

PhD report

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Research activity

The research activity of my third year as a PhD student can be divided in two different parts. The first part was the systematic study of the adsorption energy of hydrogen atoms in palladium nanoparticles (NPs). Palladium is in fact well known to be one of the most promising materials to store hydrogen at the nanoscale due to its structural robustness against charging and discharging of relatively high hydrogen loads. Many nanoparticles shapes have been produced experimentally, including face-centered-cubic, decahedral and icosahedral, and their different ability to adsorb hydrogen was observed. In particular, it was shown in the literature that face-centered-cubic NPs are better candidates for hydrogen storage than non-crystalline shapes such as icosahedra. It is guessed in the literature that the reason of such difference may be found in the presence of high strain in the inner part of icosahedral nanoparticles. Our goal was then to systematically study the adsorption energies of hydrogen atoms inside palladium NPs of different shapes, including a face-centered-cubic one and an icosahedral one. In order to do so, we considered all the tetrahedral and octahedral sites available in a regular Mackay icosahedron and in a cuboctahedron, both composed of 147 atoms. Adsorption energies were calculated by $E_{ads} = E_{Pd_{147}H} - E_{Pd_{147}} - \frac{1}{2}E_{H_2}$, where $E_{Pd_{147}H}$ is the total energy of the palladium nanoparticle with the hydrogen atom adsorbed in one of its sites, $E_{Pd_{147}}$ is the total energy of the palladium nanoparticle alone without hydrogen and finally $E_{Pd_{147}H}$ is the total energy of the hydrogen molecule. All these energies were estimated by Density Functional Theory (DFT) calculations. Consistently with experiments, we found that inner sites of the icosahedron are not even stable, meaning that hydrogen atoms naturally escape these positions towards outer sites that accommodate position of local minima. Finally we tried to correlate these results with our physical quantities such as the average pressure in each site, as calculated by atomistic simulations. Work is in progress. The second part was the employment of DFT calculations for the study of different properties of metallic nanoparticles. One of these works involved platinum-palladium nanoparticles. Among the most common shapes adopted by metal nanoparticles, there are truncated octahedra, decahedra and icosahedra. Less common is the tetrahedral shape. It is known in the literature that only very small metal nanoparticles adopt the tetrahedral shape as their lowest-energy state, i.e. up to the 20-atom regular tetrahedron for Au nanoparticles. Larger nanoparticles can grow within the tetrahedral shape, but only as unstable structures that are more prone to change their shape, as equilibrium driving forces act on them. In this work, we found a family of magic nanoparticles of tetrahedral symmetry by global optimization searches and Density Functional Theory calculations on Pt-Pd nanoalloys. This system owes its interest to the exceptional catalytic activity that is well known to be superior than that of pure metals for several chemical reactions. We showed that these structures are not energetically favorable for elemental clusters, i.e. those made by pure metals, but they are stabilized by alloying at intermediate compositions, up to N=180 atoms (approximately 1.6 nm). Finally, a thermodynamic analysis by the harmonic superposition approximation showed that

