Size-Dependent Phase Transfer of Gold Nanoparticles from Water into Toluene by Tetraoctylammonium Cations: A Wholly Electrostatic Interaction

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Received: August 24, 2003; In Final Form: November 3, 2003

In this study, it is demonstrated that the tetraoctylammonium cation can be used directly as a phase-transfer reagent of negatively charged water-based gold nanoparticles. The transference is size-dependent and is based on a wholly electrostatic interaction.

The chemical synthesis and surface modification of metallic nanoparticles are significant for their utilization as building blocks in future nanodevices from both fundamental and applied consideration.[1] However, the as-produced nanoparticles are often soluble in either the aqueous phase or the organic phase but not both. Nevertheless, the ability to direct nanoparticles into various physicochemical environments (different liquid phase) in possible catalytic and sensoric applications is often needed. Thus, growing research efforts have been directed toward the study of the phase transfer of nanoparticles from an aqueous phase into an organic phase[2] (or an organic phase into an aqueous phase[3]). In regard to transference from the aqueous phase into the organic phase, nanoparticles must be rendered hydrophobic by complexation with molecules by covalent[2a−c] or electrostatic interactions.[2e−h] From a catalysis viewpoint, electrostatic-force-induced phase transfer is advantageous over covalent forces, because covalently bound molecules will adversely affect the catalytic reactivity of the nanoparticles.[4] Underwood et al. used a nonadsorbed polymeric comb to accomplish the transfer of gold nanoparticles from water into an organic solvent;[2a] however, the polymer is complex synthetically. In this letter, we observe that cationic tetraoctammonium (TOA$^+$) can also transfer water-based, electrostatically protected gold nanoparticles into the organic phase. Although TOA$^+$ has been used previously as a phase-transfer reagent of carboxylate-ω-functionalized alkanethiolate-modified gold nanoparticles from water into an organic phase,[2f−h] covalent bonds for both transferred and untransferred (original) particles still exist in their work,[2f−h] which would adversely affect their catalytic activities.[4] However, the gold nanoparticles used in this study are stabilized by physically bound anions, and both transferred and original nanoparticles are free of Au−S covalent interaction, which would not have an adverse affect on their catalytic activities. In addition, the phase-transfer process was observed to be size-dependent, which might help us separate nanoparticles with different sizes.

TOA$^+$ is a positively charged surfactant with four alkane chains and is commonly used as a phase-transfer reagent[5] of AuCl$_4^-$ from water into an organic phase in the well-established two-phase liquid/liquid synthesis of thiol-derivatized gold nanoparticles. In fact, the four alkane chains in TOA$^+$ provide enough hydrophobic forces so that negatively charged water-

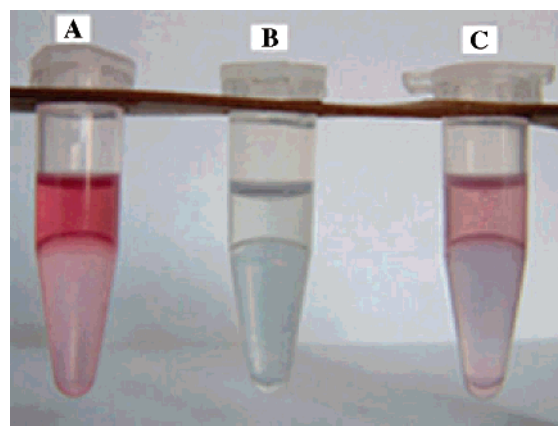* Author to whom correspondence should be addressed. E-mail: ekwang@ciac.jl.cn.

