Stepwise Size-Selective Extraction of Carboxylate-Modified Gold Nanoparticles from an Aqueous Suspension into Toluene with Tetraoctylammonium Cations

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Ion-pair formation between carboxylate anions on particle surfaces and tetraoctylammonium cations caused the phase transfer of well-characterized, water-soluble gold nanoparticles into an organic phase. Stepwise extraction procedures demonstrated for the first time that the initially fractionated solution included gold nanoparticles smaller than those in the following extractions, indicating that the smaller nanoparticles can transfer into an organic phase more easily than the larger ones. The systematic stepwise extraction is expected to provide a new and effective methodology for precise size selections. The particle size dependence of the transferred gold nanoparticles could be qualitatively explained by a phenomenological model for ion-pair extraction.

Introduction

In recent years the interest in the synthesis and characterization of nanostructured materials has grown widely due to their distinctive physical and chemical properties.[1,2] In particular, metal nanoparticles whose surfaces are modified with thiolate molecules have attracted extensive attention because of their potential electronic, optical, magnetic, and catalytic applications under high stabilities.[3−5] So far, the surfaces of metal nanoparticles have been modified by long-chain thiolates containing an aromatic moiety,[6] ω-substituted alkanethiolates,[7] polyhetero-ω-functionalized alkanethiolates[8] and small molecular thiolates, such as (3-mercaptopropyl)trimethoxysilane,[9] tiopronin,[10] and 4-mercaptophenol.[11] These surface-modified nanoparticles can be isolated in dry powders without flocculation, and exhibit not only good air and thermal stability but also solubility in organic solvents or water depending on the structure and/or polarity of the surface modifiers. In the past few years, many investigations have been focused on the control of the size of nanoparticles and their self-assembly into two- or three-dimensional superlattice structures, which will provide a new horizon to study collective physical behaviors.[12,13] A tight size distribution is required for well-ordered packing of nanoparticles. Furthermore, manipulating the surface properties, such as the molecular structures of the modifiers, the hydrophobicity, and the reactivity, plays an important role in constructing such ordered nanostructures.[14] Therefore, strict controls of the surface structure and the size distribution for the relevant nanoparticles are inevitable.

We have developed a large-scale synthesis of water-soluble, carboxylate-modified gold nanoparticle powders by use of mercaptosuccinic acid as a surface stabilizer.[15] Since the carboxylate-functionalized gold nanoparticles are well-characterized as a common molecular compound,[15] the characteristic features of the surface can be strictly controlled by a reaction of carboxylate anions. We have already demonstrated that the water-soluble carboxylate-modified gold nanoparticles were transferred into an organic phase by stoichiometric (1:1) ion-pair formation between a hydrophilic carboxylate anion and a hydrophobic tetraoctylammonium cation.[16] It should be emphasized that the phase transfer of gold

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nanoparticles occurred as that of the well-defined “molecule”. For the transferred gold nanoparticles, particle size narrowing was observed due to a truncation of larger nanoparticles, suggesting that the results can lead to a new methodology for an easy size control of nanoparticles. However, a precise size selection has not been examined because the extraction experiments were conducted with a single-step procedure. In this paper, therefore, we will describe the notable features of systematic stepwise extraction of carboxylate-modified gold nanoparticles from an aqueous phase into toluene. For the first time, size-dependent phase transfer of gold nanoparticles on the basis of the surface reaction is presented.

Experimental Section

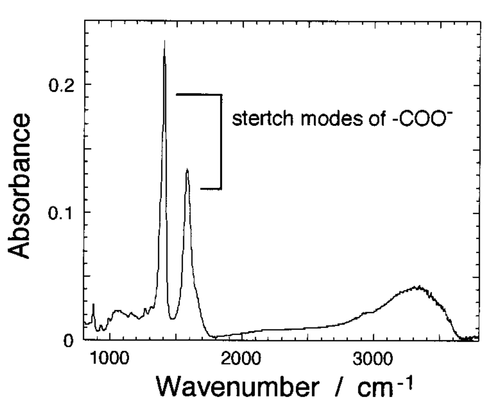
Chemicals. Hydrogen tetrachloroaurate tetrahydrate ($HAuCl_4{\cdot}4H_2O$; 99%), sodium borohydride ($NaBH_4$; >90%), mercaptosuccinic acid ($HSCH(COOH)CH_2(COOH)$, abbreviated as MSA; 97%), methanol (GR grade), ethanol (GR grade), and toluene (GR grade) were received from Wako Pure Chemicals (Osaka, Japan), and used without further purification. Tetraoctylammonium bromide ($[CH_3(CH_2)_7]_4NBr$, abbreviated as TOABr) was purchased from Aldrich (Milwaukee, WI), and was used as received. Pure water of high resistivity (>18 MΩ cm) was obtained by using an Aquarius GSR-200 (Advantec Co. Ltd., Japan) water distillation system.

