

## 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.**

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

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

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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***

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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.



	<b>Experiment title:</b> Sulfidation kinetics of silver nanoparticles reacting with polysulfide under anoxic conditions	<b>Experiment number:</b> 01-01-976
<b>Beamline:</b>	<b>Date of experiment:</b> from: 08.04.2015 to: 12.04.2015	<b>Date of report:</b>
<b>Shifts:</b>	<b>Local contact(s):</b> Dipanjan Banerjee ( email: banerjee@esrf.fr )	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists):  *Dr. Ralf Kaegi Basilius Thalmann Dr. Andreas Voegelin		

## Report:

The aim of the original proposal was to investigate the sulfidation kinetics of silver nanoparticles reacting with polysulfide under anoxic conditions. However, unfortunately, our experimental samples were not stable under the X-ray beam (although we have conducted the measurements at 80 °K) and all spectra exclusively revealed metallic Ag (These finding were also supported by transmission electron microscopy analysis conducted on additional samples that we later synthesized in the lab. In the electron microscope, we observed the reduction of Ag-S species to Ag(0) in-situ, within a few seconds). Thus, we decided to investigate the kinetics of Ag-NP with bisulfide ( $\text{HS}^-$ ) in the presence humic acid (HA). The complied results from that study are summarized in a manuscript that will be submitted to Environmental Science Nano shortly. A brief summary of the paper in provided below:

## Summary

Metallic silver nanoparticles (Ag-NP) are sulfidized in urban wastewater systems (Kaegi et al., 2011; Kaegi et al., 2013; Thalmann et al., 2014; Ma et al., 2013) which dramatically reduces the Ag toxicity (Reinsch et al., 2012). However, the kinetics of this transformation is only poorly understood and the influence of natural organic matter (NOM) on AgNP sulfidation has not been studied to date. We therefore investigated the sulfidation kinetics of AgNP with bisulfide ( $\text{HS}^-$ ) in the absence and presence of NOM and evaluated different kinetic models to describe the observed reaction kinetics.

Citrate-stabilized AgNP of different sizes (20 – 200 nm) were reacted with an excess of  $\text{HS}^-$  in the absence of humic acid (HA, used as proxy for NOM) as well as at HA concentrations from 50 – 1000 mg L<sup>-1</sup>. The extent of AgNP sulfidation after selected reaction times was determined by X-ray absorption spectroscopy (XAS). The sulfidation rate increased with decreasing AgNP size and increasing HA concentration. The sulfidation kinetic of the AgNP was best described by a diffusion-limited solid-state reaction model (Jander model). The derived half-life times of the AgNP ranged from minutes to hours. The increase of the sulfidation rate with increasing HA concentration may be explained by the replacement of citrate by HA which may facilitate the access of  $\text{HS}^-$  to the AgNP surface. Results from analytical transmission electron microscopy suggest that the AgNP sulfidized asymmetrically in the absence of HA. In the presence of HA

initially formed, concentric core-shell Ag<sub>0</sub>-Ag<sub>2</sub>S structures developed into hollow Ag<sub>2</sub>S nanoparticles with increasing reaction time, possibly via the nano-Kirkendall effect. The XAS analyses required for this study were obtained within the current experiment 01-01-976.

## Experimental results

In time resolved experiments AgNP (20, 40, 100, 200 nm) were reacted with HS<sup>-</sup> (2.5 mM, HS<sup>-</sup> in fivefold excess compared to Ag) in the presence of HA (0, 50, 250, 1000 mgHA L<sup>-1</sup>) for up to 60 min and the reaction progress was monitored by determining the sulfidic and the metallic fraction of the suspension using Ag K-edge XAS. The recorded EXAFS spectra and the corresponding LCF results are given in Figure 1. In all experiments, the metallic fraction steadily decreased with increasing reaction time and the decrease was faster for smaller particles. After 30 min reaction (1000 mgHA L<sup>-1</sup>) the 20- and 40-nm AgNP were fully sulfidized, whereas the 100- and 200-nm were still to 6 and 20 % metallic. An increasing sulfidation rate (faster decrease of the metallic fraction) was observed for increasing HA concentrations at constant particle size. The sulfidation was completed after 15 min for the 20-nm AgNP in the presence of 1000 mgHA L<sup>-1</sup>, but a metallic fraction of 43 % was still observed after the same reaction time without HA.

Out of 4 different kinetic models which were evaluated to describe the sulfidation rates, a parabolic rate law known as the Jander rate law (Jander, 1927), described the data best. The half-life time ( $t_{1/2}$ , were 50 % of the total Ag was transformed to Ag<sub>2</sub>S) of AgNP derived from the Jander model was decreasing from 11.5 to 1 min with an increase of the HA concentration from 0 and 1000 mgHA L<sup>-1</sup> for the 20-nm AgNP

To study the mechanism of AgNP sulfidation in more detail, analytical STEM analyses were performed. Samples were collected from partially and fully sulfidized 20 and 100-nm AgNP after specific reaction times (5 and 45 min for 20-nm and 5 and 15 min or 4 h for 100-nm AgNP) in the absence and presence of HA (250 mgHA L<sup>-1</sup> for 20-nm and 1000 mgHA L<sup>-1</sup> for 100-nm. Results from the 20 nm Ag NP reacted with 250 mgHA L<sup>-1</sup> for 5 and 45 min are provided in Figure 2.

