| ESRF | **Experiment title:** Crystallization of ultrathin metal nanowires with tetrahedrally close packed structure: the role of surface chemistry and precursors | **Experiment number**: CH-6071 |
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| **Shifts: 9** | **Local contact(s)**: Stefano Checchia | *Received at ESRF:* |

**Names and affiliations of applicants** (* indicates experimentalists):

*Guillaume Viau, LPCNO, INSA-Toulouse, France

*Lise-Marie Lacroix, LPCNO, INSA-Toulouse, France

*EzgiYildirim, LPCNO, INSA-Toulouse, France

*Valeri Petkov, Department of Physics, Central Michigan University, United States

*Raj Kumar Ramamoorthy, LGC, INP-Toulouse, France

*Rohan Parmar, LGC, INP-Toulouse, France

**Objective and preliminary results:**

Our objective was to follow in situ the crystallization/re-crystallization process of ultra-thin gold nanowires (AuUNWs) and utrasmall nanospheres with non-classical structure in presence of different ligands in hexane solvent. In case of UNWs, we aimed to follow this complex process by applying an alternating current (AC) electric field to align the wires perpendicular to the X-ray direction. In total, we used three sample environments for the total X-ray scattering (TXS) experiment: (i) static capillary holder (for precursors and final nanospheres), (ii) flow cell environment (for in-situ crystallization experiments), and (iii) capillary holder inside two toroid electrodes separated by a gap of 1 mm for the UNWs alignment experiments.

*Summary of the main observations*. The first analysis shows that the Au UNWs produced in our synthesis take a non-classical crystalline structure instead of the face-centered cubic (FCC) strutcure of the bulk gold. The extent of structural correlation along and perpendicular to the nanowires confirms their anisotropic structure. Changes in the local structure around Au in the precursor solutions, as a function of the concentration of oleylamine (OY), were identified. In addition to this proposed work, in situ crystallization from precursor to ultra-small icosahedra gold nanospheres (UIAuNSs) was followed using TXS. Futher, we have shown that an aging process of UIAuNSs, at high temperature, transform the icosahedra to decahedra, which provides a recipe to produce a non-classical structure as well as prospects for further synchrotron sessions.

**Anisotropic structure and in situ crystallization of UAuNWs**

To understand the crystalline structure and the growth direction, AuUNWs, synthesized by the reduction of $HAuCl_4.3H_2O$ by triisopropylsilane (TIPS) in 400 mM OY dissolved hexane solution, were aligned by applying 40 kHz AC voltage (250 V/mm). Strongly anisotropic patterns were recorded in agreement with previous SAXS data. Intensity was integrated horizontally (angle range = -179, -149°) i.e. in the direction parallel to the electric field and vertically (angle range = -121, -91) i.e. perpendicular to the electric. The resulting atomic pair distribution functions (PDFs) of AuUNWs parallel and perpendicular to the applied ac electric field - are plotted in Fig. 1a. The correlation length measured perpendicular to the electric field is consistent with the diameter of the wires. On the other hand, an extended coherence length is observed in the parallel direction. This preliminary result indicates that the Au UNWs are aligned and that they present a good crystallinity in their long axis. The position and intensity of correlation peaks do not fit with a FCC model. The next step will be to

generate PDF of anisotropic crystal with different structures to describe precisely the structure and the crystallographic orientation of the Au UNWs. TXS of Au UNWs grown under ac electric field and outside the field have been recorded as well as Au UNWs grown with different surface ligands. This will allow to show the influence of both parameters on the UNWs unusual structure.

Synthesis of ultra-thin nanowires carried out under electric field was followed using TXS. Time-resolved atomic PDFs during the crystallization of AuUNWs, along with the precursor solution: 400 mM OY (0 h), are show in Fig. 1b. Initially, at t = 0 h, the first Au-Au correlation peak in PNCs are weak and positioned at a far distance. As reaction proceeds, this correlation distance shrinks, along with the emergence of long-distance peaks, during the crystallization process. This result suggests that the AuUNWs have emerged through non-crystalline PNCs.