Preparation of MSA-Modified Gold Nanoparticles. MSA-modified gold nanoparticles were prepared by the method reported earlier.[15] Briefly, 0.5 mmol of $HAuCl_4$ dissolved as an aqueous solution (0.121 M) and 0.5 mmol of MSA were at first mixed in methanol (100 mL) with bubbling of Ar gas, followed by the addition of a freshly prepared 0.2 M aqueous $NaBH_4$ solution (25 mL) at a rate of 7 mL/min under vigorous stirring. A dark-brown precipitate was produced, and then separated by centrifugation (10000 rpm). The precipitate was thoroughly washed with a water/ethanol (1:4) solution and ethanol to remove any inorganic and organic impurities. Finally, the precipitate was dried under vacuum (MSA−Au sample).

Size Separations by Stepwise Extraction. Stepwise extraction of water-soluble nanoparticles into an organic phase was conducted by an immiscible two-phase method. When 20 mL of an aqueous solution containing an MSA−Au sample of 5 mg and 40 mL of toluene containing TOABr ($[\mathrm{TOABr}] = 5.0 \times 10^{-5}$ M) were mixed and stirred vigorously, a yellow color was transferred into a toluene phase, indicating that the very small gold nanoparticles were transferred from an aqueous phase into toluene across the water/toluene interface (extract 1). After the toluene phase containing small gold nanoparticles was removed, 40 mL of a fresh TOABr/toluene solution ($[\mathrm{TOABr}] = 5.0 \times 10^{-5}$ M) was added again to the water phase, and then stirred vigorously. In this case, a dark-brown color was transferred into an organic phase, indicating that larger gold nanoparticles compared to those in extract 1 were transferred into toluene (extract 2). When the third extraction was conducted with the same procedure, a light-blue color was transferred into toluene (extract 3).

For comparison, the MSA−Au sample in a water phase was also extracted by a single-step procedure as follows: After mixing/stirring of 20 mL of an aqueous MSA−Au (5.0 mg) solution and 40 mL of TOABr/toluene solution ($[\mathrm{TOABr}] = 1.5 \times 10^{-4}$ M; this concentration is 3 times higher than that used under each multistep procedure), a dark-brown color was transferred into toluene (single-step extract).

Apparatus. Centrifugation of suspensions was conducted by using a Kubota-1720 centrifuge (Tokyo, Japan). Transmission electron microscopy (TEM) was conducted by using a Hitachi-8100 electron microscope operated at 200 kV. Absorption spectra were recorded on a Hitachi U-3210 spectrometer by using cuvettes with a 1 cm optical path length. FT-IR spectra were measured by using a Horiba FT-210 infrared spectrophotometer using a KBr disk dispersed with the powder sample. Elemental analyses of C, O, Au, S, and Na were conducted by using energy-dispersive X-ray spectroscopy (EDX) with an EDAX DX-4 system attached to the XL-20 scanning electron microscope (Philips Electronics, The Netherlands) operated under an acceleration voltage of 6 or 9 kV.



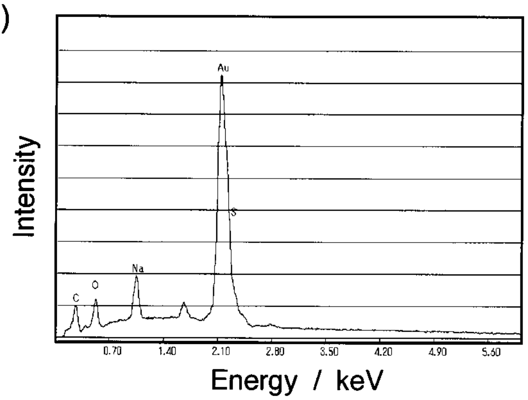


Figure 1. (a) FT-IR and (b) EDX spectra of the MSA−Au sample.

