Phase Transfer of Gold Nanoparticles across a Water/Oil Interface by Stoichiometric Ion-Pair Formation on Particle Surfaces

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The transfer of surface-modified gold nanoparticles across a water/toluene interface was demonstrated. Stoichiometric ion-pair formation between carboxylate anions on particle surfaces and tetraoctylammonium cations brought about the phase transfer, and was revealed by transmission electron microscopy (TEM), IR, UV-vis absorption, and energy dispersive X-ray (EDX) spectroscopies. A surface structure of the transferred gold nanoparticles was also presented. During the nanoparticle transfer from water into an organic phase, an improvement in the dispersibility and a slight decrease in the average diameter were observed (3.6 → 2.9 nm) accompanied by a slight narrowing in the size distribution (standard deviation: 0.80 → 0.54 nm). The phenomena could lead to a new methodology for size and/or dispersibility selections.

Metal nanoparticles whose surfaces are functionalized with thiolate molecules are of considerable interest because of their potential electronic, optical, magnetic, and catalytic applications under high stabilities.[1,2] In particular, manipulating the surface properties, such as molecular structures of the modifiers, the hydrophobicity, and the reactivity plays an important role for constructing nanostructures.[3,4] So far, the surfaces of metal nanoparticles have been modified by long-chain thiolates containing an aromatic moiety,[5] ω-substituted alkanethiolates,[6] as well as small molecular thiolates, such as (3-mercaptopropyl)trimethoxysilane[7] and 4-mercaptophenol.[8] Recently, we have developed a large-scale synthesis of water-soluble, carboxylate-modified gold nanoparticle powders using mercaptosuccinic acid as a surface stabilizer.[9] Since carboxylate-modified gold nanoparticles are well-characterized as a common molecular compound,[9] the characteristic features of the surface can be controlled by a reaction of carboxylate anions.

It can be considered that hydrophilic ions would interact with oppositely-charged lipophilic ions through an electrostatic attraction, leading to highly hydrophobic ion-pairs represented by a phase-transfer catalyst.[10] Such ion-pairs are produced stoichiometrically, and are often extracted into an organic phase. It should be emphasized that the reaction occurs between "molecules". Therefore, ion-pair formation and extraction involving "nanoparticles" have not been well investigated, since the surfaces of nanoparticles were poorly-defined, although nanoparticle extraction into an organic phase had already been reported.[11,12]

In this article, we describe the phase transfer of gold nanoparticles across a water/oil interface by stoichiometric ion-pair formation between carboxylate anions on the surface and hydrophobic cations. The surface structure of transferred nanoparticles is presented. Furthermore, the characteristic features in the transfer phenomena of gold nanoparticles on the particle size distributions and dispersibility will also be discussed.

Experimental

Chemicals. Hydrogen tetrachloroaurate tetrahydrate ($HAuCl_4 \cdot 4H_2O$, 99%), sodium borohydride ($NaBH_4$, > 90%), mercaptosuccinic acid ($HS-CH(COOH)-CH_2(COOH)$; abbreviated as MSA, 97%), methanol (GR grade), ethanol (GR grade) and toluene (GR grade) were received from Wako Pure Chemicals, and used without further purification. Tetraoctylammonium bromide ($[CH_3(CH_2)_7]_4NBr$; abbreviated as TOABr) was purchased from Aldrich, and was used as received. Pure water was obtained by an Advantec GS-200 automatic water-distillation supplier.

Sample Preparations. Carboxylate-modified gold nanoparticles were prepared by a method reported earlier.[9] Briefly, 0.5 mmol of $HAuCl_4$ dissolved as an aqueous solution (0.121 M, $M = mol\,dm^{-3}$) and 0.5 mmol of mercaptosuccinic acid (MSA) was at first mixed in methanol (100 mL), followed by the addition of a freshly prepared 0.2 M aqueous $NaBH_4$ solution (25 mL) at a rate of 5 mL min^{-1} under vigorous stirring. A dark-brown precipitate was produced, and thoroughly washed with a water/ethanol (1/4) solution, methanol, and ethanol in order to remove any inorganic and organic impurities. Finally, the precipitate was dried under vacuum (Au–MSA sample).

