Titre du projet : Nucléation, Croissance et Réactivité de Nanocristaux (bi-) métalliques

The recent decades have shown that nanocrystals (NCs) can play an important role in a lot of different fields such as biology, magnetism and catalysis, which enable a wide range of promising application. In catalysis, metallic surfaces or NCs of platinum or palladium are often used, nevertheless, from a sustainable point of view it is necessary to limit the use of these rare metals as catalyst. Due to their low cost and low toxicity, cobalt NCs and their derivatives are appealing materials. However, to gain valuable electronic and chemical properties, a careful design of the nano-object is required, i.e. its shape, size, phase and composition. In several industrial domains, the production of nanomaterials used as catalysts in fuel cells, batteries, etc.. needs to be improved. This calls for a better understanding of their structure at the atomic level in relation with their properties, not only in vacuum, but also in real conditions. Nevertheless, despite important research efforts in the field of colloid chemistry, the understanding of the growth mechanisms of nanomaterials is still incomplete, because of i) the impossibility of directly visualizing dynamical processes at the nanoscale in liquids, ii) the complexity of the chemicals reaction itself due to the number of components and of the role of the chemical byproducts. Thus the preparation of high quality NCs is still challenging, depicted the fact there is in the literature a large number of synthetic protocol focusing on the control of NCs size and shape but also in the last decade on the purity, composition crystallinity, stability and monosdispersity. Furthermore, for industrial application the reproducibility of the chemical process is crucial as the reported synthesis are often highly sensitive to any fluctuations of purity of the chemical products, experimental trick or physical parameters as temperature or environment. Therefore, the influence of the physical and chemical parameters (concentration of precursors, time of reaction, temperature, role of organic ligands..) are still in debate. These problems are strongly correlated with the nucleation and growth process of the NCs in solution, which is now possible to study with in- and ex-situ measurements. Indeed, modern studies of nanoscale materials are being revolutionized by in-situ and operando characterization. It is now possible to follow in real-time the reactivity and evolution of nanomaterials in response to chemical, thermal, mechanical, or electrical stimuli i.e, in operando conditions, but also the growth of NCs in solution or the atomic structure of NCs in liquids. These cutting-edge techniques (E-TEM, NAP-XPS, in situ STM) should lead to advanced understanding of the mechanisms of nanomaterials synthesis (nucleation and growth) with functional properties, e.g. nanoalloys or core-shell nanoparticles and to their behavior in operando conditions. This is a prerequisite to the extension of the use of NCs in rational industrial process. In the last decade, organometallic synthesis has made it possible to carry out mass production of well-designed nanoparticles. However, at present, there are no studies combining different in-situ measurement in order to reach deeper understanding of the synthesis and reactivity of metallic NCs. This deals also with the complexity of the synthetic method. However we recently demonstrate that it is possible to synthetize nanoparticles of metal like cobalt, platinum or palladium by using a simple bi-component system.

Thus the aim of this project is to study in situ the nucleation and growth process and the reactivity of metallic NCs, and their further reactivity in paradigmatic reactions combining the state of art in situ techniques applied to a really simple system with high potentiality in applications. We propose complementary approaches to in situ characterization. The comparison of the results will make possible to go beyond the limitations of each of these techniques individually and thus to provide a global response to these challenges. First the formation of the

monometallic NCs by liquid chemistry will be examined starting from a simple reaction with only two chemical components, as recently demonstrated. In a second step it will be extended to bi-metallic NCs using the same protocol. The program will be organized as follow:

1 -Synthesis of the NCs by liquid chemistry. It will be examined starting from a simple reaction with only two chemical components, as recently demonstrated. Starting from the results obtained on cobalt it will be extended to metallic (Ni, Pt, Fe) and derivated bi-metallic nanocrystals as CoNIi, CoPt, CoFe or FePt. We will consider the parameters allowing size, shape anc composition control.

2- We then consider the nucleation and growth process of NCs by using in situ techniques such as E-TEM or XPS or liquid-STM. We aim at controlling the NCs synthesis from a deeper knowledge of the nucleation and growth process in real conditions. These studies will be extended to the case of bimetallic nanocrystals that have prompted considerable interest in catalysis.

The application

For the applications, the following documents should be submitted: (i) CV, (ii) Possible publications and other scientific works in internships, (iii) Reference letters.

Laboratory information

The successful candidate will be working in MONARIS at Sorbonne University, Paris. (formerly UPMC) , Sorbonne Universités, 04 place Jussieu, 75005 Paris and located on the campus Jussieu. He/She will collaborate with the other partners of the project NUMEN (LCP-MR and IPCM at Sorbonne University and CINAM at University Aix-Marseille).

The thematic is in the field of physical chemistry and nanoscience. Knowledge on synthesis physical properties and characterization of nanomaterials would be an advantage.

Mots clés : nanomatériaux, nucléation, croissance, caractérisation in-situ , operando

Contact : Christophe.petit@sorbonne-universite.fr

Tel : 01 44 27 29 06

www.monaris.cnrs.fr