

## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



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|---|--|--|
|   | <b>Experiment title:</b><br>Transformation of Ag nanoparticles during their transport in sewer systems | <b>Experiment number:</b><br>01-01-878 |
| <b>Beamline:</b><br>BM26A   | <b>Date of experiment:</b><br>from:13.07.2012 to:17.07.2012  | <b>Date of report:</b><br>01.09.2012   |
| <b>Shifts:</b><br>12  | <b>Local contact(s):</b><br>Sergey Nikitenko, Dipanjan Banerjee  | <i>Received at ESRF:</i>               |
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## Report

Silver nanoparticles (Ag-NP) are increasingly used in consumer products, mainly cosmetics and textiles, due to their antimicrobial properties. Release of Ag-NP from such products to the municipal wastewater has been demonstrated and may represent the main transfer path for Ag-NP into environmental systems. To assess environmental risks associated with the increasing use of Ag-NP, detailed information on their transfer and transformation in urban wastewater systems is therefore needed.

Studies in wastewater treatment plants (Kim et al., 2010; Kaegi et al., 2011) and laboratory systems (Levard, Reinsch, et al., 2011; Liu, Pennell, et al., 2011) suggested that Ag-NP will be largely transformed to Ag<sub>2</sub>S during wastewater treatment, but did not systematically address the effect of Ag-NP size and surface coating. Furthermore, previous studies focused on the behaviour of Ag-NP during wastewater treatment, but did not consider physical – chemical transformations that may already occur during transport in the sewer system.

We therefore performed a Ag-NP spike experiment in a field-scale sewer channel with a length of 5 km. In addition, we conducted batch experiments in which we spiked Ag-NP with different sizes (10, 50, 100 nm) into raw wastewater and activated sludge. Changes in Ag speciation were monitored using Ag-K edge XANES spectroscopy, and nanoparticle morphology and composition was investigated by transmission electron microscopy. The respective XAS analyses were proposed within the current experiment 01-01-878. Due to the timing of beamtime and experiments, however, most of these analyses were performed at the SuperXAS beamline at the SLS, and only few samples were analyzed at DUBBLE. The compiled results have been submitted for publication (Kaegi, Voegelin, et al.). They indicate that Ag-NP are not substantially retained in the sewer system and that they are sulfidized to various degrees depending on transport distance (reaction time) and size of Ag-NP. In addition, these measurements revealed a gradual transformation of amorphous Ag-sulfide into crystalline Ag<sub>2</sub>S during Ag-NP sulfidization. For linear combination fit (LCF) analysis, we included a reference synthesized by reacting AgNO<sub>3</sub> with freshly precipitated CuS to account for

the fact that most sulfide for Ag-NP sulfidation in wastewater systems may not be available in free form, but as colloidal metal sulfide.

During our beamtime 01-01-878 at DUBBLE, we analyzed further samples from continuing more detailed laboratory experiments on Ag-NP transformation in the presence of metal sulfides. So far, all laboratory studies on the sulfidation of Ag-NP have been conducted with dissolved sulfide. In the wastewater, however, a substantial fraction of the sulphides is present as metal sulphides, most importantly Cu, Zn and Fe – sulphides. We therefore initiated preliminary investigations addressing the role of metal sulfides, namely CuS, in the sulfidation process of Ag-NP. We reacted Ag-NP of different sizes and coatings (10nm, 100nm, citrate or PVP coated) with previously synthesized CuS in order to evaluate whether also the sulfide bound to Cu could be liberated and thus contribute to the sulfidation of Ag-NP. Furthermore, separate suspensions containing the reacted Ag-NP were exposed to oxygen saturated conditions for one week in order to assess the stability of the freshly formed silver sulfides under oxic conditions. Nanoparticles from sulfidation experiments were flocculated using sodium nitrate and centrifuged (10 min, 4000 x g) after adding 0.1g cellulose. The supernatant was decanted and the sediment was put in a copper mould, dewatered with a paper tissue and immediately frozen in liquid nitrogen and kept frozen at -20 °C until analysis at the synchrotron. All synchrotron analyses conducted at the DUBBLE beamline were performed at 80 °K using a Cryostat.

Ag K-edge XANES spectra from the starting materials (10nm and 100nm, citrate or PVP coated), from the reacted samples (72h reaction time) and spectra from selected samples which were exposed to oxygen saturated conditions for one week together with references of Ag<sub>2</sub>S and metallic Ag(0) foil are given in Figure 1. In parallel high resolution transmission electron microscopy (TEM) analysis was performed on selected samples (Figure 1, right).

