₀-FePt Matrix As Model Nanocomposite
O6 Magnets
Charles Paleo, Institut Lumière Matière, Lyon, France

12h20 – 14h00 *Lunch*

Session 3 **Chair : Christine Mottet**

14h00 – 14h20 Elucidating Structural Transitions In Nanoalloys
O7 **Francesca Baletto, King's College, London, UK**

14h20 – 14h40 Core-shell vs Multi-shell Formation In Nanoalloys Evolution From
O8 Disordered Configurations
Diana Nelli, Università di Genova, Italy

14h40 – 15h00 Atomic-Resolution Imaging And Ab Initio Modelling Of Surface
O9 And Core Melting Of Supported, Size-Selected Au Nanoclusters
Richard Palmer, University of Swansea, UK

15h00 – 15h20 Structure And Chemical Ordering In Nanoalloys From
O10 Constrained Monte Carlo Simulations
**Magnus Rahm, Chalmers University of Technology,
Göteborg, Sweden**

15h20 – 15h50 *Coffee Break*

Session 4 **Chair : Ignacio Garzon**

15h50 – 16h10 DFTB Parametrization And Global Optimization Of 55-Atom
O11 $\text{Cu}_x\text{M}_{55-x}$ (M=Pd, Pt, Au) Nanoclusters
**Maxime Van den Bossche, Institut des NanoSciences de
Paris, CNRS, France**

16h10 – 16h30 Facile Route Towards Mono And Bimetallic Nanocrystals With
O12 Size And Shape Control
Christophe Petit, Sorbonne Université, Paris, France

16h30 – 16h50 Modeling Transition Metals And Nanoalloys: Fixing The Misuse
O13 Of Cohesive-Energies
**Micha Polak, Ben-Gurion University of the Negev, Beer-
Sheva, Israel**

17h00 – 23h00 *Excursion and Social Dinner*

Thursday, June 6

Session 5 **Chairman : Magali Benoit**

9h10 – 9h30
O14 Application Of Structure Descriptor For Rational Design Of Transition Metal Catalysts
Daojian Cheng, Beijing University of Chemical Technology, People's Republic of China

9h30 – 9h50
O15 Catalytic (And Optical) Properties Of (Supported) Alloy (Ultra)NanoStructures
Alessandro Fortunelli, CNR-ICCOM & IPCF, Pisa, Italy

9h50 – 10h10
O16 Catalysis By Bimetallic Subnanometer Clusters
Stefan Vajda, Academy of Sciences of the Czech Republic, Prague, Czech Republic

10h10– 10h30
O17 Dynamic Structure Of Low Temperature CO Oxidation Catalysts Based On Gas-phase PdNi Nanoclusters Deposited On Alumina Powder Unraveled By Operando XAFS And DRIFTS
Anupam Yadav, KU Leuven, Belgium

10h30 – 11h00 *Coffee Break*

Session 6 **Chair: Veronique Dupuis**

11h00 – 11h20
O18 Atomistic Simulation Of Trimetallic Nanoparticle Growth By Cluster Beam Deposition
Panagiotis Grammatikopoulos, OIST, Okinawa, Japan

11h20 – 11h40
O19 Tailored Multi-element Nanoparticles For Wide Spectrum Antibacterial Coatings
Luca Gavioli, Università Cattolica del Sacro Cuore, Brescia, Italy

11h40 – 12h00
O20 Environmental Plasmonic Spectroscopy Of Silver-Iron Nanoparticles: Chemical Ordering Under Oxidizing And Reducing Conditions
Emmanuel Cottancin, Université de Lyon, France

12h00 – 12h20
O21 Ag-Pt Nanoalloys: An Intriguing Hybrid System Between Chemical Ordering And Phase Separation
Christine Mottet, CINaM, CNRS, Marseille, France

12h20 – 14h00 *Lunch*

Session 7

Chair: Panagiotis Grammatikopoulos

14h00 – 14h20 Vibrations Of Atomically Defined Metal Clusters And Nanoalloys
O22 **Ignacio Garzón, Universidad Nacional Autónoma de México, México City, México**

14h20 – 14h40 LoDiS: Low Dimensional System Molecular Dynamics. A 0D
O23 Computational Engine For Investigations At The Nanoscale
Raphael Pinto-Miles, King's College, London, UK

14h40 – 15h00 A New Basin Hopping Suite For Multi-Component Nanoparticles
O24 **Daniele Rapetti, Università di Genova, Italy**

15h30 – 16h00 *Meeting of the IRN groups*

16h00 – 18h30 *Poster session with refreshments*

Friday, June 7

Session 8 **Chair: Luca Gavioli**

9h10 – 9h30
O25 The Surface Segregation Of Gold In Pd_nPt_{13-n}Au₄₂ Trimetallic Clusters: A DFT Study
Ali Kemal Garip, Zonguldak Bulent Ecevit University, Zonguldak, Turkey

9h30 – 9h50
O26 Nanoparticle-Support Interactions And Catalytic Activities Of Noble-Metal Nanoparticle-Based Catalysts
Theodoros Pavludis, Swansea University, UK

9h50 – 10h10
O27 Physical Synthesis And Characterization Of Plasmonic Ag@CaF₂ Nanoparticles
Sergio D'Addato, Università di Modena e Reggio Emilia, Modena, Italy

10h10 – 10h30
O28 Plasmonics Of Noble Metal Nanoparticles In A Hot Thermodynamic Bath
Michele Magnozzi, Università di Genova, Italy

10h30 – 11h00 *Coffee Break*

Session 9 **Chair: Riccardo Ferrando**

11h00 – 11h20
O29 Capturing Spatial Contributions To Excitations Through Fourier Transform Of Induced Density Obtained In δ -kick RT-TDDFT Calculations
Rajarshi Sinha-Roy, Aix-Marseille University, Marseille, France

11h20 – 11h40
O30 How Metallic Are Tiny Pieces Of Noble Metals? Metallicity And Screening In Gold & Silver Clusters
Hans-Christian Weissker, Aix-Marseille University, Marseille, France

11h40 – 12h00
O31 Origin Of Circular Dichroism In Noble Metal Alloy Clusters: A Combined Experimental And Theoretical Spectroscopic Investigation
Mauro Stener, Università di Trieste, Italy

12h00 – 12h20 Concluding remarks

12h20 – 14h00 *Lunch*

Poster session

- P1** Tuning The Magnetic Moment Of Small Late 3d-transition-metal Oxide Clusters, **R. H. Aguilera-del Toro et al., Universidad de Valladolid, Spain**
- P2** Metallic Nanoparticles: Morphological And Structural Stability Dependence Due To Metal And Support Nature, **F. Ait Hellal et al., ICMN Orléans, France**
- P3** Stability And Bonding Patterns In ZnMg Nanoalloys, From A Combined Empirical Potential/DFT Approach, **P. Alvarez-Zapatero et al., Universidad de Valladolid, Spain**
- P4** Unexpected Composition And Size Dependence Of L1₁ Chemical Order In Ag-Pt Nanoalloys, **C. Andreazza et al., ICMN Orléans, France**
- P5** Ageing Of Ag_cPt_{1-c} Thin Films And Nanoparticles, **F. Berthier et al., CNRS, Orsay Cedex, France**
- P6** Experimental Investigation Of Thermal Properties Of Binary Metal Alloys, **T. Boruvka et al., Masaryk University, Brno, Czech Republic**
- P7** Stern-Gerlach Deflection Of Cr_nO_m Clusters, **K. De Knijf et al., Laboratory of Solid-State Physics and Magnetism, Leuven, Belgium**
- P8** Low Temperature Synthesis Of Nanosized Pd-X (X=Mg, Zn) Metallic Systems, **S. Delsante et al., Università di Genova, Italy**
- P9** From Bulk To Size-Dependent Melting Properties Of Au-Ge Nanoparticles, **R. Novakovic et al., CNR Genova, Italy**
- P10** Ligand-Protected AuNPs In Lipid Raft., **A. L. de Marco et al., Università di Genova, Italy**
- P11** The Role Of Metal Traces In Bottom-up Porous Gold Structures In Oxidative Catalysis, **C. Demirci et al., IIT Genova, Italy**
- P12** Structure And Orientation Effects In The Coalescence Of Au Clusters, **R. Ferrando et al., Università di Genova, Italy**
- P13** Thermo-Optical Response Of Plasmonic Arrays Of Metallic Nanoalloys, **M. Ferrera et al., Università di Genova, Italy**
- P14** Ag-Pt Nanoalloys In A Tight Binding Ising Model: Chemical Ordering On FCC Nanoparticles, **A. Hizi et al. CINaM, Marseille**
- P15** Structural Characterization Of Subnanometer Particles, **J. Jašík et al., J. Czech Academy of Sciences, Prague, Czech Republic**

- P16** Interactions Between Liposomes Induced By Functionalized Au Nanoparticles,
E. Lavagna et al., Università di Genova, Italy
- P17** Deuterium Adsorption On Cobalt-Fullerene Complexes, **G. Libeert et al.,
Laboratory of Solid-State Physics and Magnetism, Leuven, Belgium**
- P18** Shape Transformation Of (Bi-)Metallic Nanocrystals, **A. Moisset et al.,
Sorbonne Université, Paris, France**
- P19** Structural Transformations In AuCo Nanoalloys Studied By Metadynamics,
D. Nelli et al., Università di Genova, Italy
- P20** Probing The Evolution Of PdCu And PtCu Bimetallic Nanocrystal Catalysts
Under Operando Conditions By In-situ X-ray Absorption Spectroscopy,
L. Pasquale et al., IIT Genova, Italy
- P21** CeO₂ (111) Electronic Reducibility Tuned By Ultra-Small Supported Bimetallic
Pt-Cu Clusters, **L. O. Paz-Borbón et al., Universidad Nacional Autónoma
de México, Mexico**
- P22** A Gold-Sulphur Atomistic Potential For Molecular Dynamics, **D. Rapetti et al.,
Università di Genova, Italy**
- P23** (Ni,Co) Alloy Nanoparticles: Synthesis, Characterization And Catalytic
Application, **P. Riani et al., Università di Genova, Italy**
- P24** Thermal Gradients Around Irradiated Au NPs In The Biological Environment,
S. Salassi et al., Università di Genova, Italy
- P25** Surface Assisted Synthesis Of C-based Nanostructures On Ag(110), **L. Savio et
al., Università di Genova, Italy**
- P26** Monitoring Oxidation And Reduction Of FeO₂ Islands On Pt(111) Using HREELS
And XPS, **M. Stojkovska et al., Università di Genova, Italy**
- P27** Improving Accuracy Of The Topological Approach For Nanoalloys: Case Study
Of PtCu Nanoparticles, **L. Vega et al., Universitat de Barcelona, Spain**
- P28** Time Dependent Density Functional Theory Calculation For Nano-Plasmonics,
W. Zhao et al., King's College London, United Kingdom

Oral communications

Atomic Ordering In Large Bimetallic Particles From DFT+Topological Calculations

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ABSTRACT

Bimetallic particles (nanoalloys) often become systems of choice for various applications. However, determining atomic ordering in nanoalloys, which largely defines their properties is very challenging. We developed a method to search for thermostable atomic orderings in nanoalloys by first-principles (DFT) calculations combined with a topological description [1,2]. The method allows to reliably predict energetically most stable in vacuum structures of bimetallic crystallites with up to thousands atoms and to estimate, how their surface atomic ordering will be modified in a given reactive environment [3-5].

The talk will overview our recent results of application of this novel approach to nanoalloys of Pd [1,2,4,5], Pt [6-8] and Ni [3] with *d*- and *s,p*-metals. Usage of this method can radically accelerate design of tailor-made nanoalloys for broad variety of technological needs and deepen general understanding of the bonding in nanoalloys.

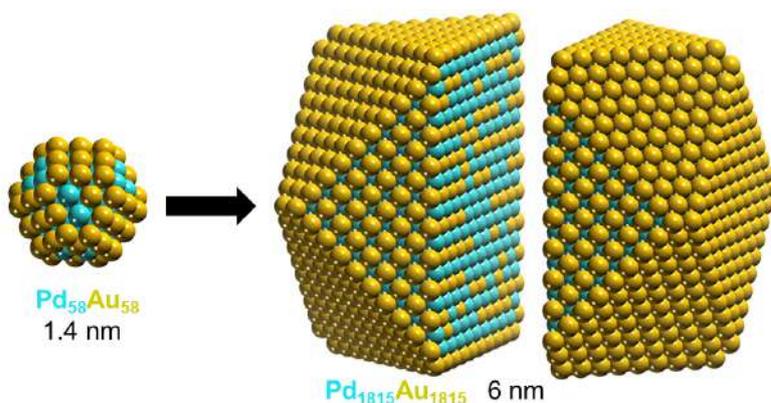


Fig. 1: Topological descriptors derived from DFT calculations of several dozen different atomic orderings of a bimetallic nanocrystallite open a way to predict atomic ordering in much larger nanoparticles not assessable for DFT treatment.

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3. A. Wolfbeisser, G. Kovács, S.M. Kozlov, K. Föttinger, B. Klötzer, K.M. Neyman, G. Rupprechter et al., *Catal. Today* **283**, 134 (2017).
4. M. Mamatkulov, I.V. Yudanov, A.V. Bukhtiyarov, I.P. Prosvirin, V.I. Bukhtiyarov and K.M. Neyman, *J. Phys. Chem. C* **123**, (2019), doi: 10.1021/acs.jpcc.8b07402
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8. A. Neitzel, G. Kovács, Y. Lykhach, S.M. Kozlov, M. Vorokhta, V. Matolín, K.M. Neyman, J. Libuda et al., *Top. Catal.* **60**, 522 (2017).

Site-Specific Wetting Of Iron Nanocubes By Gold Atoms In Gas-Phase Synthesis

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ABSTRACT

Cluster beam deposition offers a physical synthesis method to achieve nanomaterials with tailored characteristics. However, the simultaneous control of size, shape, and elemental distribution within a single nanoparticle in a small-size regime (around 10nm and below) is still a major challenge, equally limiting physical and chemical approaches. Here, a single-step nanoparticle fabrication method based on magnetron-sputtering inert-gas condensation is reported, which relies on selective wetting of specific surface sites on pre-condensed iron nanocubes by gold atoms. Using a newly developed Fe-Au inter-atomic potential, the growth mechanism is decomposed into a multi-stage model implemented in a molecular dynamics simulation framework. The importance of growth kinetics is emphasized through differences between structures obtained either experimentally or computationally, and thermodynamically favourable configurations determined via global optimization techniques. These results provide a roadmap for engineering complex nanoalloys towards targeted applications.

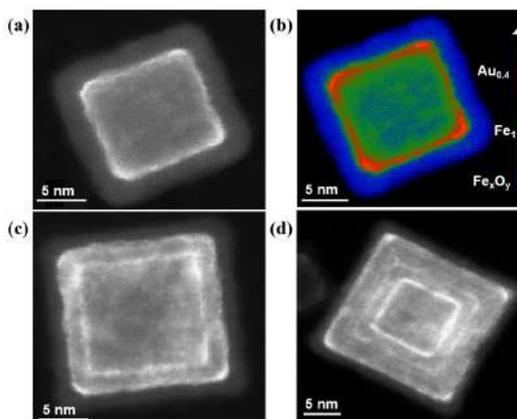


Fig. 1 : High-angle annular dark-field images of Fe-Au nanocubes with increased Au concentration.

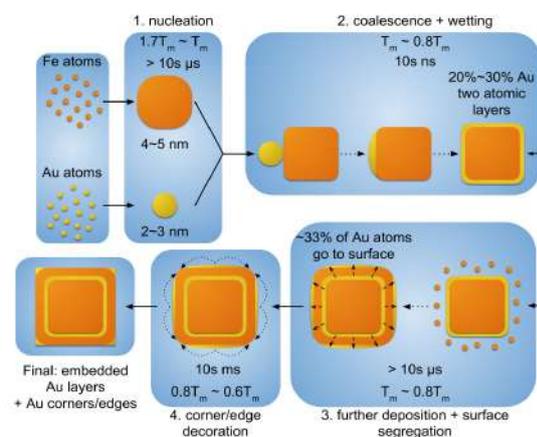


Fig. 1 : Overview of the multi-step Fe-Au nanocube growth model.

Shell Thickness Induced Core Transformation In Core(Fe)-Shell (Au) Magnetic Nanoparticles

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ABSTRACT

The nature of the exposed facets is of particular importance in many applications as catalysis or drug delivery. We will report the evolution of the morphology of core(Fe)-shell(Au) nanoparticles (NPs) with the shell thickness, as a result of the Fe core transformation. The nanoparticles were successfully synthesized at 600°C by sequential deposition using magnetron sputtering. The samples differ by the deposited thickness of the two metals, particular focus being put on the influence of the Au/Fe ratio. Their morphology and structural details were studied by transmission electron microscopy (HREM and probe-corrected HAADF/STEM). Two different types of Au/Fe interfaces are evidenced in NPs having thin Au shell whereas only one type of interface remains after further Au atoms deposition, leading to a drastic Fe core transformation from a Wulff shaped crystal towards a cube. This important finding is attributed to the large difference in the energy cost of the two different interfaces as calculated by atomic modelling. In addition, our experiments show that the ferromagnetic properties of the Fe core are preserved by the Au shell and that the size of the grown nanoparticles (in the 5-10 nm range) leads to a superparamagnetic behavior at room temperature.

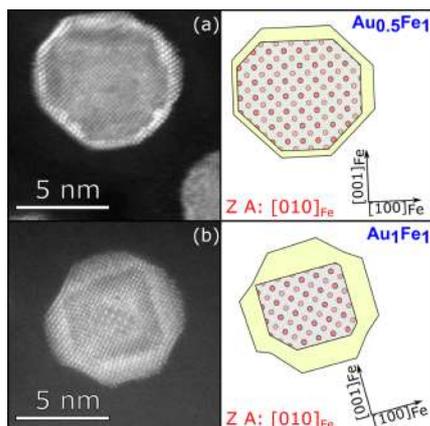


Fig. 1 : Illustration of the core transformation upon increasing the Au shell thickness. The indices x and y in Au_xFe_y samples stand for the nominal deposited thickness of each metal in nms.

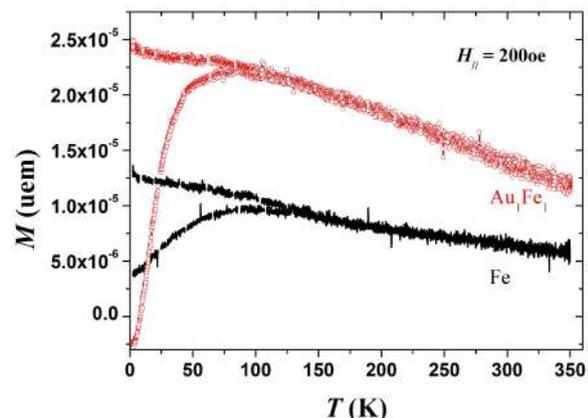


Fig. 2 : Zero field cooling and field cooling magnetization curves measured at 200oe.

