UMR INSA-CNRS-UPS 135 av. de Rangueil
31077 Toulouse Cedex 4
http://lpcno.insa-toulouse.fr/
Equipe Nanostructures et Chimie Organométallique (NCO)

Guillaume Viau gviau@insa-toulouse.fr
Lise-Marie Lacroix lmlacroi@insa-toulouse.fr
Tel. 05 67 04 88 33

PhD position 2019

Sub-nanometric metal wires: at the frontier between metallic nanostructures and supramolecular self-assemblies

The recent efforts on size reduction of metallic nanoparticles leads to a wide variety of objects with tunable morphology and properties. From now on, the new frontiers to be explored, to obtain unprecedented properties, lie between supramolecular organizations and solid nano-objects. For instance, ultrafine metallic nanowires with a diameter of less than 2 nm and a micrometric length (Figure 1) have excellent electronic conduction properties, which make them particularly interesting for applications in flexible and transparent electronics. Very recently we have shown that gold nanowires adopt a tetrahedrally close packed atomic structure (tcp), totally different from the cubic face-centered structure of solid gold. This structure is related to the strongly confined growth and significant contribution of surface effects [1]. In addition, under the effect of external stress (temperature, electron beam ...) nanowires tend to fracture, leading to the appearance of mono-atomic metal chains, which open the way to confinement effects [2].
The growth of gold nanowires is carried out at the LPCNO in an organic medium and in the presence of surfactants. The self-organizing phenomena of organic molecules, in solution and on the surface of the metal, participate in the final shape of the particles. The unique morphological properties and the importance of the organic shell confer to these nanowires original properties, intermediate between metal and supramolecular organizations [3,4].

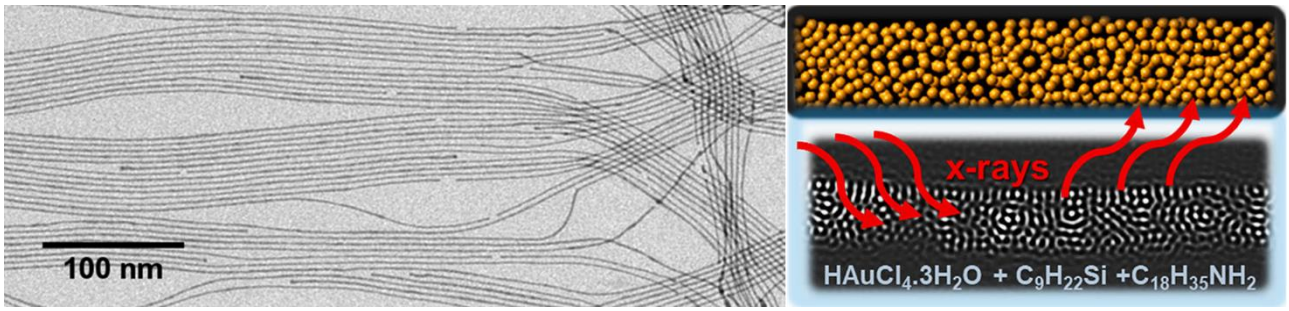

Figure 1. Transmission electron microscope image (TEM) of ultrathin Au nanowires exhibiting the tcp structure.

The objectives of the PhD are :

- The synthesis of bimetallic (Au-Pd, Au-Pt, Au-Ag) ultrathin nanowires [1] ;
- The structural characterization of ulltrathin nanowires by high energy X-ray diffraction on synchrotron and atomic resolution electron microscopy ; the study of the effect of alloying on the growth of quasiperiodic 1D metal nanoparticles;

- The study of the growth mechanism by small angle X-ray scattering (SAXS) and X-ray absorption spectroscopy (XANES, EXAFS) using microfluidic techniques;
- The development of a dielectrophoresis cell for nanowires alignment in solution and *in situ* characterization of parallel assemblies of nanowires; it will allow to complete the structural characterization and to study the effect of high frequency electric fields on the anisotropic growth.

Collaborations

The PhD work will rely on several French and International collaborators, top level specialists of:

- X-ray scattering and microfluidics for the *in situ* growth studies (S. Teychené, P. Roblin, LGC, Université de Toulouse and M. Imperor, LPS Université Paris Saclay) ;
- *In situ* X-ray diffraction (V. Petko, Central Michigan University) and atomic resolution electron microscopy (R. Arenal, Instituto de Nanociencia de Aragon, Espagne ; B. Warot-Fonrose, CEMES, Université de Toulouse)

Profile of the candidate

The candidate must have a strong background in inorganic chemistry, an experience in nanochemistry and a good knowledge of crystallography and X-ray diffraction characterization tools.

At the end of the PhD thesis, the candidate will be a specialist of metal nanoparticles synthesis by liquid phase methods and of their characterization using X-ray scattering and X-ray diffraction techniques on synchrotrons. As the work will be carried out in the context of international collaborations, the candidate will have to present his(her) work in English during advancement meetings, workshops and conferences. The thesis will lead to a stay abroad funded by the Labex Next.

References

[1] Ultrathin Gold Nanowires with the Polytetrahedral Structure of Bulk Manganese
J. A. Vargas, V. Petkov, E. S. Nouh, R. Ramaamorthy, L.-M. Lacroix, R. Poteau, G. Viau, P. Lecante, R. Arenal, *ACS Nano.*, **2018**, *12* (9), pp 9521–9531.

[2] Dynamic HAADF STEM observation of single atom chain as transient state of Au ultrathin nanowire breakdown
L.-M. Lacroix, R. Arenal, G. Viau, *J. Am. Chem. Soc.,* **2014**, *136*, 13075–13077.

[3] Growth and Self Assembly of Ultrathin Au Nanowires into Expanded Hexagonal Superlattice Studied by in situ SAXS
A. Loubat, M. Impéror-Clerc, B. Pansu, F. Meneau, B. Raquet, G. Viau, L.-M. Lacroix, Langmuir, **2014**, 30, 4005–4012.

[4] Surface-engineering of ultrathin gold nanowires: tailored self-assembly and enhanced stability
E. S. Nouh, E. Baquero, L.–M. Lacroix, F. Delpech, R. Poteau, G. Viau, *Langmuir,* **2017**, *33*, 5456–5463.