

Fractionation of Au Nanomaterials Using Selective Adsorption of a Long-chain Amidoamine Derivative

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Two-step phase transfer using C18AA molecules as the transfer agent was found to be very useful for the fractionation of large Au nanoparticles (NPs) (average diameter 7.7 nm), small Au NPs (average diameter 4.9 nm), and Au nanowires (NWs) according to their surface structural distinction. We also demonstrated that the use of organic solvents with different solubilities for C18AA was effective for the fractionation of Au nanocrystals.

Au nanomaterials are very important for potential applications in several technological fields of nanoscience, such as electrochemistry, electronics, magnetic storage, sensing, catalysis, and biotechnology.¹ The properties of metal nanomaterials are strongly dependent on their size and shape; therefore, effective fractionation and synthesis techniques are essential to obtain nanomaterials with desired properties. To date, fractionation methods, such as magnetic separation,² selective precipitation,³ filtration/difiltration,⁴ electrophoresis,⁵ and chromatographic methods,⁶ have been successfully applied to various nanoparticle (NP) systems to obtain a narrow size distribution. For example, it has been demonstrated that the density gradient method has powerful potential for the separation of NPs according to their chemical, structural, or size differences.⁷ Bai et al. have successfully applied this method to fractionate Au nanowires (NWs) from Au NPs.⁸

Very recently, we reported that Au NPs with an average diameter of 15.7 nm can be fractionated by a phase-transfer process between organic solvent and aqueous phases according to the difference in their surface structures.⁹ Interestingly, although the average particle size of the Au NPs in both chloroform and aqueous phases was the same, the former has a larger proportion of (111) crystal facets. The key material for the phase-transfer process is 1,9-bis(2-aminoethyl)-5-octadecyl-2,8-dioxodipropylenetriamine (C18AA, Figure S1, Supporting Information¹³),^{9–12} because C18AA molecules selectively adsorb on specific gold surfaces; C18AA molecules do not adsorb on (111) crystal facets but do adsorb on the (100) and (110) crystal facets of Au surfaces.⁹

Here, we expected that the size and shape selective fractionation of Au NPs would be possible by the use of the selective adsorption properties of C18AA, because the crystal facet content of Au nanocrystals is generally dependent on their size and shape.¹⁴ In this paper, we apply the phase-transfer fractionation method to a Au NW dispersion containing Au NPs as by-products and demonstrate that the method is very effective for the fractionation of Au NWs from Au NPs. Furthermore, we first demonstrate that changing the organic solvent to that with different solubility for C18AA is very useful for the further separation of Au nanocrystals.

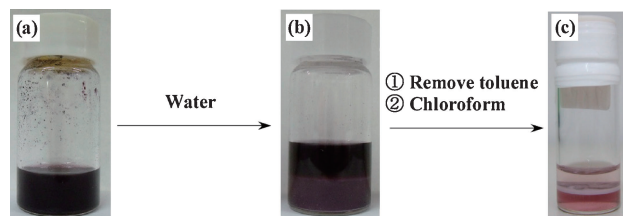


Figure 1. Dispersions of Au NPs and NWs before and after phase transfer.

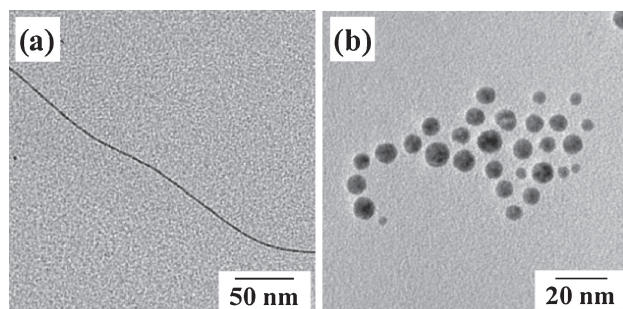


Figure 2. TEM images of as-prepared (a) Au NWs and (b) Au NPs.

