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SAXS Studies of the Formation Mechanisms of Metal Clusters in Micelles of Surfactants

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Introduction

Control of size and dispersity of metal clusters in colloidal dispersions is very important for improving electrical and optical properties of materials. The precise control requires knowledge of the formation mechanism of colloidal metal particles in dispersions. Platinum and gold colloids can be prepared by photo-reduction of $H_2PtCl_6 \cdot 6H_2O$ and $HAuCl_4 \cdot 4H_2O$, respectively, in the presence of stabilizer such as polymers [1] and surfactants [2]. In this study, in order to pursue the particle formation where metal ions are reduced to metal atoms and metal atoms are then associated into metal clusters (and aggregates), photo-reduction of metal ions in aqueous solution of surfactants is employed. In this 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 colloids (0.66mM) were prepared from $H_2PtCl_6 \cdot 6H_2O$ and $HAuCl_4 \cdot 4H_2O$ by irradiation of 500W super-high-pressure mercury lamp in 100mM aqueous solution of surfactants (SDS: Sodium Dodecyl Sulfate, DTAC: Dodecyltrimethylammonium Chloride, PEG: Polyethylene Glycol Lauryl Ether) with benzoin as a photo-activator, respectively. The 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 $HAuCl_4 \cdot 4H_2O$ (before reduction) and Au colloids (after reduction at the designated duration) prepared in SDS 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 ($q < 0.7$ nm^{-1}), the scattered intensity of solution after reduction (reduction time > 15 min) is much stronger than that of $HAuCl_4 \cdot 4H_2O$ solution before reduction (reduction time = 0 min).

On the other hand, the maximum intensity appears around q = 1.8 nm^{-1} in any samples, even though the reduction time is increased. This indicates the formation of micelles of SDS occurs in solution and Au colloids created by photo-reduction does not affect the morphology of micelles.

Thus, the Au colloids are strongly stabilized in micelles of surfactants in solution and become very stable at room temperature, because the concentration (100mM) of SDS is significantly higher than the critical micelle concentration (cmc) to form a lot of micelles.

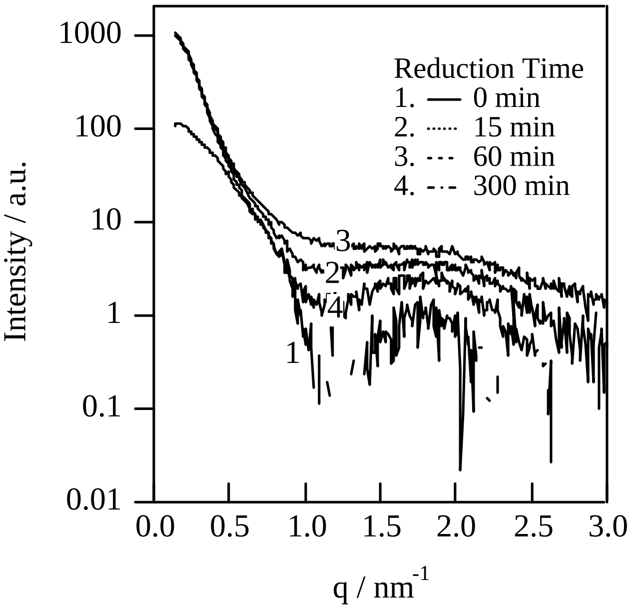

Fig. 1 SAXS profiles obtained from Au solutions dissolving SDS before and after photo-reduction.

References

[1] M. Harada et al., J. Phys. Chem. **98**, 2653 (1994).
[2] T. Yonezawa et al., Langmuir, **11**, 4601 (1995).
[3] T. Hashimoto et al., J. Chem. Phys. **109**, 5627 (1998).

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