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2. P. Benzo et al. (2019) to be submitted

Magnetic Properties Of Ferromagnetic/Antiferromagnetic Metallic Nanocomposites: Influence Of alloying At The Interface

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ABSTRACT

Magnetic nanoparticles are the focus of increasing interest from both fundamental and technological point of view for their applications in a number of different fields (magnetic memories, permanent magnets, biomedicine, sensors...). In core/shell nanoparticles, the exchange coupling between the ferromagnetic (F) core and the antiferromagnetic (AF) shell has been demonstrated to increase the actual particle anisotropy, leading to an increase of the blocking temperature, thus shifting the superparamagnetic limit to lower size. In this context, films of ferromagnetic nanoparticles dispersed in an antiferromagnetic matrix provide good model systems to control the F/AF interface exchange coupling in view of exploiting as a tool for controlling the anisotropy and then the magnetic stability of magnetic nanoparticles. In this paper, the effect of the F/AF interface exchange coupling on the magnetic properties has been investigated in three different films of nanoparticles (~ 2 nm) dispersed (~ 5 % in volume) in an antiferromagnetic matrix: Co particles in Mn matrix (Co@Mn), Fe particles in Mn matrix (Fe@Mn) and Fe particles in Cr matrix (Fe@Cr). The structural and magnetic properties of the films were investigated by using EXAFS, XMCD, magnetometry, and theoretical modeling. For all samples, the experimental data show that the antiferromagnetic matrix provides a strong interface exchange coupling with the ferromagnetic particles, leading to a remarkable enhancement of thermal stability with respect to the same particles (same size and concentration) dispersed in a non-magnetic Ag matrix. For Co@Mn films, EXAFS measurements show the presence of a significant degree of alloying, suggesting that the well-defined particles, originally deposited, become center of high Co concentration of CoMn alloy that evolves from pure Co at the nanoparticle center to the pure Mn matrix within a few nm. XMCD measurements show that the Co moment is much smaller than in Co@Ag films. Electronic structure calculations confirm that the small magnitude of the core Co moment can be understood only if significant alloying occurs. Magnetization measurements show that the antiferromagnetic matrix provides through interface exchange coupling an effective long range interparticle correlation. This gives rise to a superspin glass (SSG) type freezing. This picture is confirmed by the observation of non-equilibrium dynamics at low temperatures, as shown by memory effects in zero-field-cooled magnetization curves.

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Magnetoplasmonic Nanoalloys

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ABSTRACT

The active modulation of the optical response of plasmonic nanoparticles (NPs) by means of an external magnetic field, i.e. magnetoplasmonics, can improve the performance of plasmonic devices, such as optical switches, modulators or more efficient refractometric sensors [1]. In a previous work we demonstrated that small magnetic field-induced energy shifts of the plasmonic modes in simple Au NPs are easily detectable by Magnetic Circular Dichroism (MCD) [2]. Nevertheless, the MCD signal of Au NPs is too small for applications in devices. The enhancement of the magnetic modulation of surface plasmons is a challenging goal in magnetoplasmonics, and a few approaches have been reported in the literature [3,4]. In our work we propose an approach based on the hybridization of plasmonic and magnetic properties in a single NP, a nanoalloy made of a magnetic and a plasmonic metal. In these nanoalloys, the interaction between the conduction electrons of Au and *d* electrons of Fe can lead to an increase of the magnetic modulation. By colloidal chemistry we prepared AuFePt nanoalloys, where the presence of Pt helps to overcome the miscibility gap between Au and Fe, allowing us to tune the Au-to-Fe ratio in a range where the NPs have both magnetic and plasmonic properties. The formation of alloys was confirmed by X-ray Powder Diffraction, while Transmission Electron Microscopy revealed spherical NPs of about 9 nm. We then investigated the interplay between magnetic and plasmonic properties in AuFePt nanoalloys of different compositions (Figure 1) through MCD at room temperature. We found that with 7% of iron, the typical plasmonic derivative-like shape of the MCD signal is observed, centered at the extinction peak. On the other hand, if we increase the iron content up to 35%, the MCD signal is dominated by the magnetic part. With 11% of iron we also observed a derivative-like shape, but with an increase of the peak to peak signal with respect to what expected for pure Au [2]. This work has been financed by the EC through grant 737093 — FEMTOTERABYTE — H2020-FETOPEN-2016-2017.

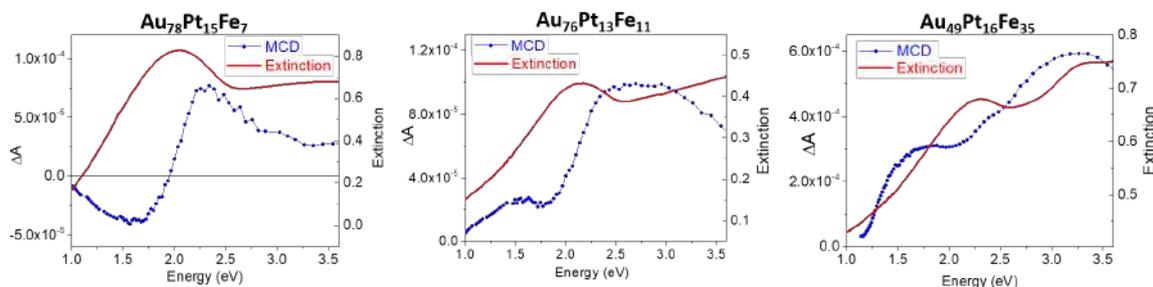


Fig. 1 : MCD spectra (blue) at 1.4 Tesla, and extinction spectra (red) of three AuFePt nanoalloys with different composition.

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Fcc-Co Clusters In L1₀-FePt Matrix As Model Nanocomposite Magnets

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ABSTRACT

Nanocomposite magnets, consisting of a fine mixture between a large magnetocrystalline anisotropy phase and a large magnetization phase, is a promising route to develop new permanent magnets with unprecedented performances. Theoretical calculations predicted a potential energy product of 1 MJ/m³, twice as large as the one of best Nd₂Fe₁₄B magnets produced today [1]. These calculations also revealed the necessity of confining the soft phase in grains of typical size less than 10 nm, which cannot be obtained with standard material fabrication processes. So far only very few experimental works with encouraging results have been reported on such exchange-spring magnet [2].

We recently prepared Co@FePt transition metal (TM)-based nanocomposite films from low energy cluster beam deposition technique (LECBD) of mass-selected Co clusters, in-situ embedded in FePt matrix independently produced by alternative electron gun evaporation on the same substrate [3,4]. This nanofabrication technique permits to have a fine control over the microstructure. Annealing is a crucial step to drive the initial Fe and Pt multilayers to the high-magnetic anisotropy L1₀ phase with a limited diffusion of the clusters in the matrix. Specular X-rays Diffraction revealed a thermal transition to a chemically ordered L1₀-FePt alloyed matrix with a partial texture on Si substrate while environmental-TEM and EDX analyses allowed us to observe the partial diffusion of the Co clusters in the hard matrix.

Recently, X-ray absorption spectroscopy measurements (EXAFS, XLD and XMCD) were performed on annealed Co@FePt nanocomposite with various clusters concentrations and compared to equivalent multilayer samples at Fe and Co K-edges at BM30 and ID12 beamlines at the ESRF. The structural analysis proved that the Co cluster doesn't entirely mix with the matrix during annealing contrary to multilayers. The study of such model system could give insights about the role of the nanostructure on magnetic hardness and could thus guide the development of mass scale synthesis processes.

Support is acknowledged from ANR SHAMAN: Soft in HARd MAGnetic Nanocomposites (2017-2020).

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Elucidating Structural Transitions In Nanoalloys

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ABSTRACT

The control of structural and chemical transitions in bimetallic nanoalloys at finite temperatures is one of the challenges for their use in advanced applications. Here we show how molecular dynamics, employing interatomic potentials based on the second-moment approximation of the tight-binding, can provide useful and novel insights on detecting polymorphisms at the nanoscale.

In order to classify concerted structural transitions in various bimetallic systems, such as AgCu, AgAu and PdPt we compared results and transitions using metadynamics -as available in LoDiS- as well as double-ended methods [1]. Furthermore, we investigate the phase changes of CuPt nanoalloys with the aim to elucidate the role of kinetic effects during their solidification and melting processes. The comparison of Nested Sampling and Molecular Dynamics simulations enables us, for the first time, to establish the thermodynamical limit for the nucleation of (CuPt)₃₀₉ at 965 +/- 10 K, and then to determine possible kinetic effects and the opening of a hysteresis in the caloric curve [2]. For CuPt nanoparticles we explore the phase changes in a wider size range and we found that classical predictions of their melting point depression can be recovered only above 5 nm.

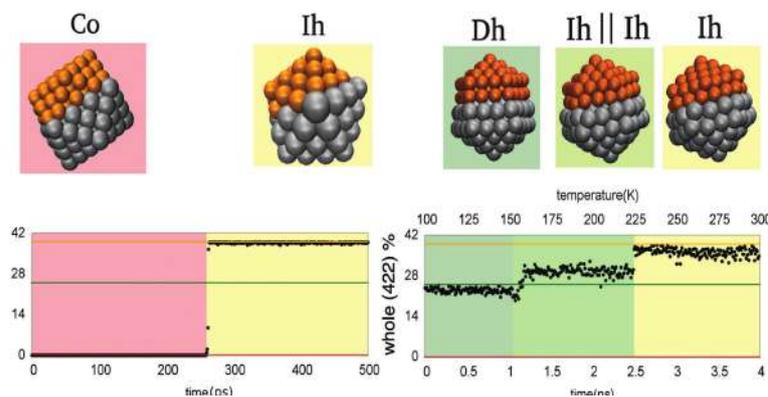


Fig. 1 : Structural transitions of Janus-like AgCu nanoalloys of 147 atoms, from Ref. 1

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Core-shell vs Multi-shell Formation In Nanoalloys Evolution From Disordered Configurations

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ABSTRACT

The evolution towards equilibrium of AuCo, AgNi and AgCu nanoparticles is studied by molecular dynamics simulations. Nanoparticle sizes of about 2.5 nm are considered, in the temperature range from 300 to 700 K. The simulations reveal complex equilibration pathways, in which geometric structure and chemical ordering change with time. These nanoparticles present the same type of strong tendency to phase separation and to surface segregation of either Au or Ag [1], which lead to the same type of core@shell equilibrium structures [2]. In spite of these similarities, the equilibration pathways of these nanoparticles from chemically disordered configurations present both quantitative and qualitative differences [3]. Quantitative differences are found in the equilibration time scale, which is much longer in AgCu than in AgNi and AuCo. Qualitative differences are found in the presence or absence of geometric structure transformations, and in the formation of different types of three-shell metastable chemical ordering during evolution. It is also shown that surface segregation depends on the geometric structure, being faster in icosahedra than in fcc nanoparticles.

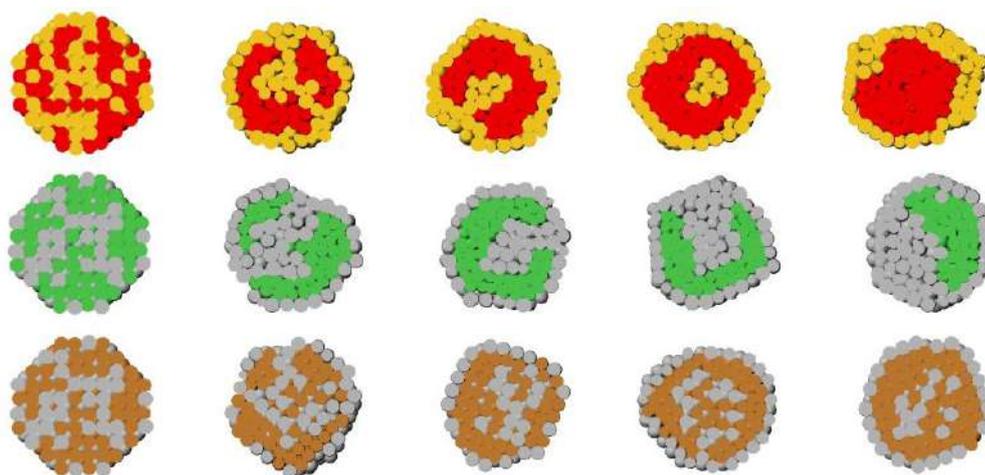


Fig 1: Equilibration stages of chemical ordering in AuCo (top row), AgNi (middle row) and AgCu (bottom row) starting from randomly intermixed structures. The images show cross-sections of the clusters.

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Atomic-Resolution Imaging And Ab Initio Modelling Of Surface And Core Melting Of Supported, Size-Selected Au Nanoclusters

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ABSTRACT

Melting is one of the most familiar and visible phase transitions in the macroscopic world but the mechanism by which nanoparticles melt remains an open question in nanoscience. The behavior of nanoclusters at elevated temperatures is both interesting from a fundamental perspective but also relevant to process that operate above room temperature, such as catalysis. We employ variable temperature, aberration-corrected scanning transmission electron microscopy (ac-STEM) to image nanoparticle surface and core melting in real space in individual size-selected Au clusters [1]. The cluster sizes (e.g. Au₅₆₁) were below 5nm; the clusters were supported on amorphous carbon films. The formation of solid core/liquid shell structures is clearly visible at elevated temperatures. The melting mechanism is broadly consistent with the liquid nucleation and growth model, but both cluster-surface and cluster-core melting temperatures are notably higher than predicted. To explore the effect of the carbon support on the melting of the clusters, we employ a novel very large-scale ab initio simulation approach, that mimics the effect of the support by imposing a “frozen-facet” on the nanoclusters. We obtain quantitative results that are in good agreement with the experiments and thus identify the cluster-support interaction as the major source of the deviation between previous theory and the experiments. The simulations also reveal the different size and location of the core in free and frozen-facet nanoclusters. The Au clusters studied in this work lie in the catalytically active size regime; therefore the results may be relevant to the performance of novel nanocluster-based catalysts.

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Structure And Chemical Ordering In Nanoalloys From Constrained Monte Carlo Simulations

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ABSTRACT

Computational modeling of nanoalloys represents a challenge owing to the many degrees of freedom involved, including structure, shape and chemical ordering. This difficulty often restricts computational studies to small particle sizes or narrow regions of the composition axis. We have recently approached this problem with combined Molecular Dynamics-Monte Carlo simulations using the variance-constrained semigrand canonical (VCSGC) ensemble [1]. In this contribution, we will highlight the pros and cons of this method as applied to structural optimization of mono-elemental nanoparticles [2] as well as chemical ordering in nanoalloys of Au-Pd and Ag-Cu with more than 5,000 atoms [3]. The latter alloys represent, respectively, a mixing and a non-mixing system, and a comprehensive scan of the composition axis allowed us to place observed equilibrium structures in a bigger picture.

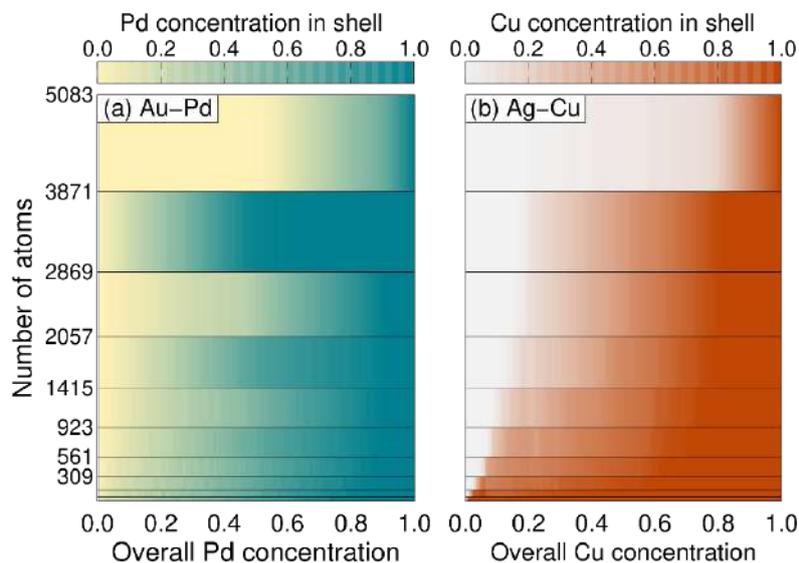


Fig. 1 : Concentrations per atomic shell in icosahedral nanoalloys with 5,083 atoms.

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DFTB Parametrization And Global Optimization Of 55-Atom $\text{Cu}_x\text{M}_{55-x}$ (M=Pd, Pt, Au) Nanoclusters

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ABSTRACT

The detailed atomic arrangement of metal clusters lies at the heart of our understanding of their physicochemical properties. However, the global optimization (GO) problem of finding the most energetically favourable structures (already challenging in the mono-elemental case) typically becomes even more daunting in the case of alloyed nanoclusters. Even with comparatively cheap density functionals and advanced GO algorithms, studying clusters of 30-40 atoms in this way already requires vast computational resources.

Interatomic potentials such as embedded atom models and Gupta potentials have therefore been widely applied as low-cost substitutes to DFT. It is, however, getting increasingly recognized that for certain metals such descriptions are too crude. The tendency towards open structures in the case of Au and Pt (see Fig. 1 below), for example, is not reproduced [1,2]. Density functional tight-binding (DFTB) is a semi-empirical electronic structure method which promises a better trade-off between accuracy and computational efficiency.

Here, I will present my recent work [2,3] on how to generate accurate DFTB models within the context of a global optimization problem. Focusing first on neutral 55-atom late-transition metal clusters, I will describe how DFTB parameters derived from bulk properties can be used to create a set of cluster geometries whose DFT energetics allow to refine the DFTB parameters and further explore the potential energy landscape. Next, I will present how this approach can be extended to alloy clusters, addressing the structure of 55-atom Cu-Pd, Cu-Pt and Cu-Au clusters as a function of the copper content.

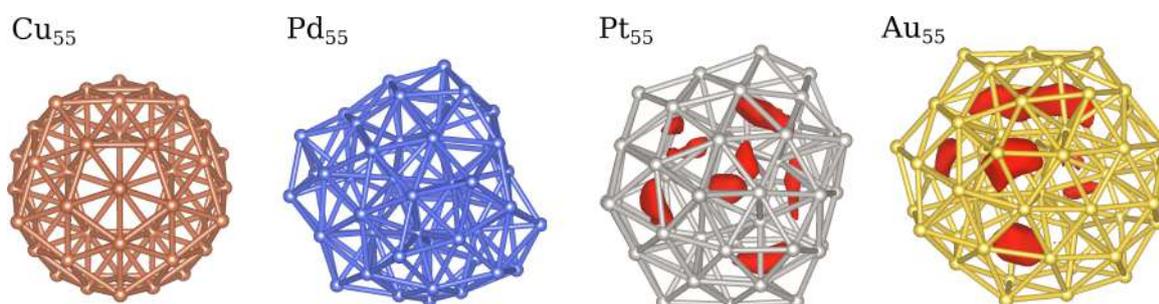


Fig. 1 : Putative global minima obtained for the pure 55-atom clusters of Cu, Pd, Pt and Au. Subsurface cavities in the case of Pt and Au are highlighted by means of isosurfaces of low electron density.