Results

According to the characterizations of the MSA−Au sample powder by elemental analysis and IR absorption spectroscopy similar to those reported previously,[15,16] gold nanoparticles were surface-modified by carboxylate−MSA moieties ($-SCH(COO-)CH_2(COO-)$, abbreviated as c-MSA) of 1.0×10^{-3} mol per g of the powder. Briefly, the FT-IR spectrum (Figure 1a) showed that MSA anchors on the gold surface through the S atom in the mercapto group (as revealed by the disappearance of the S−H stretch mode observed at 2548 cm^{-1}), and exists in the form of a carboxylate anion (as revealed by two characteristic peaks at 1404 and 1580 cm^{-1} for the stretch modes of COO−). Figure 1b shows the typical EDX spectrum of the MSA−Au sample excited by an electron beam (9 kV). Peaks for the elements C, O, Na, Au, and S were observed together with that for Si (1.74 keV). The Si peak is probably due to the EDX detector. Since the relative peak intensities were somewhat scattered depending on the observation regions, the elemental analyses by EDX were repeatedly conducted at various sample positions. Accordingly, we

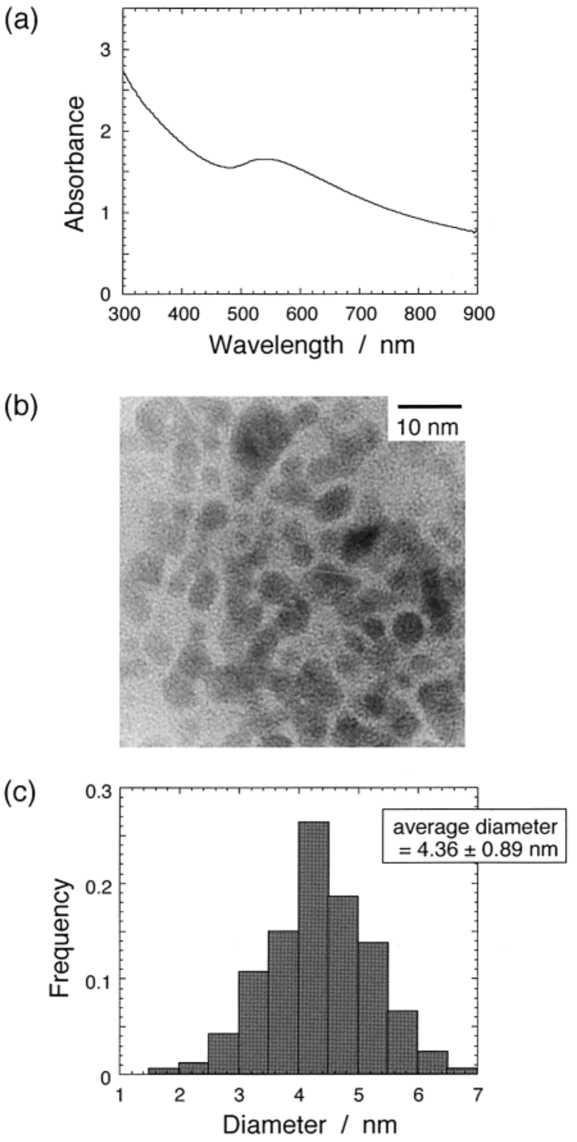


Figure 2. (a) Absorption spectrum of gold nanoparticles for the aqueous mother MSA−Au sample solution. (b) TEM image of the MSA−Au sample. (c) Particle size distribution of the MSA−Au sample.

could determine the molecular formula of the MSA−Au sample to be (c-MSA)Na_2Au_4, suggesting that the modifier component (c-MSA)Na_2 was contained at 19.7 wt % in the MSA−Au powder.

Figure 2a shows the absorption spectrum of the aqueous mother solution of the MSA−Au sample ([MSA−Au] = 5.0 mg/20 mL), in which the broad surface plasmon band appears at 540 nm. Parts b and c of Figure 2 show a TEM image and the particle size distribution of the MSA−Au sample, respectively. The mean particle diameter and the standard deviation were obtained as 4.36 and 0.89 nm, respectively. It is noteworthy that some nanoparticle aggregation occurred, reflecting relatively large absorbance in the longer wavelength regions in Figure 2a. By knowing the weight fraction of (c-MSA)Na_2 in the sample powder (19.7 wt %) and the bulk density of gold (19.3 g cm^{-3}), the average occupation area (S_0) of c-MSA on the gold surface can be estimated to be 0.12 nm^2.