A surface ion-pair formation reaction was conducted by a two-phase method. When 2 mL of an aqueous Au–MSA mother solution (5 mg/20 mL) and 4 mL of a toluene solution containing tetraoctylammonium bromide (TOABr) at a different concentration (0.35—8.0×10^{-4} M) were mixed and stirred vigorously, a dark-red color was transferred into a toluene phase, indicating that the gold nanoparticles were transferred from an aqueous phase into toluene across the water/toluene interface. After the evaporation of toluene, a dark-brown powder was obtained. Typically, an Au–MSA–TOA sample is abbreviated as that obtained under the condition at [TOABr] = 5.0×10^{-5} M.

Apparatus. Transmission electron microscopy (TEM) was conducted by a Hitachi-8100 electron microscope operated at 200 kV. Electronic absorption spectra were recorded on a Hitachi U-3210 spectrometer by using cuvettes with 1-cm optical path length. The FT-IR spectra were measured by a Horiba FT-210 infrared spectrophotometer using a KBr disk dispersed with the powder sample. Elemental analyses of C, H, O and S were conducted commercially. An energy dispersive X-ray spectroscopy (EDX) was performed by an EDAX DX-4 system attached to the Phillips XL-20 scanning electron microscope operated under an acceleration voltage of 6 kV.

Results and Discussion

According to similar characterizations of an Au–MSA powder sample by elemental analysis and IR absorption spectroscopy to those reported previously,[9] gold nanoparticles were surface-modified by carboxylate–MSA moieties ($-S-CH(COO^-)-CH_2(COO^-)$, abbreviated as c-MSA) of 8.6×10^{-4} mol per gram of the powder. Briefly, the FT-IR spectrum showed that MSA anchors on the gold surface through the S atom in the mercapto group, and exists in the form of a carboxylate anion.[13] The elemental analysis showed that the molecular formula of organics can be apparently described as $C_4H_3O_4S\cdot0.7H_2O$, and the component was contained with 13.8 wt% in the Au–MSA powder.

Figures 1a and 2a show a TEM image and the particle size distribution of the Au–MSA sample, respectively. The mean particle diameter or standard deviation was obtained to be 3.6 or 0.80 nm, respectively. In the particle-transfer experiments, the phase transfer of gold nanoparticles across a water/toluene interface could not be observed in the absence of TOABr, suggesting that ion-pair formation between carboxylate anions and tetraoctylammonium cations is necessary for extraction into an organic phase.[14] Figures 1b and 2b also show a TEM image and the size distribution of transferred gold nanoparticles in toluene (Au–MSA–TOA sample), respectively. The inset in Fig. 1b shows a high-resolution image of one particle. A (111) lattice plane image of gold (d_{111} = 2.35 Å) was clearly observed.[9] The results indicate that, for the Au–MSA–TOA sample, the mean particle diameter became slightly small (2.9 nm) along with the size distribution to be narrower (standard deviation: 0.54 nm), as compared to that of the Au–MSA sample. This phenomenon was caused by a decrease in the number of particles larger than 4.5 nm in diameter as shown in Fig. 2. Therefore, we expect that this finding will lead to a new methodology for the size selection of surface-modified nanoparticles.[15] Furthermore, the TEM images also show that gold nanoparticles were better-dispersed in toluene than those in water. Namely, nanoparticles in toluene are considered to be well-isolated from each other, while they tend to aggregate in water, suggesting that a tetraoctylammonium cation (TOA^+) plays an important role for improving the dispersibility.

Figure 3a shows the absorption spectra of transferred gold nanoparticles at a different TOABr concentration in toluene. The inset shows the absorption spectrum of the aqueous mother solution of Au–MSA, which is similar to that of the transferred gold nanoparticles. However, the surface plasmon band observed in toluene (520 nm) showed a slight blue shift as compare to that observed in water (533 nm). It is reported that a higher refractive index of the solvent renders the surface plasmon energy of metal nanoparticles to be lower;[16] thus, the observed shift would be mainly due to a change in the aggregation state of gold nanoparticles on the basis of the TEM images shown in Fig. 1.[17] The absorbance increased linearly with an increase in the TOABr concentration, and saturated above ca. 1.0×10^{-4} M (Figure 3b). Therefore, gold nanoparticles were transferred from an aqueous phase into toluene under a constant molar ratio (r_0) of c-MSA to TOA^+ at a low TOA^+ concentration region.