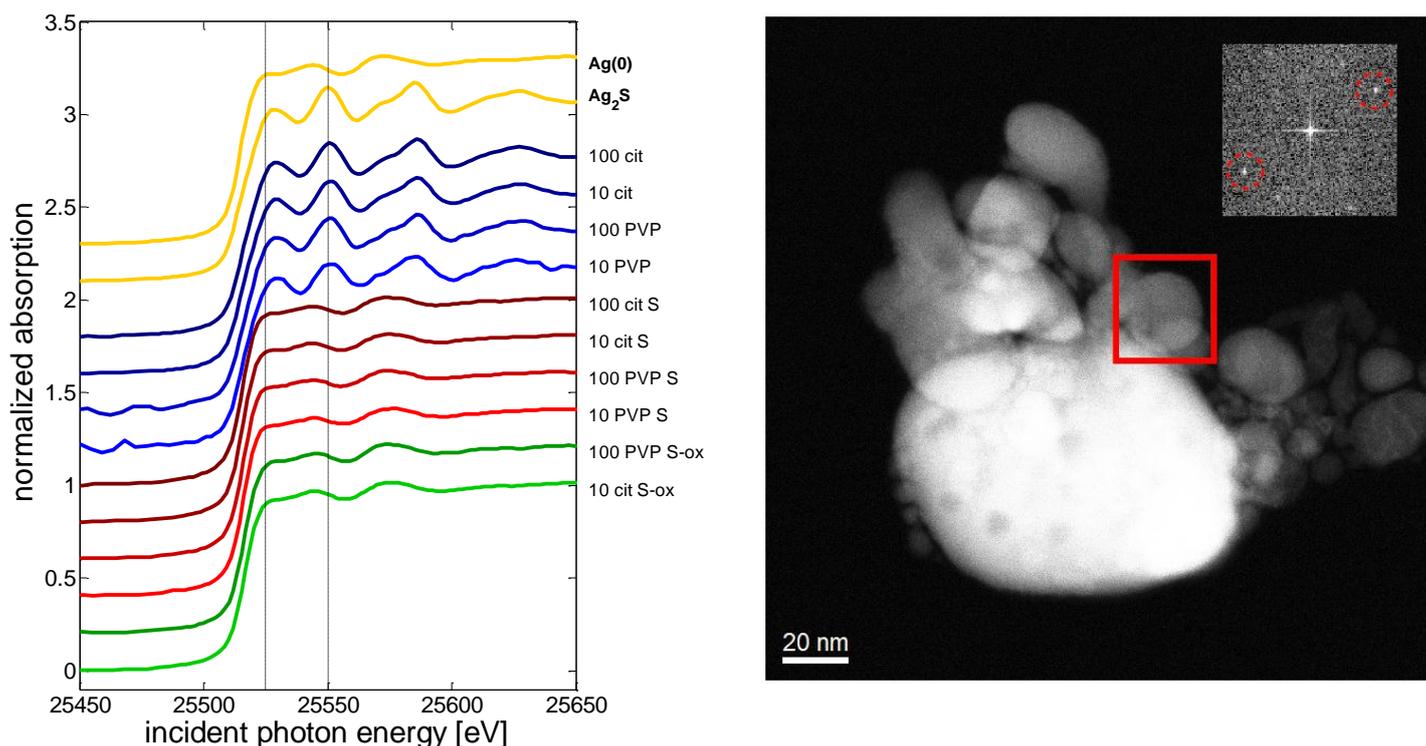


Figure 1: left: XANES spectra of reference materials (yellow), starting materials (blue), reacted Ag-NP (72h) and reacted Ag-NP oxygenated for one week (green). Right: High angular annular dark field (HAADF) image of reacted Ag-NP (100nm citrate coated). Inset is showing the fast fourier transform of the area marked in red.

XANES analysis confirmed that the starting materials (10nm, 100nm, citrate and PVP coated) were metallic (Figure 1, blue spectra) and LCF consistently returned a very high metallic fraction of > 95%. High resolution TEM results indicated that the particles were well crystalline (data not shown). After 3 days of exposing the Ag-NP to freshly precipitated CuS colloids under low oxygen contents (1ppm) in the dark, Ag-NP in all experiments were dominantly transformed to silver sulfides (Figure 1, red spectra). LCF of the of the reacted samples including Ag<sub>2</sub>S and Ag(0) as reference spectra always returned a sulfidic fraction of

>90%. Fast Fourier Transform (FFT) analysis of high resolution TEM images (inset in Figure 1 (right)) revealed that crystalline Ag<sub>2</sub>S formed after 3 days of reaction. XANES spectra recorded on reacted Ag-NP that were exposed to oxygen saturated conditions for one week were almost identical to the spectra from the reacted Ag-NP that were not exposed to oxygen saturated conditions indicating the high stability of the newly formed silver sulfides.

Taken together, these first results suggest that sulfur contained in metal sulfides is available for the sulfidation of Ag-NP and that the freshly formed Ag-sulfides are rather resistant to oxidation. These results have important consequences for the fate of Ag-NP in urban wastewater systems, especially during the transport in the sewer system. Sulfides produced in the anaerobic zones of the sewer biofilm may be temporarily preserved as metal sulfides which are more resistant to oxidation than dissolved sulfides. These metal sulfides contribute to the sulfidation of the Ag-NP that may be discharged to the wastewater stream. Whether also other sulfides such as ZnS or FeS are also available for the sulfidation of Ag-NP needs to be investigated. In addition, the influence of the structure of the metal sulfides, e.g. crystalline vs. amorphous, on the sulfidation kinetics of the Ag-NP warrants further investigations.

## References

- Kaegi, R., Voegelin, A., Ort, C., Sinnet, B., Thalmann, B., Krismer, J., Hagendorfer, H., Elumelu, M., and Mueller, E. Fate and Transformation of Silver Nanoparticles in Urban Wastewater Systems. submitted to Water Research, minor - moderate revisions required.
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- Kim, B., Park, C.-S., Murayama, M., and Hochella, M. F. (2010) Discovery and Characterization of Silver Sulfide Nanoparticles in Final Sewage Sludge Products. *Environmental Science & Technology*, **44**(19), 7509–7514.
- Levard, C., Reinsch, B. C., Michel, F. M., Oumahi, C., Lowry, G. V., and Brown, G. E. (2011) Sulfidation Processes of PVP-Coated Silver Nanoparticles in Aqueous Solution: Impact on Dissolution Rate. *Environmental Science & Technology*, **45**(12), 5260–5266.
- Liu, J., Pennell, K. G., and Hurt, R. H. (2011) Kinetics and Mechanisms of Nanosilver Oxysulfidation. *Environmental Science & Technology*, **45**(17), 7345–7353.