Figure 1. Photograph of gold nanoparticles after phase transfer from water (bottom layer) into toluene (top layer) by TOAB. Vial A shows the transference of 0.4 mL of 10^{-4} g/mL 5-nm aqueous gold nanoparticles into 0.4 mL of 0.13 M TOAB toluene solution; vial B shows a biphasic mixture of 0.4 mL of 10^{-4} g/mL 10-nm aqueous gold nanoparticles and 0.4 mL of 0.13 M TOAB toluene solution; and vial C shows a biphasic mixture of an aqueous colloidal solution (0.2 mL of 10^{-4} g/mL 5-nm gold nanoparticles + 0.2 mL of 10^{-4} g/mL 10-nm gold nanoparticles) and 0.4 mL of 0.13 M TOAB toluene solution.

based gold nanoparticles (free of alkanethiol modification) can also be pulled easily into toluene. To demonstrate this phenomenon, aqueous gold nanoparticles that were ∼5 nm in size were used[6] in the phase-transfer experiment. Typically, 0.4 mL of 0.13 M TOAB toluene solution was mixed with 0.4 mL of the 10^{-4} g/mL ∼5-nm aqueous gold nanoparticle solution, and, as a result, "red" gold nanoparticles move swiftly from the water layer (at the bottom) into the top toluene layer under stirring, as shown in Figure 1A. In the control experiment, a phase transfer never occurred under the same conditions, except in the absence of TOAB addition into toluene. This demonstrates clearly that it is the interactions between gold nanoparticles and TOAB molecules that result in the phase transfer. Figure 2 shows transmission electron microscopy (TEM) micrographs of ∼5-nm gold nanoparticles before and after phase transfer. A slight change in the nanoparticle size before and after the phase transfer was observed, which might be due to particle ripening. The UV−Vis spectra of the gold nanoparticles before and after phase transfer were also recorded, because nanoparticle aggregation and changes in the dielectric surrounding enviroment can be detected optically.[7,8] The ∼5-nm gold nanoparticles (in

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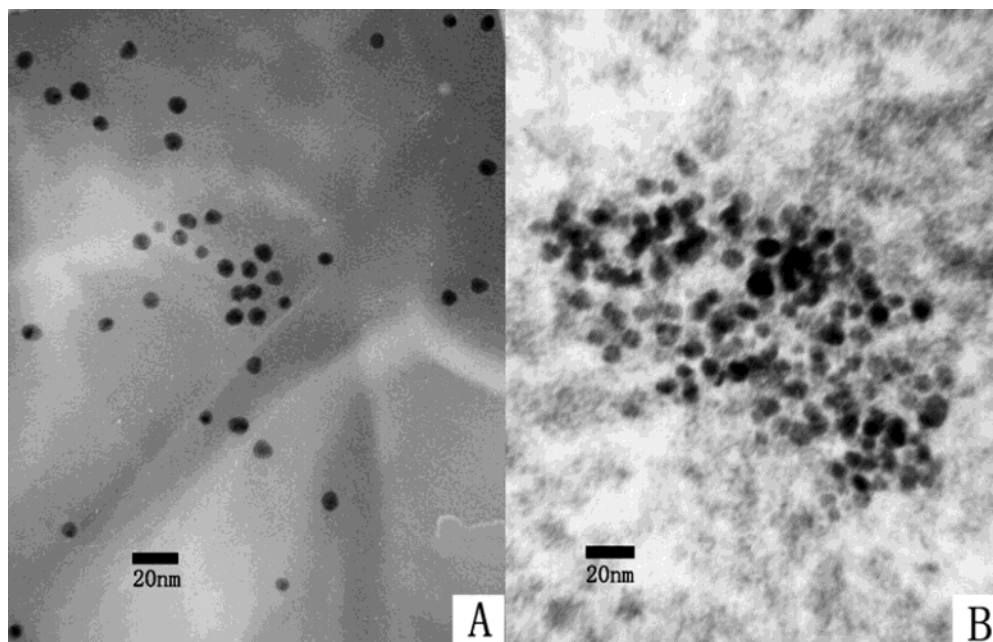*J. Phys. Chem. B, Vol. 108, No. 1, 2004* **25**