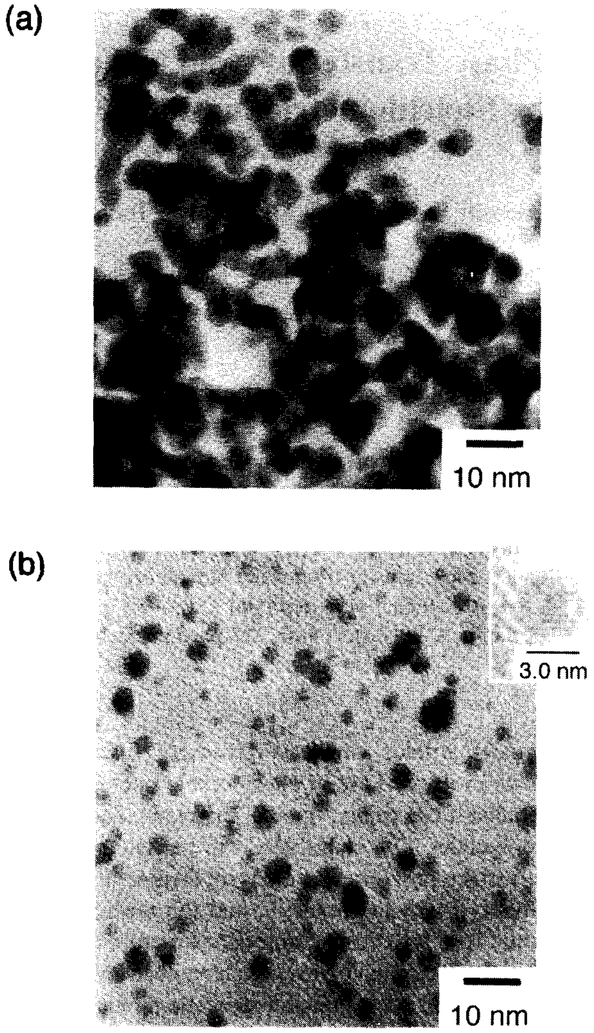

Fig. 1. Transmission electron microscopic (TEM) images of gold nanoparticles. (a) Au–MSA sample; (b) Au–MSA–TOA sample.

Figure 4 shows the FT-IR absorption spectra of Au–MSA–TOA and TOABr together with that of an Au–MSA sample. The Au–MSA sample has two characteristic peaks at 1580 and 1404 cm^{-1}, which can be attributed to the asymmetric and symmetric stretch modes of a carboxylate group (COO^-), respectively.[9] On the other hand, the IR spectrum of the Au–MSA–TOA sample was similar to

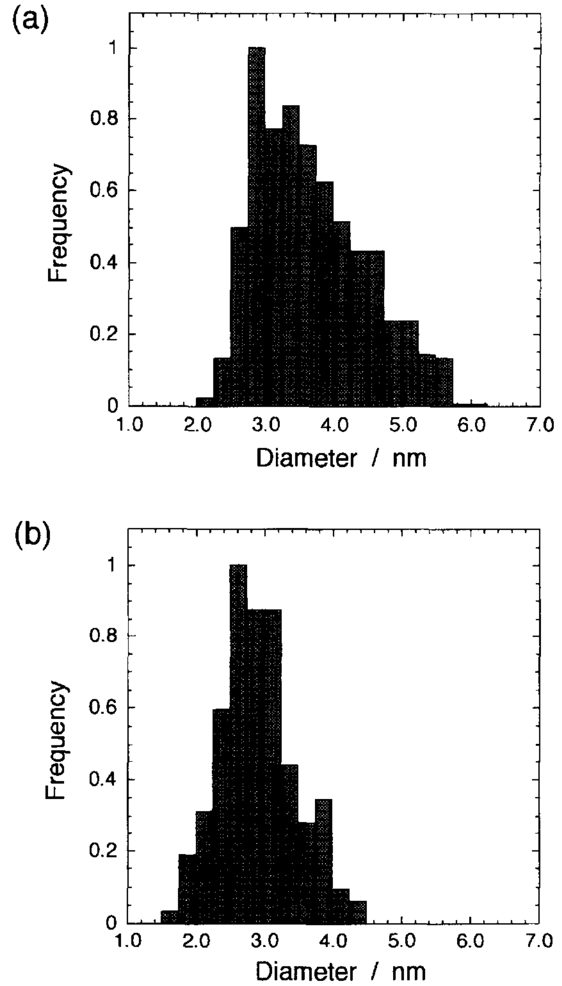

Fig. 2. Particle size distributions of gold nanoparticles. (a) Au–MSA sample; a mean particle diameter and a standard deviation were 3.6 and 0.80 nm, respectively. (b) Au–MSA–TOA sample; a mean particle diameter and a standard deviation were 2.9 and 0.54 nm, respectively.