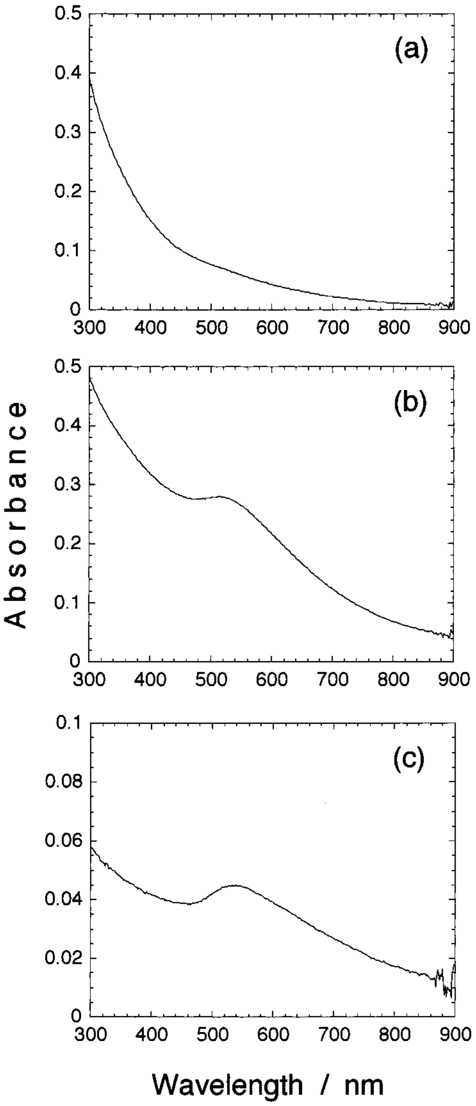


Figure 3. Absorption spectra of transferred gold nanoparticles in toluene obtained by the stepwise extraction procedures. (a), (b), and (c) show absorption spectra for extracts 1, 2, and 3, respectively.

Parts a, b, and c of Figure 3 show absorption spectra of gold nanoparticles for extracts 1, 2, and 3, respectively, which were fractionated by stepwise extraction procedures under [TOABr] = 5.0 × 10^{-5} M. Extract 1 showed no surface plasmon band in the absorption spectrum. On the other hand, extracts 2 and 3 showed a similar surface plasmon band (∼530 nm) in the absorption spectra.

To examine the particle diameter for each of them, TEM was conducted. Parts a, b, and c of Figure 4 show typical TEM images of gold nanoparticles for extracts 1, 2, and 3, respectively. The particle size distributions are also summarized in the insets in each figure.

Discussion

Stepwise Size-Selective Extraction. Our previous results on the single extraction of MSA-modified gold nanoparticles from an aqueous phase into toluene by using tetraoctylammonium cations (TOA^+) showed that (i) the amount of extracted nanoparticles increased

