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ESRF

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://wwws.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.

ESRF	**Experiment title:** Kinetics of Silver Nanoparticle Sulfidation by Metal Sulfides	**Experiment number**: 01-01-906
Beamline:	**Date of experiment**: from: 04.04.2013 to: 08.04.2013	**Date of report**:
Shifts:	**Local contact(s)**: Dipanjan Banerjee (email: banerjee@esrf.fr) Sergey Nikitenko (email: nikitenko@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Dr. Ralf Kaegi
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Report:

The complied results from these experiments have been published in Environmental Science and Technology (Thalmann, Voegelin, Sinnet, Morgenroth, and Kaegi, 2014). A brief summary of the paper is provided below.

Recent studies have documented that the sulfidation of silver nanoparticles (Ag-NP), possibly released to the environment from consumer products, occurs in anoxic zones of urban wastewater systems and that sulfidized Ag-NP exhibit dramatically reduced toxic effects. However, whether Ag-NP sulfidation also occurs under oxic conditions in the absence of bisulfide has not been addressed, yet.

We, therefore, investigated whether metal sulfides that are more resistant towards oxidation than free sulfide, could enable the sulfidation of Ag-NP under oxic conditions. We reacted citrate-stabilized Ag-NP of different sizes (10 – 100 nm) with freshly precipitated and crystalline CuS and ZnS in oxygenated aqueous suspensions at pH 7.5. The extent of Ag-NP sulfidation was derived from the increase in dissolved Cu^{2+} or Zn^{2+} over time and linked with results from X-ray absorption spectroscopy (XAS) analysis of selected samples. The morphological changes of individual Ag-NP occurring during the sulfidation reaction was evaluated based on transmission electron microscopy (TEM) analyses. The respective XAS analyses were proposed within the current experiment 01-01-906.

The degree of sulfidation derived from the dissolved Cu^{2+} and Zn^{2+} concentrations by UV-vis measurements were in good agreement with the results from LCF analyses of XAS spectra (Tabel 1). The results of the LCF analyses of the experimental spectra using Ag(0), Ag_2S and Ag-CuS (used as a proxy for Ag adsorbed to metals sulfides and/or poorly crystalline Ag_2S) as reference materials are given in Figure 1. In addition, the metallic fractions derived from XANES and EXAFS spectra were also in good agreement.

Table 1: Metallic Ag fractions derived from UV-Vis measurements and from speciation analysis resulting from LCF of EXAFS spectra using Ag^0, Ag-CuS, and Ag_2S as reference spectra. MS refers to metal sulfides and size to the diameter of the Ag-NP.

No.	MS	Ag-NP size (nm)	Reaction time (h)	UV-Vis Ag^0	EXAFS Ag^0
1	CuS_{ppt}	10 nm	6	45%	36%
2	CuS_{ppt}	10 nm	72	0%	2%
3	CuS_{ppt}	100 nm	22	15%	7%
4	CuS_{ppt}	100 nm	72	10%	8%
5	ZnS_{ppt}	10 nm	8	36%	30%
6	ZnS_{ppt}	10 nm	72	0%	8%
7	ZnS_{ppt}	100 nm	26	69%	72%
8	ZnS_{ppt}	100 nm	72	48%	63%
9	CuS_{cryst}	10 nm	9	50%	37%
10	CuS_{cryst}	10 nm	72	7%	14%
11	CuS_{cryst}	100 nm	72	61%	54%
12	ZnS_{cryst}	10 nm	72	94%	75%
13	ZnS_{cryst}	100 nm	72	94%	84%

