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**Report:**
## Background and aim of the proposal

Due to the large possible applications of nanorods and anisotropic gold nanoparticles, the mastery of large scale of synthetic routes without pollution by other shape is a very active domain. Anisotropic shape of nanoparticles is generally obtained after a seeded growth method based on isotropic seeds. However all the types of seeds are not leading to nanorods and recent studies have evidenced the importance of the seed crystal structure as a guide to obtain different anisotropic final shape. Liu and guyot-sionnest[1] were the first to indentify the preferential growth of single crystal seeds into single crystal nanorods while multitwinned seeds grow preferentially into multitwinned nanoparticles. On another side, using TEM it has been noticed that the minimum size above which the anisotropy starts to appear was 5 nm. Today, the initial repartition of facets on seeds and particles in formation below the bifurcation point is clearly the bridge stone to understand the symmetry breaking in the nanorods formation.

The general objective of the proposal was to use *in situ* X-Ray Diffraction to follow the seeded growth synthesis of gold anisotropic nanoparticles whose chemistry scheme is well controlled in the group.[2,3]

## Experimental conditions

The chosen reactions of gold nanoparticles synthesis are optimized at room temperature in mild conditions. The synthesis starts with the addition of some seeds to a fresh growth solution constituted of $HAuCl_4$ (1-10 mM), $AgNO_3$ (1 mM), cetyltrimethylammonium bromide (CTAB 0,2 M) and ascorbic acid (2-12 mM). The reaction is typically completed in 20 minutes. It was followed by measuring X-Ray diffraction of the colloïdal solution circulating from reservoir in a flowing capillary with a simultaneous UV-Vis acquisition, a setup well controlled in our group.[2,4]

The experiment was done at 77.84 keV ($\lambda$=0.15929 Å) using the FReLoN CCD camera positioned at 16.1983 cm from sample position, yielding $Q_{max1}$ ~0.35 Å$^{-1}$ and $Q_{max2}$ ~24.9 Å$^{-1}$.

The different chemical conditions were summarized in the table 1. The modification of the nature of the seeds and the presence (or absence) of silver nitrate in growth solution strongly influence the final shape. The chosen conditions were based on preliminary characterizations of final state obtained in laboratory by complementary techniques (UV-Vis, SAXS, TEM). Because, XRD measurements could not be synchronized with the addition of seeds so we had to adapt the protocol in place.

The acquisition time was 15s and kinetic time was fixed between 30 and 45 mn depending on the chemical conditions.

*Table 1: Chemical conditions used to prepare different anisotropic shape from three different seed batches.*

| Sample conditions | AgNO$_3$ | Seed batch | V seed | pH | Final shape |
|---|---|---|---|---|---|
| A | yes | 1 | 120 µl | 2 different initial pH | nanorods |
| B | no | 1 | 120 µl | One initial pH | spheres |
| C | yes | 2 | 50 µl | One initial pH | bipyramids |
| D | no | 2 | 50 µl | One initial pH | spheres |
| D | yes | 3 | 100 µl | One initial pH | stars |

We have dedicated a non-negligeable part of the run to the acquisition of references, backgrounds, initial states and repeability of kinetics to improve the post-data treatment of XRD diagram. Unfortunatly, we do not succed in the extraction of seeds signal from diluted water solution.

Kinetic evolutions were obtained for the four final geometries, nanorods, nanospheres, bipyramids and stars. The fig.1 shows a typical temporal evolution of XRD diagramms obtained in the case of nanorods. The growth of nanoparticles is clearly visible with the increase of the Bragg peaks in intensity over time.
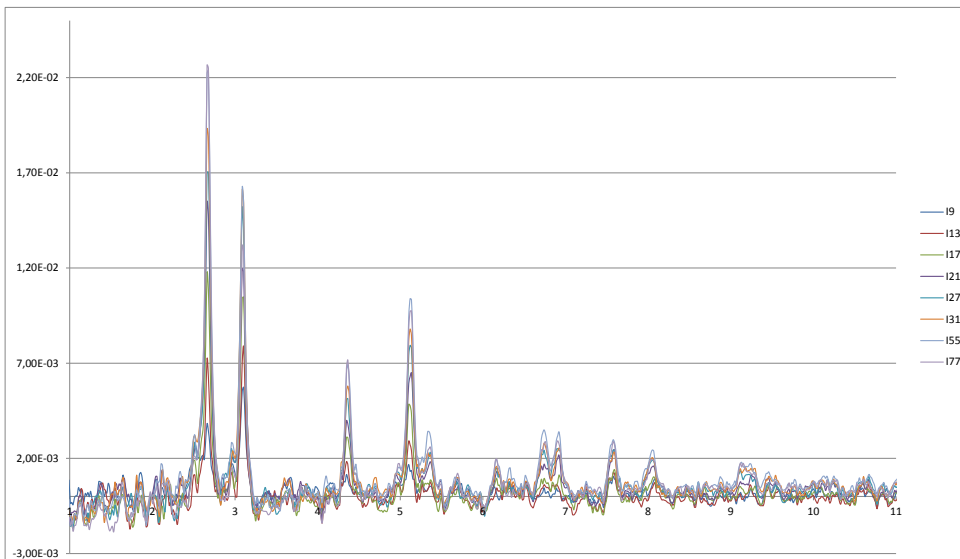


*Figure 1: XRD diagrams obtained for nanorods by in situ registration after addition of CTAB seeds in a gold(I)-silver(I) growth solution.*

While the growth speed is similar for all the geometries, individual signature encoded in the diagrams were found. A remarkable feature is the strong kinetic variation of the intensity ratio between the first two peaks. This observation also observed for the other geometries is actually under treatment by a comparison between experiences and XRD patterns calculated on relaxed model of nanoparticles obtained from Molecular dynamics calculations.

## Conclusions:

- We didn't have any trouble during the run, all the scheduled experiment were realised within the 2 days. The data tratement were realized with PyFAI and python homemade programs.
- The major difficulty of this experiements was the location of the chemistry laboratory really far from the experimental hutch while each new kinetic acquisitions needs fresh solutions to be prepared in the chemistry laboratory.
- Results are very promising to go towards a better understanding of the anisotropic growth of gold nanoparticles.

## References

1. Liu M et al, P. J. Phys. Chem. B 2005, 109, 2219222200.
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4. Fleury B. et al,  ACS Nano, (2014), 8, 2602−2608