

SAXS studies of the formation mechanisms of metal clusters in micelles of surfactants

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Introduction

Hydrophobic field produced by the micelles of surfactants in aqueous solutions plays an important role for the control of size and dispersity of the metal nanoparticles when prepared [1]. Colloidal dispersions of platinum and gold particles can be prepared by photo-reduction of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, respectively, in the presence of stabilizer such as surfactants [2]. In the photo-reduction process, we attempt to characterize the structures of primary metal particles and secondary metal particles (aggregated particles) [3] in solution of various surfactants as well as the change of average particle size in reduction by means of small angle X-ray scattering (SAXS).

Experimental

Platinum and gold colloidal dispersions (0.66mM) were prepared from $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ by irradiation of 500W super-high-pressure mercury lamp in 5 wt% aqueous solution, with benzoin as a photo-activator, of fluorinated surfactants (FTERGENT 110 and FTERGENT 250) kindly provided from NEOS Co. Ltd. Similarly, these Pt and Au colloids in emulsions were also prepared by the photo-reduction in 500 mM AOT(bis(2-ethylhexyl) sodium sulfosuccinate) solutions of the mixture of benzene and water. These reduced samples prepared in quartz cell at the designated duration of reduction were then poured into cells (optical length: 1mm) sealed with Kapton film for SAXS measurements.

SAXS measurements were performed at BL-15A station. X-ray beam was monochromatized to 0.150 nm in wavelength and the scattering data was collected by the position sensitive proportional counter (PSPC). The accumulating time for an intensity measurements of each sample was 600 sec.

Results and Discussion

Figure 1 shows SAXS profiles ($\log I(q)$ vs. q) of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (before reduction) and Au colloids (after reduction) prepared in FT 110 aqueous solutions. 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 tends to increase with the reduction time increasing. At a small q range ($q < 0.5 \text{ nm}^{-1}$), the scattered intensity of solution after

reduction (reduction time longer than 1 hour) is much stronger than that of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ solution before reduction (reduction time = 0).

On the other hand, the maximum intensity appears around $q = 0.8 \text{ nm}^{-1}$ (before reduction) and $q = 0.7 \text{ nm}^{-1}$ (after reduction), respectively, although the reference solution has the maximum intensity at $q = 0.9 \text{ nm}^{-1}$. This indicates that the addition of Au ions to micelles of FT 110 reference solution leads to change the size of micelles created in solution and Au particles created after photo-irradiation make the size of micelles much larger. Thus, the Au ions as well as Au particles are strongly stabilized in micelles of fluorinated surfactant without precipitates. The similar trends are also observed in the case of Au colloids in AOT/ H_2O /Benzene emulsion system.

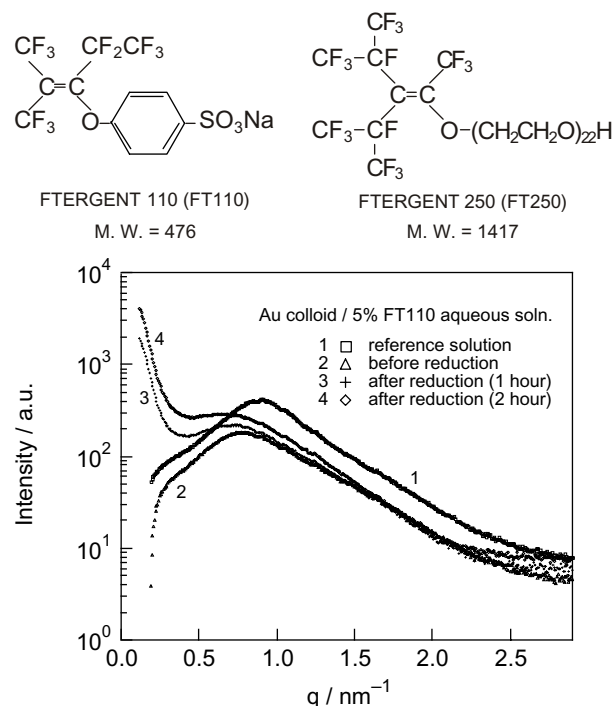


Fig. 1 SAXS profiles obtained from Au solutions dissolving FT 110 before and after photo-reduction.

References

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