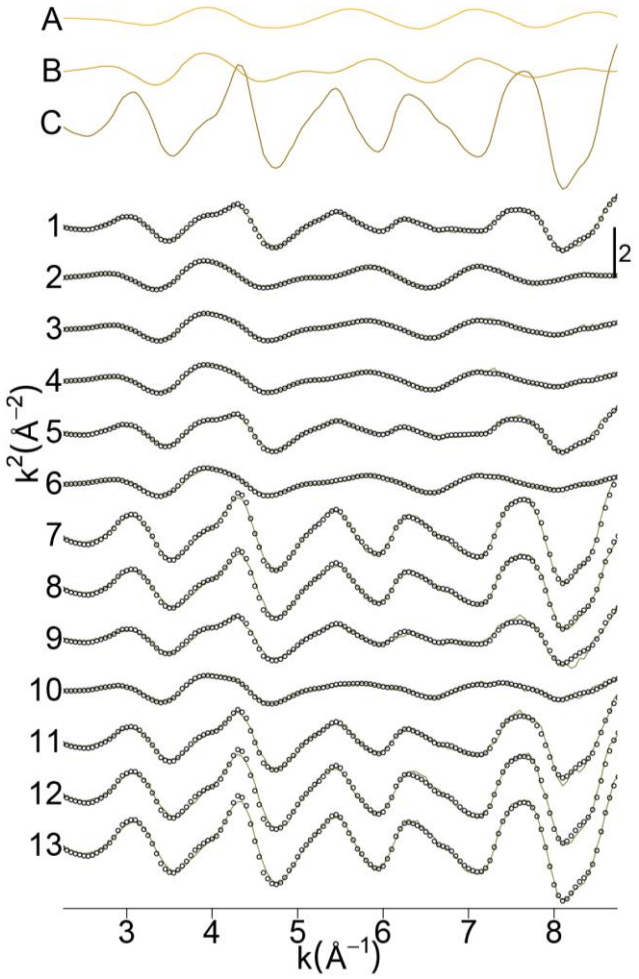

Figure 1. EXAFS spectra (lines) and LCF results (dots) using Ag-CuS (A), Ag_2S (B), and Ag-foil (C) as references. Numbers on the left correspond to the numbers given in Table 1. Spectra are plotted with an offset of 2 for clarity.

The sulfidation of Ag-NP followed pseudo first-order kinetics, with rate coefficients increasing with decreasing Ag-NP diameter and increasing metal sulfide concentration and depending on the type (CuS and ZnS) and crystallinity of the reacting metal sulfide.

Results from analytical electron microscopy revealed the formation of complex sulfidation patterns that seemed to follow preexisting subgrain boundaries in the pristine Ag-NP (Figure 2). The kinetics of Ag-NP sulfidation observed in this study in combination with reported ZnS and CuS concentrations and predicted Ag-NP concentrations in wastewater and urban surface waters indicate that even under oxic conditions and in the absence of free sulfide, Ag-NP can be transformed into Ag_2S within a few hours to days by reaction with metal sulfides.

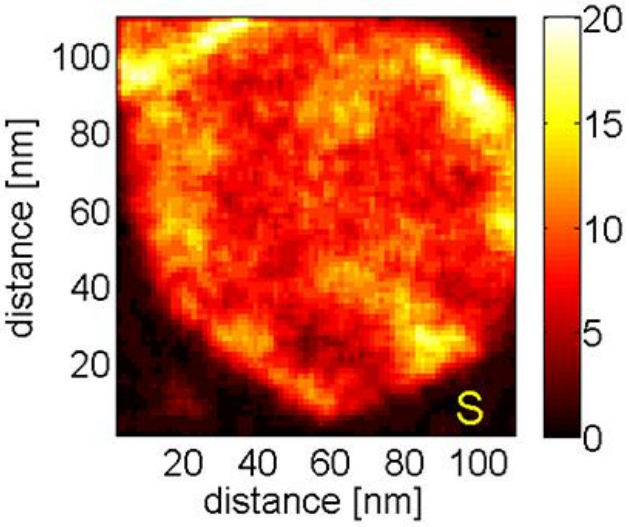

Figure 2:Sulfur distribution map derived from STEM – EDX measurements recorded on a partially sulfidized 100-nm Ag-NP. The color bar indicates the signal intensities.

References

Thalmann, B., Voegelin, A., Sinnet, B., Morgenroth, E., and Kaegi, R. (2014) Sulfidation Kinetics of Silver Nanoparticles Reacted with Metal Sulfides. Environmental Science & Technology, 48(9), 4885–4892.