

## 1. Crystal growth at the nanoscale

### Nanoparticles of complex shape and composition

#### a. Complex shapes

The growth of metal nanoparticles (NPs) in liquid media containing surfactants, can lead to complex forms resulting from the succession of several growth stages. These forms correspond to a modification of the growth conditions with the progress of the reaction, which is due to the fact that the long-chain ligands play several roles: ligands of the molecular precursors, molecular structuring agents of the liquid phase and stabilizers of the metal NPs.

#### Pt

Concave nanocubes of pure Pt exposing {110} facets were synthesized for the first time by reduction under H<sub>2</sub> of a simple platinum precursor (PtCl<sub>2</sub>), in the presence of octadecylamine, and at a temperature of 20 °C, the lowest ever used in the literature for Pt nanocubes (Fig. 1a, *Nanoscale* 2018). Their formation requires a balance between the rate of deposition of new Pt atoms on the vertices of cubic seeds and the rate of diffusion of these atoms to lower energy sites. At 20 °C, the rate of deposition is slowed down, which allows the diffusion of the atoms deposited on the vertices towards the edges. By increasing the temperature to 60 °C, the deposition rate becomes much higher and the diffusion is not fast enough to compensate for it. In this case, the atoms of Pt remain on the vertices, thus forming octopodes, exposing different facets. Since the catalytic properties are dependent on the type of exposed faces, these NPs of Pt are of interest for studying the modification of the catalytic and electrocatalytic properties as a function of their shape.

#### FeCo

Monocrystalline FeCo particles having a complex three-dimensional shape, which can be described as stars or octopodes, have recently been obtained. Although this octopode morphology is classically reported on materials with a fcc crystalline structure (eg Pt, Ni ...), it is, to our knowledge, unique for a material with a cubic centered structure (Fig. 1b). These objects are of great interest for fundamental studies concerning their magnetic configuration (NanoMag and C. Gatel collets, CEMES) and for catalysis applications, the exposed faces being faces of high Miller indices{311}.

#### Ru

The originality of ultrathin ruthenium stars recently obtained is their very small thickness, between 0.85 nm (5 atomic layers) and 1.07 nm (6 atomic layers). The exposed faces are the crystallographic planes (0001) of the hexagonal structure of ruthenium. Their original form comes from two growth stages where the lateral facets {10-10} and {11-20} are successively stabilized (Fig. 1c).

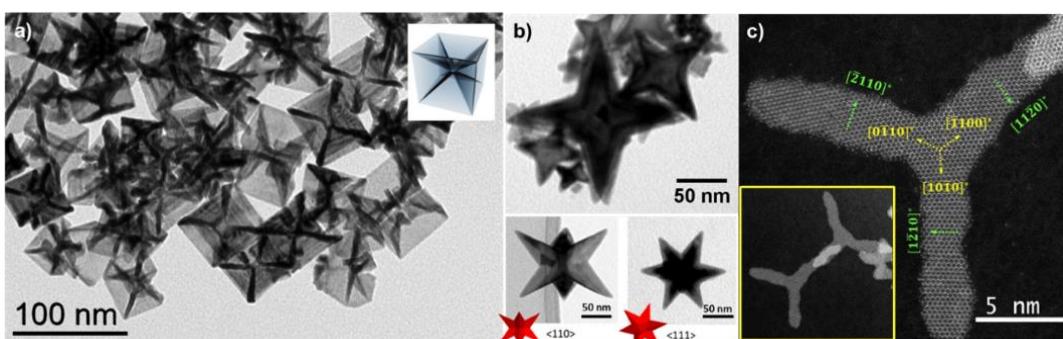


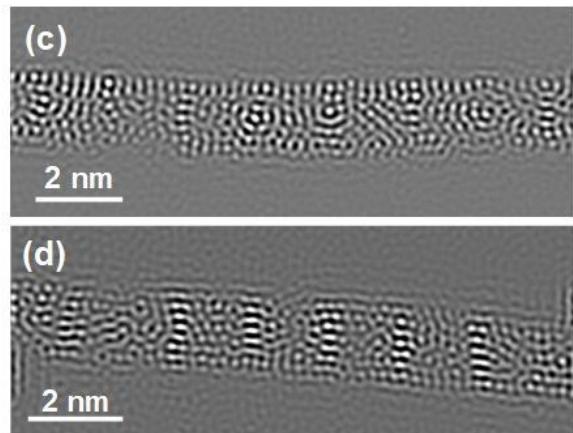
Fig. 1. (a) Concave Pt nanocubes obtained at 20 °C, exposing (110) facets; (b) FeCo nanostars obtained by the organometallic approach. In insert: isolated stars seen along the direction <110> et <111>; (c) ultrathin Ru stars.

