Post-doctoral position

"Modeling Surface Reactions on Ligand-Covered Metallic Nanoparticles"

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About the consortium. The team *Nano* is hosted by *Sorbonne University* and *CNRS*. It is internationally recognized for the **design and applications of nanomaterials**. Metal oxides nanomaterials, and more recently metal-alloys nanomaterials that contain lighter elements (eg. phosphorus, carbon, sulfur) are prepared and studied both in academic and industrial projects for their applications in several fields: optical materials, automobile and aeronautics, energy harvesting and storage, industrial catalysis, nanomedicine. **We have a strong experimental knowledge** on metal nanoparticle design and reactivity.

The team *Theoretical Chemistry* at *ENS de Lyon* has an internationally recognized expertise in the theoretical **modeling of metallic nanoparticles and more generally of catalysts and reactive interfaces, at the atomic scale, on the basis of density functional theory, in various contexts including energy, environment, medicine, etc**. Over the past two decades, the team has gained a strong background in the description of thermodynamic, kinetic, spectroscopic and optical properties from static approaches to the predictions of stability and reactivity of catalytic materials by *ab initio* molecular dynamics (AIMD).

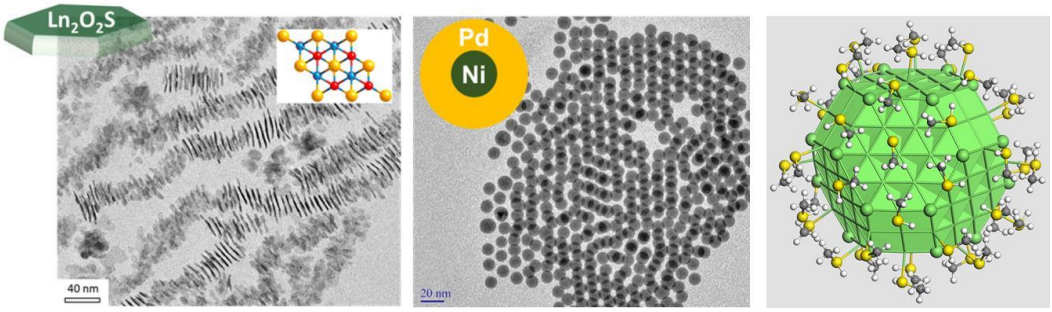

Figure 1: (Left) Some nanoparticles routinely prepared in Paris. (Right) Example of DFT modeling on a methane-thiol-covered silver nanoparticle from AIMD simulations, at ENS Lyon in collaboration with CEMES Toulouse.

Context of the project. Metal nanoparticles are astonishing objects at the cross-road between condensed mater and molecular clusters. As such, few descriptors are routinely available to describe and understand their chemical structure and their reactivity towards smaller organic molecules. This is however critical to the development of nanocatalysts efficient under mild conditions, highly desirable not only for energy saving but also to broaden the scope of products.[1] In this context, the research program *NanoFLP*, funded by ERC, is interested in boosting the reactivity of transition metal nanoparticles (eg. Ni) with the help of adequate organic ligands, typically strong Lewis bases such as phosphines (generic formula PR_3).[2,3] Today, a large amount of experimental data was collected on these objects, dealing with the mechanism of their synthesis,

the coverage by the ligands and the resulting efficiency in catalysis. These raise a number of questions that can hardly be approached by experimental means but could be investigated by using DFT modeling and AIMD.

