

Structural Change of Emulsions in Forming of Metal Colloids in the Emulsions

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Introduction

Metal nanoparticles are of particular interest due to their potential applications including optical, electronic and magnetic device and catalysis. One route to prepare metal nanoparticles is to utilize water-in-oil (w/o) microemulsions, as a template, where a metal precursor is reduced to metallic nanoparticles in the water pools. The particle size can be almost precisely controlled by an appropriate choice of the water-to-surfactant molar ratio. In general, gold and silver colloidal particles are known to be synthesized by photo-reduction of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ and AgNO_3 in w/o microemulsions, respectively [1]. In the photo-reduction process, we attempt to characterize the structure of aggregated metal nanoparticles in w/o microemulsions [2], and to estimate the change of average size of water pool including silver nanoparticles during the reduction by means of small angle X-ray scattering (SAXS) measurements.

Experimental

Gold colloids (18 mM) and silver colloids (22 mM) were prepared from $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ and AgNO_3 solution by the irradiation of 500W high-pressure Hg-lamp, respectively. The HAuCl_4 solution was composed of 4.3 vol% distilled water, 43.5 vol% petroleum solvent (main compounds: paraffin > 90%, naphthen < 10%), and 52.2 vol% surfactants, and AgNO_3 solution was also composed of 8.3 vol% distilled water, 41.7 vol% petroleum solvent, and 50 vol% surfactants. The mixture of distilled water and petroleum solvent contained two cationic surfactants (A and B), and Ag^+ or Au^{3+} , as shown in Table 1. The volume ratio of cationic surfactant A to B was 5 to 1. All the surfactants were kindly provided from Nikka Co. Ltd. The obtained samples were then poured into cells sealed with Kapton film for SAXS measurements. The measurements were performed at BL-15A. The scattering data was collected by the position sensitive proportional counter (PSPC).

Results and Discussion

Figure 1(a) shows SAXS profiles (log $I(q)$ vs. q) of Au^{3+} solutions (before and after photo-reduction) prepared in the mixture of water and petroleum solvent, containing two kinds of cationic surfactants A and B. 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 of peak around $q = 0.61 \text{ nm}^{-1}$ increases with an increase in reduction time, while the peak around $q = 1.17 \text{ nm}^{-1}$, corresponding the distance between water pools in the emulsion, does not change in the photo-irradiation. On the other hand, Figure 1(b) shows SAXS profiles of Ag^+ solutions prepared in the same mixed solution dissolving surfactants A and B. The peak around $q = 0.61 \text{ nm}^{-1}$ does not appear. The intensity of solutions at a small q range ($q < 0.5 \text{ nm}^{-1}$) becomes higher immediately after Ag^+ ions are added in the emulsion, although the intensity keeps almost unchanged in the addition of Au^{3+} ions as shown in Fig. 1(a). Further the intensity does not change when the reduction time increases. Thus, in the case of Au, the water pools are well dispersed after the addition of Au^{3+} and crystallization of aggregates of Au nanoparticles proceeds during the photo-irradiation, while in the case of Ag, the aggregation of water pools takes place at the early stage of the irradiation and a lot of nucleate formation of Ag rapidly proceeds in these aggregated water pools. The investigation for the change of water pools in forming of metal nanoparticles during photo-reduction is in progress.

Table 1. Surfactants used in this experiment

Surfactant	Molecular formula
Cationic A	$(\text{C}_{18}\text{H}_{32})_2\text{CH}_3\text{-N}^+\text{-CH}_2\text{CH}_2\text{OH X}^-$
Cationic B	$\text{C}_{12}\text{H}_{25}(\text{CH}_3)_2\text{-N}^+\text{-CH}_2\text{CH}_2\text{OH X}^-$

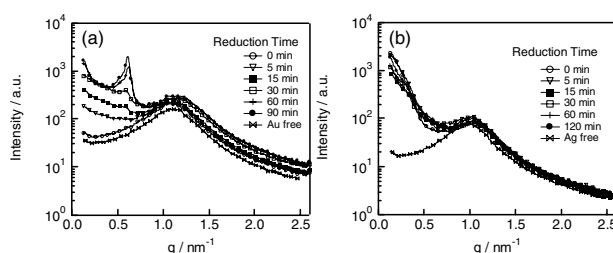


Fig. 1. SAXS profiles obtained from the colloidal dispersions containing both cationic A and B surfactants in petroleum solvent with (a) Au^{3+} and (b) Ag^+ aqueous solutions, before and after photo-reduction, comparing with metal ion free solutions.

References

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