Stepwise Size-selective Extraction of Aqueous Silver Nanoparticles by a Series of Organic Solvents

Yang Yang and Keisaku Kimura*
Department of Material Science, University of Hyogo, 3-2-1 Koto, Kamigori-cho, Ako-gun, Hyogo 678-1297

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Using various organic solvents in turn, stepwise size-selective extraction of aqueous mercaptosuccinic acid (MSA)-modified silver nanoparticles is achieved through a cation surfactant-induced water–oil transference process.

In recent years, metal nanoparticles have been intensely investigated because of their unique size- and shape-dependent optical and electrical properties.[1–4] Among the plethora of existing synthesis procedures, wet-chemical methods are most widely used to synthesize metal nanoparticles over a range of sizes. We have prepared water-soluble metal nanoparticles in large scale by introducing mercaptosuccinic acid (MSA) as a surface stabilizer.[5,6] Though the average size of the obtained metal nanoparticles can be primarily controlled through varying the initial molar ratio of MSA to metal ions during synthesis process, further control of the size and narrowing of the size distribution for the relevant nanoparticles are still essential.[7,8] In this letter, we utilized MSA-modified silver nanoparticles as an example and proposed a simple and comprehensive route to achieve stepwise size-selective extraction of aqueous MSA-modified nanoparticles into organic phase under the help of various organic solvents, which was well verified by UV–vis absorption spectra and transmission electron microscopy (TEM) observations.

MSA-modified silver nanoparticles were prepared using a method reported previously.[6] The average size of the obtained silver nanoparticles was confirmed to be 4.9 nm by X-ray diffraction (XRD) measurement. Subsequent TEM observation revealed that most of the nanoparticles are in the size of ca. 5.1 nm, but accompanying a rather wide size distribution from 2 to 10 nm. The aqueous phase of silver nanoparticles was obtained by dissolving 2.0 mg of product in 10 mL of water with pH value adjusted to 11. The organic phase used for particle extraction was prepared by dissolving 3.65 mg (1.0×10^{-5} mol) of cetyltrimethylammonium bromide (CTAB) in 10 mL of xylene, toluene, carbon tetrachloride, dichloromethane, or chloroform. After vigorous shaking for the sufficient bonding of CTA^+ cations with MSA-modified silver nanoparticles through electrostatic interaction,[7] water–oil biphasic solution was left quiet until two clearly separated layers formed.

From Figure 1a, it can be seen that the as-prepared aqueous silver nanoparticles display a characteristic surface plasmon resonance (SPR) band centered at 417 nm (curve 1). Addition of CTAB achieved the extraction of silver nanoparticles into various organic phases, as shown in curves 2–6. However, by comparing the relative absorption intensity, it was found that the yield of transference for various solvents is quite different. When the organic solvent was taken turns from chloroform, dichloromethane, carbon tetrachloride, toluene, to xylene, the yield of transference was calculated to be 81, 66, 26, 22%, and less than 1%, respectively. Thus, the efficiency of phase transfer is strongly influenced by nature of the solvent even at the same surfactant concentration and volume ratio of water–oil biphase.

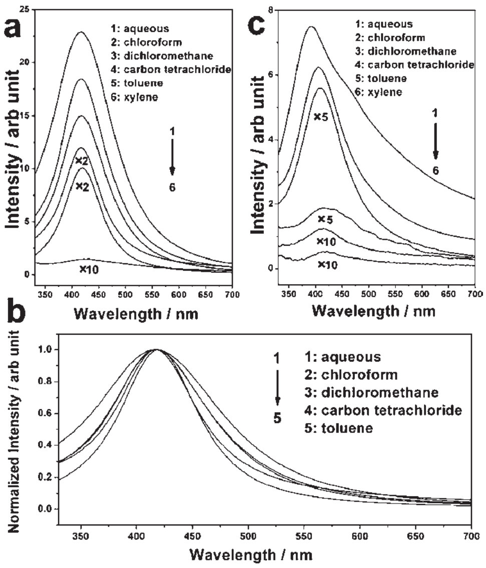

Figure 1. Absorption spectra of aqueous silver nanoparticles and those transferred in different organic solvents. (a) and (c) correspond to spectra of silver nanoparticles in the average size of 5.1 and 7.5 nm, respectively. (b) is the normalized spectra of (a).

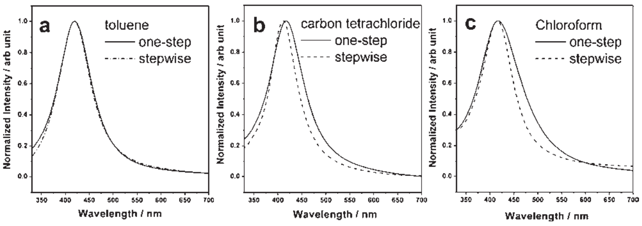

Figure 2. Normalized absorption spectra of silver nanoparticles in toluene (a), carbon tetrachloride (b), and chloroform (c) by single-step and stepwise extraction processes.