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Facile Route Towards Mono And Bi Metallic Nanocrystals With Size And Shape Control

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ABSTRACT

Herein, we described the first synthesis of pure mono-dispersed spherical hcp-nanocrystals ferromagnetic at room temperature. Our strategy, based on the simple combination of oleylamine and $\text{ClCo}(\text{PPh}_3)_3$, allows the one-pot synthesis of size controlled hcp-nanocrystals. (Figure 1). It is highlighted an original disproportionation mechanism for formation of hcp cobalt nanoparticles starting from low-valent cobalt complexes. By coupling experimental and theoretical studies, we demonstrate that oleylamine promotes the disproportionation of the starting metal complexes and controls the growth of the nanocrystals, in contrast to the role of reducing reagent proposed elsewhere. We also decipher the sensitivity of the synthesis in regard to the nature of the phosphine and of the halogen ligands in the starting cobalt precursors. Understanding of the mechanism allows the development of a less expensive and less toxic synthesis of these nanoparticles by decreasing the amount of oleylamine in alkane solvent.

Finally, an extension of this process is presented and allows reaching size and shape controlled nanospheres and nanorods nickel nanoparticles and bi metallic CoNi nanoalloys (Figure 2).

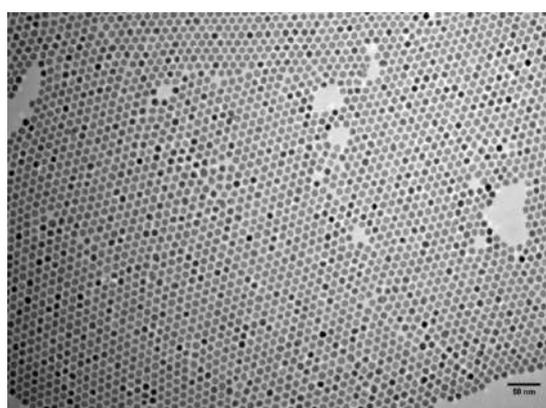


Fig. 1 : hcp cobalt nanocrystals

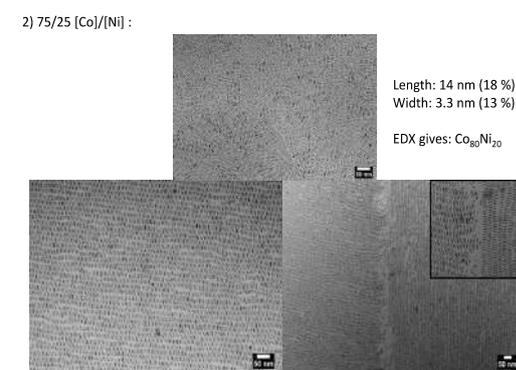


Fig. 2 : hcp $\text{Co}_{75}\text{Ni}_{25}$ nanorods

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Modeling Transition Metals And Nanoalloys: Fixing The Misuse Of Cohesive-Energies

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ABSTRACT

In spite of free-atom electronic-relaxation contributions to transition-metal cohesive-energies, numerous studies have misused the latter instead of using the interatomic bond-energies in modeling bulk and surface properties [1-2], including atomistic-potential parametrization for nanoalloys. This work first reveals that eliminating the free-atom contributions from experimental cohesive-energies leads to highly accurate linear correlations of the resultant bond-energies with melting temperatures and enthalpies (Fig. 1), as well as with inverse thermal-expansion coefficients, specifically for the fcc transition-metals. In addition, predictions of surface segregation phenomena in Cu-Pd and Au-Pd bulk alloys on the basis of the correct energetics are in much better agreement with reported LEISS experimental results. A distinctive demonstration of the problem and its solution involves the significant impact of the cohesive-energy modification on segregation (separation) phase transitions in Cu-Ni TO nanoparticles. In particular, without the correction destabilization of Janus configuration in favor of Core-Shell is erroneously obtained (Fig. 2). Preliminary computations for Cu-Ni-Pd NPs reveal significant effects of Pd and of the fixed energetics on chemical-order and transition temperatures.

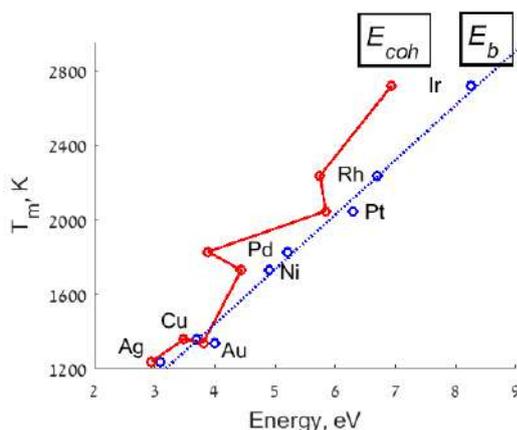


Fig. 1 : Plots of the melting-temperatures vs. experimental cohesive-energies (E_{coh}) and the corresponding interatomic bond-energies (E_b) of fcc transition-metals. The remarkable improvement in linear correlation in the case of E_b is due to the elimination of free-atom electronic-relaxation contributions to E_{coh} .

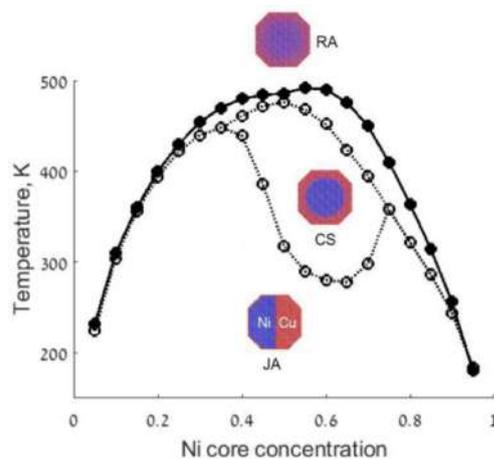


Fig. 2 : Nanophase diagrams computed for CuNi 1289-atom truncated-octahedron (TO) by means of the FCEM/CBEV/CGLM methodology [2]: solid and dotted lines correspond to E_b - and E_{coh} - based modelings, respectively.

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Application Of Structure Descriptor For Rational Design Of Transition Metal Catalysts

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ABSTRACT

We present an overview of some exciting results from our recently proposed structure descriptor¹⁻⁵, mapping the quantitative relationship between intrinsic structural feature and catalytic performance for transition metal catalysis, as well as its application in the high-throughput screening on catalyst and rational construction of catalytic sites. The central concept of our structure descriptor contains following points: (1) The features parameters inside structure descriptor have to be unique in representing electronic and geometric structures of a catalytic site. (2) The features parameters inside structure descriptor must be easily computed, experimentally quantified or readily available physical properties from databases, which is conveniently used for rapid screening. (3) Most importantly, structure descriptor should be physically intuitive to ensure model robustness and direct inference of chemical insights, the variation of which is unambiguously linked to changes in adsorption energies or catalytic activity. With the constructed structure descriptor for each transition metal catalyst system, such as single-atom catalyst, nanocluster, alloy and so on, it is helpful for fundamental understanding of structure–activity relationships between catalytic activity and the physical properties of transition metal catalysts, which is validated by available experimental data.

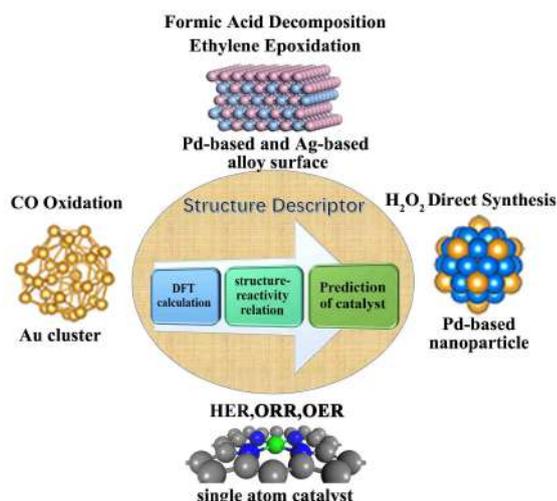


Fig. 1 : Schematic illustration for rational design of transition metal catalyst by structure descriptor.

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Catalytic (And Optical) Properties Of (Supported) Alloy (Ultra)NanoStructures

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ABSTRACT

First, we will present our results on computational modeling of catalysis by alloy nanostructures. We start from an extensive study of ammonia synthesis via the Haber-Bosch (HB) process over Fe bcc(111) and bcc(211) via a computational protocol combining Quantum-Mechanics in the form of Density-Functional Theory plus dispersion to unveil the mechanistic steps at the atomic level, and kinetic Monte Carlo (kMC) modeling to predict steady-state catalytic reaction rates under realistic conditions, thus allowing us to validate our predictions against experimental kinetic data from literature. We then use the detailed knowledge derived for this system to consider modifications of the catalyst such as alloying the first few surface layers via a hierarchical high-throughput screening (HHTS) approach to catalyst design. The HHTS approach singles out the most promising alloying elements and configurations as a function of catalyst structure and specific alloying site. The approach is validated in several test cases, such as Rh 0.25 ML substitutional top layer, by reconstructing the complete free-energy diagram, conducting a full kinetic analysis, and comparing the results from those estimated on the basis of the HHTS, finding very good agreement [1].

Focusing then on optical properties, we will present a first-principles time-dependent density-functional theory (TDDFT) study of the optical response of (M/M')₆ and (M)₃(M')₃ six-atom clusters (M, M': Cu, Ag, and Au), both in the gas-phase and supported on the MgO(100) surface as a model of a simple oxide substrate. UV-vis spectra are predicted and analysed to rationalize origin and features of optical absorption in these systems. The interaction with the electric field generated by the charge-separated substrate is found to induce a fragmentation and a shift toward lower energies of the absorption peaks, which is in tune with experiment and can be beneficial in applications as photo-enhancers or promoters. The orientation of the transition dipole moment with respect to the support (parallel or perpendicular) is analysed in view of translating these results to optically active semi-conducting supports to tune interaction with substrate excitations [2].

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Catalysis By Bimetallic Subnanometer Clusters

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ABSTRACT

This paper discusses the catalytic performance of bimetallic clusters as the function of cluster size, atomically varied composition and support. The samples of supported size- and composition-selected clusters are fabricated by soft-landing of cluster cations of desired size and stoichiometry on oxide- and carbon-based supports, followed by interrogation under realistic conditions of pressure and temperature. The catalysts are characterized with *in situ* techniques to determine their stability and the oxidation state of their components under working conditions. Fundamental understanding of the function of the catalysts and the role of their individual components emerges from accompanying theoretical calculations. Comparisons with the performance of monometallic clusters will be made, along with the effect of the supports used.

The applicability and promises of this approach will be illustrated on three examples: i) low-temperature oxidation of CO on Ag-Pt and Pt clusters in bridging the materials and pressure gap [1-2], ii) oxidative dehydrogenation of cyclohexane on Co, Cu-Pd, Cu and Pd clusters with control of selectivity and activity [3-4], and iii) conversion of propane on Cu-Pd, Cu and Pd clusters into selected products [4].

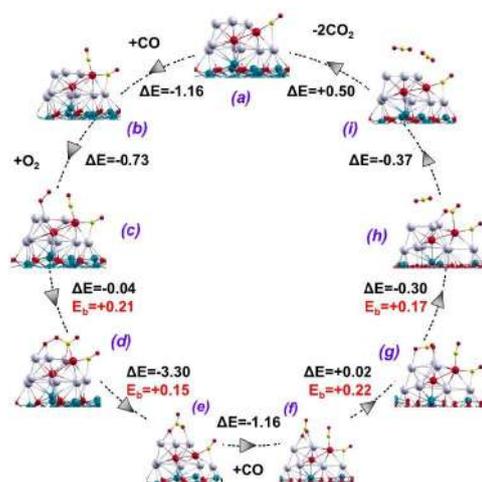


Fig. 1: Ag-Pt clusters in CO oxidation – understanding the catalytic cycle from theory [2].

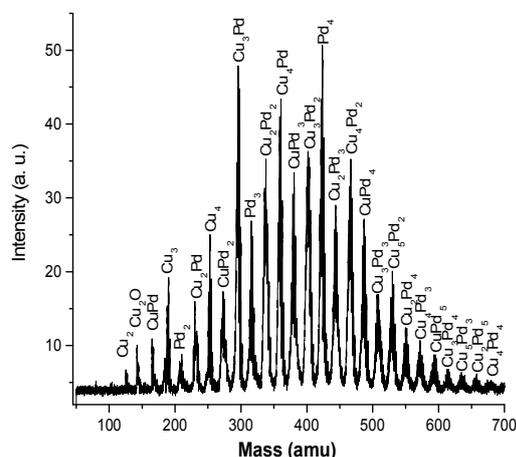


Fig. 2: Tuning of cluster size and composition with atomic precision

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Dynamic Structure Of Low Temperature CO Oxidation Catalysts Based On Gas-phase PdNi Nanoclusters Deposited On Alumina Powder Unraveled By Operando XAFS And DRIFTS

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ABSTRACT

Development of superior catalytic systems has been limited by the lack of precisely synthesized model catalysts that can aid in establishing the active catalyst structures under reaction conditions. Here, we design a highly homogeneous low temperature CO oxidation model catalyst by depositing well-defined gas-phase monometallic Pd and bimetallic PdNi Nanoclusters (NCs) directly on γ -alumina powder, with an ultra-low loading of 0.1 wt%, using the Cluster Beam Deposition (CBD) technology. STEM-HAADF confirmed that nearly monodispersed Pd and PdNi NCs of ca. 4 nm were discretely loaded on the γ -alumina powder.

As-prepared Pd and PdNi NCs on alumina catalyze the complete oxidation of CO at 150 °C with a remarkable stability. Upon mild H₂ reduction, the reaction temperature of PdNi NCs is further lowered to a remarkable 100 °C while that of pure Pd NCs remains unchanged. Correlation of the catalytic activity of PdNi and pure Pd NCs with their dynamic structure and surface properties was unraveled by a unique combination of in operando XAFS and DRIFTS. XAFS spectroscopy revealed that PdNi NCs possess a unique structure in comparison to PdOx@Pd structure of Pd NCs that are interacting weakly with the γ -alumina support. The structure of PdNi NCs consists of disordered NiOx and PdOx phase with underlying Pd rich Pd-Ni alloy at the surface of pure Pd NCs whose Pd-Pd bonds are substantially lengthened under CO oxidation. DRIFTS complemented the XAFS analysis by pointing out the detailed surface reconstruction occurring in Pd-Ni alloy and monometallic Pd NCs under hydrogen activation and reaction conditions. This work highlights the potential of the CBD approach to design and optimize the next generation of supported metal nanoparticle based catalysts.

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Atomistic Simulation of Trimetallic Nanoparticle Growth by Cluster Beam Deposition

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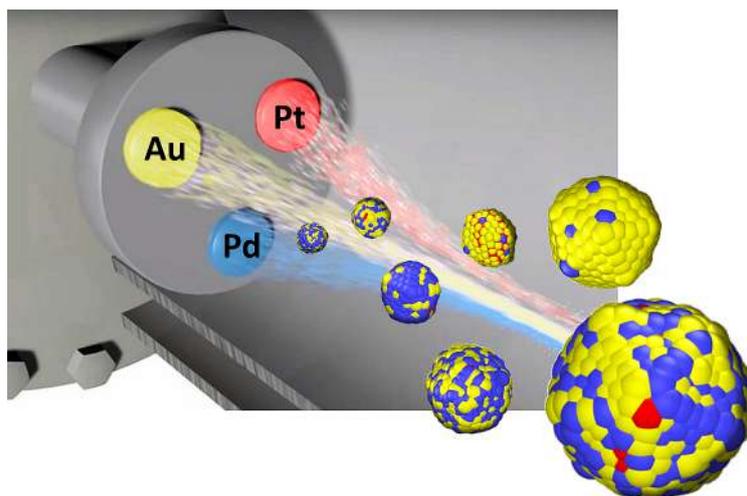
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ABSTRACT

Even though the fabrication of multimetallic nanoalloys by physical deposition methods has been technically possible for some time now, the vast majority of reports worldwide are still discussing mono- or bimetallic nanoparticles. The reason is clear: co-deposition of many elements is very complicated, due to the non-equilibrium processes it entails, with kinetic factors playing a more important role than energetics. One just cannot enhance or inhibit growth by adding or removing chemical precursors or surfactants; it all happens in-flight during aggregation, and the only viable strategy is by understanding the kinetics and dynamics of nucleation and growth. This is what makes tackling this problem both challenging and exciting at the same time.

Here, we will present the growth of trimetallic Au-Pt-Pd nanoparticles grown by concurrent co-sputtering of independent targets from the simulation point of view [1]. We will show which parameters dictate the individual growth rate of each species, and how this determines the resultant composition and chemical order of the deposited nanoparticles. Further, we will expand on how the simulated nanoparticles show a remarkable agreement with experimentally fabricated ones in shape, structure, and composition.



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Tailored Multi-element Nanoparticles For Wide Spectrum Antibacterial Coatings

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ABSTRACT

Combination of materials at the nanoscale may result in unprecedented functional properties [1], and nano-sized coatings with bactericidal action are very promising for hindering pathogens indirect transmission through cross-contaminated surfaces [2,3]. The challenge stands in the ability of tailoring the main coating's physicochemical properties, namely composition, bactericidal spectrum, adhesion to the substrate. Here we engineer a new family of nanoparticle-based, bactericidal coatings composed of Ag, Cu and Mg and synthesized by a green gas-phase technique, the supersonic cluster beam deposition (SCBD). We link the material and functional properties by a multi-disciplinary, multi-technique approach [5]. The NPs are characterized by phase-segregated incomplete core-shell clusters of metallic Ag_{core}Cu_{shell}, partially embedded on a magnesium oxide matrix. This structure is replicated into the coatings, forming a smooth (RMS roughness $\leq 5\text{nm}$) and porous (20% voids) granular film. These coatings present a wide-spectrum bactericidal activity on both Gram-positive and Gram-negative reference strains and tunable physicochemical properties of relevance in view of their "on-field" deployment. Our results pave the way towards engineering bio-functional, fully tunable nanoparticles coatings, exploiting an arbitrarily wide number of elements in a straightforward, eco-friendly, high-throughput one-step process.

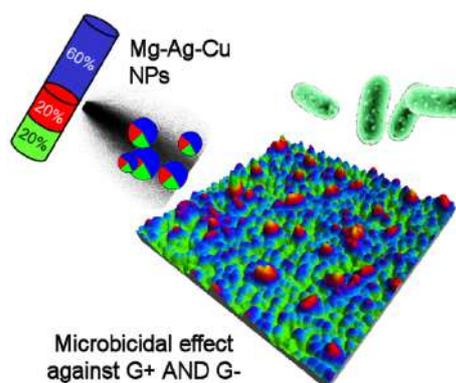


Fig. 1 : scheme of deposition process, including the surface morphology of the film and schematized bacteria.