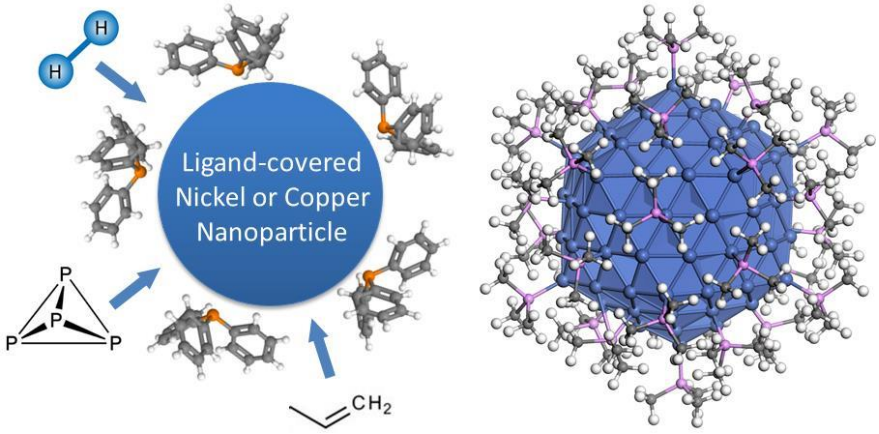

Figure 2: (Left) Overview of the project: modeling the reactivity of copper and nickel nanoparticles covered with organic ligands (phosphines or amines). (Right) Example of a DFT model of phosphine-covered Ni nanoparticle.

The robustness of *ab initio* codes and the ultra-high performance of computational national and local resources currently allow to converge routinely DFT models, composed of more than ten thousand valence electrons in a reasonable CPU time, such as functionalized metallic nanoparticles of a few nanometers.[4,5] In this project, we aim to study two main aspects: first, the influence of the nature of the ligand (amine vs. phosphine) and its adsorption shell on the stability order of the nanocrystal symmetries in competition and second, the chemical reactivity at the surface of these ligand-covered nanoparticles. We will investigate model reactions with small molecules such as H_2, P_4 or alkenes. The theoretical results related to catalytic activity tuned by the ligand nature will be compared to already available experimental data.

Description of the post-doctoral fellow missions. The post-doctoral fellow will be hired in the consortium for his/her expertise in ab initio modeling related to nanochemistry. A good knowledge of DFT in periodic boundary conditions is a real plus. He/she will model nanoparticles with state-of-the-art tools. He/she will develop the theoretical models and analyze the predictions, under the supervision of ENS Lyon team and in close collaboration with experimentalists at Sorbonne Université.

Candidate Profile. The candidate should have a good knowledge of DFT applied to materials science and chemistry or catalysis. He/she may have already worked on the theoretical modeling of metallic nanoparticles at various scales or methodologies.

Application. CV with publication list (mentioning the nature and extent of your contributions in the most relevant papers), as well as a short cover letter. Please specify the names of your previous advisors (as a PhD student and/or in a previous post-doctoral stay) in your CV.

References:

[1] S. Carenco, Describing inorganic nanoparticles in the context of surface reactivity and catalysis. *Chem. Commun.* **2018**, *54 (50)*, 6719–6727.
[2] A. Palazzolo, S. Carenco. Phosphines Modulating the Catalytic Silane Activation on Nickel–Cobalt Nanoparticles, Tentatively Attributed to Frustrated Lewis Pairs in a Colloidal Solution. Chem. Mater. **2021**, *33 (19)*, 7914–7922.
[3] X. Frogneux, F. Borondics, S. Lefrançois, F. D'Accriscio, C. Sanchez, S. Carenco. Surprisingly high sensitivity of copper nanoparticles toward coordinating ligands: consequences for the hydride reduction of benzaldehyde. *Catal. Sci. Technol.* **2018**, *8 (19)*, 5073–5080.
[4] C.-H. Chan, F. Poignant, M. Beuve, E. Dumont, D. Loffreda, Effect of the Ligand Binding Strength on the Morphology of Functionalized Gold Nanoparticles. *J. Phys. Chem. Lett.* **2020**, *11 (7),* 2717-2723 (front cover);
[5] N. Tarrat, D. Loffreda, Morphological sensitivity of silver nanoparticles to the environment. Environ. Sci.: Nano, **2023**, Advance Article, DOI :10.1039/D2EN01129H (front cover).