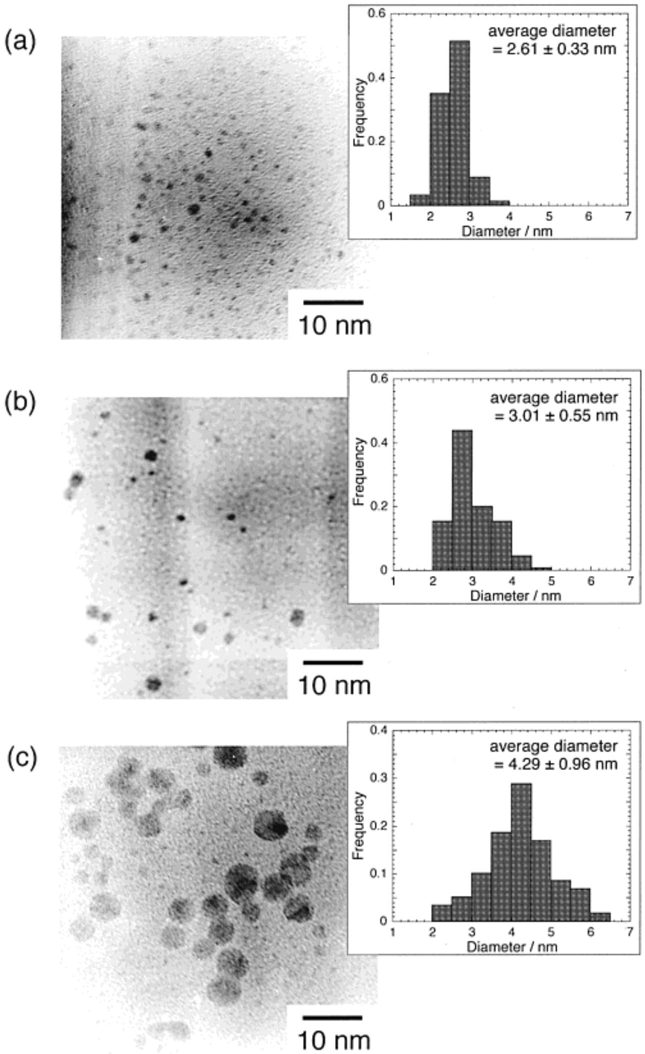


Figure 4. TEM images of transferred gold nanoparticles in toluene obtained by the stepwise extraction procedures. (a), (b), and (c) show the micrographs for extracts 1, 2, and 3, respectively. Particle size distributions for these extracts are also shown in the insets in each figure.

linearly with an increase in that of TOABr in toluene, and the extracts contained trace amounts of Br^- under these conditions and (ii) the extraction was saturated (maximum yield ~50%) when the amount of TOA^+ in toluene became larger than that of c-MSA in water, because large-sized nanoparticles (>4.5 nm in diameter) could not transfer across a water/toluene interface.[16,17] Therefore, we concluded that stoichiometric (1:1) ion-pair formation between carboxylate anions on a particle surface and tetraoctylammonium cations caused the phase transfer of MSA-modified gold nanoparticles across a water/toluene interface. It was possible to form an ion pair between two large TOA^+ moieties and one c-MSA moiety when two carboxylate anions in the c-MSA were almost perpendicular. As a result, a slight decrease in the average diameter has been observed accompanied by a slight narrowing in the size distribution. However, a precise size selection could not be achieved because the extraction experiments were conducted by a single-step procedure. Therefore, *stepwise* extraction experiments were conducted.

According to the absorption spectra for the fractionated solutions, extract 1 showed no surface plasmon band, indicating that small gold nanoparticles of less than ~2−3 nm diameter are considered to transfer into toluene.[18] However, comparing the spectra between extracts 2 and 3, damping of the surface plasmon band for extract 2 was larger than that for extract 3. It is demonstrated that damping of the surface plasmon band has been determined by the nanoparticle size under the same capping organic layer and the solvent because of the surface scattering of conduction electrons.[19] Thus, we can expect that an average particle diameter of gold nanoparticles for the extracted solution increases as extract 1 < 2 < 3.

Actually, an average diameter and a standard deviation of transferred gold nanoparticles also increase with an increase in the steps of extraction. For any case, average particle diameters decreased compared to that for the original MSA−Au sample. The results clearly show that stepwise extraction is quite effective for size selection of water-soluble gold nanoparticles. Therefore, we expect that this finding will lead to a new methodology for easy and precise size selections of surface-modified nanoparticles.

Comparison between the Single-Step and Stepwise Procedures. We can compare physical properties between the single-step and stepwise extraction procedures. Figure 5a shows the absorption spectrum for the single-step extract under the condition of [TOABr] = 1.5×10^{-4} M ($3 \times 5.0 \times 10^{-5}$ M) together with that of the calculated sum of extracts 1, 2, and 3. Similar absorption spectra could be obtained, indicating that the sum of the three absorption spectra quantitatively reproduces that for the single-step extract under [TOABr] = 1.5×10^{-4} M. The results show that the phase transfer of gold nanoparticles occurred under stoichiometric ion-pair formation between TOA^+ cations and c-MSA anions.

If we can determine the ratio of the number of particles in each extracted solution, a particle size distribution is calculated from Figure 4. For extracts 2 and 3, similar absorption spectra were obtained. The absorption spectrum of gold nanoparticles surely depends on the particle size and surrounding media of particles (the capping layer and solvent).[18,19] However, for small gold nanoparticles (<~5 nm in diameter) accompanied by a large damping of the surface plasmon band under the same surrounding media, the extinction coefficients near the surface plasmon band are similar.[19] Therefore, we here assume that the ratio of the number of particles corresponds to that of the absorbance around the surface plasmon band, and we could estimate the ratio to be 0.163 between extracts 3 and 2. On the other hand, since the absorption spectra were quite different between extracts 1 and 2, similar consideration cannot

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(17) Correctly, 95% or 5% of carboxylate anions on the gold nanoparticle were proved to be bound to TOA^+ cations or protons, respectively. For simplicity, however, we depict the stoichiometry as 1:1 ion-pair formation between carboxylate anions and TOA^+ cations. This approximation does not affect the following discussion.