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Environmental Plasmonic Spectroscopy Of Silver-Iron Nanoparticles: Chemical Ordering Under Oxidizing And Reducing Conditions

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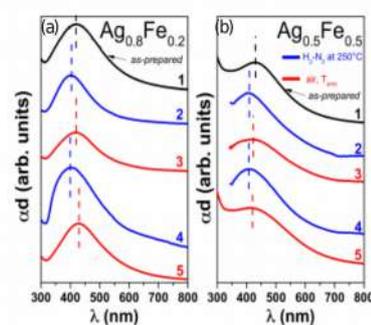
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ABSTRACT

By combining a plasmonic metal with a reactive one, nanoalloys become valuable systems for optical purposes by using the Localized Surface Plasmon Resonance (LSPR) as the probe for chemical processes. It is thus crucial to develop experimental devices allowing the *in situ* or in operando monitoring of these nanoparticles in order to identify the mechanism involved during restructuring processes. For this purpose, we developed a new setup allowing *in situ* optical measurements of a nanoparticle (NP) assembly, complementary to single NP environmental transmission electron microscopy (ETEM) observations [1]. The set-up was tested on iron-silver NPs, which combine a plasmonic material with a ferromagnetic element [2].

A detailed study of the Ag-Fe bimetallic system was thus conducted for two silver compositions (50% and 80%), by investigating the chemical properties of the NPs through TEM and environmental optical spectroscopy, and interpreting the combined physico-chemical observations with the help of parallel tempering Monte Carlo (MC) simulations of their structural stability at finite temperature. We show that these metals are initially segregated with a silver-enriched surface and that oxidation induces some iron migration towards the surface. *In situ* optical measurements carried out successively under oxidizing and reducing atmospheres indicate that iron oxidation and reduction are reversible processes that are directly mirrored in the LSPR changes (see Figure 1), in good agreement with optical simulations. Based on these results we propose a scenario of the evolution of the chemical ordering under reducing and oxidizing atmospheres.

Fig. 1: Cycles of *in situ* optical absorption measurements of Ag_xFe_{1-x} NPs embedded in silica for (a) $x=0.8$ and (b) $x=0.5$, either after reducing under H_2-N_2 atmosphere at 250°C for 10-15 minutes (blue curves) or after air exposure at room temperature (red curves). The black curves correspond to the spectra of the as-prepared samples recorded just after air exposure.



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Ag-Pt Nanoalloys: An Intriguing Hybrid System Between Chemical Ordering And Phase Separation

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The Ag-Pt bulk alloy displays at low temperature an L₁ phase with an alternation of pure atomic planes in the (111) orientation and also a phase separation at high temperature between two solid solutions respectively Pt-rich and Ag-rich [1,2]. This makes the study of Ag-Pt nanoalloys very intriguing because of finite size effects in the stabilization of one or the other phase. STEM-HAADF observations (Fig. 1) together with DFT calculations and Monte Carlo simulations using semi-empirical potentials (Fig. 2), have shown a reversed size-dependent stabilization of the ordered L₁ nanophase [3]. High resolution STEM-HAADF profile analysis reveal an L₁ ordered phase located in the core accompanied by a silver surface shell. The DFT confirms that the L₁ phase without Ag skin is highly unstable. But it leads to internal stress between the core and the shell increasing with cluster size. The way to release the stress for larger sizes is to make an almost perfect Pt subsurface shell as illustrated on the Fig. 2.

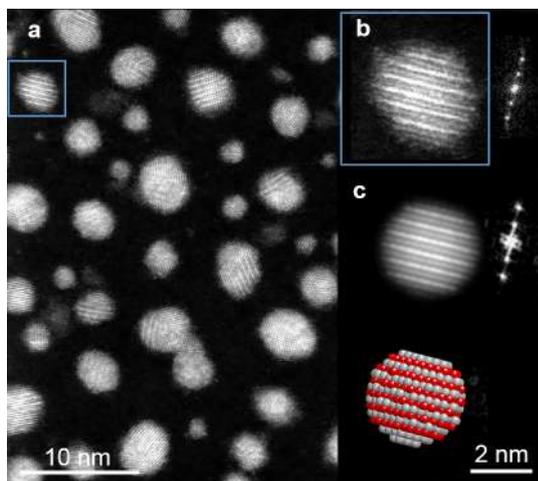


Fig. 1: Annealed AgPt NPs after UHV deposition. a) STEM-HAADF image; with b) experimental image and c) simulated NP (using the model showed below) oriented along the [01-1] zone axis showing the L₁ phase and its corresponding FFT.

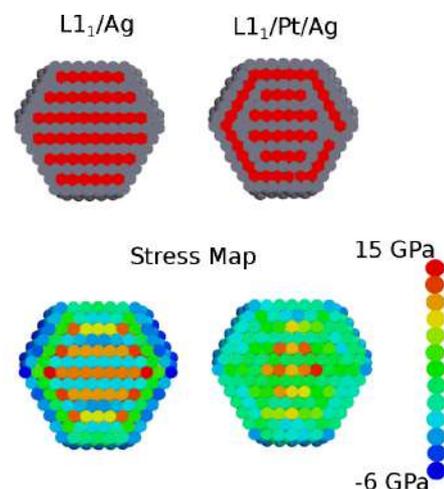


Fig. 2: L₁ nanophase in the core with silver and possibly Pt subsurface segregation (Ag atoms in grey and Pt ones in red) and their associated stress map.

As a consequence, the L₁ domain becomes narrower inside the core of the nanoparticle because of local stress due to the lattice mismatch between the Ag skin and the orthorhombic L₁ ordered phase.

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Vibrations Of Atomically Defined Metal Clusters And Nanoalloys[#]

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ABSTRACT

The elastic behavior at lower sizes (<1–2 nm), where nanoparticles become molecular clusters made by few tens to few atoms, is still little explored. The question remains to which extent the transition from small continuous mass solids to discrete-atom molecular clusters affects their specific low-frequency vibrational modes. Theoretical calculations based on density functional theory (DFT) predict, in the case of bare gold clusters, that vibrational periods corresponding to the breathing and quadrupolar modes scale linearly with size down to diatomic molecules. For ligand-protected gold clusters, it is found a pronounced effect of the ligand molecules, related with a mechanical mass-loading effects due to the protecting layer.

We also investigate experimentally by ultrafast time-resolved optical spectroscopy the acoustic response of atomically defined ligand-protected metal clusters $Au_n(SR)_m$ with a number n of atoms ranging from 10 to 102 (0.5–1.5 nm diameter range). Two periods, corresponding to fundamental breathing- and quadrupolar-like acoustic modes, are detected, with the latter scaling linearly with cluster diameters and the former taking a constant value. This study shows that clusters characteristic vibrational frequencies agree with DFT calculations. The combined theoretical-experimental study also indicates that acoustic vibrations of small bare nanoparticles are still ruled by continuum mechanics laws down to diameters of a few nanometers whose period is classically expected to linearly scale with diameter. [1,2]

In this work, we also present theoretical results regarding the vibrational density of states (VDOS) of Ag–Au icosahedral nanoparticles with a core–shell structure in the size range 147–923 atoms. The results are obtained by changing the size and type of atoms in the core–shell structure. For all sizes investigated, a smooth and monotonic variation of the VDOSs from Ag to Au is obtained by increasing the number of core Au atoms, and vice versa.

[#] In collaboration with: P. Maioli, T. Stoll, H. E. Saucedo, I. Valencia, A. Demessence, F. Bertonelle, A. Crut, F. Vallée, G. Cerullo, and N. del Fatti.

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LoDiS: Low Dimensional System Molecular Dynamics. A 0D Computational Engine For Investigations At The Nanoscale

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ABSTRACT

We present a Classical Molecular Dynamics suite designed to study processes for finite-sized systems between 10 - 10^6 atoms, abbreviated as LoDiS. The source code along with documentation is available via GitHub. LoDiS provides an extensive yet simplistic input scheme to enable flexible tuning of simulations of 0D materials, including their energy classification [1], phase transitions [2], growth [3], coalescence and free-energy sampling [4]. The core of the engine uses velocity-Verlet to integrate the Newton's equations, supporting both NVE and NVT simulations [5]. LoDiS primarily employs Rosato-Guillope-Legrand potentials for metallic clusters, with a secondary focus on noble gases and C_{60} systems modelled by Lennard-Jones and Pacheco-Girifalco potentials, respectively [6]. For mono- and bi-metallic systems, a recent implementation allows to include the effect of an external environment and/or an MgO substrate [7].

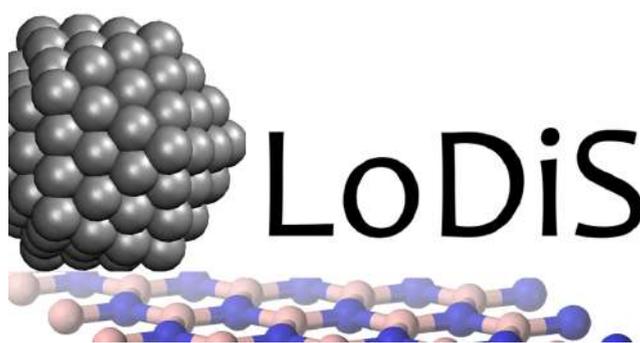


Fig. 1 : Low Dimensional System Molecular Dynamics logo..

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A New Basin Hopping Suite For Multi-Component Nanoparticles

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ABSTRACT

A new basin hopping (BH) suite for the optimization of multi-component nanoparticles has been developed. The algorithm evolves a population of BH walkers, which may either evolve independently or interact in the space of a suitable order parameter¹. In this new implementation, each walker can evolve according to its own specific rules and parameters. Therefore, different walkers may evolve at different temperatures, and also the interaction between walkers may be asymmetric. Walkers can be also forced to stay outside a given region of the order parameter space. Many types of elementary moves are possible. Local minimization can be made both at the atomistic and at the DFT level.

Along with the presentation of the new features, results about some specific systems are shown: DFT optimization of chemical ordering in AgAu² and AgPt³; full global optimization of large nanoalloys.

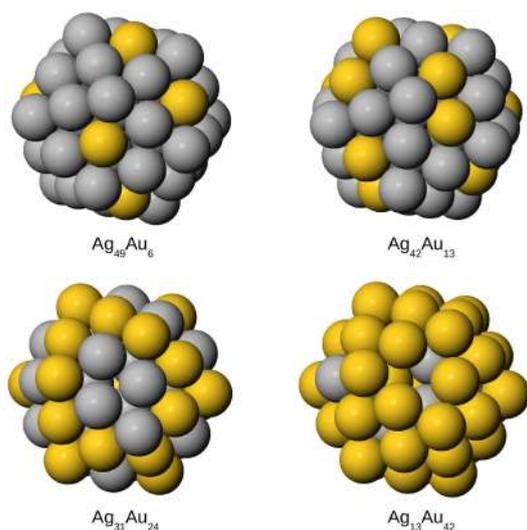


Fig. 1 : Some of the best minima obtained in the BH-DFT for AuAg nanoclusters at various compositions.

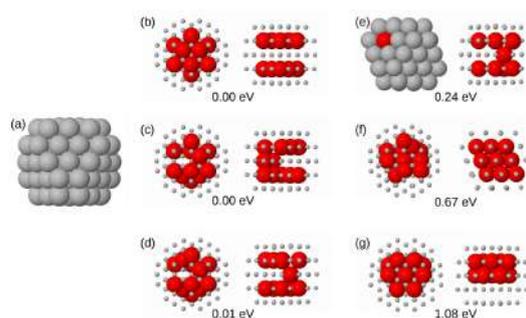


Fig. 2 : The search with BH-DFT, for the best configuration in an Ag67Pt12 truncated octahedron.

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The Surface Segregation Of Gold In Pd_nPt_{13-n}Au₄₂ Trimetallic Clusters: A DFT Study

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ABSTRACT

The chemical ordering of Pd-Pt-Au trimetallic clusters is investigated at Gupta and DFT levels. A systematic search is performed first to show that Au atoms tend to occupy the surface sites of the cluster. Compositions Pd_nPt_{13-n}Au₄₂ are considered. The Gupta level calculations show that the icosahedral structures are energetically more favorable than decahedral structures as confirmed by DFT relaxations. The lowest energy structures at Gupta level have surfaces completely occupied by Au atoms. The DFT relaxation results also confirm that the surface occupation of Au atoms is more favorable, as supported by DFT relaxations with different geometrical homotops. When the single palladium atom which is in the center of the Pd₁Pt₁₂Au₄₂ cluster is replaced by a gold atom, DFT relaxation for these shows that this is less favorable than the initial case. The DFT relaxation result for Pd₁Pt₁₂Au₄₂ cluster in which the single Pd atom occupies the center of the cluster shows that the Pd-Pt bonds are expanded and Pt atoms show the tendency to get closer to the Au atoms which are at the surface.

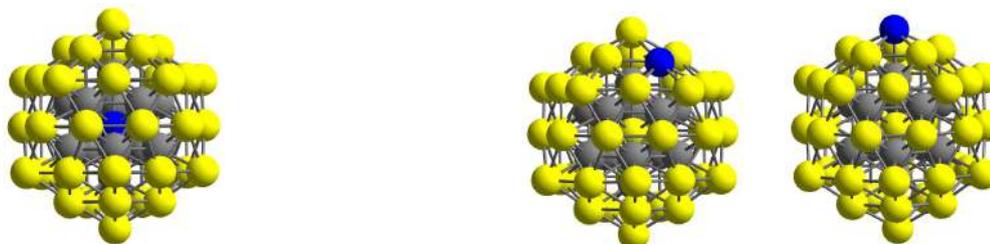


Fig. 1 : Pd₁Pt₁₂Au₄₂ with Au surface and central Pd atom. Fig. 2 : The less favorable two homotops for Pd₁Pt₁₂Au₄₂.

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Nanoparticle-Support Interactions And Catalytic Activities Of Noble-Metal Nanoparticle-Based Catalysts

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ABSTRACT

Size-selected nanoparticles (NPs) are known to exhibit remarkable catalytic properties, which diverge significantly from the properties of the respective bulk materials. Major issues for the performance of deposited clusters are their structure, composition and interactions with the support; two such issues are addressed here. (i) We investigate the binding of Au NPs on graphene sheets via very large scale (10^3 -atom) *ab initio* spin-polarized calculations incorporating van der Waals interactions. We build models of 561-atom NPs of the cuboctahedral, decahedral and icosahedral isomers on graphene for two distinct cases: i) where the Au NPs sit with their (111) facets on the graphene plane and ii) where the NPs are pinned by their vertices to the graphene. We find that in all cases the presence of a point defect (vacancy) improves the binding of the clusters to the graphene. Significantly, in the vertex-on-graphene case the binding energy is considerably increased, by several eVs, and becomes similar to the (111) facet-on-graphene case. The strain in the NPs is found to be minimal and the displacement of the C atoms in the immediate neighborhood of the vacancy is only on the 10 pm scale. (ii) The selective hydrogenation of alkyne and alkene molecules on Pd clusters and PdTi nanoalloy clusters is investigated. We map the binding sites and binding energies of the pentyne, pentene and pentane molecules on Pd and PdTi 55-atom NPs. We evaluate the performance of the alloy catalyst clusters compared with the elemental catalyst, and investigate previously proposed electronic interactions between Pd and Ti as well as binary Pd-Ti active sites for the reaction.

This work was financially supported by the Engineering and Physical Sciences Research Council through fellowship EP/K006061/2 and by the European Union and the Welsh Government through the Horizon 2020 programme Marie Skłodowska-Curie Actions Sêr Cymru II COFUND fellowship No. 663830-SU165.

Physical Synthesis And Characterization Of Plasmonic Ag@CaF₂ Nanoparticles

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ABSTRACT

Synthesis, study and applications of NanoParticles (NPs) have been playing a major role in material science and technology over the last 20 years, although some important examples of NP presence in manufactured goods can be dated back to ancient history [1]. Physical synthesis with a bottom-up approach presents some advantages, as it can be single-step and ligand-free, and these characteristics can result in a more accurate analysis of the NP structure and of their electronic and magnetic behaviour. During the last years we prepared and studied different types of NPs. Co-deposition and sequential layer deposition methods have been used to obtain core@shell NPs. These methods gave us the possibility of realizing non-native oxide shells [2], and to investigate metal@metal oxide core@shell NPs by varying independently the core diameter and the shell thickness. We report here the results of experimental activity on physically synthesized Ag@CaF₂ and Ag@MgO NP, of technological interest because of the possibility of exploiting the Ag Surface Plasmon Resonance (SPR) in order to increase power cell efficiency in photovoltaic devices [3]. Scanning electron microscopy, in situ X-ray photoelectron spectroscopy and surface differential reflectivity have been used to characterize the NP assembly, relating the SPR behaviour with film morphology and core/shell interface properties, emphasizing the importance of an accurate synthesis procedure on the tailoring of the optical properties of these systems.

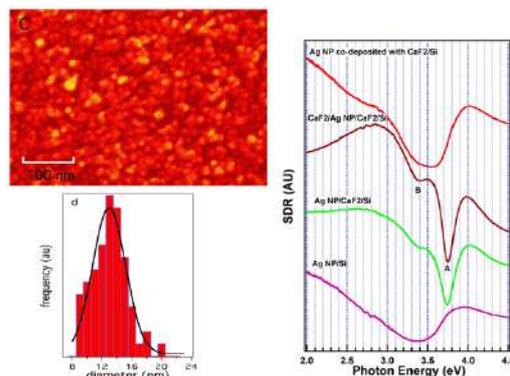


Fig. 1 : Left: SEM image of Ag@CaF₂ NP films and relative size distribution. Right SDR spectra of NP films

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Plasmonics Of Noble Metal Nanoparticles In A Hot Thermodynamic Bath

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ABSTRACT

We report a temperature-dependent investigation of the optical response of densely-packed 2D arrays of gold nanoparticles supported on an insulating nanopatterned substrate [1]. Spectroscopic ellipsometry (SE) measurements were acquired in the 245-1450 nm spectral range, under high-vacuum conditions and in the 25-350 °C temperature interval [2]. Using a dedicated effective medium approximation developed for this kind of systems [1], we are able to reproduce the complex anisotropic optical response of this system employing morphological parameters deduced by *ex-post* AFM analysis. A satisfactory agreement is attained introducing an effective correction to the Drude term of the dielectric function of Au, that keeps into account morphological effects affecting the NPs surface - such as surface premelting - that enhance the surface electron scattering rate (see Fig. 1) [3]. Our analysis thus shows that the T-dependent optical properties of metal NPs deviate from simplified expectations, and validates SE as a valuable tool to study the complex, anisotropic properties of plasmonic NPs systems.

