

Structural Change of Emulsions in Forming of Metal Colloids in Water-in-scCO₂ Microemulsions

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Introduction

Many approaches using supercritical fluids (SCFs) have been developed to control the size and shape of metal nanoparticles. Recently, water-in-scCO₂ microemulsions have been applied for the synthesis of metal nanoparticles. For example, water-in-scCO₂ microemulsions were used as "microreactors" to synthesize cadmium sulfide and silver (Ag) nanoparticles [1-3]. In the present study we have tried to synthesize Ag nanoparticles by the photoreduction of AgClO₄ using UV-light in the presence of Aerosol-OT (AOT) in water-in-scCO₂ microemulsions. We investigated the reduction process of Ag⁺ ions and the size of aggregates of Ag nanoparticles by *in-situ* small angle X-ray scattering (SAXS) measurements.

Experimental

Ag nanoparticles were synthesized in a high-pressure SUS 316 cell (inner volume of 13.5 mL) equipped with four optical windows: two of them were diamond windows for *in-situ* SAXS measurements and the other two were quartz windows for the irradiation of UV-light from a 500W high-pressure Hg lamp. Water-in-scCO₂ microemulsions containing AgClO₄ were prepared by adding CO₂ into the cell which contained a mixture of AOT and AgClO₄ (6.32×10^{-4} mol) aqueous solution. The water-to-surfactant molar ratios (*w*) was fixed to 10, and water content and metal concentration [Ag⁺] were 1.628 wt% and 46.8 mM, respectively. The cell was then kept at 35°C and 25MPa for 2-3 h with continuous stirring to form microemulsions. After stirring, the microemulsions were irradiated with UV light for the designated time to achieve the reduction of Ag⁺ to Ag⁰ nanoparticles. The *in-situ* SAXS measurements were performed at BL-15A. The scattering data was collected by a position sensitive proportional counter (PSPC).

Results and Discussion

Fig. 1(a) shows the SAXS profiles of water-in-scCO₂ microemulsions before and after the photo-irradiation. Here *q* is the magnitude of the scattering vector, defined as $q = (4\pi/\lambda) \sin(\theta/2)$ where θ is the scattering angle and λ is the wavelength of X-ray. The intensity at a small *q* range ($q < 0.5 \text{ nm}^{-1}$) tends to increase with the reduction

time increasing. The intensity of irradiated samples for longer time is much stronger than that of irradiated ones for shorter time. The corresponding Guinier plots are shown in Fig. 1(b), and the size of water pool in the microemulsions was calculated. The radii of water pool keeps almost constant values ranging from 18.1 to 20.2 nm. It is probable that the surfactant molecules in the microemulsions do not stabilize Ag oligomeric clusters so strongly, so that the formation of larger aggregates consisting of Ag clusters occurred in a water pool.

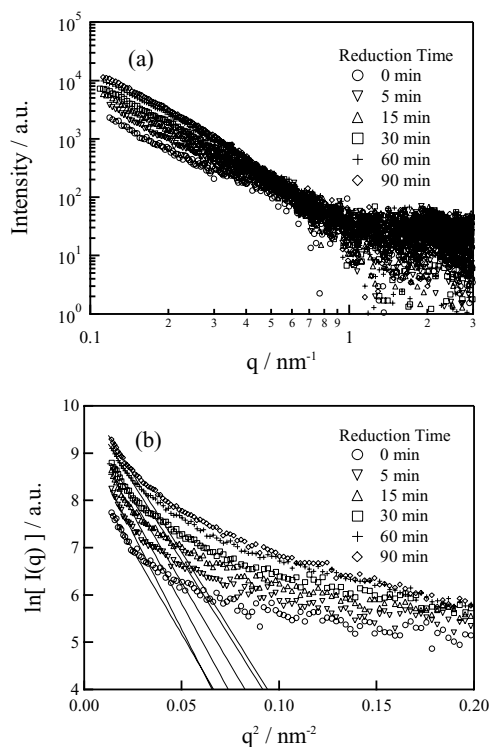


Fig. 1. SAXS profiles of (a) log-log plots and (b) Guinier plots of Ag ionic solutions prepared by the irradiation of UV light in the presence of AOT in water-in-scCO₂ microemulsions.

References

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