Figure 2. TEM micrographs of ∼5-nm aqueous gold nanoparticles (A) before and (B) after phase transfer into toluene.
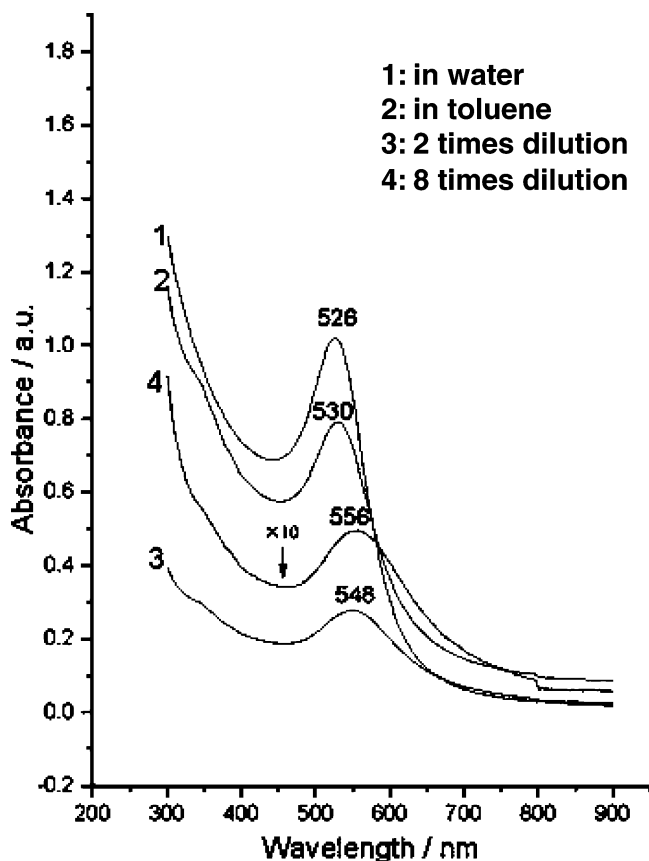

Figure 3. UV-Vis spectra of ∼5-nm gold nanoparticles in water (curve 1) and after phase transfer into toluene (curve 2). Curves 3 and 4 show spectral changes with dilution.

the surface plasmon band was observed after the transference of gold nanoparticles from water into toluene, which is indicative of an absence of nanoparticle aggregation or fusion.[7−9] Thus, UV−Vis spectral results provide solid evidence that TOA$^+$-induced phase transfer of gold nanoparticles yields well-dispersed nanoparticles in toluene.

Interestingly, it was also noted that the TOA$^+$-induced phase transfer of gold nanoparticles from water into toluene is size-dependent. Aqueous gold nanoparticles ∼10 nm in size[6] were also used in the phase-transfer experiment, following the same procedure as that for the ∼5-nm aqueous gold nanoparticles. Vigorous stirring of the biphasic mixture of ∼10-nm aqueous gold nanoparticles and TOA$^+$ toluene solution results in only a partial transfer of the gold nanoparticles from water into toluene. However, almost all the gold nanoparticles in toluene accumulate at the liquid/liquid interface instantaneously after several seconds, still giving a transparent toluene phase, as shown in Figure 1B. Simultaneously, the water phase at the bottom changes to light blue, which is indicative of nanoparticle aggregation. This indicates that the efficiency in the phase transfer of aqueous gold nanoparticles is critically dependent on size. To confirm further this, gold nanoparticles ∼2.6 nm in size were synthesized by NaBH$_4$ reduction, following Natan's strategy.[9] These as-prepared gold nanoparticles are electro-statically stabilized by citrate anions and exhibit an easier phase transfer into toluene than the aforementioned ∼5-nm gold nanoparticles, under the same TOAB concentrations. Also, we prepared gold nanoparticles ∼13 nm in size (stabilized by citrate anions) by Fren's method[10] and utilized them in similar phase-transfer experiments; as a result, these particles never were transferred into the toluene phase. These results indicate that we can separate gold nanoparticles with two dominant size distributions by virtue of size effects on phase transfer. Figure 1C clearly supports our speculation. In the case of a mixture of gold nanoparticles with two sizes (5 nm + 10 nm), the ∼5-nm particles move swiftly into toluene, whereas the ∼10-nm particles still reside at the liquid/liquid interface and in the water phase.