Figure 2b exhibits normalized spectra derivate from Figure 1a, in which two phenomena are very noticeable. According to the Mie theory and the results of other groups, the refractive index of the medium greatly affects the SPR peak position of metal particles and the peak will shift to lower energy when the refractive index of the solution increases.[9–12] However, in our system, it can be seen that no matter which solvent the silver nanoparticles is dispersed in, the position of SPR band remains unchangeable at about 417 nm. Since the phase transfer through electrostatic interaction is based on the formation of ion pairs between CTA^+ cations and carboxylate anions, the formed dense bilayer structure on the particle surface could be estimated to screen the influence of surrounding medium on the electric field of silver core. Meanwhile, it can be observed that all the full width at half-maximum (fwhm) values of the symmetric SPR band become narrower when silver nanoparticles were extracted into organic phase. Especially, the degree of band narrowing has direct relation to the type of organic solvents employed. For example, compared to 1.05 eV of fwhm value for hydrosols, the value of silver nanoparticles in chloroform is 0.79 eV, but it is only 0.61 eV in toluene. Though organic solvent directly affects the SPR absorption, the band narrowing is not the case as already stated above. Hence, the relatively narrow absorption band indicates rather narrow size distribution for a particle system with polydispersity,[12] and it can be suggested that the lower yield of extraction of aqueous silver nanoparticles into toluene is partially due to more captious size-selection in transfer process than that in chloroform.

By decreasing the initial molar ratio of MSA to silver ions, larger silver nanoparticles in the size of 7.5 ± 2 nm were obtained. Figure 1c shows the absorption spectra of these aqueous silver nanoparticles extracted by various organic solvents under the same conditions. The yield of transference by toluene significantly reduces from 22% for the particle with average size of ca. 5.1 nm to 1.7%. However, the yield under the assistance of chloroform is still up to 83%. Considering the fraction of smaller-sized particles in this sample is apparently less than that of the former, we can conclude that toluene is only competent for the phase transfer of particles in small size via CTAB-induced process. On the contrary, chloroform presents more compatibility in this transference process. Behavior of other organic solvents such as dichloromethane and carbon tetrachloride is intervenient for this system.

MSA-modified metal nanoparticles have been well characterized as a common molecular compound whose properties are adjustable with the particle size. After fully bonding with CTA^+ cations by the electrostatic interaction, all the silver nanoparticles are changed from the hydrophilic to the hydrophobic owing to the coverage of long-chained surfactant. But small-sized nanoparticles are likely to obtain more hydrophobic force since their average polarization is relatively lower that that of the big-sized.[13] As a result, small particles are more preferential to enter the solvent like toluene with low polarity ($\varepsilon = 2.37$, 25 °C) and transfer of big particles are prevented for lack of enough hydrophobic force. As for chloroform with higher polarity ($\varepsilon = 4.81$, 25 °C), most of the silver nanoparticles can achieve phase transfer and only some oversize particles fail which leads to a bit decrease of absorption intensity after phase transfer. However, on the basis of the data from the present organic solvents, solvent polarity cannot be proved to be the exclusive factor to determine the phase transfer of nanoparticles with different polarization. Other physical properties of organic solvent such as viscosity, surface tension, and dipole moment might also affect this process because of the complexity of solubility, which requires further investigation.

Subsequently, stepwise extraction experiments for silver nanoparticles in the average size of 5.1 nm were conducted as follows. Firstly, we used toluene to extract aqueous silver nanoparticles repeatedly until nearly no silver nanoparticles could be detected in the newly added toluene. Every portion of the toluene solution after extraction was incorporated for the following absorption measurement. After toluene was removed, carbon tetrachloride was added to repeat the above process, followed by chloroform. Figure 2 shows the comparison of SPR absorption between single-step and stepwise processes. For the normalized absorption spectra of toluene solution (Figure 2a), no obvious change of fwhm value could be observed between these two processes though their relative concentrations are quite different, which indicate that repetitious extractions only achieve sufficient transfer of smaller particles into toluene. From Figures 2b and 2c, it can be clearly seen that the fwhm values of silver nanoparticles in carbon tetrachloride and chloroform obviously reduce from 0.69, 0.79 to 0.51, 0.65 eV, respectively, by stepwise extraction procedure. Since most fractions of the particles in smaller size have been removed by toluene, only the residual bigger silver nanoparticles could enter carbon tetrachloride and chloroform in turn, which contributes to the narrowing of size distribution for these extracts. By TEM observation as shown in Figure 3, the change of size and narrowing of size distribution on each extract could be clearly observed, well consistent to the results of absorption. On the basis of the mechanism for the size-selective extraction of this process discussed above, it is reasonable to consider the extension of this method to other carboxylate-modified water-soluble nanoparticles for size selection. Further investigation is in progress.

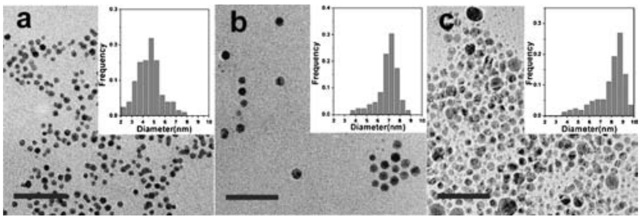

Figure 3. TEM images and corresponding histograms of size distributions of silver nanoparticles transferred in toluene (a), carbon tetrachloride (b), and chloroform (c) by stepwise extraction process. The bar for all figures is 50 nm.

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