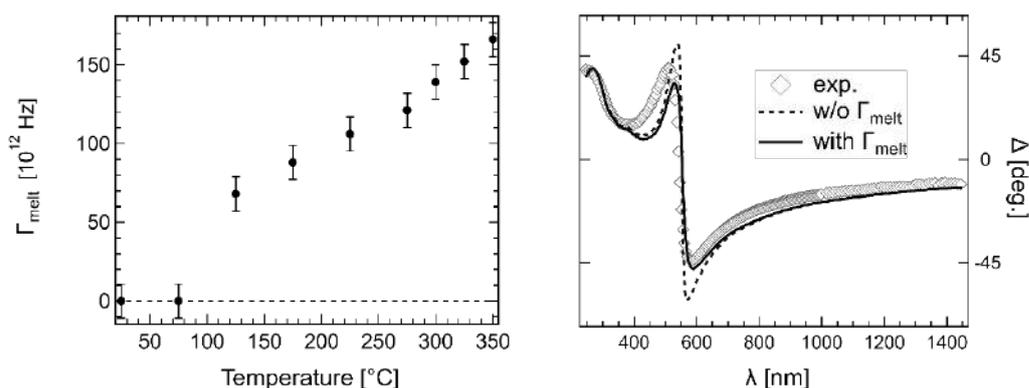


Fig. 1 Left: magnitude of the effective correction required to obtain the best match with experimental SE data. Right: comparison between uncorrected (dashed line) and corrected (continuous line) Δ spectra at 350 °C. Experimental data are reported as open markers.

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Capturing Spatial Contributions To Excitations Through Fourier Transform Of Induced Density Obtained In δ -kick RT-TDDFT Calculations

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ABSTRACT

The dynamics of electrons in a metal cluster under the influence of an optical perturbation can give important information regarding the nature of the excitations, the contribution of different chemical species to a given excitation, etc. Within the framework of Time-Dependent Density-Functional Theory (TDDFT), the real-time propagation scheme of Yabana and Bertsch (RT-TDDFT) gives direct access to the density dynamics and related quantities (dipole, absorption spectra, etc.). However, the results are relatively difficult to interpret due to the lack of direct information on the origin of spectral features, at least in comparison with transition-based linear-response calculations. To this end, spatially resolved Fourier transformation has been successfully applied to analyze the time-dependent density from δ -kick time-evolution calculations, in order to obtain spatial information about the origin of individual peaks in the spectra [1]. Individual modes can be identified using color maps, and also recovered from the Fourier coefficients to obtain animations. The differences between collective plasmonic excitations and the excitations involving d-electrons, as well as the interplay between them are captured in this analysis. In a more complex ligand-protected cluster, $\text{Ag}_{29}\text{P}_4\text{S}_{24}\text{C}_{144}\text{H}_{108}$. The spatially resolved Fourier transform of the time-dependent induced density reveals that the low-energy excitations are confined to the Ag core of the compound, unlike the strong high-energy excitations, which are found to have principal contributions from the benzene rings of the surrounding ligands. The analysis works for general systems and in particular for nanoalloys as well as for monometallic metal clusters.

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How Metallic are Tiny Pieces of Noble Metals? Metallicity and Screening in Gold & Silver clusters

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Metallicity of nanoparticles can be defined in different ways. One commonly used possibility is to look at the degree to which external fields will be screened inside the object. This screening would be complete in a classical perfect metal where surface charges arrange on the classical – i.e., abrupt – surface such that no internal fields exist. However, it is obvious that this situation is modified for very small clusters: the surface charges are “smeared out” at the surface, and the screening might be less complete.

In the present work we ask the question as to how close small noble-metal clusters are to the classical situation. We show that, indeed, the screening is almost complete already for as little as two atomic layers of the metals, silver and gold alike. At the same time, we show that quantum effects play a role, meaning that the clusters cannot be described solely using the concept of classical screening in a classical metal. We demonstrate these points using realistic atomistic pseudopotential density-functional theory (DFT) calculations, along with jellium-based DFT calculations which can be interpreted more easily than their pseudopotential counterparts. The dynamic response of the system to a time-dependent external perturbation is discussed using induced densities from time-dependent DFT.

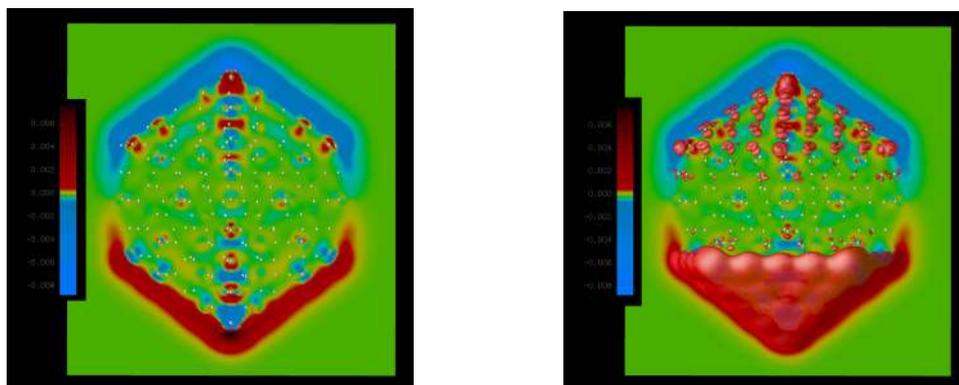


Fig. 1 : Induced density of a 309-atom silver cluster under a static homogeneous external electric field. Color map shows values from positive to negative. We show a cut through the center (left panel), as well as the same cut overlaid by a 3d iso-surface representation of the positive densities (right panel).

Origin Of Circular Dichroism In Noble Metal Alloy Clusters: A Combined Experimental And Theoretical Spectroscopic Investigation

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ABSTRACT

We probe the origin of Circular Dichroism (CD) of a class of atomically precise noble metal alloy clusters, $\text{Ag}_{24}\text{Au}_1(\text{DMBT})_{18-2x}(\text{BINAS})_x$ (DMBT = 2,4-dimethylbenzenethiolate) using experimental measurements and density functional theory (DFT) calculations. In order to impart chirality to the achiral $\text{Ag}_{24}\text{Au}_1(\text{DMBT})_{18}$ cluster, a chiral ligand, *R/S*-1,1'-[binaphthalene]-2,2'-dithiol (*R/S*-BINAS) was incorporated. The icosahedral $\text{Ag}_{12}\text{Au}_1$ core undergoes a transition from achiral to chiral and back to achiral from pure $\text{Ag}_{24}\text{Au}_1(\text{DMBT})_{18}$ to $\text{Ag}_{24}\text{Au}_1(\text{R/S-BINAS})_x(\text{DMBT})_{18-2x}$, by increasing the number of incorporated BINAS ligands. The CD spectroscopic measurements, in conjunction with DFT calculations, suggest that the CD response in $\text{Ag}_{24}\text{Au}_1(\text{R/S-BINAS})_x(\text{DMBT})_{18-2x}$ originates from transitions from metal-ligand occupied orbitals to ligands virtual orbitals. This work suggests that the chiroptical spectroscopic techniques such as circular dichroism represents a useful tool to understand the nature of electronic transitions in ligand protected metal clusters. This approach opens the way for gaining deeper insights into the structure-property relationships of the electronic transitions of such molecule-like cluster systems.

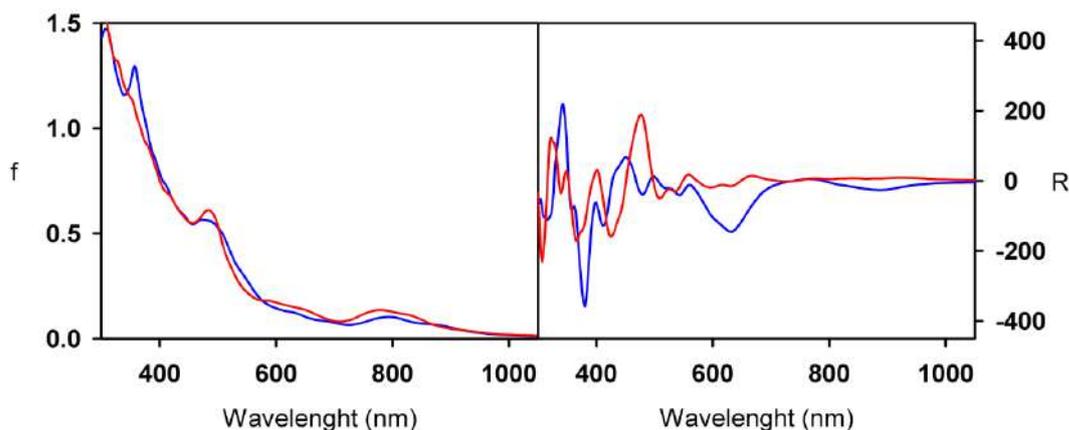


Fig. 1 : Photoabsorption oscillator strength (*f*, left box) and Circular Dichroism rotatory strength (*R*, right box) calculated at the TDDFT/LB94/TZV level for two geometries of the $[\text{Ag}_{24}\text{Au}(\text{DMBT})_{10}(\text{BINAS})_4]^-$ cluster anion.

Poster communications

P1

Tuning The Magnetic Moment Of Small Late 3d-Transition-Metal Oxide Clusters

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ABSTRACT

Oxidation of magnetic transition-metal (TM) clusters generally induces antiparallel (AP) magnetic couplings due to the metal-oxygen interactions that weaken metal-metal interactions. This render most TM oxide clusters to be in a low-spin state, and consequently to have a small total magnetic moment. To overcome this issue, attempts have been made to increase the total moment of TM oxide nanoparticles (NP) by their doping with another element[1][2]. We explore, by means of first principles calculations, the possibility of inducing ferromagnetic-like order and to promote a high-spin state in TM oxide NP (TM= Fe, Co, Ni) by mixing of the different 3d TM elements to form oxide TM binary nanoalloys of small sizes (dimers, trimers and tetramers) of all possible compositions. The goal of this systematical study is to identify optimal mixed TM oxides from the magnetic point of view, that is with high net magnetic moment and/or robust magnetic moments against different rates of oxidation which can take place in either environmental conditions or in certain applications. We also aim at finding qualitative trends that might help to design best magnetic TM nanoalloys of larger sizes.

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P2

Metallic Nanoparticles: Morphological And Structural Stability Dependence Due To Metal And Support Nature

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ABSTRACT

It is well known that nanosystems show different properties from those of the bulk due to the size reduction. Indeed, experimental and numerical studies demonstrate that the relative stability of nanoparticles and their evolution depend on the support's nature which is used for their elaboration, despite the weak interaction in the case of amorphous substrates. Our work combines molecular approach based on effective potential and experimental one using both X-ray scattering and transmission electron microscopy [1] for further comprehension of Pt-Ag alloy system [2], through the studies of pure Pt and Ag nanoparticles.

The objective of our numerical simulation is to predict the structural stability of free and supported nanoparticles on amorphous silica, especially the effect of the roughness and the surface chemistry. The tight binding semi-empirical potential within the second moment approximation (TB-SMA) [3] describes the metal-metal interaction. An mTTAM potential for the silica support and a Lennard Jones potential for metal-silica interaction.

Experimentally, the nanoparticles were prepared by atomic evaporation under ultra-high vacuum conditions on amorphous silica and amorphous carbon substrates. Morphological studies carried out by GISAXS and TEM show different behavior depending on annealing temperature and support nature. The alloy effect is showed with respect to pure particles in terms of wetting, atomic mobility and coalescence on substrate.

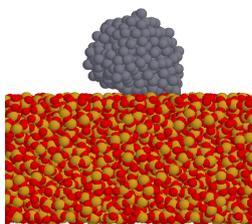


Fig. 1 : annealing temperature effect on silver supported on amorphous silica[4]

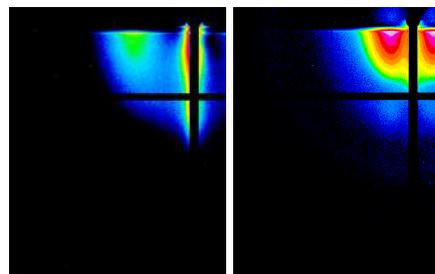


Fig. 2 : GISAXS image of annealing temperature effect on platinum nanoparticles supported on amorphous carbon

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Stability And Bonding Patterns In ZnMg Nanoalloys, From A Combined Empirical Potential/DFT Approach

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ABSTRACT

First-principles calculations are reported for a small Zn-Mg nanoalloy to get insight into relevant properties which can be important for an improved efficiency of Zn-Mg coatings against corrosion [1]. Zn-Mg nanoalloys exhibit a clear preference for mixing (i.e. a larger number of Mg-Zn hetero-bonds) favored by charge transfer effects promoted by the electronegativity difference between Zn and Mg. The most stable composition is the equiatomic ratio, further stabilized by the charge transfer effect. Although the bonding is predominantly metallic, charge transfer must be taken into account.

We show that Bader atomic charges can be accurately predicted using an order parameter dependent on both chemical and geometrical local environments. They can be used to feed improved interatomic potentials accounting for charge transfer effects. Some preliminary calculations demonstrating the advantages of using empirical potentials that incorporate coulombic interactions are shown for Zn-Mg clusters of different sizes and compositions. In particular, better predictions regarding the preferred chemical order (most stable homotop) are obtained as compared to bare tight-binding based interatomic potentials for metallic systems.

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Unexpected Composition And Size Dependence Of L₁ Chemical Order In Ag-Pt Nanoalloys

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ABSTRACT

Increasing the size of a nanoscale material is commonly associated to a widening of the stability range of its ordered phases at equilibrium [1]. Well-known examples are the melting point temperature increase with nanoparticle size, which widens the stability range of the ordered solid phase, and the increase of the order-disorder transition temperature in nanoalloys, such as CoPt, to approach the bulk limit [2]. In this study, we show that this is not a general rule, since an increase of the system size can have the opposite effect: in small AgPt clusters, up to 2.5 nm, a well-ordered intermetallic phase is stabilized at equilibrium, but, above this size, either the ordered phase breaks down into less-ordered multi-domains, or its regular arrangement is interrupted by faults. The small-size stable nanophase is characterized by a specific surface segregation effect, while stress accumulation contributes to the breaking of the ordered phase in larger objects. Macroscopic Pt-Ag alloy shows an interesting but complex phase diagram [3] especially at low temperature: an ordered alloy L₁ is formed only at the equi-stoichiometry of Ag-Pt, and a quasi-complete immiscibility for the rich-Pt side compared to a partial immiscibility for an important Ag concentration. In this study, the alloying and segregation effect competition in Pt-Ag nanoalloys prepared by atomic evaporation under UHV conditions were investigated by transmission electron microscopy (HRTEM, HAADF) and grazing incidence small and wide angle X-ray scattering (GISAXS, GIWAXS). The structural study shows a disordered/ordered phase transition depending on the annealing temperature and the composition. For the quasi-equiatomic composition an alloy phase L₁ (alternative planes of Ag and Pt in the [111] direction) with an important rhomboedral deformation is observed in a core-shell arrangement. However, an unexpected behavior is observed as a less stability of L₁ structure as the size increase [4]. The experimental results are interpreted with the aid of a multiscale modelling approach comprising full-DFT global optimization calculations and atomistic modelling.

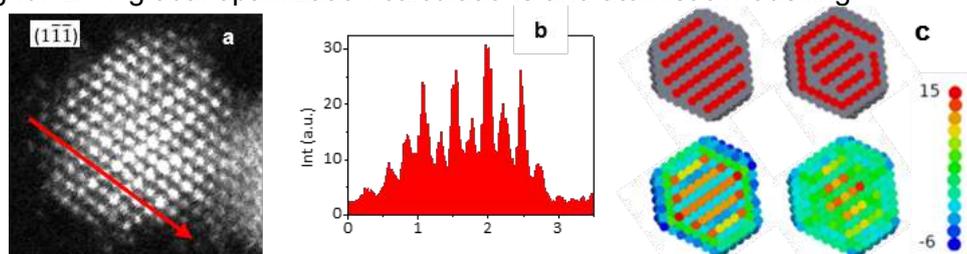


Fig. STEM-HAADF image a) and intensity profile b) of 2.8 nm PtAg cluster and c) Chemical maps and stress (in GPa) maps of core L₁-shell Ag (as STEM image) and multi-shell structures.

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Ageing Of $\text{Ag}_c\text{Pt}_{1-c}$ Thin Films And Nanoparticles

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ABSTRACT

We investigate the $\text{Ag}_c\text{Pt}_{1-c}$ alloy which has interesting properties in the field of catalysis. This system forms a $L1_1$ ordered phase at low temperature and a tendency to phase separation at higher temperatures (Fig. 1) [1-3]. Moreover, whatever the surface and the nominal composition, Ag tends to segregate. Ag-Pt-Ag thin films and Pt@Ag core-shell nanoparticles are thus expected at high temperatures whereas more complex configurations at lower temperatures with an ordered core and a silver enrichment at the surface (Fig. 2).

First we determine the equilibrium configurations at equiatomic composition of thin films and nanoparticles as a function of temperature using a Tight Binding Ising Model. Then we explore the ageing kinetics of $\text{Ag}_c\text{Pt}_{1-c}$ thin films and nanoparticles under thermal annealing using both Kinetics Monte Carlo (KMC) simulations and a kinetic mean-field description which provides the time evolution of the concentration for *each site* called MFA-SK approach (Mean-Field Approximation, Site Kinetics), based on the same atomic model [4].

The aim of this talk is then to compare the kinetics obtained for thin films and nanoparticles starting from out-of-equilibrium states or configurations which correspond to the equilibrium state at another given temperature.

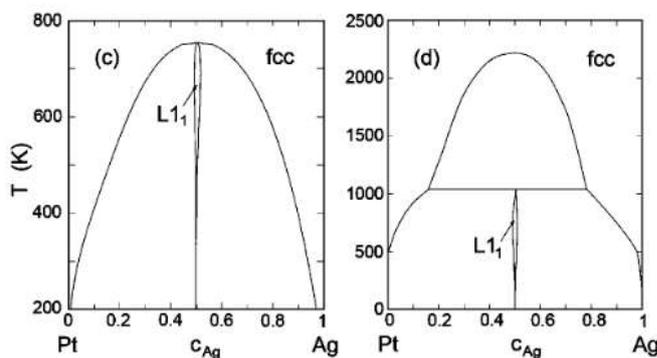


Fig. 1 : $\text{Ag}_c\text{Pt}_{1-c}$ phases diagram [1].

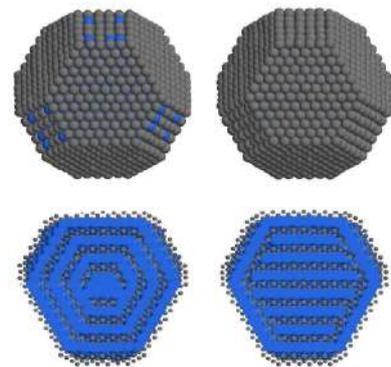


Fig. 1 : Ordered structures of TOh_{2951} at 300 K [5].

