

Phase transfer of Au nanoparticles using one chemical inducer: DDAB

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Abstract Au nanoparticles in aqueous medium were transferred to organic solution via a remarkably simple one-step route under the effect of phase transfer inducer dimethyldioctadecylammonium bromide (DDAB). The feature of our method is that only one reagent (DDAB) was added purposely for the phase transfer. This is different from the literatures, where two reagents were used for the phase transfer of Au nanoparticles. One is an Au nanoparticle stabilizer; the other is a phase transfer agent. The effect of the inducer DDAB concentration was checked, and it was found that the optimum concentration of DDAB was 1×10^{-5} mol dm⁻³ for phase transfer of Au nanoparticles. The organosol, Au nanoparticle, and phase transfer were characterized by UV–vis spectra, TEM, EDS, ED, and FT-IR. Molecular structure of quaternary ammonium salt was used to explain the unique effect of DDAB for the phase transfer of nanoparticles.

Keywords Phase transfer · Au nanoparticles · DDAB · Synthesis

Introduction

Owing to the fact that surface atoms have a very high surface area to volume ratio, nanoparticles hold many novel physical and chemical properties. This makes them to have possible future applications in electronics (Templeton et al. 2000), optics (Guoa et al. 1999), catalysis (Mukherjee et al. 2002), ceramics (Ray et al. 2002), and magnetic storage (Sun et al. 2000). Coinage metals nanoparticles such as Au, Ag, and Cu have been studied most extensively (Tzhayik et al. 2002; Wang et al. 1998). While studied earliest, Au nanoparticles still have great interest because of their potential application of cyto-labeling, catalysis, solid-state physics, and colloidal crystal applications. Much effort has been focused on the synthesis of Au nanoparticles in aqueous systems (Templeton et al. 2000; Mukherjee et al. 2002; Enustun and Turkevich 1963; Tan et al. 2002) and organic media (Brust et al. 1994; Zhou et al. 2002). Among these reports, Turkevich's method is a simple but effective one to fabricate monodispersed Au nanoparticle in aqueous medium.

One of the main challenges in the preparation and application of nanoparticles is the transfer of the particles into different physicochemical environments

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(Hirai et al. 1992; Hirai and Aizawa 1993). Organosols of nanoparticles are attractive because they can be used to obtain packed structures of nanoparticles by self-assembly. Under the effect of HCl, Au nanoparticles were transferred to toluene containing dodecanethiol from hydrosol (Sarathy et al. 1997a, b). Tetraoctylammonium bromide (TOAB) was also used as phase transfer agent to transfer mercaptosuccinic acid (MSA)-modified Au nanoparticles and glutathione, reduced form (GTR)-modified Au nanoparticles from hydrosol to toluene (Yao et al. 2001; Chen et al. 2001). Capping with valine, Au nanoparticles can be transferred from water into toluene by electrostatic coordination with octadecylamine (Kumar et al. 2000). Xanthate-capped Au nanoparticles were transferred from water into chloroform or dichloromethane by adding sodium phosphate (Tzhayik et al. 2002). On the other hand, the phase transfer of Au nanoparticles from organic to aqueous solution has been investigated because particles in organic solvents can be synthesized at relatively high concentrations (up to 1 M of reactant) than in aqueous solution (about 5×10^{-4} M of reactant). For example, TOAB-modified Au nanoparticles were transferred from toluene to water under the effect of 4-dimethylaminopyridine (DMAP) (Gittins and Caruso 2001). Through adjusting the dissociation states of carboxylate groups on the Au particle surface using HCl, the Au particles were redispersed from toluene into water because of the desorption of TOAB molecules from the particle surface, and the reversible transference of Au nanoparticles was achieved (Chen et al. 2001).

In the phase transfer of Au nanoparticles there should be two reagents at least. One is an Au nanoparticle stabilizer, such as dodecanethiol, MSA, GTR, valine, or xanthate. The other is a phase transfer agent like HCl, TOAB, octadecylamine, and DMAP. In this study, a facile, rapid method for Au nanoparticle phase transfer was reported. Only one reagent was used, without special stabilizer of nanoparticles. Au nanoparticles were synthesized according to the method of Turkevich et al. (Enustun and Turkevich 1963) by using citrate to reduce AuCl_4^- in aqueous solution. This particle can be transferred into organic solvent under the effect of DDAB. The novelty feature of our method is that only one rather than two reagents was added purposely for phase transfer. The effect of DDAB concentration on the phase transfer was investigated.