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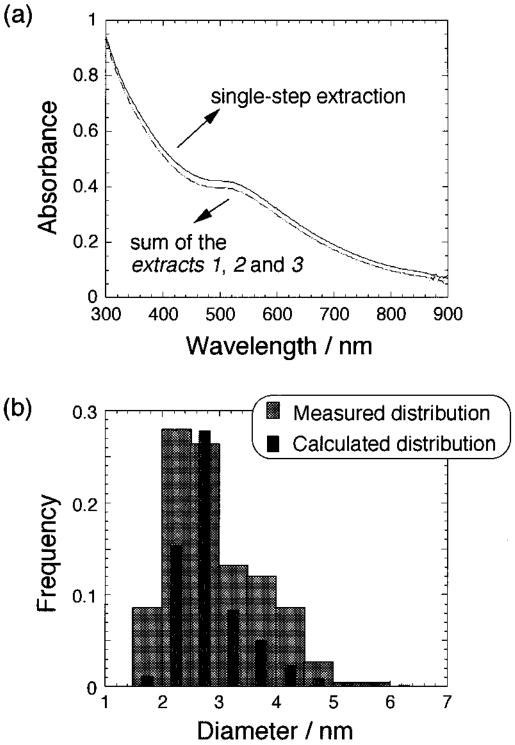

Figure 5. Comparison between the single-step and the stepwise extraction procedures. (a) Absorption spectra for the single-step extract and the sum of three extracts (extracts 1−3). (b) Particle size distributions for the single-step extract and the calculated sum of the three extracts.

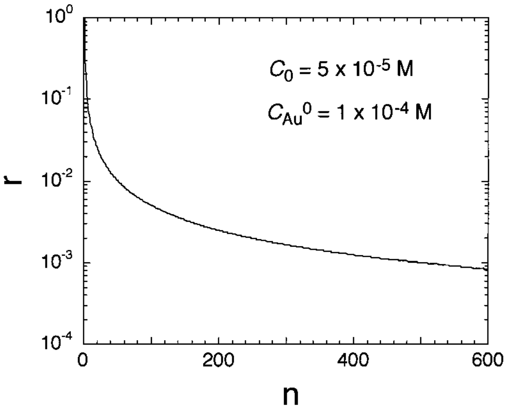

Figure 6. *n* dependence of the distribution ratio (*r*) of gold nanoparticles. The value *n* indicates the amount of carboxylate anions on one particle surface.

be applied. For extracts 1 and 2, all TOA^+ molecules in toluene are considered to contribute to the phase transfer of gold nanoparticles.[20] The ratio of the number of particles can be reduced to that of the inverse of the average surface area. Because the ratio of the average surface area of gold nanoparticles for extract 2 to extract 1 is calculated to be 1.33, we thus determined the ratios of the number of particles, extract 1:extract 2:extract 3 = 1.33:1:0.163.

Figure 5b shows the calculated particle size distribution by using these factors together with that obtained for the single-step extract. Note that the single-step extraction makes the particle size distribution narrow compared to that of the original MSA−Au sample. Although they show similar size distributions, slight differences between the measured and calculated distributions remain. The discrepancies are probably due to those in the number of counting nanoparticles between the single-step and the stepwise extracted solutions, and/or ambiguities of factors for reproducing size distributions.

Phenomenological Model for Nanoparticle Extraction. Size-selective fractionation of water-soluble nanoparticles can be explained qualitatively by considering phenomenological mass and charge balances for ion-pair extraction.[21] Since the MSA-modified gold nanoparticles can be regarded as a common molecular compound, we can consider that a single particle is one of the *n*-valent anions ($\mathrm{P_{Au}}^{n-}$) with $n\bullet\mathrm{Na}^+$ countercations. Furthermore, since the stoichiometric ion-pair formation between c-MSA anions on particle surfaces and TOA^+ cations causes the phase transfer, the extracted particle is considered to have the formula $\mathrm{P_{Au}}^{n-}\cdot n\mathrm{TOA}^+$). It is noteworthy that the value *n* corresponds to the amount of carboxylate anions on one particle surface, indicating that *n* directly relates to the particle size. For instance, a sphere nanoparticle of 2, 3, 4, or 5 nm in diameter possesses an *n* value of 105, 236, 419, or 654, respectively, which is calculated under $S_0 = 0.12\ \mathrm{nm}^2$.