#### b. Original structures

The control of precursor reduction rates, the nature of the metal particle stabilizers and the confined growth in cylindrical micelles are the tools that allowed the synthesis of metallic particles with novel atomic structures. The structural studies were carried out by X-ray diffraction in the laboratory or on a synchrotron (Argonne APS) or by high-resolution electron microscopy in STEM-HAADF mode (UMS Castaing platform and INA Zaragoza in the LIA TALEM framework).

In the framework of the Tours 2015 project with STMicroelectronics, FeCo NPs, of a CsCl type ordered structure (structure B2) were obtained by decomposition of two organometallic Fe and Co precursors under H<sub>2</sub> in the presence of a pair of amine / ammonium chloride (HDA/ HDA-HCl) ligands. The local order was probed by cobalt zero-field NMR (C. Meny coll., IPCMS Strasbourg), by Mössbauer spectroscopy of iron and by the detection of the superstructure peak by X-ray diffraction. Modification of the reaction conditions by replacing HDA/HDA-HCl with HDA/PA (PA: palmitic acid) leads to the modification of the reactivities of the introduced Fe and Co precursors, leading to NPs having a concentration gradient, from the cobalt core up to the iron surface ([NanoLett 2019](#)).

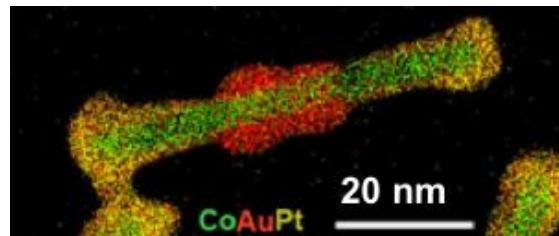
Ultrafine gold nanowires (dm < 2 nm) were synthesized by reduction of a HAuCl<sub>4</sub> / oleylamine complex in hexane ([Langmuir 2015](#), [Langmuir 2017](#), [J Phys Chem 2015](#)). The structure of the wires in the growth medium was studied by high-energy X-ray diffraction (HE-XRD). Analysis of the pair distribution function (PDF) of the X-ray diffractogram showed that the wires (Fig. 2) adopt a tetrahedrally close packed (tcp) type structure, analogous to the so-called Frank-Kasper phases (FK) with a structural model close to the α-Mn phase ([ACS Nano 2018](#)). The interpretation of the formation of this atomic arrangement is the search for a maximum atomic compactness for metal growth confined in a cylinder whose radius is about six times the atomic radius of gold. This very original result was obtained thanks to a collaboration with V. Petkov (Central Michigan University) who is one of the best specialists in PDF analysis of metallic nanostructures. It also opens up new collaborations with solid-state physicists, specialists in FK phases and quasi-periodic structures.



*Fig. 2. HAADF-STEM images of gold nanowires of tetrahedrally close packed (tcp) structure.*

### ***c. Original compositions***

For biomedical applications requiring high magnetization, purely metallic magnetic nano-objects, such as the ones synthesized at the LPCNO, have magnetic properties superior to those of the oxides. However, they are easily oxidizable, which limits their competitiveness compared to the more commonly used oxides. In this context, the possibility of entirely covering Co nanorods (NRs) with a noble metal, preferably gold, offers the possibility to protect them against oxidation and to render them appropriate for the *in vitro* biodetection of cancer cells in aqueous media. Since cobalt and gold are not miscible, the complete coverage by a continuous layer of gold is not favorable. By using as a buffer tin, which is compatible both with cobalt and gold, we developed a continuous layer of gold. The treatment with tin of bare NBs before depositing the noble metal is the key step for the formation of a continuous shell of Au or Pt. Tin plays a double role: (a) it reduces the interface energy between the Co core and the shell, and (b) it is not very selective with respect to the different types of facets of the NBs thus, it homogenizes the surface for subsequent reaction with the noble metal, enabling the subsequent deposition of a uniform shell. We have shown that the Au layer developed using tin was continuous and protected the Co from oxidation in air but not in water. On the other hand, a combination of the two noble metals (Au and Pt) on the same layer produced water-stable nanorods (Fig. 3) ([ACS Nano 2015](#)). After transfer into water and bio-functionalization with specific antibodies (Coll. W. Parak, Marburg Univ.), tests carried out by the Austrian Institute of Technology (Coll J. Schotter) employing a magneto-optical detection method have shown the efficiency of these NRs as probes for the detection of proteins associated with cancer ([Scientific Reports 2012](#)). This work was financed through the FP7Large project [NAMDIATREAM](#) (2009-2014), voted best European project in 2015.



*Fig. 3 : STEM-EDX image showing the location of the elements sur on an isolated Co nanorod (Co: green, Au: red Pt: yellow).*