the superposition of that of Au–MSA and TOABr; however, it shows another characteristic small peak at around 1727 cm^{-1}. This peak can be ascribed to the C=O stretch mode of a carboxylic acid different from that of COO^-, indicating that the surface of transferred Au nanoparticles possesses both $-COO^-$ and –COOH.

It is reasonable that the transfer yield of gold nanoparticles is assumed to be approximately the ratio of the absorbance of the surface plasmon band in toluene to that in water under the same volume. According to this assumption, the maximum transfer yield was calculated to be ca. 55% ($[TOABr] \geq 1.0 \times 10^{-4}$ M), indicating that nanoparticles still remain in a water phase. Indeed, gold nanoparticles can be observed in water; however, most of them would tend to precipitate. The results are consistent with those described in Figs. 1 and 2, that is, the existence of components which cannot be transferred into toluene makes the particle size distribution narrow through phase transfer. On the other hand, since the concentrations of transferred c-MSA moieties and TOA^+ in toluene can both be determined by knowing the transfer yield at a low TOA^+ concentration (< ca. 1.0×10^{-4} M),[18] r_0 was calculated to be 0.53, indicating that one c-MSA can bind 1.9 TOA^+ molecules. Considering that c-MSA possesses two $-COO^-$ groups, most of $-COO^-$ (ca. 95%) are able to combine with TOA^+ to produce a hydrophobic ion-pair $[-COO^-\ TOA^+]$. It is surprising that almost two bulky

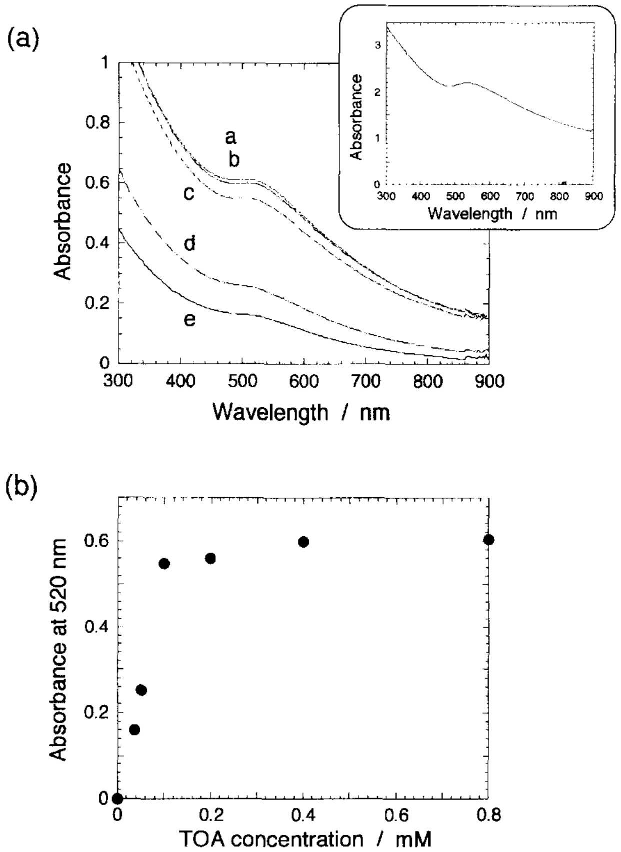

Fig. 3. (a) Absorption spectra of transferred gold nanoparticles in toluene at a different TOABr concentration. [TOABr] = **a**: 8.0×10^{-4}, **b**: 4.0×10^{-4}, **c**: 1.0×10^{-4}, **d**: 5.0×10^{-5}, **e**: 3.5×10^{-5} M. The inset shows the absorption spectrum of the aqueous mother Au–MSA solution. (b) TOA^+ concentration dependence of the surface plasmon band (520 nm) of the transferred gold nanoparticles.