All water-based gold nanoparticles used in this study are electrostatically stabilized by tannic or citrate anions, with a

water) displayed a maximum absorbance in the surface plasmon band at ∼526 nm (see curve 1 in Figure 3). A 4-nm red shift in the wavelength of the surface plasmon band peak was observed after the phase transfer (see curve 2 in Figure 3) of the gold nanoparticles. The observed shift may result from the combined effect of the change in refractive index of the medium on transfer (from 1.33 to 1.47) and the exchange of the adsorbed molecules on transfer.[7a] It is also noted that almost no peak broadening of

CHART 1: Schematic Graph Showing the Formation of a Surface Ion Pair between $(C_8H_{17})_4N^+$ and Surface-Bound Anions. The Shell of Gold Nanoparticle is Composed of Hydrophobic Alkane Chains, which Renders the Gold Nanoparticles Hydrophobic to Result in Phase Transfer. For Clarity, the Relative Sizes of the Gold Core and Tetraoctylammonium Are Not to Scale.
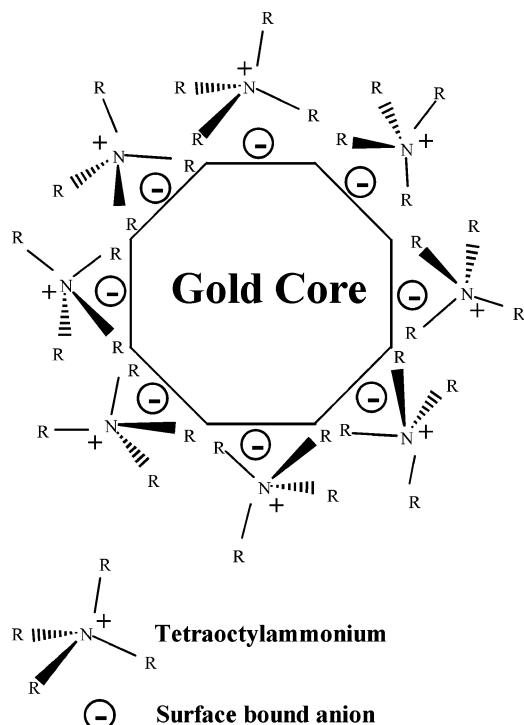
different surface chemistry from previous reports;[2f–h] thus, Au–S linkage is absent for both before- and after-transfer nanoparticles in this study. The formation of surface ion pairs based on electrostatically attractive forces is thought to be the cause of the TOA^+-induced phase transfer of gold nanoparticles. The mechanism is illustrated in Chart 1. Note that all the gold nanoparticles described previously are protected by negatively charged ions. These negatively charged ions will strongly attract positively charged TOA^+ cations to form surface ion pairs by electrostatically attractive interactions. The formation of surface ion pairs changes the protecting layer from being hydrophilic to being hydrophobic, which drives the phase transfer of gold nanoparticles from the water into the toluene. In regard to the size-dependent properties of phase transfer, it is thought to be due to surface-area-ratio effects: The smaller the nanoparticle size, the higher the surface-area ratio. This would result in larger coverage of TOA^+ on the particle surface (this speculation is consistent with the studies of Murray et al.,[11] who demonstrated that absorbent molecules have greater coverage on nanosized gold surfaces than on a planar gold surface); as a result, greater hydrophobic forces are expected for TOA^+ capping layers on the smaller gold core. In contrast, the TOA^+ layers on the larger gold core would provide hydrophobic forces that are too weak to pull the gold core into the toluene efficiently.

Remarkably, such electrostatic-force-induced phase transfer is different from previous covalent-force-induced phase transfer.[2a–c] The stability of extracted gold nanoparticles is largely dependent on the TOA^+ concentration. Curves 3 and 4 in Figure 3 show the absorbance spectral changes of transferred gold nanoparticles with dilution. The observed red shift and widening of the surface plasmon peak upon dilution indicate an aggregation of gold nanoparticles.[7,8] The observed concentration-dependent spectral responses demonstrate that the extracted nanoparticles are kinetically stabilized by TOA^+, in sharp contrast with thermodynamically stabilized alkylthiol-capped gold nanoparticles.[2a–c]

In a word, TOA^+ acted directly as a phase-transfer reagent of negatively charged water-based gold nanoparticles. Both transferred and original particles are electrostatically stabilized, which would not adversely affect their catalytic activities. The phase transfer is size-dependent, which might help us to narrow the size distribution of polydisperse gold nanoparticles. To some extent, this type of size-selective phase transfer is thought to be comparable to the well-known size-selective precipitation[12,13] in the distillation of gold nanoparticles.

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