

# Structural Analysis of Silver Nanoparticles in Microemulsions Composed of Water/Alkane/AOT Systems.

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## 1. Introduction

A technique that utilizes reverse micelles of surfactants in solution as “nanoreactor” has been developed over the past decade. The utilization of reverse micelles or microemulsion systems has received considerable attention for preparing many kinds of nanoparticles. The nanometer-sized water pools of the reverse micelles or water-in-oil (w/o) microemulsion systems can provide an appropriate stabilized environment to produce the specified size of metal nanoparticles [1], because the monolayers of surfactant molecules on the water pools can effectively prevent metal nanoparticles from aggregating excessively. As it is important to control the size of metal nanoparticles in the water pools and requires knowledge of the formation mechanisms, we have investigated the formation mechanism of silver (Ag) nanoparticles prepared by the photoreduction of silver perchlorate ( $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ ) in the presence of benzophenone as a photoactivator in water/alkane/sodium bis(2-ethylhexyl) sulfosuccinate (AOT) water-in-oil (w/o) microemulsions by means of in-situ X-ray absorption fine structure (XAFS) and small angle X-ray scattering (SAXS) technique [2]. Although these SAXS results clearly show the size changes of Ag nanoparticles (or their aggregates of Ag nanoparticles) in water pools during the photoreduction, it is difficult to quantitatively evaluate the size changes of water pools in the water/alkane/AOT w/o microemulsions. This is due to the fact that SAXS intensities of Ag nanoparticles (or their aggregates) are too strong to distinguish their intensities from those of water pools in microemulsions.

On the other hand, there are a few literatures which had reported the shell thickness and solvation structure of alkanethiol ligands on metal nanoparticles dispersed in mixtures of organic solvent and antisolvent (for example, mixture of *n*-hexane- $d_{14}$ /ethanol- $d_6$ ) by means of the contrast variation small angle neutron scattering (CV SANS) measurements [3,4]. However, as far as we know, there is no report investigating the quantitative evaluation for the size change of water pools during the metal particle formation by employing CV SANS measurements. Based on these grounds, in order to overcome the difficulty for the separation of X-ray scattering contribution between Ag nanoparticles and water pools, we have performed some preliminary CV SANS measurements to elucidate the size change of water pools and the shell thickness of AOT layers in water/d-benzene/AOT w/o microemulsions during the photoreduction.

## 2. Experiment

### *Preparation of the Ag nanoparticles in $\text{D}_2\text{O}$ /d-benzene/AOT w/o microemulsions.*

Colloidal dispersions of Ag nanoparticles were synthesized in the presence of AOT by the photoreduction of the  $\text{Ag}^+$ -containing water/d-benzene/AOT w/o microemulsions. Briefly, 1 mmol of AOT was added to 1.9 mL of d-benzene followed by the addition of both 0.1 mL  $\text{D}_2\text{O}$  solution of  $\text{AgClO}_4 \cdot \text{H}_2\text{O}$  (1.32 M) and 40 mg benzophenone, and the mixture was then stirred vigorously. The  $\text{Ag}^+$ -containing w/o microemulsions were poured into a quartz cell and irradiation by UV-light was started by using a 500W super-high-pressure mercury lamp. Here, the concentration of  $\text{Ag}^+$  ion in  $\text{D}_2\text{O}$ /d-benzene/AOT w/o microemulsions was 66 mM.

### *SANS experiments of the Ag nanoparticles in $\text{D}_2\text{O}$ /d-benzene/AOT w/o microemulsions.*

SANS experiments were performed using a time-of-flight diffractometer, on the BL15 (TAIKAN) at J-PARC, Japan, in the  $q$  range of  $0.07$ - $14 \text{ nm}^{-1}$  at room temperature with neutron wavelengths between  $0.1$  and  $0.7 \text{ nm}$ . All data were normalized to an absolute intensity by the coherent scattering of a glassy carbon as a reference sample

after the necessary data corrections such as air scattering, empty-cell scattering, and the transmission factor. A sample changer was mounted on the goniometer. The solution samples were placed into a quartz cell. The thickness of the cell was 1.0 mm for all the samples. For the CV SANS measurements, the scattering length density (SLD) of Ag atom is  $3.47 (10^{-6}/\text{\AA}^2)$ . Here the SLDs of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  are  $-0.561 (10^{-6}/\text{\AA}^2)$  and  $6.402 (10^{-6}/\text{\AA}^2)$ , respectively. Hence, since the SLD of the Ag particles is matched to that of the mixture for  $\text{H}_2\text{O}/\text{D}_2\text{O}=42/58$ , we can estimate the average size of the water droplets that consisted of aggregates of Ag nanoparticles after photoreduction. In addition, to estimate the size of AOT layers, mixture solvent of d-benzene and benzene (d-benzene/benzene) is available for the SLD matching point between water pool and bulk d-benzene/benzene (=54/46) mixture.