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Experimental Investigation Of Thermal Properties Of Binary Metal Alloys

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ABSTRACT

Metallic nanoparticles and recently to a greater extent also metallic nanoalloys are studied for their thermal properties such as melting point depression or phase transformation depression for neat metals and metal alloys, respectively. Melting point depression is explained by the Gibbs-Thomson equation (1) and it was reported and experimentally studied in many papers which are dealing with metallic nanoparticles [1], [2]. Thanks to further research and to development of modern methods of modeling of phase diagrams it is possible now to model phase diagrams of nanoparticle alloys by the combination of the CALPHAD method with the ab initio calculations [3], (Fig. 1).

In our work we developed synthetic strategies for preparation of alloy nanoparticles of Bi, Ni and Sn in which we used a reduction route. NaBH₄ and BH₃·H₂NiBu were used to reduce particular metal salts to obtain nanoparticles of zero-valent metal alloys. Polyvinylpyrrolidone or 1,10-phenanthroline were used as surfactants to stabilize their surface.

Prepared NPs, their phases and phase transformations were studied by Powder X-Ray Diffraction (PXRD), Transmission and Scanning Electron Microscopy (TEM, SEM/EDS) (Fig. 2) and Differential Scanning Calorimetry (DSC). The results were compared with both bulk and nano phase diagrams and were in good agreement with theoretical predictions.

$$\Delta T_m = T_m - T_m(d) = \frac{4\sigma_{sl}T_m}{d\Delta H_f\rho_s} \quad (1)$$

T_m is melting point, σ_{sl} is surface energy of liquid solid interface, d is diameter of particle, H_f is bulk enthalpy of fusion and ρ_s is density of solid

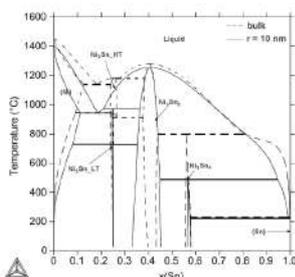


Fig. 1 : Assembled phase diagram for Ni-Sn binary system for bulk and 20 nm nanoparticles [3]

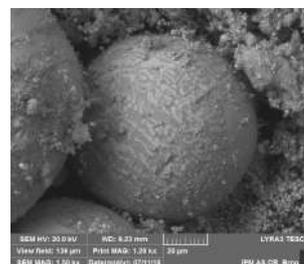


Fig. 2 : SEM micrograph of Bi-Sn near eutectic alloy after heating and aggregation. Eutectic two-phase pattern on aggregated ball and relict nanoparticles.

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Stern-Gerlach Deflection Of Cr_nO_m Clusters

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ABSTRACT

Bulk transition metal oxides (TMO) are used in diverse interesting technological applications [1, 2]. Similarly, TMO clusters composed of a small number of atoms show a rich variety of magnetic properties and their understanding is likely to provide clues about the development of magnetic interactions in bulk TMOs.

So far, mainly computational studies about the evolution of magnetic order in TMO clusters have been carried out. The results are fascinating, showing a range of possible spin coupling configurations, and suggesting that the addition of a single transition metal or oxygen atom can drastically change the magnetic order. However, there is a huge lack of experimental data.

The concept of chemical control of magnetic properties was suggested by combining DFT calculations with photo-electron spectroscopy (PES) on anionic Cr_2O_n^- ($n=1-3$) clusters [3]. And recently, infrared multiple-photon dissociation (IRMPD) spectroscopy in combination with computational analysis of the electronic and magnetic properties of cationic chromium oxide clusters indicated that the magnetic configuration of the clusters varies with the size and oxidation state [4]. None of those experimental studies, however, directly assessed the magnetic properties of the clusters.

In this study, Stern-Gerlach magnetic deflection experiments are performed on Cr_nO_m clusters ($n \leq 10$, $m \leq 10-15$) and some previous postulated results are confronted with our experimental outcomes. The choice of chromium was motivated by the notable availability of theoretical studies on its cluster oxides. In our setup at KU Leuven, clusters are formed by ablation with a frequency doubled Nd:YAG laser and by the help of an oxygen enriched He carrier gas. The latter also gives the clusters their initial momentum that steers them into the inhomogeneous field of the Stern-Gerlach magnet. The deflected neutral clusters are postionized by an excimer laser and orthogonally extracted into a high-resolution ($m/\Delta m = 5000$) time-of-flight chamber. A position sensitive MCP permits the simultaneous measurement of both the cluster's stoichiometry and magnetic deflection.

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Low Temperature Synthesis Of Nanosized Pd-X (X=Mg, Zn) Metallic Systems

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ABSTRACT

Palladium nanoparticles (NPs) have been extensively used as one of the primary catalysts for many organic reactions; in addition, the possible employment of Pd-based bimetallic materials has also been explored in dechlorination studies of PCB, in systems such as Pd/Al and Pd/Mg [1,2] and as hydrogen storage [3,4] materials in systems such as Pd/Mg.

A chemical route to nanotaylor Pd-X (X= electronegative metal) particles could be the cementation reaction, a spontaneous electrochemical process that involves the reduction of the noble species Pd²⁺ by “sacrificial” metals such as Fe, Zn, Al, Mg etc [5]. This strategy has been employed in this work in order to explore the possibility to synthesize in mild conditions bimetallic systems having Pd NPs supported on less-noble metal powders.

The chemicals used were Mg powders 325#, Zn powders 200# and a 0.1M solution of PdCl₂; the reaction was conducted in ethanol at room temperature under Ar flux. The obtained product was filtered, washed with ethanol and dried. Samples were investigated by X-ray diffraction (XRD) and Field Emission Gun Scanning Electron Microscope (FEGSEM) in order to check their composition, morphology and particles dimensions.

XRD results confirmed the formation of Pd NPs and the presence of Mg or Zn; the FEGSEM images revealed the presence of ~10 nm Pd NPs supported on the less noble metal powders having micrometric dimensions. The thermal behavior of the bimetallic systems has been investigated by using a Differential Scanning Calorimeter (DSC).

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From Bulk To Size-Dependent Melting Properties Of Au-Ge Nanoparticles

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ABSTRACT

The melting temperature and the heat of melting of Au-Ge eutectic alloy were measured by Differential Scanning Calorimetry (DSC), while the sessile drop method was used to determine its surface tension. Starting from bulk thermodynamics, solid-liquid phase equilibria in Au-Ge nanosized system has been studied analysing the melting phenomena of Au and Ge pure components and Au-Ge eutectic alloy. For the last one, own experimental data were used. It is well known that the melting points of pure metallic materials decrease with decreasing the size of their particles [1,2]. The large surface / volume ratio in nanosized particle systems has significant effects on their thermodynamic properties and phase relations. In the present work the phase diagram of Au-Ge nanoalloys is evaluated qualitatively from the macroscopic thermodynamic point of view and it is calculated as a function of temperature (T), composition (c), size (d) and taking into account that the phase relations are dependent on the size of particle and its surface property [3].

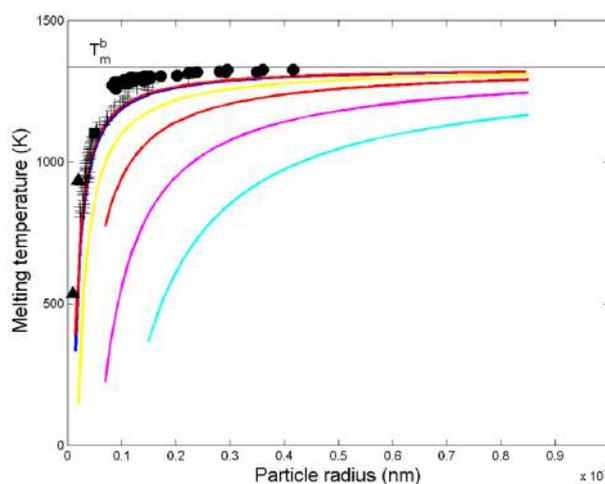


Fig. 1 : A comparison between different thermodynamic models describing the melting behaviour of Au nanoparticles together with available literature data.

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Ligand-Protected AuNPs On Lipid Raft

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ABSTRACT

Ligand-protected gold nanoparticles (AuNPs) are extensively studied for their potential application in nanomedicine, e.g. drug and gene delivery, and imaging. In order to understand how NPs impact on biological systems it is fundamental to clarify the driving forces regulating the interaction between NPs and biologically relevant interfaces, specifically cell membranes.

Over the last years, coarse-grained simulations have clarified the NP-membrane molecular mechanism of interaction, specifically for single-phase model lipid membranes [1], [2], [3], [4]. More realistic membrane models might comprehend lipid rafts. Lipid rafts are liquid-ordered (Lo) phase nanodomains in living cells typically enriched in cholesterol and saturated lipid species like sphingolipids and gangliosides embedded in a liquid disordered phase (Ld) mostly consisting of unsaturated lipids; they form phase-separated functional platforms on the cell membrane and there are evidences they are involved in signaling and trafficking cellular processes.

For a deeper understanding of NPs bioactive role, it is meaningful to investigate the interaction between NPs with lipid rafts. To this aim we use coarse-grained molecular simulations to self-assemble heterogeneous membranes with composition DIPC:DPSM:DPG1:CHOL (56:18:9:17). We investigate the interaction of this lipid membrane with an anionic ligand-protected AuNP. As a first result, we find that the same mechanism of NP internalization observed in homogeneous membranes takes place in the Ld phase. The second and more interesting observation is that, as the NP approaches the membrane, the Lo-phase starts to melt until its full disruption after few microseconds.

In order to identify the driving forces for this phenomenon, we performed specific analysis on the membrane structural changes by the calculation of the Sz order parameter, lateral diffusion coefficient and bending modulus showing the long-range effect of the NP-lipid raft interaction. We discuss the results in comparison with experimental data, focusing on the role AuNPs might have in actively regulating phase separation in cell membranes.

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The Role Of Metal Traces In Bottom-Up Porous Gold Structures In Oxidative Catalysis

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ABSTRACT

In the last decades, nanoporous gold (NPG) structures gained more and more interest in the field of heterogeneous catalysis. These kind of structures, usually synthesized by a top-bottom approach, are showing high activities and selectivity for different reactions, exhibiting catalytic properties that are not displayed by the corresponding supported catalysts. According to the currently employed synthesis method, the pure miscible metals like gold, silver, copper or aluminum are alloyed and afterwards the less noble metal is selectively etched by chemical or electrochemical methods. Yet, there is no possibility to synthesize pure nanoporous gold without residuals of metals after the dealloying step, leaving the role of the metal traces still under discussion.

In our work, we chose a bottom up approach, based on the self-assembly of nanoscale units, i.e. metallic nanoparticles (NPs), through the cryogelation method to build 3D disordered porous structures (i.e. cryogels). The cryogelation of Au NPs enabled us to synthesize pure, self-standing, porous gold gels, without the presence of any residual metal trace, while the addition of metal salts (Cu, Ce and Pd) to the system resulted in decorated gold gels. This allowed us to study the role of metal traces in two oxidative reactions (oxidative methanol coupling reaction and carbon monoxide oxidation) and to overcome the compositional restrictions of gold alloys.

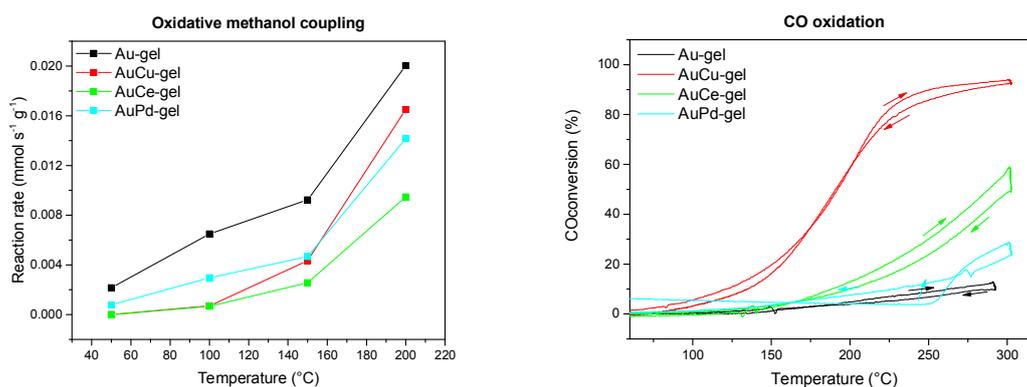


Fig. 1: Oxidative methanol coupling (left) and CO oxidation (right) experiments on synthesized porous gold structures.

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P12

Structure And Orientation Effects In The Coalescence Of Au Clusters

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ABSTRACT

The coalescence of Au clusters is studied by Molecular-Dynamics simulations. As colliding units, two Au clusters of the same size of 147 atoms are considered, analyzing the effects of the different initial structures (being decahedral, icosahedral and truncated octahedral) and their mutual orientations on the final result of the process. The simulations are run for times of more than 1 μ s at constant temperature. We consider two temperatures, 400 and 500 K. At 400 K, our results show that the final outcome of coalescence produces a variety of structures, including multidecahedra, icosahedral fragments and mixed fcc/decahedral structures. These structures are still quite far from equilibrium. At 500 K, we find that the final result still depends both on the initial structures of colliding fragments and on their orientation, but the lowest-energy structures of the different motifs are often reached during the simulations, and that, after the initial transient, transitions between different motifs are uncommon. These results are a clear indication of equilibration within each motif, but not between different motifs.

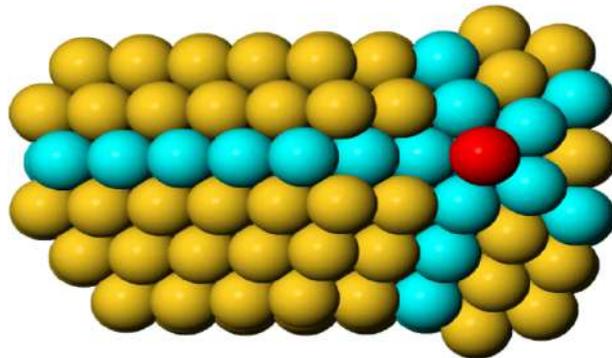


Fig. 1 : A comet-like structure, made of a decahedral part and of an fcc part.

Thermo-Optical Response Of Plasmonic Arrays Of Metallic Nanoalloys

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ABSTRACT

Noble-metal-based nanosystems easily lend themselves to tuning their Localized Surface Plasmon Resonance (LSPR) frequency, for example varying their chemical composition [1]. Nanoparticles (NPs) with finely-tuned LSPR, for example precisely matching a selected laser wavelength, can then be exploited as efficient nanoscale heaters.

In order to better understand this potential application, in this contribution we report the fabrication and investigation of the thermo-optical response of plasmonic nanoalloys of different composition in a variable-temperature (T) thermodynamic bath. We fabricated 2D ultra-dense arrays of metallic nanoparticles with graded composition, $Au_xAg_{(1-x)}$ by means of template-driven metal deposition and subsequent dewetting. From AFM images, we observed that the morphology of the system is independent from composition (Fig. 1 a). The thermo-optical characterization was performed within a roll-on/roll-off HV chamber equipped with a heating stage, placed between the arms of a spectroscopic ellipsometer (J.A Woollam M-2000). The explored temperature interval was from RT to 350°C. SE spectra at RT are a direct confirmation of the possibility of tuning LSPR as a function of the composition (Fig. 1 b). All investigated systems present a remarkable temperature dependence of their optical properties in LSPR spectral region. We discuss such a behavior in terms of reversible and irreversible effects taking place as a function of thermal cycling.

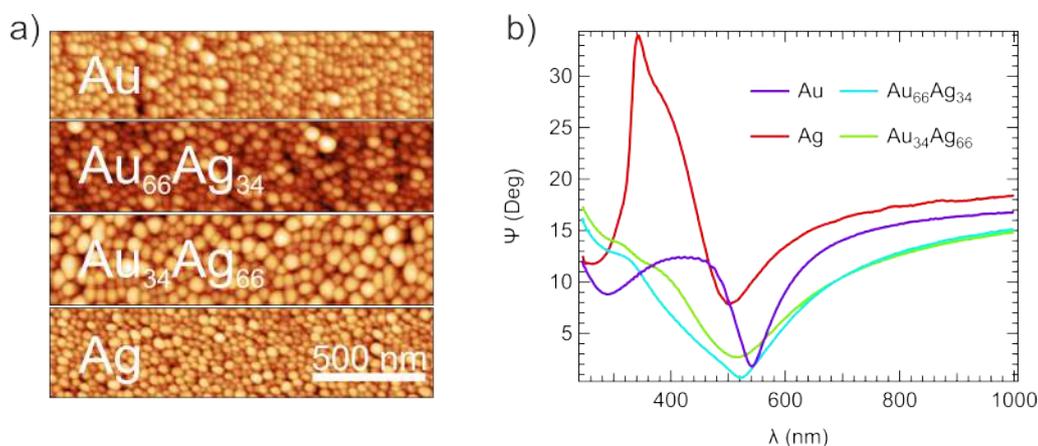


Fig. 1 : a) AFM images of 2D arrays of metallic NPs with graded composition; b) corresponding SE spectra at RT.

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Ag-Pt Nanoalloys In A Tight Binding Ising Model: Chemical Ordering On FCC Nanoparticles

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ABSTRACT

The chemical ordering of $\text{Ag}_c\text{Pt}_{10c}$ nanoalloys is characterized by a simple model on rigid lattice with effective pair interactions derived from the Tight Binding Ising Model (TBIM) [1]. This model integrates the main chemical ingredients of the bulk Ag-Pt alloys that means the ordered $L1_1$ phase at low temperature and the phase separation tendency between the two solid solutions respectively the Pt-rich one and the Ag-rich one [2-4]. The bulk phase diagram obtained within the TBIM is shown in Fig. 1. Introducing a driving force for the silver surface segregation, we get a more complicated model to study core ordering and surface segregation in nanoparticles of Ag-Pt with the truncated octahedral (TOh) morphology. Some results on the TOh of 1289 atoms are illustrated in fig. 2 for different compositions around the equiconcentration where we see that the $L1_1$ core ordering can present different domains depending on the concentration.

The next step is to integrate in our TBIM effective misfit effects not only the segregation driving force (making the silver segregating to the surface) but also to take into account subsurface stress induced by lattice misfit between the Ag skin and the $L1_1$ orthorhombic phase in the core [5].

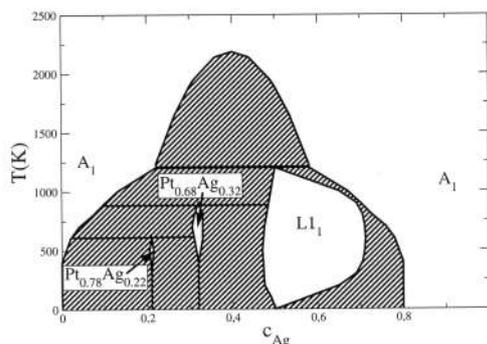


Fig. 1 : Ag-Pt phases diagram.

