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Small-angle X-ray scattering study of metal nanoparticles prepared by photoreduction in aqueous solutions of sodium dodecyl sulfate

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ABSTRACT

Photoreduction formation mechanisms of metal particles (gold (Au) and platinum (Pt) particles) in aqueous solution of sodium dodecyl sulfate (SDS) have been investigated using transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and extended X-ray absorption fine structure (EXAFS) measurements. The anionic surfactant SDS was used as a stabilized reagent to disperse metal particles in aqueous solutions. The average particle diameter of Au and Pt particles was estimated from TEM as 4.5 and 2.7 nm, respectively. The SAXS analysis showed that in high concentration of SDS the size of Au and Pt particles is consistent with those obtained from TEM and EXAFS measurements, and the micelles of SDS retain a core–shell structure in aqueous solutions after the formation of metal particles. In the particle formation process, metal particles were photochemically produced in the core of micelles and they did not significantly affect the morphology of micelles, although these metal ions were almost randomly distributed in solution before the photoreduction. The particle growth rate of Au and Pt could be evaluated on the basis of the weight fraction of these metal particles, and it was found that Au particle growth occurs more rapidly than Pt particle growth in the aqueous SDS solutions.

1. Introduction

Some surfactants have been utilized as surface stabilizers [1] and/or templates [2] in the synthesis of metal particles. These moieties, by their binding to the metal particle surface, decrease the surface energy, control the growth and shape of the metal particles, and act as a stabilizer against precipitation. Charged surfactants such as alkyltrimethylammonium chloride (C_nTAC: $n = 10$, 12, 14, and 18) [3], sodium dodecyl sulfate (SDS) [4], and sodium bis(2-ethylhexyl)sulfosuccinate (AOT) [5] are often used as stabilizers in the synthesis of various metal nanoparticles and nanowires. For example, in the photochemical preparation of Ag particles with the photolysis of $AgClO_4$ in the presence of anionic surfactant SDS, the surfactant plays an important role of the stabilization of Ag particles to prevent their aggregation [4a,4b].

The size and shape of the finally synthesized metal particles depends on the spatial distribution of ionic precursors incorporated in the micellar systems, and it is determined from the interactions between metal particles and surfactants during the nucleation and growth process of metal particles. There are some examples relevant to the metal–surfactant interactions such as the binding of anionic $[PdCl_4]^{2-}$ [6], $[AuCl_4]^-$ [7], cationic Ru(II) [8], and cationic Pd(II) complexes [9] to a variety of oppositely charged surfactants in aqueous solutions. Since the particle formation begins when ionic precursors of transition metal incorporated in micellar systems are reduced to zerovalent metal atoms, the interactions between ionic precursors and charged surfactant molecules should be carefully investigated so as to control the rate of the particle growth.

In the present study, in order to evaluate the particle growth mechanisms of Au and Pt particles in the presence of SDS, we have examined the structural change of micelles as well as that of the colloidal dispersions of Au and Pt particles before and after photoreduction by means of the small-angle X-ray scattering (SAXS) measurements. Additionally, we have attempted to characterize the metal particles in aqueous SDS solutions produced by the photoreduction by means of UV–vis, transmission electron microscopy (TEM), and extended X-ray absorption fine structure (EXAFS) measurements.

2. Experimental

2.1. Preparation of colloidal dispersions of Au and Pt particles

Colloidal dispersions of Au and Pt particles were synthesized by the UV-irradiation of $AuCl_4^-$ and $PtCl_6^{2-}$ ions, respectively, in

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aqueous surfactant SDS solutions. Tetrachloroauric(III) acid (hydrogen tetrachloroaurate(III), $HAuCl_4{\cdot}4H_2O$, guaranteed reagent), hexachloroplatinic(IV) acid (hydrated hydrogen hexachloroplatinate(IV), $H_2PtCl_6{\cdot}6H_2O$, guaranteed reagent), and distilled water were purchased from Nacalai Tesque, and used without further purification. SDS (supplied from Wako Chemicals) was also used without further purification. The purity of SDS was checked using surface tension measurements.

Dilute (0.66 mM) and concentrated (6.6 mM) colloidal dispersions of Au and Pt particles were prepared from $HAuCl_4{\cdot}4H_2O$ and $H_2PtCl_6{\cdot}6H_2O$ by irradiation with a 500 W super-high-pressure mercury lamp for 8, 100, and 250 mM aqueous surfactant solution of SDS with benzoin as a photo-activator [10,11]. Briefly, in preparing the dilute Au and Pt colloidal solutions in the presence of 100 mM SDS, 5 mL of 1.32 mM aqueous solution of $HAuCl_4{\cdot}4H_2O$ and $H_2PtCl_6{\cdot}6H_2O$ was added to 5 mL of 200 mM SDS aqueous solution, respectively, followed by the addition of 4 mg benzoin powder and stirring vigorously. The obtained ionic solutions were poured into a quartz cell, and the irradiation of mercury lamp was started. The reduced samples irradiated for 5 h were poured into polyethylene bags (optical path length about 2 mm) for EXAFS measurements. For SAXS measurements, the reduced samples irradiated with a designated reduction time up to 5 h were poured into cells (optical path length 1 mm) sealed with Kapton film. The reduced samples prepared in the quartz cell with a designated reduction time were also measured by means of UV–vis and TEM.