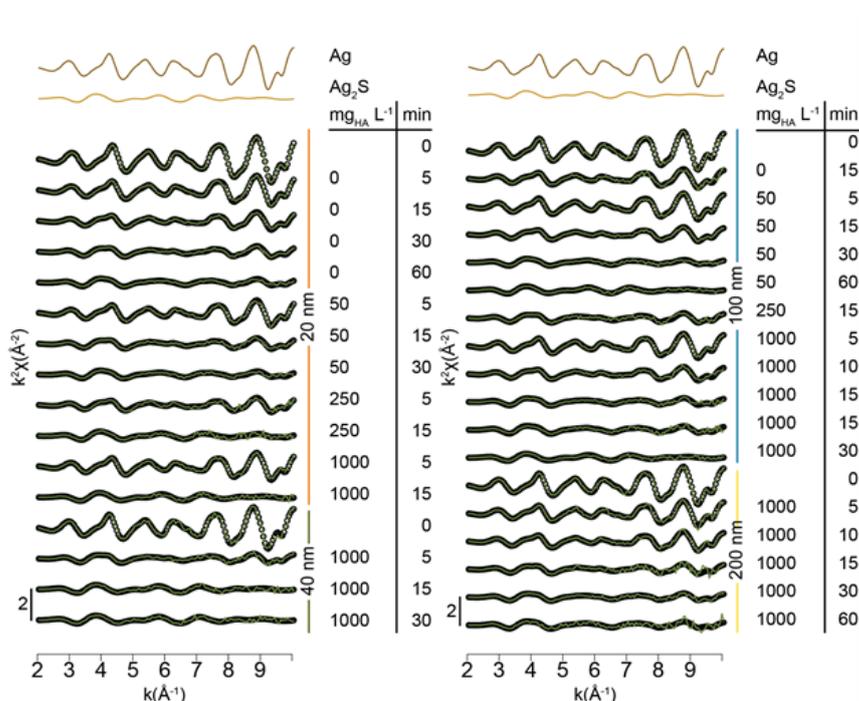


Figure 1: EXAFS spectra (lines) and LCF reconstructions (dots) of Ag-NP (20nm – 200 nm) reacted with HS<sup>-</sup> for up to 60 min in the presence of HA (0 – 1000 mg L<sup>-1</sup>).

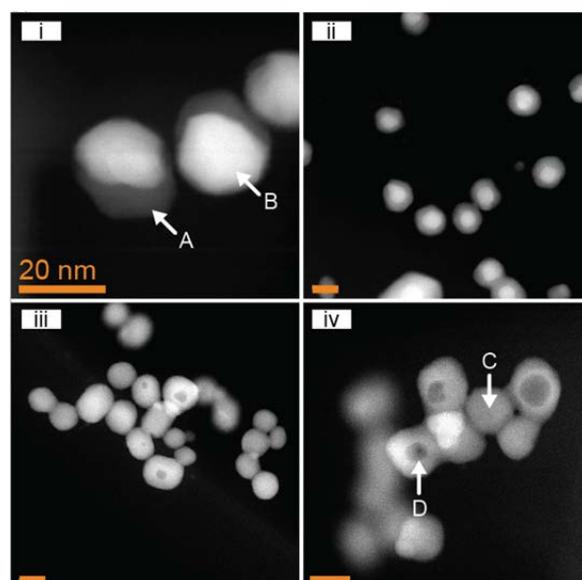


Figure 2. HAADF image of partially to fully sulfidized 20nm AgNP in the absence (left) and presence of 250 mgHA L<sup>-1</sup> after 5 min (top) and 45 min (bottom) reaction time. A: Ag<sub>2</sub>S, B: Ag<sub>0</sub>, C: void.

In the absence of HA and after 5 min, HAADF images of the 20-nm AgNP revealed a bright, spherical area with an adjacent grey sickle-shaped part. EDX analysis revealed that the bright part corresponded to metallic Ag and the grey areas represented Ag<sub>2</sub>S (Figure 5i, A, B). With increasing reaction time, the Ag<sub>2</sub>S increasingly replaced the metallic Ag resulting in mostly light-grey, spherical particles (Figure 5iii).

In the presence of 250 mgHA L<sup>-1</sup> and after 5 min reaction time, the metallic Ag (bright areas) was concentrically surrounded by a grey (Ag<sub>2</sub>S) shell, forming core-shell type structures (Figure 5ii). After 45 min reaction time, the contrast of the core-shell structures was reversed and a dark core was often surrounded by a light-grey shell. EDX analysis of the core and the shell revealed that both parts consisted of Ag<sub>2</sub>S (Figure 5iv, C, D), suggesting the formation of hollow Ag<sub>2</sub>S spheres. Most probably, these hollow spheres formed via the nanoscale Kirkendall effect.

### Environmental implications

Based on the results from the current study, it is likely that the sulfidation of AgNP in the presence of natural organic matter (HA was used as a proxy for natural organic matter) is substantially accelerated and completed within one hour or less. The sulfidation of AgNP in the presence of HA initially led to the formation of core (Ag<sup>0</sup>) – shell (Ag<sub>2</sub>S) particles that transformed into hollow –Ag<sub>2</sub>S particles via the nano-Kirkendall effect. Similar core-shell structures as reported in this study may also have been obtained by (Impellitteri et al., 2013) from AgNP that were sulfidized in real wastewater samples, demonstrating that Kirkendall-like core-shell structures also form in real wastewater. The occurrence of hollow AgNP may therefore be indicative for the release of (engineered) AgNP into the wastewater.

The sulfidation kinetics were best described by the Jander model, implying that neither the overall Ag nor the HS<sup>-</sup> concentration influence the sulfidation rate. Therefore, in the presence of sufficient amounts of HS<sup>-</sup> to completely sulfidize all AgNP (which should be the case in urban wastewater systems) the half life time of AgNP can be estimated based on their size and the concentration of the HA in the respective water.

### References

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