A toluene dispersion of ultrathin Au NWs with diameters of 2–5 nm, lengths of a few hundred nanometers, and growth direction of the (111) crystal facet, together with a by-product of Au NPs with an average diameter of 6.3 nm and the relative standard size distribution of 27%, was prepared according to a previous report (Figures 1a and 2, Figure S2¹³).¹⁰ The toluene dispersion (5 mL) was gently poured onto water (5 mL), and the two-phase system was left to achieve a phase-transfer equilibrium of the products. After a few hours, the color of the aqueous phase had changed to magenta (Figure 1b), which indicated that Au NPs had been transferred from the toluene phase into the aqueous phase. UV–vis spectra of both phases were measured to examine the dispersion state of Au NPs in the phase-transfer process. The surface plasmon bands of Au NPs in toluene and in water appeared at 526 and 528 nm, respectively, which were almost the same peak position of the as-prepared Au NPs in toluene (Figures S3–S5¹³). This indicates that Au NPs were in the dispersed state in both toluene and water phases and were not aggregated during the phase-transfer process. No precipitation was observed in either of the phases, which confirmed that the loss of Au products was negligible during the phase-transfer process. To confirm the transfer of Au NPs, the products in both phases were examined by transmission electron microscopy (TEM) observation. TEM images showed that Au

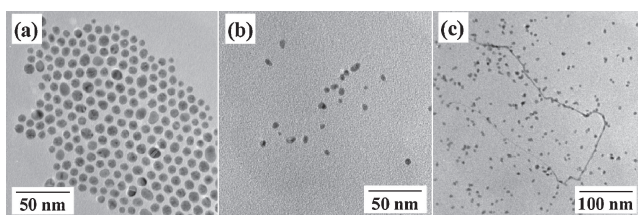


Figure 3. TEM images of (a) large Au NPs in the toluene phase and (b, c) Au NWs and small Au NPs in the aqueous phase.

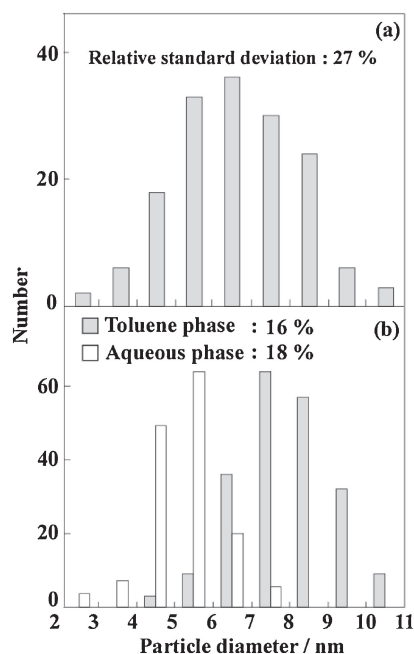


Figure 4. Particle distributions of Au NPs and NWs (a) before and (b) after phase transfer.

NWs were transferred into the aqueous phase, together with Au NPs, but some Au NPs remained in the toluene phase (Figure 3). The TEM images showed that the size of the Au NPs remaining in the toluene phase was larger than those in the aqueous phase. Figure 4b shows that the size distributions of NPs in both phases have normal distributions with different average sizes. The sum of the two histograms was similar to the original size distribution histogram of the as-prepared Au NPs with an average size of 6.3 nm (Figure 4a). The average diameters and the relative standard size distributions of the Au NPs in the toluene and aqueous phases were measured as 7.7 nm and 16%, and 4.9 nm and 18%, respectively. The values of the size distribution were smaller than 27% of the as-prepared Au NPs. These results indicated that the phase-transfer process was highly effective to divide the as-prepared Au NPs with a broad size distribution into two Au NPs groups with narrow size distributions (Figure 4). Namely, this suggested that it is possible to fractionate the Au NPs according to their particle size.

Au NPs in toluene and aqueous phases were examined using high-resolution TEM. The crystal forms of the larger Au NPs in the toluene phase were decahedral or icosahedral covered by (111) crystal facets, while those of the smaller Au NPs in the

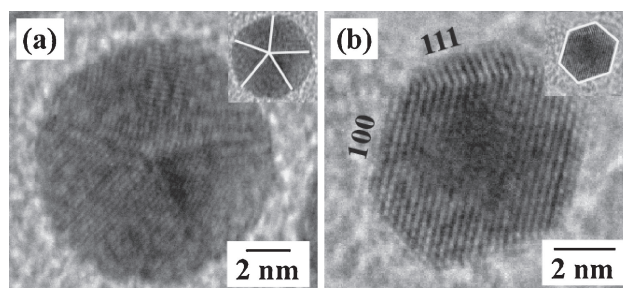


Figure 5. HRTEM images of Au NPs in the (a) toluene and (b) aqueous phases.