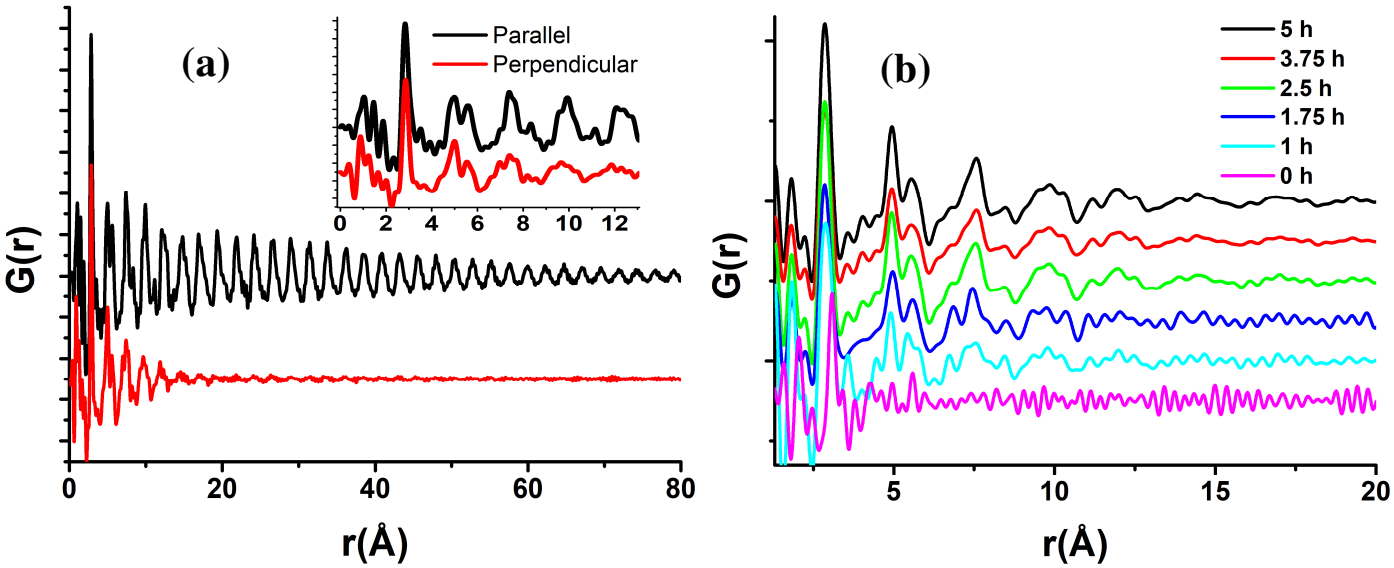


**Figure 1**. (a) Atomic PDFs along with the parallel and perpendicular directions (with respect to the applied electric field) of AuUNWs. (b) Time-resolved atomic PDFs during the crystallization of AuUNWs under ac electric field.

**Precursors structures**

TXS of precursor solutions were recorded - as a function of OY concentration – using a static sample holder. The extracted PDFs of precursor solutions are shown in Fig. 2. The variation in intensity and position of correlation peaks demonstrate that the local environment around Au, in the precursors solutions, modifies as a function of OY concentration, the main peak at 2.25 Å (Au-Cl distance) being progressively replaced by a peak at 2.04 Å (Au-N distance) with increasing [OY]. Irrespective of the OY concentration, a peak at 3.1 Å corresponding to Au-Au aurophilic bond is observed.

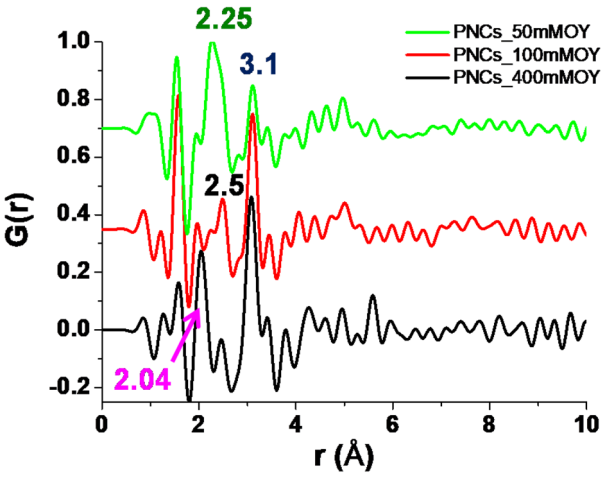


**Figure 2.** Atomic PDFs of precursor solutions as a function of OY concentration

As we know from small-angle X-ray scattering (SAXS), the precursor solutions contain nanostructured objects. In the following, these objects will be called pre-nucleation clusters (PNCs). Irrespective of the OY concentration, the structural correlation length in r-space is found to be ≤ 5 Å which is contrary to the mean size of scattering objects as observed by SAXS (*ca*. 43 Å). This difference indicates that the nanostructured objects recorded using TXS are non-crystalline in nature.

