



	Experiment title: In situ study of the sulfidation of silver nanoparticles	Experiment number:
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Shifts: 9	Local contact(s): Carlotta Giacobbe	<i>Received at ESRF:</i>
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Report:

Silver nanoparticles (AgNPs) are one of the most prevalent metallic nanoparticles in consumer products. Their use leads to the release of AgNPs to wastewaters. Sewage sludge produced by wastewater treatment plants, which contain AgNPs and their secondary products, are applied on soils as fertilisers. There is an urgent need to better evaluate the risk associated to these practices. The aim of this study was to gain knowledge about one of the most environmentally relevant transformations of Ag nanoparticles in the environment, the sulfidation. Main gaps on the literature about this process are related to the absence of morphological and crystallinity characterization of both the intermediate products of the reaction and the resulting nanoAg₂S. We proposed to perform a time resolved and *in situ* HEXRD measurements followed by PDF analysis on the sulfidation of non-coated and PVP coated AgNPs exposed to different sources of S (Na₂S, mackinawite (FeS) or glutathione). Results on morphology and crystallinity should help to understand the formation mechanisms and the environmental fate of nanoAg₂S.

Experiment

This experiment was conducted at room temperature, with an incident energy of 61 keV. XRD patterns were obtained with a CCD camera (Perkin Elmer XRD 1611CP3). The counting time was 2 min per sample.

First, we studied the sulfidation product *ex situ*, after centrifugation of a suspension of AgNPs reacted with a source of sulfide in polypropylene tubes. Dry samples (powders) were placed in 1 to 1.5 mm diameter kapton capillaries. Three sources of Ag were tested: uncoated and PVP-coated AgNPs, and ionic Ag. Three sources of S were tested: Na₂S, GSH and mackinawite (FeS) and three ratios of Ag:S were also tested: 2:1, 1:1, 1:3. Different reactions times were also evaluated: 12, 24, 48 and 96h. Then, we studied *in situ* the sulfidation of AgNP-PVP using Na₂S. AgNPs were placed in a quartz capillary, and a solution containing the S source was circulated with a peristaltic pump.

In both cases, very good quality XRD patterns were obtained up to high Q values (24 Å⁻¹) (Figure 1).

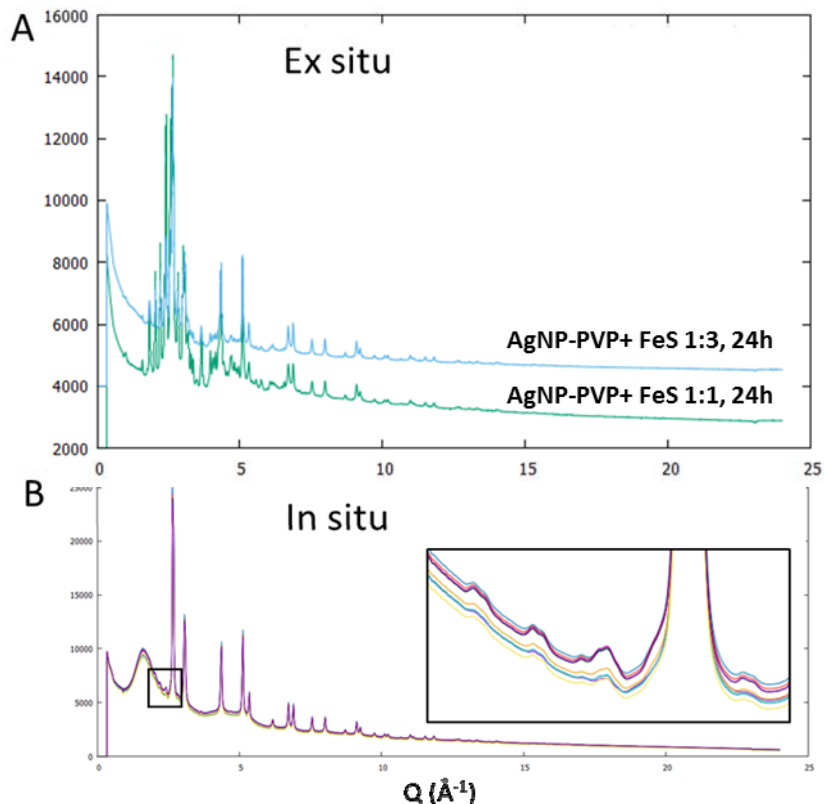


Figure 1: Examples of XRD patterns obtained for the *ex situ* and *in situ* reactions.

The analysis of the results for the *ex situ* sulfidation showed an efficiency in the order $\text{AgNO}_3 > \text{PVPAgNPs} > \text{AgNPs}$, probably due to the better dispersion of PVPAgNPs relative to AgNPs. The limiting factor was the access to oxygen, necessary for the oxidation of Ag^0 into Ag^+ before sulfidation. Related with the S source, the higher sulfidation rates were found for FeS followed by Na_2S . Almost no sulfidation was found for the reaction with GSH.

The sulfidation did not follow a linear trend over time (12, 24, 48 and 96h). This might be due to some insufficient dispersion, or attachment of some nanoparticles on the polypropylene tubes.

The setup for the *in situ* reaction worked well, but the reaction was too slow compared to the timeframe of the experiment (only small peaks corresponding to Ag_2S were observed on the XRD patterns after 8h of reaction, Fig. 1B). Some modifications are planned, including a better dispersion of the AgNPs in the capillary, and an aeration of the Na_2S solution.

To conclude, results are encouraging and shed light on the complexity of Ag-NPs sulfidation and the high number of variables that influence this reaction. We hope to get beamtime to complement these results.