aqueous phase were composed of (111) and (100) crystal facets, such as truncated octahedral structure (Figure 5, Figures S6 and S7¹³).^{15,16} This indicates that the larger Au NPs in toluene have a larger proportion of (111) crystal facets than those in the aqueous phase. Thus, the adsorption density of C18AA for smaller Au NPs would be larger than that for larger Au NPs, because C18AA molecules preferably adsorb on (100) and (110) facets.⁹ Furthermore, C18AA can form a bilayer structure on (100) and (110) crystal facets, which causes the Au NPs to exhibit high hydrophilicity due to the high adsorption density of C18AA.⁹ In contrast, C18AA cannot form a bilayer structure on (111) crystal facets due to the low adsorption density. Therefore, smaller Au NPs would exhibit high hydrophilicity due to the formation of the C18AA bilayer structure on the (100) and (110) crystal facets. Consequently, the small Au NPs with high hydrophilicity are transferred into the aqueous phase. Thus, the difference in the crystal structure of Au NPs, such as decahedral and truncated octahedral is the origin of the fractionation of Au NPs into two groups (Figure 4b) by the phase-transfer process.

On the other hand, the side and both end surfaces of Au NWs consist of (100) and (110) crystal facets and (111) crystal facet, respectively. Namely, Au NWs have a large content of (100) and (110) crystal facets. Thus, Au NWs would also be transferred into the aqueous phase, together with the smaller Au NPs. Here, Au NWs and small Au NPs were both present in the aqueous phase, although Au NWs are thought to have a larger content of (100) and/or (110) crystal facets than the small Au NPs. We then attempted to separate these small Au NPs and Au NWs by the same approach. A dispersion (2 mL) was gently poured into toluene (2 mL) to maintain the phase boundary, and the two phases were left for 1 day; however, no color change was observed and no Au NPs and NWs were evident in TEM images of the toluene phase. The concentration effect of C18AA on the fractionation of Au NWs and small NPs was then examined, and a successive phase-transfer process using the same combination of solvents was found to be ineffective for the further separation of Au NWs and Au NPs.

Successive phase transfer was then attempted using chloroform, which is a good solvent for C18AA, rather than toluene, which is a poor (gelation) solvent for C18AA. Contact between the chloroform and the aqueous dispersion resulted in color change of the chloroform phase to magenta and the aqueous phase from magenta into pale magenta, as shown in Figure 1c. The TEM images shown in Figure 6 revealed that Au NPs were transferred to the chloroform phase and that Au NWs remained in the aqueous phase. It is worth noting that it was difficult to

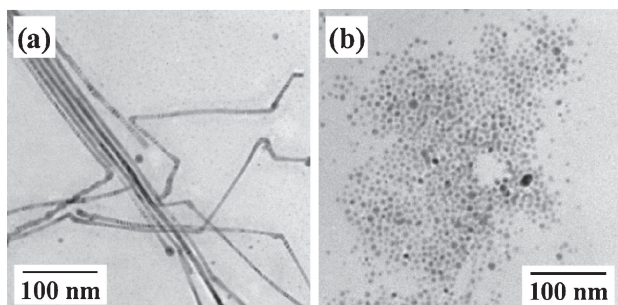


Figure 6. TEM images of (a) Au NWs in the aqueous phase and (b) Au NPs in the chloroform phase.

find Au NWs in the chloroform phase, and vice versa Au NPs in the aqueous phase. Furthermore, UV-vis spectra (Figure S8¹³) showed that the surface plasmon band at 526 nm arising from the small NPs was not observed in the spectra of the aqueous phase. Therefore, Au NWs were successfully separated from small Au NPs using different immiscible solvents. The mechanism for the separation is not clarified yet, so further investigation is required. A possible explanation is given as follows.

Chloroform is a good solvent for C18AA, so that contact between the chloroform phase and aqueous phase of C18AA containing dispersed Au NPs and Au NWs results in a large decrease in the C18AA concentration of the aqueous phase. Thus, the content of C18AA bilayer adsorbed on Au NPs and Au NWs is thought to decrease, which leads to a decrease in the hydrophilicity of these nanocrystals. Consequently, small Au NPs would transfer to the chloroform phase from the aqueous phase. However, Au NWs still have sufficiently high hydrophilicity to disperse them in the aqueous phase, because they have a large content of (100) and (110) crystal facets that enable formation of the C18AA bilayer structure.

In summary, this communication presents the separation of large Au NPs (average diameter 7.7 nm), small Au NPs (average diameter 4.9 nm), and Au NWs. The use of organic solvents with different solubilities for C18AA effectively resulted in the further separation of Au nanocrystals.

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