2.2. Characterization of the Au and Pt particles prepared by photoreduction

The UV–vis absorption spectra of the colloidal dispersions of Au and Pt particles as well as the corresponding ionic precursors were measured by a Hitachi U-3010 spectrophotometer to pursue the reduction of ionic precursors in the aqueous SDS solutions.

TEM micrographs of the colloidal dispersions were obtained using a JEM-2000FX instrument operated at 200 kV as the acceleration voltage. The high-resolution carbon-supported copper mesh was used to support the samples of colloidal dispersions. The diameter of each particle was determined from enlarged photographs. The histogram of the particle size distribution and the average diameter were obtained by measuring about 200 particles in the enlarged photograph.

2.3. EXAFS measurements and data analysis of the Au and Pt particles

EXAFS measurements at the Au–L_3 and Pt–L_3 edge of the colloidal dispersions of Au and Pt particles ([Au] = [Pt] = 0.66 mM) stabilized by SDS were carried out at room temperature in the fluorescence mode using a Lytle type detector in BL-12C station [12] of the Photon Factory, High Energy Accelerator Research Organization (KEK-PF). Monochromatic synchrotron radiation was obtained using a Si(1 1 1) double crystal. The storage ring was operated at 2.5 GeV with currents between 150 and 400 mA. The beam size was 5 mm × 1 mm. For the measurements of Au and Pt colloidal dispersions, an ionization chamber was used both for I_0 (incident intensity) filled with $Ar(15)N_2(85)$ gas and I (transmitted intensity) filled with Ar gas. The Au and Pt samples were sealed in 1 cm × 1 cm polyethylene bag with the optical path length of about 2 mm for the fluorescence EXAFS measurements. In order to acquire coordination numbers and bond distances, EXAFS measurement of Au and Pt foil was performed as a reference compound.

EXAFS spectra were analyzed by the program package REX2000 Ver. 2.0.7 (supplied by Rigaku Corp.) [13]. EXAFS analyses were performed as described in detail elsewhere [14]. The spectra were extracted using the cubic spline method and normalized to the edge height. The k^3-weighted EXAFS function was Fourier transformed into r space, and the Fourier transformation range was typically between 3 and 14 Å^{-1}. For the following curve-fitting, the high-frequency noise was removed by a Fourier filtering technique, and the inverse Fourier transformation was performed. The Fourier-filtered EXAFS functions were fitted with empirically derived phase shift and amplitude functions from the reference sample (Pt–Pt contribution from the Pt foil and Pt–Cl contribution from $H_2PtCl_6{\cdot}6H_2O$, and Au–Au contribution from the Au foil and Au–Cl contribution from $HAuCl_4{\cdot}4H_2O$) to obtain the structural parameters, such as coordination number (C.N.), bond distance (r), Debye–waller factor (σ) and R factor, of the colloidal dispersions of Au and Pt particles.

2.4. SAXS measurement and data analysis of the Au and Pt particles

SAXS experiments were performed for the colloidal dispersions of Au and Pt particles ([Au] = [Pt] = 0.66 or 6.6 mM) stabilized by SDS before and after UV-irradiation, at BL-15A station in KEK-PF, by using SAXS instruments constructed at the stations [15]. By the bent mirror and a bent monochrometer made of Si single crystal, X-ray beams of 1.5 Å in wavelength were selected and the beam was focused to 1.2 mm × 0.8 mm, and the scattering data was collected by a position sensitive proportional counter (PSPC). The camera distance was about 2400 mm, and 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 was equipped with two 20 μm thick Kapton windows. The accumulating time for measurement of each sample was 10 min.

Various corrections for the observed scattering intensities were made, i.e., the subtraction of instrumental backgrounds, the absorption correction, and the correction for the fluctuation of the beam intensity during the experiments. However, no corrections, for either slit width or slit length, were performed, since these effects were negligibly small on the SAXS curves under the present experimental conditions.

The scattering intensity from a set of monodispersed particles is given by [16–18]

$$I(q) = \gamma n_p(\Delta\rho)^2 V^2 P(q) S(q) \tag{1}$$

where γ is a factor related to the instrumental effects; n_p corresponds to the particle number density; $\Delta\rho$ is the electron density contrast between the scattering particle and the medium; V is the scattering particle volume; $P(q)$ is the particle form factor ($P(0) = 1$); and $S(q)$ is the structure factor that accounts for the interparticle interference effects on scattering intensity produced by the particle spatial correlation. Here q is the magnitude of the scattering wave vector defined as,

$$q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right) \tag{2}$$

where θ is the scattering angle and λ is the wavelength of X-ray.

In the present study, the SAXS profile is composed of the scattering from metal particles (Au or Pt particles) and that from the SDS micelles. In order to treat the SAXS profile of the colloidal dispersions, we carefully consider these two scattering contributions. Generally, the metal particle would be modeled as a spherical particle and the micelles would be modeled as a sphere with a core–shell structure [5,19,20], which consists of regions with two different electron densities, i.e., an inner core of paraffinic (hydrocarbon) moiety and an external shell with a polar headgroup including the hydrated water. The detailed analytical procedure of SAXS profiles will be described later in Section 3.