In the extraction experiments, an initial concentration of TOABr (C_0) in toluene is assumed to be much lower than that of the nanoparticle ($C^{\mathrm{Au}}{}_0$) in water. Therefore, all TOABr molecules will change into $\mathrm{P_{Au}}^{n-}\cdot n\mathrm{TOA}^+$ in toluene after the extraction. Br^- anions are simultaneously transferred into water to keep the charge balance.[16] Assuming that TOABr and $\mathrm{P_{Au}}^{n-}\cdot n\mathrm{TOA}^+$ are insoluble in water, chemical species in the organic and water phases in an equilibrium state can be expressed as

organic phase:

$$n\mathrm{TOA}^+{}_{(o)} + \mathrm{P}^{n-}_{\mathrm{Au(o)}} \overset{K_{\mathrm{ip}}}{\longleftrightarrow} (\mathrm{P_{Au}}^{n-}\cdot n\mathrm{TOA}^+)_{(o)} \quad (1)$$

water phase:

$$\mathrm{Na}^+{}_{(w)} + \mathrm{P_{Au(w)}}^{n-} + \mathrm{Br}^-{}_{(w)} \quad (2)$$

where K_{ip} is the equilibrium constant of ion-pair formation. The suffix (o) or (w) implies the organic or water phase, respectively. Under the conditions, the distribution ratio (*r*) can be given as

$$r = \frac{C_{\mathrm{i(o)}}/n + C_{\mathrm{ip(o)}}}{C_{\mathrm{Au(w)}}} \quad (3)$$

where $C_{\mathrm{i(o)}}$, $C_{\mathrm{ip(o)}}$, and $C_{\mathrm{Au(w)}}$ represent the concentrations $[\mathrm{TOA}^+]_{(o)}$, $[\mathrm{P_{Au}}^{n-}\cdot n\mathrm{TOA}^+]_{(o)}$, and $[\mathrm{P_{Au}}^{n-}]_{(w)}$, respectively.

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(20) For extracts 1 and 2, the total amount of TOA^+ in toluene ($2 \times 2.0 \times 10^{-6}$ mol) was calculated to be lower than that of c-MSA (5.1×10^{-6} mol) in water. The experimental conditions are involved in those under a stoichiometric linear relationship between the extracted nanoparticles and the TOA^+ concentration as described in the first paragraph in the Discussion.

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According to the mass balances for C_0 and $C^{Au}{}_0$, we can obtain the following expressions:

$$C_0 = C_{i(o)} + nC_{ip(o)} \tag{4}$$

$$C^{Au}{}_0 = C_{Au(w)} + \frac{C_{i(o)}}{n} + C_{ip(o)} \tag{5}$$

Thus, combining eqs 3−5, r can be simply expressed as follows:

$$r = \frac{C_0}{nC^{Au}{}_0 - C_0} \tag{6}$$

Figure 6 shows the n dependence of the distribution ratio (r) for extraction calculated from eq 6 with $C_0 = 5.0 \times 10^{-5}$ and $C^{Au}{}_0 = 1.0 \times 10^{-4}$ M. With an increase in n (namely, with an increase in the nanoparticle size), r decreases, indicating that smaller particles can transfer more easily into an organic phase. For instance, the distribution ratio of nanoparticles 2 nm in diameter is 4 times larger than that of nanoparticles 4 nm in diameter. It is also expected that controls of extraction by the TOABr concentration under a small S_0 value are easier and more effective than those under a large S_0. Therefore, in the extraction experiments, the initially extracted solution in the stepwise procedures contains smaller nanoparticles compared to the following solutions. These phenomenological considerations qualitatively agreed with the results of our stepwise fractionation experiments.

Conclusion

It was demonstrated for the first time that stepwise extraction procedures were very effective for easy size selections of well-characterized, water-soluble gold nanoparticles. The initially extracted solution included smaller gold nanoparticles compared to the following extracted solutions, indicating that the smaller nanoparticles can transfer into an organic phase more easily than the larger ones. The physical properties of sum of the successive extracted solutions were similar to those of the single-step extracted solution. We expect that the multistep extraction leads to a new methodology for easy and precise size selections. The particle size dependence of the transferred gold nanoparticles could be qualitatively depicted by a phenomenological model considering the mass and charge balances for ion-pair extraction.

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