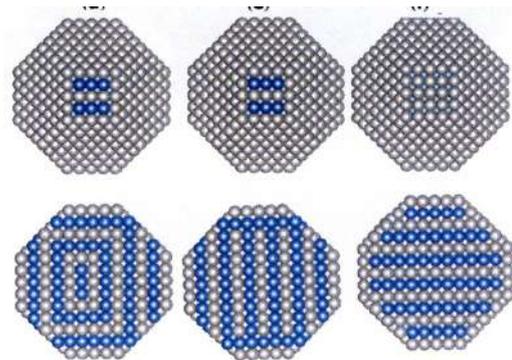


Fig. 1 : Ordered structures of TOh_{1289} at 300 K (Ag in grey, Pt in blue).

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Structural Characterization Of Subnanometer Particles

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ABSTRACT

Structural characterization of subnanometer particles is important for understanding their physical and chemical properties along the way to establish structure - function relationships. Here we present the principles of a method which can be applied to the determination of the structure of gas phase small species, on the example of a charged molecule.

Geometrical configuration of atoms within a molecule determines the vibrational energy levels that can be observed in infrared absorption spectrum of the molecule. These vibration transitions combined with those emerging from theoretical calculations allow to reconstruct the structure of the molecule. The applied experimental approach, so called Infrared Pre-Dissociation (IRPD) Spectroscopy, is based on the dissociation of mass selected tagged ions triggered by an infrared photon followed by the measurement of the depletion of the tagged ion signal on a mass spectrometer allowing single ion detection. The absorption of photons is not detected as such, but rather translated to change of mass. As a tag, here we use loosely bonded helium atom that are removed by absorption of one photon. Typically, helium tagging is accomplished in radiofrequency ion trap by collisions with helium buffer gas cooled to 3 K. At such temperature the molecule is relaxed to its ground vibrational state and its infrared pre-dissociation spectrum is free of hot bands thus it simplifies interpretation. The heart of the experiments is a cryogenic ion trap of the instrument ISORI (Infrared Spectroscopy Of Reactive Ions) [1-2], an ideal tool for spectroscopic characterization of gas-phase subnanometer charged species up to 4000 u/e, where broadband infrared radiation from an OPO (range 600 – 4700 cm⁻¹, linewidth 1.6 cm⁻¹) is used for vibrational ion spectroscopy experiments. Optionally, two-color spectroscopy can be applied to probe various structural isomers [3]. The versatility of the instrument makes also possible to investigate chemical reactions in a wide temperature range (from room temperature down to 3 K) to measure rate coefficients [4-5].

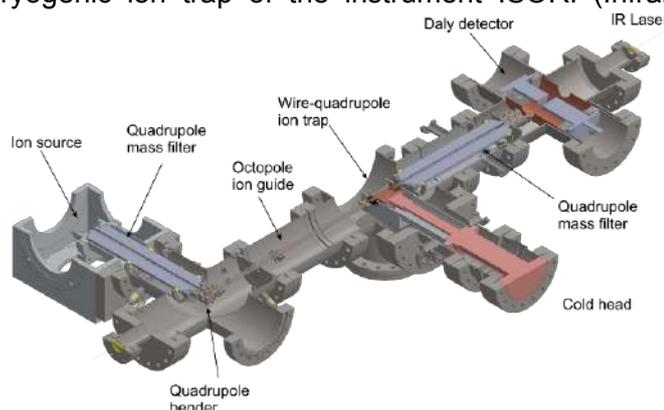


Fig. 1: Schematic of the ISORI instrument [2]

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Interactions Between Liposomes Induced By Functionalized Au Nanoparticles

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ABSTRACT

Membrane fusion is a ubiquitous and fundamental process in biological systems. The artificial synthesis of fusogenic agents can, on the one hand, shed light on the basic physical mechanisms underlying spontaneous fusion¹ and, on the other hand, it can lead to new applications, such as the directed delivery of encapsulated reagents to cells or liposomes. All fusion reactions embody an elementary process that includes membrane contact, membrane merging, and opening of a fusion pore between the water compartments of the vesicles. Here we explore the potential fusogenic activity of a class of Au nanoparticles which have been previously shown to interact favorably with neutral lipid membranes^{2,3}. We perform molecular dynamics simulations with coarse-grained resolution and show that anionic, ligand-protected Au nanoparticles (NPs) can drive liposome-liposome interactions and cause liposome clustering, as recently shown at experimental level⁴. Moreover, the NPs accumulate at liposome-liposome interfaces and can cause the formation of inter-liposome bilayer structures. These results suggest that by designing specific ligands with fusogenic activity to be covalently linked to the NP surface may be a promising route towards the development of synthetic fusogenic nanoparticles.

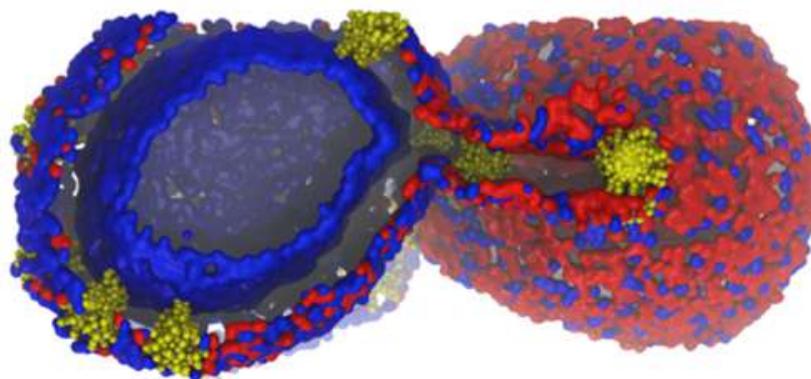


Figure 1: Two liposomes merging: a lipid bilayer bridge has developed. (In red and blue the polar heads of the lipids, in yellow the nanoparticles)

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Deuterium Adsorption On Cobalt-Fullerene Complexes

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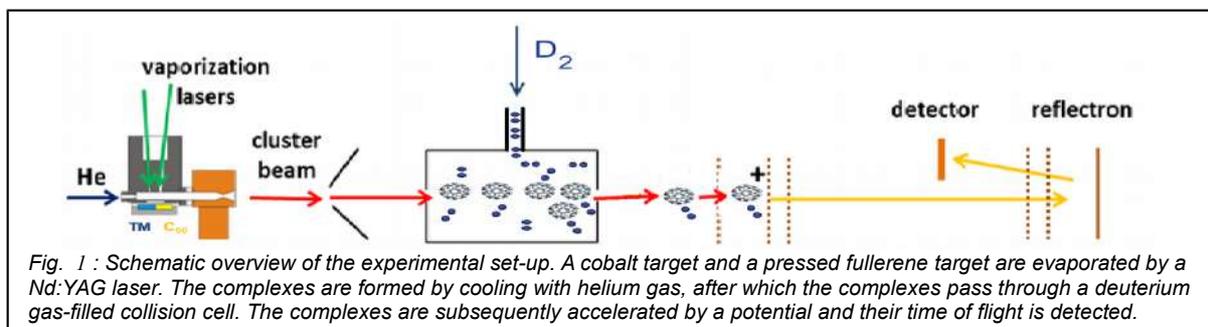
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ABSTRACT

Before hydrogen can realize its full potential as a renewable energy carrier, safe and efficient storage methods are needed. One promising strategy is the adsorption of hydrogen on nanostructured materials. For this purpose, increased fundamental understanding of the adsorption processes of hydrogen on solid-state materials is indispensable. For this reason, the interaction of hydrogen with gas-phase model systems, e.g. transition metal-doped aluminum clusters [1,2], has been studied extensively.

In this work, we present a mass spectrometric study of the adsorption of deuterium on cationic cobalt-fullerene complexes (denoted as $\text{Co}_n\text{C}_{60}^+$, with $n=1-8$). The complexes are produced in a dual-laser vaporization source by evaporating a cobalt target and desorbing fullerenes from a pressed powder target using two independent Nd:YAG lasers (see figure 1), after which the cobalt ions and fullerenes condense to form the complexes via collisions with a helium cooling gas. By measuring the time-of-flight of the $\text{Co}_n\text{C}_{60}^+$ complexes after passage through a few-collision deuterium gas-filled reaction cell, the percentage of deuterogenated complexes, with respect to the total number of complexes, could be obtained as a function of the deuterium pressure. From these curves, the formation and dissociation rate constant of the deuterogenation reaction could be inferred [3]. These rate constants are strongly size-dependent, which indicates that the cobalt atoms form a cluster on the fullerene surface. This hypothesis was tested by simulating the bare and hydrogenated $\text{Co}_n\text{C}_{60}^+$ complexes by *ab initio* density functional theory (DFT) calculations. It was found that it is indeed energetically more favorable for the cobalt atoms to form a cluster than to remain isolated on the fullerene surface. Additionally, it was found that molecular and dissociative adsorption is size dependent.



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Shape Transformation Of (Bi-)Metallic Nanocrystals

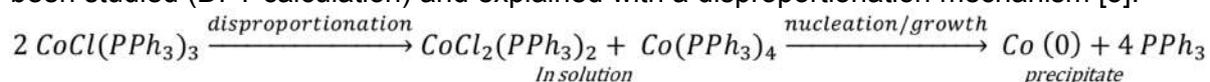
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ABSTRACT

Nanoparticles (NPs) area has known a tremendous interest since several years in the scientific community. This recent interest is stemmed from their innovative properties and their many applications in different fields like biology, optics, magnetism or catalysis. To reach the required standards in terms of selectivity (catalysis) or material efficiency (magnetism) a perfect control of the size, shape and crystallinity is mandatory. In these two fields, cobalt NPs showed in this last few decades a high potential [1]. Thanks especially to its hexagonal closed pack (hcp) structure which is giving access to a control over size and crystallinity. This structure has also one of the highest magnetic anisotropy for metallic compounds. The MONARIS group developed a one-pot synthesis of cobalt NPs spherical (hcp) with only two reagents: $\text{CoCl}(\text{PPh}_3)_3$ and Oleylamine [2]. This method showed many advantages like the reproducibility, the low size dispersity percent (10%), the NPs are well crystallized (Figure 1) and single-domain (magnetic). The process of the NPs formation has been studied (DFT calculation) and explained with a disproportionation mechanism [3]:



also an original shape transformation from nanospheres to nanorods, which is not well understood to date. During this **poster presentation**, I will present this shape transformation for cobalt NPs (hcp) e(Figure 2) with only channelling the ramp temperature and the reaction time. This shape transformation has been also observed with nickel and cobalt/nickel nanoalloys.

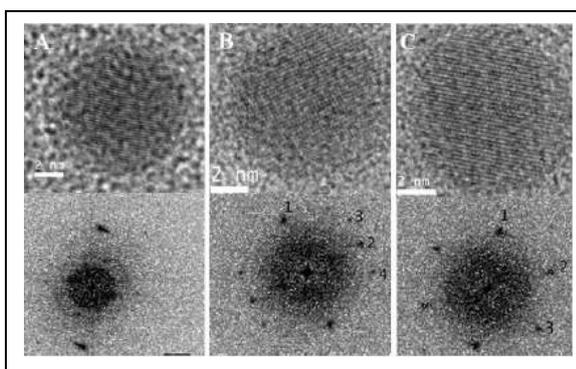


Figure 1 : HRTEM images, Co NPs 9 nm

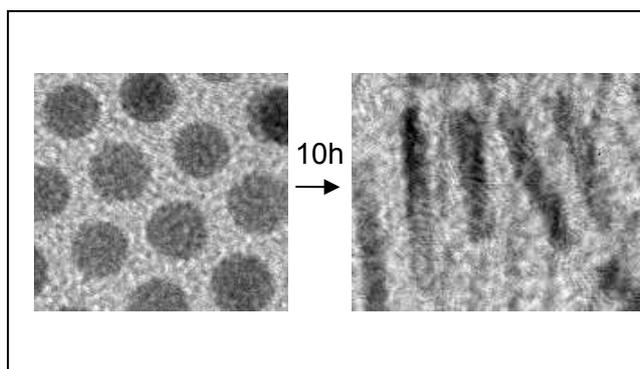


Figure 2 : Shape transformation (zoom on 80K images)

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Structural Transformations In AuCo Nanoalloys Studied By Metadynamics

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ABSTRACT

In most experiments, nanoalloys are initially produced in out-of-equilibrium states; they then evolve towards thermodynamic equilibrium undergoing transformations in geometric structure and in chemical ordering. During this evolution, metastable configurations with very long lifetime are sometimes reached; this behavior leads to long equilibration time scales, ranging from seconds to minutes or even months. The computational study of such evolution may be quite challenging: standard molecular dynamics techniques can only reach time scales up to some microseconds for nanoparticles of sizes of a few thousand atoms, therefore it is necessary to use enhanced sampling techniques, such as metadynamics, to extend the time scale of the simulations.

Here we use a recently developed form of metadynamics [1] to study the evolution towards thermodynamic equilibrium at room temperature of AuCo nanoalloys of different sizes and compositions. This type of metadynamics allows to direct the evolution from a starting configuration to a desired final configuration. In particular, transformations from reverse core-shell Au@Co to core-shell Co@Au are analysed: Co@Au configurations correspond to the lowest energy configurations for AuCo nanoalloys [2], while Au@Co metastable configurations can be produced in synthesis experiments.

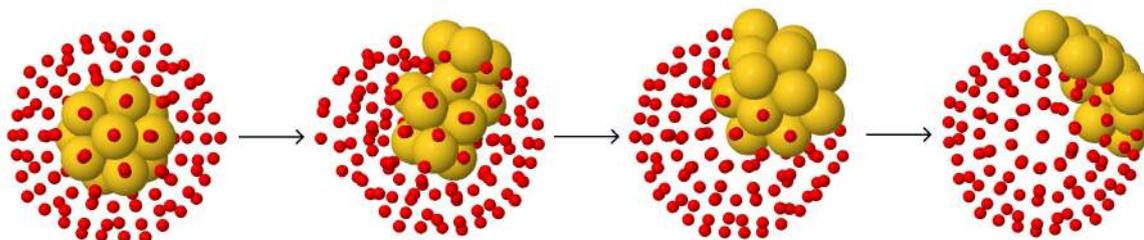


Fig 1: Evolution of $Au_{13}Co_{134}$ obtained in metadynamics simulations at $T = 300K$

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Probing The Evolution Of PdCu And PtCu Bimetallic Nanocrystal Catalysts Under Operando Conditions By *In-situ* X-ray Absorption Spectroscopy

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ABSTRACT

Thanks to the improvement of wet chemistry methods, the synthesis of bimetallic nanocrystals (NCs) experienced extensive development over the past decade. Current preparation protocols allow the precise tuning of NC size, shape and composition as well as fine control over atomic-scale features¹. While these properties can be efficiently controlled at the synthesis step, when these NCs are applied to heterogeneous catalytic processes, they undergo extensive transformations with the consequent modification of their electronic and geometric properties which affect their performances in the selected catalytic process². Extending the works related to AuCu NCs, here, we synthesized bimetallic PdCu and PtCu NCs by means of colloidal synthesis approach. We studied the transformations of these alumina supported disordered bimetallic alloy catalysts upon different redox treatments as well as the CO oxidation reaction. In this regard, we applied advanced *in situ* spectroscopy including time-resolved X-ray absorption spectroscopy (XAS) and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) under operando conditions to monitor the transient transformations on these two systems and to establish structure-activity correlations. In both cases, the initial oxidative pretreatment led to a progressive segregation between the noble metal and Cu with the formation of PdCu mixed oxide (Fig. 1a) and Pt/PtO and CuO_x species (Fig. 1b), which in turn resulted in a decreased catalytic activity (Fig. 1c). Reducing the catalyst restored the PtCu (Fig. 1b) and partially the PdCu alloyed NCs, and enhanced the catalytic activity (Fig. 1a, 1c), highlighting the importance of the interface between the noble metal and the Cu oxide species for the catalytic activity in the CO oxidation reaction.

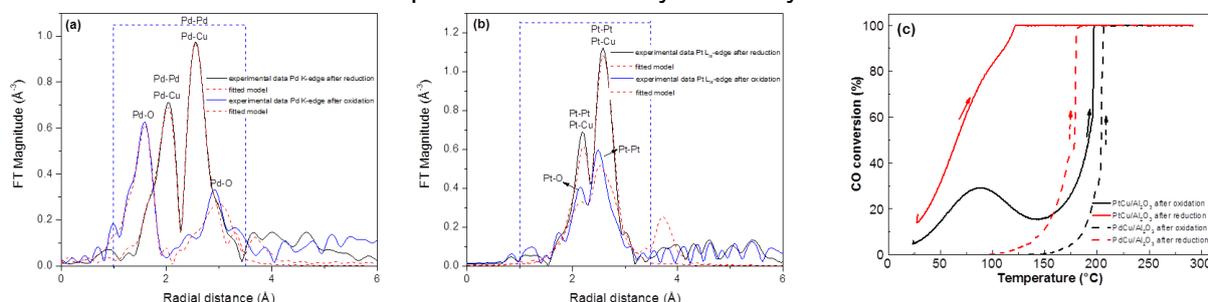


Fig. 1: Fourier transforms of the EXAFS spectra with the best fit of the components evolving during the pretreatments (a) Pd K-edge and (b) Pt L_{III}-edge collected on PdCu/Al₂O₃ and PtCu/Al₂O₃ catalysts and (c) corresponding to the transient catalytic activity in CO oxidation reaction.

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P21

CeO₂(111) Electronic Reducibility Tuned By Ultra-Small Supported Bimetallic Pt-Cu Clusters

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ABSTRACT

Controlling Ce⁴⁺ to Ce³⁺ electronic reducibility in a rare-earth binary oxide such as CeO₂ has enormous applications in heterogeneous catalysis, where a profound understanding of reactivity and selectivity at the atomic level has yet to be reached. In this work we report an extensive DFT-based Basin Hopping global optimization study to find the most stable bimetallic Pt-Cu clusters supported on the CeO₂(111) oxide surface, involving up to 5 atoms in size for all compositions [1]. Our PBE+U global optimization calculations indicate a preference for Pt-Cu clusters to adopt 2D planar geometries parallel to the oxide surface, due to the formation of strong metal bonds to oxygen surface sites and charge transfer effects [2]. Calculated adsorption energy values (E_{ads}) for both mono- and bimetallic systems are of the order of 1.79 up to 4.07 eV, implying a strong metal cluster interaction with the oxide surface. Our calculations indicate that at such sub-nanometer sizes, the number of Ce⁴⁺ surface atoms reduced to Ce³⁺ cations are mediated by the amount of Cu atoms within the cluster, reaching a maximum of three Ce³⁺ for supported Cu₅ cluster. Our computational results have critical implications on the continuous understanding of the strong metal-support interactions over reducible oxides such as CeO₂, as well as the advancement of frontier research areas such as heterogeneous single-atom catalysts (SAC) and single-cluster catalysts (SCC) [3,4].

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A Gold-Sulphur Atomistic Potential For Molecular Dynamics

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ABSTRACT

We aim at developing a new atomistic potential for the gold-sulphur interaction¹ in the case of thiolates on gold surfaces^{2,3}, and in particular on a gold nanoparticle.