**In situ crystallization and phase transformation of UIAuNSs**

In situ crystallization of ultra-small gold nanoparticles (in presence of 50 mM OY in hexane) was followed using TXS. The time-resolved atomic PDFs during the crystallization process of UIAuNSs, along with

the precursor solution containing PNCs: 50 mM OY, are shown in Fig. 3a. The Au-Au correlation peak at 3.1 Å in the PNCs (t= 0) shifts to 2.86 Å when the nucleation of the metal particle takes place, i.e. before 3 min. At 3 min, the structural correlation is identified only until ~ 10 Å (possibly nuclei for further growth). Then, an increasing correlation length is observed with time corresponding to metal particle growth. The structure of the final particles is not the fcc structure of bulk but reminds an icosahedral structure. These results inidcated that nanoparticles with an icosahedral structure and a mean size of ca. 20 Å are produced from non-crystalline pre-nucleation clusters (average size of about 43 Å: from SAXS). Additional TXS have recorded between 0 and 3 min. Their analysis should provide a complete picture of the nucleation and growth of the 2 nm particles with a temporal resolution on the second scale and a spatial resolution on the Å scale.

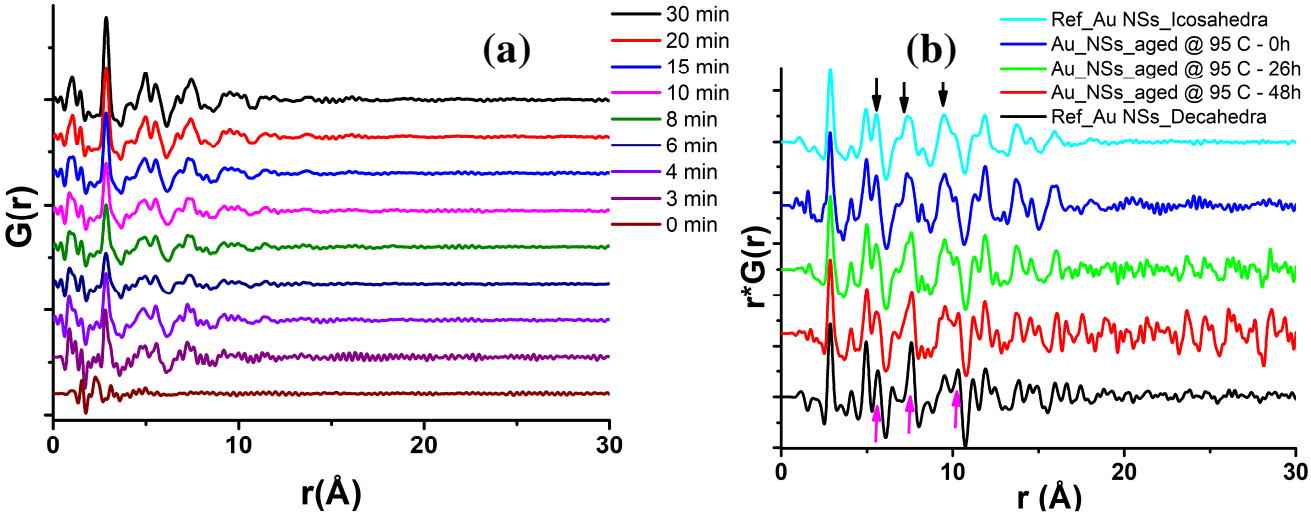


**Figure 3.** (a) Time-resolved atomic PDFs during the crystallization of ultra-small gold nanospheres. (b) Total PDFs of aged (@ 95 °C) gold nanospheres.

These synthesized nanoparticles were aged (at 95 °C for 26 h and 48 h) and recorded using TXS. The resulted experimental PDFs, along with the PDFs of Au ultra-small icosahedra and Au decahedra used as reference are plotted in Fig. 3b. As can be seen, aging resulted in an increase in the size of Au nanospheres along with the modification in its crystalline structure that becomes closer to the structure of decahedra (Fig. 3b). Further analysis and modelling should allow us to have a complete description of the recrytsallization process of Au icosahedra to decahedra.

**Future perspective:**

In continuation, modelling are now needed to go further in the structural analysis of ultrathin nanowires using high quality experimental data set recorded on ID15A. The initial structure of PNCs will be identified by molecular dynamics. Then, the time-resolved atomic PDFs will be modeled by reverse Monte-Carlo simulation to propose the crystallization mechanism of ultra-thin nanowires and ultra-small nanospheres.