### 3. Results

Figure 1(a) shows SANS patterns ( $\log I(q)$  vs.  $\log q$ ) of the colloidal dispersions of Ag nanoparticles before and after the photoreduction of  $\text{Ag}^+$ -containing  $\text{H}_2\text{O}/\text{D}_2\text{O}/\text{d-benzene}/\text{AOT}$  microemulsions at the matching condition ( $\text{H}_2\text{O}/\text{D}_2\text{O}=42/58$ ). The scattering patterns show the formation of micelles with a core-shell structure involving the scattering peak centered at ca.  $3.0 \text{ nm}^{-1}$ , and their patterns do not change at smaller  $q$  range ( $q \leq 1.0 \text{ nm}^{-1}$ ) after the photoreduction. This might suggest that the production of Ag nanoparticles does not so much affect the size of the water droplets. On the other hand, as shown in Figure 1(b), the SAXS patterns of the same sample indicate that the scattering intensity increases after the photoreduction in a smaller  $q$  range ( $q \leq 1.0 \text{ nm}^{-1}$ ). This should originate from the formation of Ag nanoparticles. Moreover, a broad peak centered around  $1.4 \text{ nm}^{-1}$  is also characteristic of a form factor of core-shell structure of the water droplets (core) with AOT layers (shell).

### 4. Conclusion

From the structural investigation by SANS and SAXS, the following facts were disclosed: (1) Ag nanoparticles were generated in the water pool after photoreduction. (2) SANS was able to distinguish two types of scatterings: one from the water pool containing Ag aggregates and the other from AOT layers on the water pool. Further studies to elucidate the underlying structural changes of water/alkane/AOT w/o microemulsions using the complementary use of SANS and SAXS techniques are also of great importance.

### References

- (1) M. Harada et al., *J. Colloid Interface Sci.*, **343**, 423 (2010).
- (2) M. Harada et al., *Cryst. Growth Des.*, **16**, 2860 (2016).
- (3) G. Von White et al., *J. Phys. Chem. C*, **114**, 16285 (2010).
- (4) G. Von White et al., *J. Phys. Chem. C*, **115**, 18397 (2011).

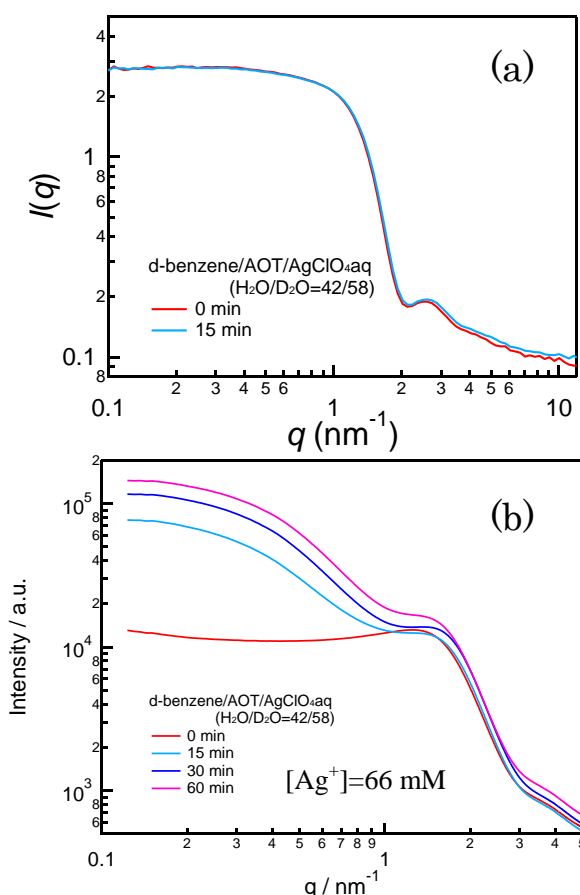


Fig. 1. (a) SANS and (b) SAXS profiles of the Ag nanoparticles prepared in water/d-benzene/AOT microemulsions at the matching condition ( $\text{H}_2\text{O}/\text{D}_2\text{O}=42/58$ ) before and after photoreduction.