To determine the parameters of the interaction, we make Density Functional Theory (DFT) calculations of methyl thiolates on gold surfaces.

From the DFT calculations, we find that the Au-S interaction depends on the coordination of the gold atom with other gold atoms.

The potential form is of Morse-like form, with the strength and the equilibrium distance between Au and S depending on the Au coordination, see Figure 2.

We have implemented the potential in the LAMMPS suite. We are testing the potential in molecular dynamics simulations using the OPLS force field.

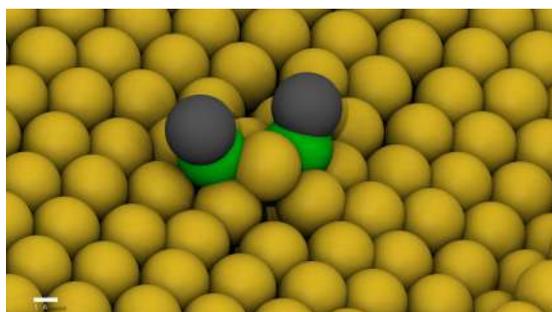


Fig. 1 : These methanethiols are about to extract a gold atom from the surface in a MD simulation with our potential.

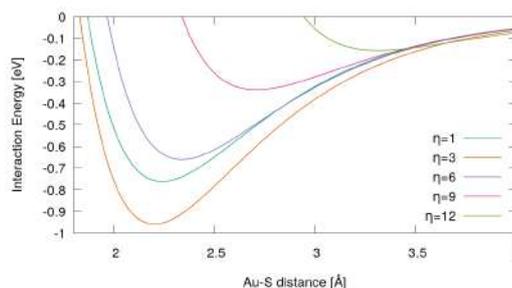


Fig. 2 : The form of the potential at various Au coordinations"

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(Ni,Co) Alloy Nanoparticles: Synthesis, Characterization And Catalytic Application

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ABSTRACT

Hydrogen production through bioethanol steam reforming is a very promising way for low temperature production (523-773 K). Up to now, the catalyst formulation is still not optimized, even if Nickel and Cobalt were identified as possible active phase for this process, being more robust and cheaper than noble metal based catalysts. With this purpose we tested (Co,Ni) nanoparticles prepared via reduction method in aqueous solution using NaBH₄ as reducing agent, starting from NiCl₂·6H₂O and CoCl₂·6H₂O salts in different stoichiometric ratio, but making sure to reach a final concentration of 10⁻² M for metals in solution, with a Me²⁺:BH₄⁻ ratio equal to 1:2.

The obtained materials have been characterized as cast and/or after annealing by means of XRD, magnetic measurements, IR spectroscopy, FESEM and TEM microscopies. The resulting nanomaterials, originally amorphous, crystallize into the cubic structure cF4-Cu as homogeneous (Co,Ni) solid solution alloy and with the additional presence of Boron containing phases due to the residual preparation impurities.

All the catalysts have been successfully prepared, characterized and tested in ESR showing promising performances. The effect of the synthetic procedure and the possible preparation residuals will be discussed since they might strongly affect both catalytic activity and catalysts stability.

Thermal Gradients Around Irradiated Au NPs in the Biological Environment

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ABSTRACT

Monolayer-protected Au nanoparticles (AuNPs), functionalized by organic and biocompatible ligands, find several applications in biomedicine among which, thanks to their plasmonic response, photothermal therapies [1]. The Au core can efficiently absorb light and convert it into heat. The capability of the NP to transfer heat from the core to the surrounding environment depends on the core diameter and shape but also on the physico-chemical properties of the NP-ligands and ligands-water interfaces. Heat transfer is influenced by the ligand coverage, ligand composition, length, hydrophobicity and charge.

At the interface between a bare hot NP and the surrounding solution the Kapitza resistance generates a sharp temperature discontinuity [2]. The aim of this work is to study, by means of non-equilibrium atomistic molecular dynamics simulations, what is the influence of ligands on the temperature profile around a coated hot AuNP.

We calculate the temperature gradients around the NP core at variance with the type of ligands covering the core. All ligands are covalently bound to the core via a thiol bond, and have a different degree of hydrophobicity. We consider the 4-mercaptobenzoic acid (pMBA), the 7-methyl-mercaptoundecanoic acid (MMUA), both negatively charged, two polyethylene glycol chains made with 3 and 7 monomers (PEG_n) and the fully hydrophobic 6-methyl-undecane thiol (MC11). We find that the temperature gradient depends on the hydrophobicity of the ligand type and on water mobility at the ligand-water interface [3].

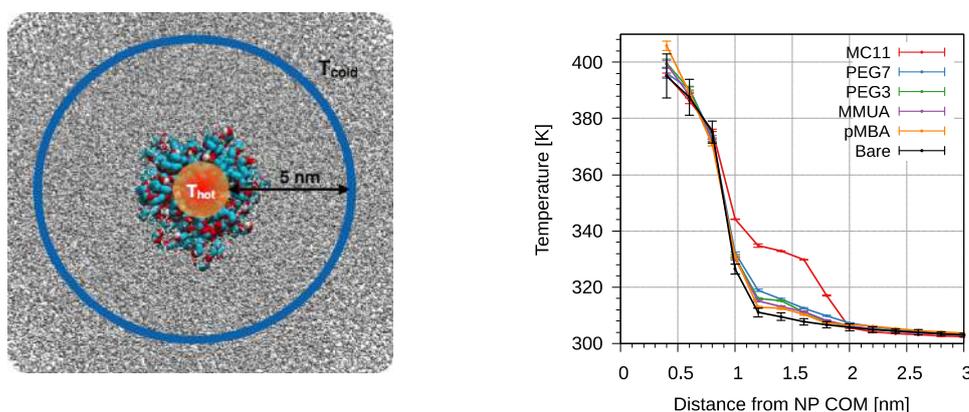


Fig. 1. Snapshot of a simulation box with a functionalized NP. Au in yellow, S in grey, C in blue, O in red and H in white. Water is shown as shaded light-grey beads. The Au atoms are thermostated at a 380 K. Water at a distance larger than 5 nm from the Au surface is thermostated at 300 K. The rest of the system is left un-thermostated.

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Surface Assisted Synthesis Of C-Based Nanostructures On Ag(110)

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ABSTRACT

Graphene is a material of exceptional properties, but its intrinsic zero-energy gap reduces the impact for applications in nanoelectronics. On the contrary, *graphene nanoribbons (GNR)* narrower than 10 nm are semiconductors, due to the electron confinement in one dimension and to edge effects [1]. The ability to grow highly ordered nano-ribbons is therefore of relevance for possible applications in nanodevices and in this frame bottom-up synthesis from molecular precursors has been proven to give the best results. Here we summarize our recent results on the formation of low dimensional C-based nanostructures on Ag(110) [2,3]. By a combination of scanning tunneling microscopy, spectroscopic techniques and density functional theory calculations, we demonstrate the formation of extended patterns of parallel graphene nanoribbons by surface assisted Ullmann coupling and de-hydrogenation of 1,6-dibromo-pyrene (DBP). The GNRs are monodispersed in width and show alternated zig-zag and armchair sites at the edges. This outcome is compared with the parallel experiment performed starting from the Br-corannulene precursor, which produces an extended network of corrugated C-based nanostructures maintaining the original curvature of the precursor molecule. Our results demonstrate the peculiarity of pyrene derivatives for the formation of GNRs on coinage metals, in particular on Ag(110) and open the possibility of engineering nanostructures of particular shape and dimension (and hence with tailored electronic properties) by choosing suitable molecular precursors.

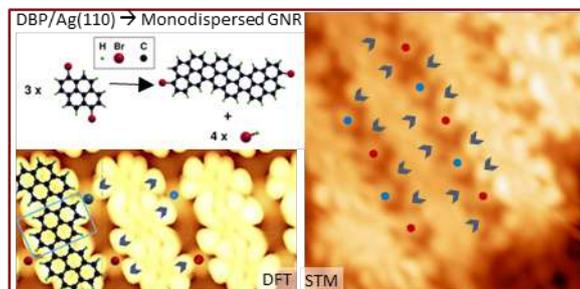


Fig. 1 : Scheme of GNR formation from DBP precursors (top left panel), experimental (right panel) and simulated (bottom right panel) STM images of the so-obtained GNR [2].

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Monitoring Oxidation And Reduction Of FeO₂ Islands On Pt(111) Using HREELS And XPS

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ABSTRACT

Iron oxides are widely used in many technological fields due to their unique electronic, magnetic and catalytic properties, combined with low cost and non-toxicity. In catalysis, they are employed in oxidation, hydrogenation, desulfurization and other reactions [1]. Ultrathin iron oxide films grown on platinum substrates exhibit superior catalytic activity for the CO oxidation reaction [2] and for O₂ dissociation. Their activity derives from the electron transfer effects allowed by the work function of the film and the electron affinity of the reacting gas molecule.

The FeO_{2-x} phase, consisting of a single O-Fe-O trilayer, is expected to show an enhanced reactivity with respect to other iron oxides due to its high oxidation state. Indeed, it was shown [3] that the CO oxidation reaction over FeO/Pt(111) proceeds through the formation of this oxygen-rich phase. Nonetheless, FeO_{2-x} is the least characterised among Fe_xO_y compounds, since a complete layer forms only in high pressure cells or using an atomic oxygen source, while FeO_{2-x} islands can be produced under UHV conditions [4].

Here we characterize the reactivity of FeO_{2-x} islands grown on Pt(111) by vibrational (HREELS) and photoemission (XPS) spectroscopy. By performing repeated oxidation/reduction cycles we identified the Fuchs-Kliever modes of FeO₂ and confirm the ability of CO to reduce the so-formed oxide at 450 K. This latter process is not fully reversible, witnessing a poisoning/modification of the active sites upon CO adsorption.

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Improving Accuracy Of The Topological Approach For Nanoalloys: Case Study Of PtCu Nanoparticles

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ABSTRACT

Chemical reactivity and other properties of bimetallic nanoparticles (NPs) depend on their composition, size, shape and mutual atom arrangement of the constituting two metals (so-called, chemical or atomic ordering). Determining the most energetically stable chemical ordering within a given structure is a very challenging task due to huge number of combinatorically possible configurations (homotops). To make practical quantum-mechanical calculations of chemical ordering in bimetallic NPs a topological approach (TOP) has been recently developed [1,2] and applied in our group for nanoalloy particles of different metals, sizes and shapes [1-5]. The TOP method relies on the decomposition of the NP energy (e.g. that from a DFT calculation) in several topological contributions allowing to pre-select groups of low-energy homotops via a Monte-Carlo approach in order to subsequently determine the minimum energy homotops by a small number of DFT calculations.

In this work, we examined accuracy of the TOP method for catalytically relevant PtCu NPs intricate due to size mismatch of Pt and Cu atoms. A series of truncated octahedral PtCu NPs containing 116, 140 and 201 atoms and featuring Pt:Cu atomic ratios 1:3, 1:1 and 3:1 were studied. In all cases the results revealed alloy formation with a clear tendency towards Cu@Pt core@shell NPs. The TOP description is applicable for both low- and high-energy homotops. Yet, the accuracy for the latter structures is still to be examined. Our analysis of DFT energies of NP structures with the same TOP revealed inaccuracies by up to ~1 eV. We will discuss how the accuracy can be improved by modifying the TOP energy expressions.

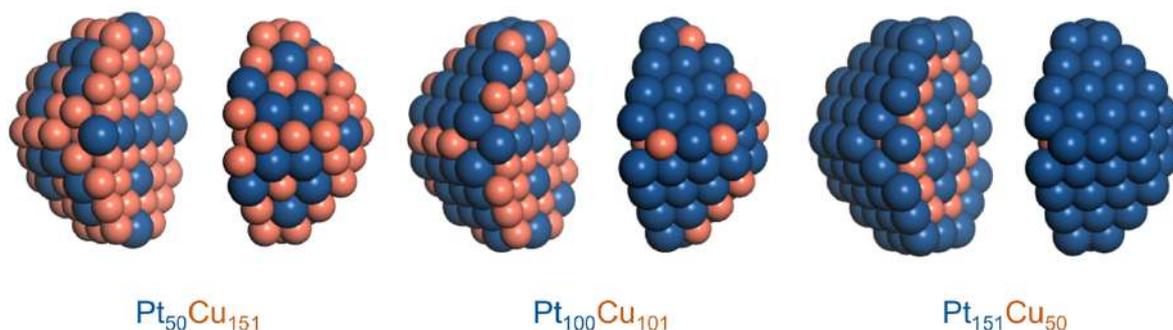


Fig. 1: Lowest-energy homotops for $\text{Pt}_{201-n}\text{Cu}_n$ nanoparticles with Pt:Cu ratios 1:3, 1:1 and 3:1.

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Time Dependent Density Functional Theory Calculation For Nano-Plasmonics

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ABSTRACT

The structural features dependence of optical properties for metallic nano-particles is of interest for its promising potential to be applied in various applications including designing of photo-catalyst with better performance. To investigate and understand the short-time plasmon dynamic, the first principle simulation using time dependent functional theory (TDDFT) has been proven to be both efficient, reliable and became a de-facto standard tool for researchers.

In this work, we illustrate and discuss numerical results on the dynamic of electrons that are confined in various noble-metal structures, especially in a family of bare gold nano-particles (AuNP) with different sizes and shapes. The simulation shows there are correlation between structure features and the optical properties such as absorption spectrum as well as charge density differences propagation under LASER. These findings indicate the possibility of tuning optical response of metallic NPs by constructing corresponding architectural features, and a theory for description beyond Jullium model is needed.

In future, we will look at the possible overlap between simulation results and experimental measurement and the optical dependence upon chemical composition and ordering, other NPs structures with doping Al and Cu will be considered.

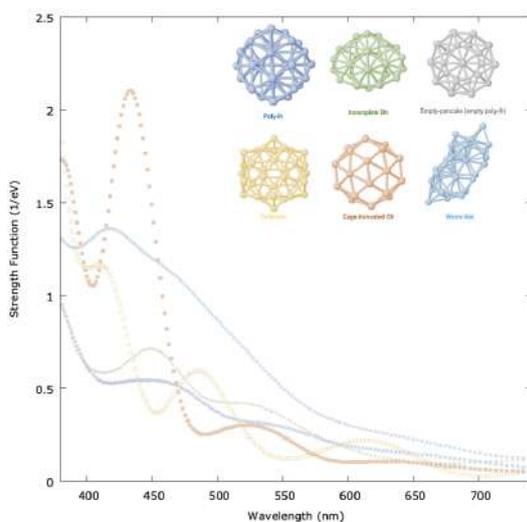


Fig. 1 : The absorption spectrum within visible light spectrum for five Au₃₂ NPs under delta-kick calculation.

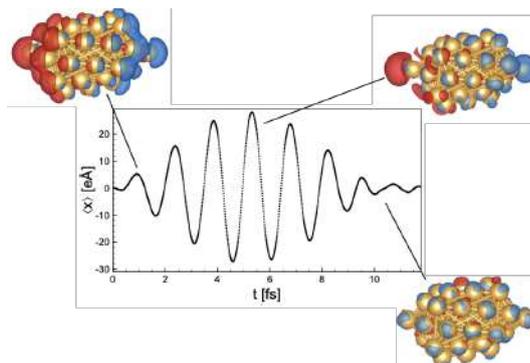


Fig. 2 : Electric dipole oscillations in a wire-like structure cluster of Au₃₂. LASER points along the major axis of the isomer, Here we show the shape of the LASER and the charge density difference with respect to the initial configuration for three given point of time, with blue positive and red negative region.

Conference venue: Physics Department



Address: Via Dodecaneso 33, Genova, Italy

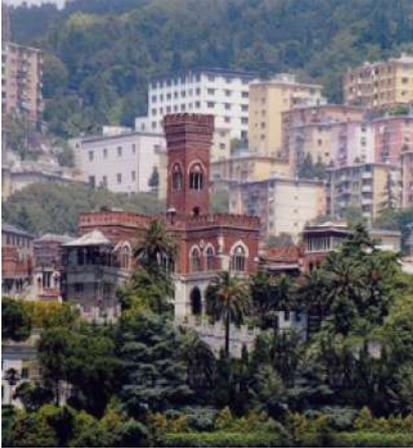
This building was designed in the seventies, and got also some kind of architecture prize (!!).

The entrance door, that you may reach by following the instructions of the next page, is on the back side of this building.

The entrance door is between the fifth and the sixth floor of the building (!?, do not worry, there is a hill on the back side of the building, so that the entrance seems to be on the ground floor, but it is not).

The lecture room is *Aula Magna* on the fifth floor. There will be indications at the entrance on how to reach it.

Social Dinner at Castello D'Albertis



Address: Corso Dogali 18, Genoa

Castello D'Albertis is located on top of the Montegalletto hill, which is just above the city center.

The Castle was built in Neo-Gothic style in 1886, on the site of a 13th-century fortified area, which had been reinforced in the 16th century. Originally, the Castle was the residence of the Genoese sea Captain Enrico Alberto d'Albertis, an explorer and ethnologist.

The Castle was donated to the city of Genoa on the death of the Captain in 1932. It currently houses the Museo delle Culture del Mondo (Museum of World Cultures).

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COMUNE DI GENOVA

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	Tuesday, June 04	Wednesday, June 05	Thursday, June 06	Friday, June 07
8:30–9:10		Registration		
9:10–9:30		Opening	O14 Cheng	O25 Garip
9:30–9:50		IRN Activity Report	O15 Fortunelli	O26 Pavloudis
9:50–10:10		O1 Neyman	O16 Vajda	O27 D'Addato
10:10–10:30		O2 J. Zhao	O17 Yadav	O28 Magnozzi
10:30–11:00		Coffee Break	Coffee Break	Coffee Break
11:00–11:20		O3 Casanove	O18 Grammatikopoulos	O29 Sinha-Roy
11:20–11:40		O4 Peddis	O19 Gavioli	O30 Weissker
11:40–12:00		O5 Gabbani	O20 Cottancin	O31 Stener
12:00–12:20		O6 Paleo	O21 Mottet	Concluding Remarks
12:20–14:00		Lunch	Lunch	Lunch
14:00–14:20		O7 Baletto	O22 Garzon	
14:20–14:40		O8 Nelli	O23 Pinto-Miles	
14:40–15:00		O9 Palmer	O24 Rapetti	
15:00–15:20	15:00 – 18:00 An introduction to metal nanoparticles and nanoalloys (Ferrando, Palmer, Ricolleau, Cottancin)	O10 Rahm	15:00 –16:00 IRN Groups Meeting	
15:20–15:50		Coffee Break		
15:50–16:10		O11 Van den Bossche	16:00 –18:30 Poster Session with refreshments	
16:10–16:30		O12 Petit		
16:10–16:50		O13 Polak		
17:00–20:00	18:00 – 19:30 Welcome Party and Registration	City Tour and approach to Castello D'Albertis		
20:00–23:00		Social Dinner		