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Annual report of the activity during the year 2019/2020

Research activity

The aim of my research activity is the study of equilibrium and out-of-equilibrium properties of nanoparticles and nanoalloys by computational methods. During this year I have mostly focused on the phenomenon of the growth of nanoparticles from an initial atomic vapour, working in close contact with different experimental groups. The combination of computational and experimental data have made it possible to better understand the growth mechanisms, and to clarify how the synthesis conditions affect the shape and chemical ordering of the nanoparticles obtained. Other topics I have investigated are the coalescence of nanoalloys and the application of advanced computational techniques to the study of nanoparticles evolution from metastable configurations. The following is a short summary of each topic I have worked on.

- Growth of core-shell PtPd nanoalloys in the gas phase

  This work has been done in collaboration with dr. Chloé Minnai (OIST, Okinawa, Japan) who performed gas phase synthesis experiments and TEM observations of PtPd nanoalloys, pointing out a composition-tunable chemical ordering effect. In the observed nanoparticles, the minority element always concentrates in the central part of the structure, while the shell is strongly enriched in the majority element. This corresponds to the formation of (PtPd)@Pd and of (PtPd)@Pt core-shell structures in the Pd-rich and Pt-rich cases, respectively. To deeply understand both the physical origin of the observed composition-tunable chemical ordering and the mechanisms leading to the formation of these core-shell structures, we rationalized the experimental results by computer simulations. By means of global optimization searches, we demonstrated that neither (PtPd)@Pd nor (PtPd)@Pt arrangements correspond to the equilibrium chemical ordering but are the result of kinetic trapping phenomena instead. The kinetic origin of these structures is further confirmed by molecular dynamics (MD) simulations of nanoparticle growth, which are able to reproduce both geometric shapes and chemical ordering in very good agreement with the experiments. The results have been published (see the list of publications below).

- Growth of octahedral and tetrahedral Pt nanoparticles in the gas phase

  This work has been done in close collaboration with the experimental group of prof. Ziyou Li (University of Birmingham, U.K.) who performed gas phase synthesis experiments and TEM observations of Pd nanoparticles. In the experiment, both octahedral and tetrahedral out-of-equilibrium shapes are obtained, and their relative abundance can be tuned by controlling the growth conditions. We performed MD simulations of the growth, which reproduced the main features of the experiment and unraveled the atomic-scale growth mechanism from octahedral to tetrahedral shaped nanoparticles. The results have been submitted (see the list of publications).

- Growth of AgCo supported clusters

  This work has been done in collaboration with the experimental group of Pascal Andreazza (University of Orléans, France) who performed synthesis experiments of AgCo supported clusters and followed the growth in situ and in real time by X-ray scattering techniques. In the experiment, Co atoms are deposited on preformed Ag clusters. Both experimental data and MD growth simulation show that Co atoms migrate from the surface towards the center of the nanoparticle, so that the final outcome of the growth is the equilibrium core-shell Co@Ag arrangement. Besides, MD simulations allow to identify the

intermediate steps of the growth, for example the formation of quasi-Janus structures. The results have been submitted (see the list of publications).

- Coalescence of PtPd nanoalloys

  This work has been done in collaboration with dr. Chloé Minnai (OIST, Okinawa, Japan) who performed gas phase synthesis experiments and TEM observations of PtPd nanoalloys. The coalescence of preformed core-shell (PtPd)@Pd and pure Pd nanoparticles is observed experimentally and reproduced by MD simulations. The combination of experimental images and simulated evolution sequences allow to identify the different stages of the process. In particular, it can bee seen that the geometric shape of the coalesced aggregate evolves much faster than its chemical ordering. This leads to the formation of compact core-shell structures with off-centered core.

- Migration of single-atom impurities from the center to the surface of icosahedral clusters studied by advanced computational techniques

  We consider pure Co and Cu icosahedral clusters of different sizes in which single-atom impurities of Au and Ag respectively are placed in the central site. The evolution towards the equilibrium configurations, in which the impurity is on the surface of the nanoparticle, is studied by MD simulations at different temperatures and by metadynamics simulations at room temperature. Unexpectedly, the migration of the impurity towards the surface takes place through the formation of vacancies in the inner part of the cluster. This work has been done in collaboration with dr. Fabio Pietrucci (Sorbonne University, Paris, France) who developed the collective variables that we used in the medadynamics simulations.

Publications

- D. Nelli, G. Rossi, Z. Wang, R. E. Palmer and R. Ferrando, Structure and orientation effects in the coalescence of Au clusters, Nanoscale 12, 7688 (2020) doi: 10.1039/c9nr10163b
- D. Nelli, A. Krishnadas, R. Ferrando and C. Minnai, One-step growth of core-shell (PtPd)@Pt and (PtPd)@Pd nanoparticles in the gas phase, J. Phys. Chem. C 124, 14338 (2020) doi: 10.1021/acs.jpcc.0c02621
- P. Andreazza, A. Lemoine, D. Nelli, R. Ferrando, A. Coati, Y. Garreau, J. Creuze and C. Andreazza-Vignolle, From metastability to equilibrium during the sequential growth of Co-Ag supported clusters, submitted
- Y. Xia, D. Nelli, R. Ferrando, J. Yuan and Z. Y. Li, Shape control of size-selected naked platinum nanocrystals, submitted

Attended courses

Aspects of Soft Matter

Attended courses and exams during the first two years

- Quantum Optics (exam passed)
- Advanced Computational Physics (exam passed)
- Elementary Electronic Structure of Solids (exam passed)
- Basic Scanning and Transmission Electron Microscopy (exam passed)
- Aspects of Soft Matter (exam passed)

One course has been replaced by the attendance to a one-week summer school (PISACMS 2019: Paris International School on Advanced Computational Material Science)