Pt-Pd tetrahedral nanoalloys can be stable even above room temperature. The work is now submitted to the Journal of Physical Chemistry A [1]. We believe that the importance of our work is double because 1) from a theoretical point of view, we proved for the first time by *ab-initio* calculations that the stability of the tetrahedral structural motif can be extended up to a relatively large size, compared to previous results, and 2) from an experimental point of view, our results show that by mixing the two metals, one can in principle produce tetrahedral nanoparticles that are more stable than those made by pure metals, so that they should be more resistant against ageing under the action of a controlled environment and possibly less prone to shape changes during chemical reactions. Another work was done in collaboration with the theoretical research group of Prof. Giacomello at Sapienza University in Rome, Italy, published by the Journal of Chemical Physics, currently available as a preprint [2]. In this work, we studied the size-dependent competition between different structural motifs of different metal nanoparticles, including Au, Ag and Cu, by combining Harmonic Superposition Approximation and Parallel Tempering Molecular Dynamics. Also in this case, DFT was needed to discuss the validity of some of the conclusions that were drawn by using atomistic calculations only, since they do not take in to account electronic interactions. A third work was done in collaboration with the experimental research group of Prof. Andreazza at Orléans University, France. In this collaboration, the growth of Ag clusters on amorphous carbon substrates was studied *in situ* by X-ray scattering experiments, whose final outcome was imaged by electron microscopy. The real-time analysis of the growth process at room temperature showed the formation of a large majority of icosahedral structures by a shell-by-shell growth mode which produces smooth and nearly defect-free structures. Interestingly, molecular dynamics simulations supported by *ab initio* (DFT) calculations revealed that the shell-by-shell mode is possible because of the occurrence of collective displacements which involve the concerted motion of many atoms of the growing shell. This work is now under review in the journal Nanoscale [3]. One more project in which I was involved was the development of new algorithms for the solution to the global optimization problem. The new algorithms are based on the concept of multiple Basin-Hopping walkers running in parallel, each with its own specialized task – the flying walker, exploring the energy landscape at high temperatures to sample different geometric structures, and the landing and hiking walkers mainly refining the optimization of chemical ordering at low temperatures. The algorithms were tested against several benchmarks (AuCu and AuRh clusters of 400 atoms and PtNi clusters of 38 and 55 atoms). In all cases, both algorithms were shown to perform very well compared to previous results in the literature. In addition, the algorithms were applied to the optimization of larger AgCu nanoparticles, with sizes up to 4000 atoms, in order to establish the behavior of the mixing energy and to compare full global optimization of shape and chemical ordering with optimization of chemical ordering alone at fixed shape. In general, our results showed that the simultaneous optimization of shape and chemical ordering is necessary in many cases, and that the flying-landing-hiking approach is especially efficient for that purpose. The work was published for the Advanced Theory and Simulations journal [4].

List of publications

- [1] Roncaglia, C.; Ferrando, R. Tetrahedral Clusters Stabilized by Alloying. Currently submitted at Journal of Physical Chemistry A.
- [2] Settem, M.; Roncaglia, C.; Ferrando, R; Giacomello, A. Structural transformations in Cu, Ag, and Au metal nanoclusters. Accepted at Journal of Chemical

Physics. Arxiv preprint available at arXiv:2308.07792v1.

- [3] Nelli, D.; Roncaglia, C.; Ferrando, R.; Kataya, Z.; Garreau, Y.; Coati, A.; Andrezza-Vignolle, C.; Andrezza, P. Sudden collective atomic rearrangements trigger the growth of defect-free silver icosahedra. Under review for *Nanoscale*.
- [4] Rapetti, D.; Roncaglia, C.; Ferrando, R. Optimizing the Shape and Chemical Ordering of Nanoalloys with Specialized Walkers. *Adv. Theory Simul.* **2023**, 2300268. <https://doi.org/10.1002/adts.202300268>
- [5] Roncaglia, C.; Swaminathan, S.; Farris, R.; El Koraychy, E. Highlights from *Faraday Discussion* on Nanoalloys: recent developments and future perspectives, London, UK. *Chem. Commun.*, 2023, **59**, 3331-3338. <https://doi.org/10.1039/D3CC90068A>

List of attended courses

- Spectroscopies and materials for Photonics

Conferences

I participated to the following conferences, where I also presented a poster:

- Non-Equilibrium and Environment Effects on Nanoalloys (Paris, France, December 7-9, 2022). Link: <https://nanoalloys-irn.cnrs.fr/thematic-workshop-2021/>
- Cluster Meeting 2023 (Prague, Czech Republic, June 18-23, 2023). Link: <https://www.clustermeeting2023.eu/>

I participated to the following conferences, where I had an oral presentation:

- 2023 International Meeting on Nanoalloys (IMN 2023) (Orléans, France, May 9-11, 2023). Link: <https://nanoalloys-irn.cnrs.fr/imn2023/>