

## Time-resolved EXAFS measurements in Forming of Ag Nanoparticles in Water-in-scCO<sub>2</sub> Microemulsions

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### Introduction

Supercritical fluids provide several processing advantages over conventional solvents in materials chemistry and especially in nanocrystal synthesis [1]. Water-in-scCO<sub>2</sub> microemulsions have been applied as "microreactors" for the synthesis of silver (Ag) nanoparticles [2, 3]. In this study, the time-resolved *in-situ* DXAFS measurements have been carried out to investigate the reduction process in ms-order time scale of Ag<sup>+</sup> ions to Ag nanoparticles by 1) the photo-reduction of AgClO<sub>4</sub> using UV-light and 2) the chemical reduction using a reducing reagent, hydrazine monohydrate (H<sub>2</sub>NNH<sub>2</sub>•H<sub>2</sub>O), in the presence of Aerosol-OT (AOT) in water-in-scCO<sub>2</sub> microemulsions.

### Experimental

Ag nanoparticles were synthesized in a high-pressure SUS 316 cell (inner volume of 14.0 mL) equipped with four optical windows: two of them were CVD diamond windows for *in-situ* DXAFS measurements and the other two were quartz windows for the irradiation of UV-light from a 500W high-pressure Hg lamp. Water-in-scCO<sub>2</sub> microemulsions containing AgClO<sub>4</sub> were prepared by adding CO<sub>2</sub> into the cell which contained a mixture of AOT and AgClO<sub>4</sub> (3.16 × 10<sup>-3</sup> mol) aqueous solution. The water-to-surfactant molar ratios (w) was equal to 2.3, and water content and metal concentration [Ag<sup>+</sup>] were 3.87 wt% and 226 mM, respectively. The cell was then kept at 35°C and 25MPa for 2-3 hours with continuous stirring to form microemulsions. In the case of the photo-reduction, the microemulsions were irradiated with UV-light for the designated time to achieve the reduction of Ag<sup>+</sup>. In the case of the chemical reduction, on the other hand, the small amount of hydrazine solution was injected into the cell under high-pressure conditions by a high-pressure syringe pump.

The time-resolved *in-situ* DXAFS measurements were carried out at NW2A beamline in PF-AR using an Si(311) bent crystal (Laue-type) and a self-scanning photodiode array coupled by a Gd<sub>2</sub>O<sub>2</sub>S(Tb)-embrocated fiber optical plate. DXAFS spectra were recorded with the acquisition time of 60 ms. DXAFS spectra for Ag-K edge were collected to evaluate the electronic state as well as the coordination number of Ag nanoparticles in the presence of AOT in water-in-scCO<sub>2</sub> microemulsions.

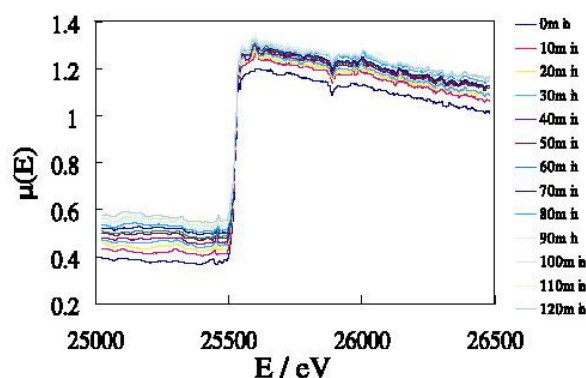


Fig. 1. Time-resolved DXAFS spectra at the Ag-K edge during the reduction process of Ag<sup>+</sup> ionic solutions after the injection of reducing agent in the presence of AOT in water-in-scCO<sub>2</sub> microemulsions.

### Results and Discussion

Figure 1 shows the time evolution of μ(E) vs E for Ag<sup>+</sup> ions in the water-in-scCO<sub>2</sub> microemulsions after the injection of the hydrazine aqueous solution. Before the injection, the spectrum is quite similar to that of the reactant (AgClO<sub>4</sub> aqueous solution, not shown here), resulting in the Ag<sup>+</sup> ions dissolved homogeneously in the water-in-scCO<sub>2</sub> microemulsions. The reduction of Ag<sup>+</sup> to Ag<sup>0</sup> and the association of Ag<sup>0</sup> into Ag nanoparticles proceed concurrently with the reduction time increasing. After the reduction of 120 min, the XAFS spectrum at the Ag-K edge energy region is the same as that of Ag foil. This means the reduction of Ag<sup>+</sup> ions completed within 2-3 hours in continuous stirring by the addition of hydrazine.

On the other hand, in the photo-reduction of the above microemulsions containing Ag<sup>+</sup> ions, the reduction does not occur remarkably, so that the XAFS spectrum before the reduction does not change even after the irradiation of UV-light more than 2 hours. The precise *in-situ* DXAFS experiments will be carried out in near future.

### References

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