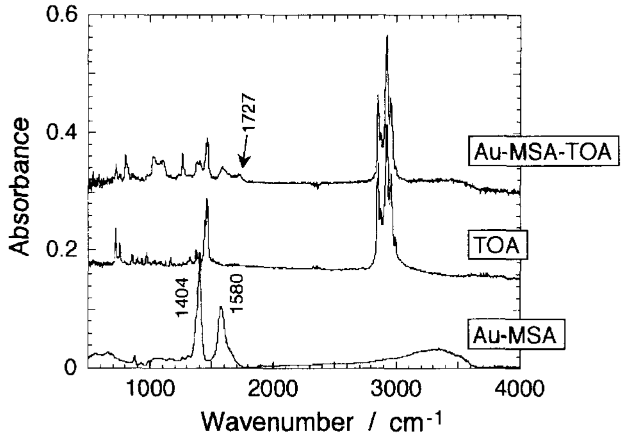

Fig. 4. FT-IR spectra of Au-MSA-TOA, TOABr, and Au-MSA samples.

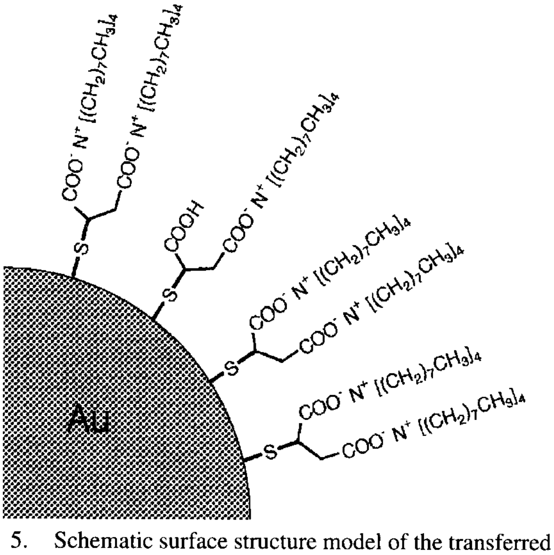

Fig. 5. Schematic surface structure model of the transferred gold nanoparticles by stoichiometric ion-pair formation across a water/toluene interface.

TOA^+ cations can produce ion-pairs with one c-MSA moiety; however, the result indicates that long alkyl chains would be extended toward the solution phase. It should also be mentioned that the IR spectrum proved the existence of –COOH groups in the Au–MSA–TOA sample. This is probably ascribed to the hydrolysis of small amounts of carboxylate anions in water (ca. 5%), i.e.; $-COO^- + H_2O \rightarrow -COOH + OH^-$.[9,19] Moreover, energy dispersive X-ray spectroscopy (EDX) excited by an electron beam revealed that the Au–MSA–TOA sample contained no Na, and trace amounts of Br (ca. 1.0 wt%), which supports the present ion-pair extraction mechanisms.

Therefore, the surface structure of gold nanoparticles transferred by ion-pair formation across a water/toluene interface is schematically illustrated in Fig. 5. Namely, 95 or 5% of carboxylate anions on the gold nanoparticles were stoichimetrically bound to tetraoctylammonium cations or protons, respectively; the interactions lead to the transfer of gold nanoparticles from water into an organic phase. This methodology can provide easy control of the surface functionality, reactivity, and/or nanoparticle dispersibility by modifying the ion-pair reagents.

Conclusion

The transfer of water-soluble, carboxylate-modified gold nanoparticles across a water/toluene interface was demonstrated. Since the surface of the prepared gold nanoparticles has been well-characterized, stoichiometric ion-pair formation between carboxylate anions on the particle surface and tetraoctylammonium cations was proved to cause a phase transfer of nanoparticles. An improvement in the dispersibility of nanoparticles was observed during phase transfer from water into an organic phase. Furthermore, the average particle diameter of gold nanoparticles changed to be small (3.6 → 2.9 nm) accompanied by a slight narrowing in the size distribution (standard deviation: 0.80 → 0.54 nm). The results suggest an easy control of surface functionality, leading to a new tool for size and/or dispersibility selections.

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