



Characterization of water/AOT/benzene microemulsions during photoreduction to produce silver particles

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ABSTRACT

Colloidal dispersions of silver (Ag) particles were prepared by the photoreduction of silver perchlorate (AgClO₄) in water/AOT/benzene water-in-oil (w/o) microemulsions consisting of sodium bis(2-ethylhexyl) sulfosuccinate (AOT), water and benzene. Formation mechanisms of Ag particles prepared in the presence of benzoin by photoreduction from Ag⁺-containing w/o microemulsions were investigated by UV-vis, transmission electron microscopy (TEM), extended X-ray absorption fine structure (EXAFS) and small-angle X-ray scattering (SAXS) measurements. By a combination of TEM and EXAFS results, Ag particles show a metallic nature after the photoreduction and the diameter of Ag particles ranges between 5 and 30 nm. In situ time-resolved SAXS measurements show that the integrated rate equation can be applied in the reduction process of Ag⁺ ions to Ag⁰ atoms, and the autocatalytic Ag particle growth proceeds in the association process of Ag⁰ atoms during the photoreduction of Ag⁺-containing w/o microemulsions. The nanometer-sized water droplets microemulsified by AOT in benzene continuous-phase regulated the size of Ag particles, and the size and shape of water droplets were retained during the Ag particle formation.

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1. Introduction

Microemulsions have been subjected to numerous theoretical and experimental studies [1,2]. The microstructure of such microemulsions has been described as droplets of water (or oil) dispersed in a continuous-phase of oil (or water) in a certain composition range. On the applied front, microemulsions are of interest in enhanced oil recovery, cutting oils, pharmaceuticals, cosmetics and so on. An important property of microemulsions is its solubilization capacity for water or oil as microdroplets dispersed in the continuous-phase. The anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) readily forms reverse micelles in a wide variety of nonpolar solvents [3–5]. It is recognized that water/AOT/alkane microemulsions have water droplets with diameters ranging from 3 to 30 nm. The water droplets are encapsulated by the AOT surfactant so that virtually all of the AOT is located at the interface shell. The size of the water droplets can be conveniently altered by adjusting the molar ratios of water-to-surfactant designated as w ($=[\text{H}_2\text{O}]/[\text{AOT}]$). The microemulsions are thermodynamically stable and optically clear since the water droplets have not enough large in size to be scattered by light source.

Surfactant-stabilized water pools are well known to provide a microenvironment for the preparation of metal particles by exchanging their contents via the fusion–redispersion process and preventing the excess aggregation of metal particles [6–8]. Since the size control of metal particles in colloidal dispersions is very important and requires knowledge of the formation mechanisms, there have been many attempts to investigate the formation kinetics of metal particles [9–13]. For example, pioneering work by Petit and co-workers [9] on the production of silver (Ag) particles in the water/AOT/alkane microemulsions was undertaken using synthetic method via the reduction of Ag⁺ ions with reducing reagents. The Ag⁺ ions was introduced into the reverse micelle system by functionalization of the AOT ionic headgroup, replacing the Na⁺ ion to form Ag(AOT) surfactant. They found that the particle size distribution of Ag particles prepared using NaBH₄ was bimodal whereas it was unimodal in using N₂H₄, suggesting that autocatalysis by an aggregated product will have a great effect for slow reactions (in using NaBH₄) than for fast reactions (in using N₂H₄). Ingelsten et al. [12] also reported the kinetics of the formation of Pt nanoparticles in water-in-oil microemulsions by the borohydride-reduction of PtCl₆²⁻, and they concluded that the fusion of water droplets is a prerequisite for the reaction to proceed and might be a rate-determining step in the reduction of PtCl₆²⁻ to metallic platinum.

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Small-angle X-ray scattering (SAXS) has been used as one of the most powerful techniques to investigate the structural change of the water droplet size of water-in-oil (w/o) microemulsions [14,15]. Most of the previously reported experimental techniques for the monitoring the formation of metal particles were not able to give a complete picture of the nucleation, crystallization, and growth processes. The high intensity of the synchrotron beam has recently allowed data collection on a sufficiently short time-scale of milliseconds to minutes. However, up to now, the elucidation for the kinetics of the particle formation has not been extensively performed by means of the in situ time-resolved SAXS method [16,17] that can provide quantitative information on the number of nuclei and particles, their size distribution and the yield of the chemical reaction during the particle formation process in a real time.

On the other hand, metal concentration of the starting materials is significantly important factor for the particle formation kinetics although there are few studies to characterize an AOT-based water-in-oil (w/o) microemulsions with high concentrations of metal ions [18,19]. The metal concentration ($[Ag] = 66 \text{ mM}$) used here is relatively higher than those previously reported by Zukoski et al. [20] and Henglein et al. [21]. The photoreduction method with assistance of benzoin is very useful for the preparation of the higher concentration of Ag particles since the benzoin plays an important role for the enhancement of Ag^+ reduction [22].

In this study we investigated the formation mechanisms of Ag particles by the photoreduction of the high concentrations of ionic precursor $AgClO_4$ in the presence of benzoin as a photoactivator in water/AOT/benzene water-in-oil (w/o) microemulsions by means of UV-vis, transmission electron microscopy (TEM), in situ EXAFS and SAXS measurements. By a combination of EXAFS and SAXS techniques, we can acquire some useful information on the morphology of Ag particles prepared in the AOT-based water-in-oil (w/o) microemulsions during the photoreduction. Especially, the kinetics and dynamics of Ag particle formation was successfully demonstrated by monitoring the real-time structural change of Ag particles during the photoreduction process by means of in situ SAXS measurements.

2. Experimental

2.1. Preparation of the Ag particles in water/AOT/benzene microemulsions

Anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT), silver perchlorate ($AgClO_4 \cdot H_2O$, guaranteed reagent), benzene, benzoin ($C_6H_5CH(OH)COC_6H_5$, guaranteed reagent) and distilled water were purchased from Nacalai Tesque and used without further purification.

Reverse microemulsions were prepared by first making a 10 mmol AOT in 19 mL of benzene solution (21.0 wt.% AOT). One milliliter of distilled water was added to the benzene solution of AOT using a glass syringe and then shaken at least for 1 min in glass bottles. The shaking action was required to overcome an energy barrier to distribute the water into the nanosized droplets, as it could not be achieved using a magnetic stirrer. The water-to-surfactant molar ratio (w) was fixed to 5.6 in all cases of this study. In order to prepare Ag^+ -containing w/o microemulsions, 1 mL of distilled water was replaced by the same amount of $AgClO_4$ aqueous solution. The metal concentration $[Ag^+]$ in the aqueous phase was 1.32 M.

The colloidal dispersions of Ag particles were synthesized in the presence of AOT by the photoreduction of the Ag^+ -containing w/o microemulsions. Briefly, 1 mL of 1.32 M aqueous solution of $AgClO_4 \cdot H_2O$ was added to 19 mL of 0.53 M benzene solution of AOT

followed by the addition of 110 mg benzoin powder and the mixture was then mixed vigorously by shaking. Here it should be noted that benzoin plays an important role as a photoactivator [23,24] to complete Ag particle formation in benzene solution. The Ag^+ -containing w/o microemulsions were poured into a quartz cell and irradiation by UV-light was started with continuous stirring using a magnetic stirrer. An irradiation of 500 W super high-pressure mercury lamp was carried out to obtain the colloidal dispersions of Ag particles ($[Ag] = 66 \text{ mM}$) in water/AOT/benzene w/o microemulsions. During the irradiation by UV-light, the reduced samples were collected in a designated reduction time up to 4 h and their UV-vis and ex situ SAXS spectra were measured.

2.2. Characterization of the Ag particles in water/AOT/benzene microemulsions

UV-vis absorption spectra for the colloidal dispersions of Ag particles as well as the corresponding ionic precursor of $AgClO_4$ in the water/AOT/benzene w/o microemulsions were measured with a Hitachi U-3010 spectrophotometer to pursue the reduction of ionic precursor to Ag particles. To measure the obtained colloidal dispersions ($[Ag] = 66 \text{ mM}$), 0.1 mL of the obtained samples were diluted in 9 mL of water/benzene (1/19) mixture to adjust the concentration of metal for the UV absorption measurements.

TEM micrograph of the colloidal dispersions of Ag particles prepared in the water/AOT/benzene w/o microemulsions was obtained using a JEM-2000FX operated at 200 kV as the acceleration voltage. The samples after the UV-vis measurements were diluted in an appropriate amount of benzene solution for the TEM observations. The high-resolution carbon-supported copper mesh was used to support the Ag colloidal samples. The diameter of each particle was determined from enlarged photographs. A histogram of the particle size distribution and the average diameter was determined from the enlarged photographs.

In situ EXAFS measurements at the Ag-K edge (25,516.5 eV) for the colloidal dispersions of Ag particles ($[Ag] = 66 \text{ mM}$) in the water/AOT/benzene w/o microemulsions were carried out to estimate the size of Ag particles as well as the structural change before and after the photoirradiation. The data were recorded in a transmission mode at the BL-NW10A station in the Photon Factory, High Energy Accelerator Research Organization (PF-AR, KEK, Japan). For the in situ EXAFS measurements, the Ag^+ -containing samples were poured into a glass cell (optical path length 50 mm) sealed with polyimide film windows (Kapton-200H, 50 μm thickness) and the samples were photoirradiated with the 500 W super high-pressure mercury lamp. EXAFS spectra of the samples were measured as described in our previous paper [24]. EXAFS spectra were analyzed by a computer program REX2000 (supplied by Rigaku Corp.) [25]. EXAFS analysis was performed according to the procedure previously reported [23,24]. Parameters for the phase shifts and the backscattering amplitudes were obtained from the reference samples (for example, Ag-Ag contribution from Ag foil and the Ag-O contribution from $AgClO_4 \cdot H_2O$).

2.3. Ex situ and in situ SAXS measurement of the Ag particles in water/AOT/benzene microemulsions

Ex situ SAXS measurements of the colloidal dispersions of Ag particles ($[Ag] = 66 \text{ mM}$) in the water/AOT/benzene w/o microemulsions were performed at the BL-15A station in KEK-PF. Using a bent mirror and a bent monochromator made of a Si single crystal, X-ray beams with a wavelength of 1.50 \AA were selected and the beam was focused to 1.2 mm \times 0.8 mm. The scattering data was collected by a position sensitive proportional counter (PSPC). The X-ray path was evacuated except at the position where the sample cell was set. The path length of the sample cell was 1 mm and it

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