The Au nanoparticle chloroform organosol was used to self-assemble order monolayer on carbon film. UV-vis spectra, TEM, energy dispersive spectroscopy (EDS), electron diffraction (ED), and FT-IR were used to characterize the organosol, Au nanoparticle, and self-assembled monolayer of Au nanoparticle. The molecular structure with two long alkane chains and two short alkane chains of DDAB would be the reason of its unique effect to the phase transfer of nanoparticles.

Experimental section

All the chemicals, including KAuCl_4 (99.99%), sodium citrate (99.9%), dimethyldioctadecylammonium bromide (DDAB, 99.98%), HPLC grade solvents such as toluene, hexane, cyclohexane, and chloroform were obtained from Aldrich Chemical Co. and used without further purification. Distilled water was passed through a six-cartridge Barnstead Nanopure II purification train consisting of Macropure pretreatment. The Au nanoparticles were synthesized using sodium citrate as reductant. A 1.0 mL of 0.40 wt% KAuCl_4 aqueous solution was added to 19.0 mL of distilled water. The mixture was heated to boiling. Then 2.0 mL of 1.0 wt% sodium citrate aqueous solution was added during vigorous stirring. After continuous boiling for 30 min, it was cooled and diluted to 40.0 mL. A 5.0 mL of the prepared ruby red Au hydrosol was added into 5.0 mL organic solution (such as toluene, chloroform, cyclohexane, and hexane) of DDAB and shook for 30 s and the mixture was quiet. Two liquid layers formed and the color of the organic phase became red, meaning Au particles were transferred into the organic phase.

UV-vis spectra were taken on a Hitachi model U-3210 spectrophotometer, and the FT-IR spectra were recorded with a Perkin Elmer Spectrum 2000. For UV-vis analysis, the Au dispersion (aqueous or organic phase) is used as it is gotten, not diluted. TEM experiments and corresponding electron diffraction were carried out on a JEOL JEM2010 transmission electron microscope operated at 200 kV, and EDS was performed with an EDAX X-ray energy-dispersive analysis system attached to the JEOL JEM2010 transmission electron microscope. TEM samples were prepared on the 400-mesh copper grid coated with carbon film. A drop of the

nanoparticle solution was carefully placed on the grid and dried in air. The size distributions of the particles were measured from enlarged photograph of the TEM image.

Results and discussion

The KAuCl_4 solution without sodium citrate is pale yellow. By adding sodium citrate into the boiling solution, the color of the solution became blue-dark. This means that the Au particles formed at first are very big (Biggs et al. 1993). After 2–3 min, the color of the solution became ruby red, indicating that Au nanoparticles formed. Keep stirring and boiling for 30 min. The UV–vis spectrum of the Au nanoparticle hydrosol is given in Fig. 1a. The examination of the spectrum shows a little absorption at long wavelengths. But at shorter wavelengths the absorption increases to a maximum at 520 nm, falling to a value of about two-thirds of the maximum at 450 nm, and finally rising steadily in the ultraviolet to the limit of the measurements at 300 nm.

Figure 2 shows a TEM image of the Au particles obtained when a drop of as-prepared Au hydrosol was placed on a copper grid coated with about 10-nm amorphous carbon film and the solvent was allowed to evaporate. From this image, clear spherical nanoparticles can be observed; however, some of the particles are aggregated. This is a common problem with TEM sample in air drying which due to surface tension aggregates particles as drying occurs when

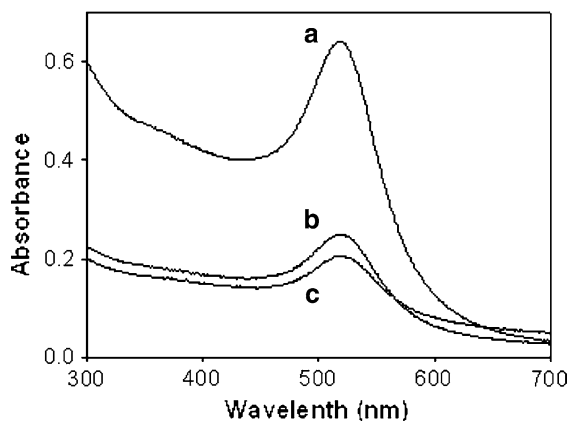


Fig. 1 UV–vis spectra of Au hydrosol before (a) and after phase transfer with (b) 6×10^{-6} M DDAB toluene solution, (c) 1×10^{-5} M DDAB toluene solution

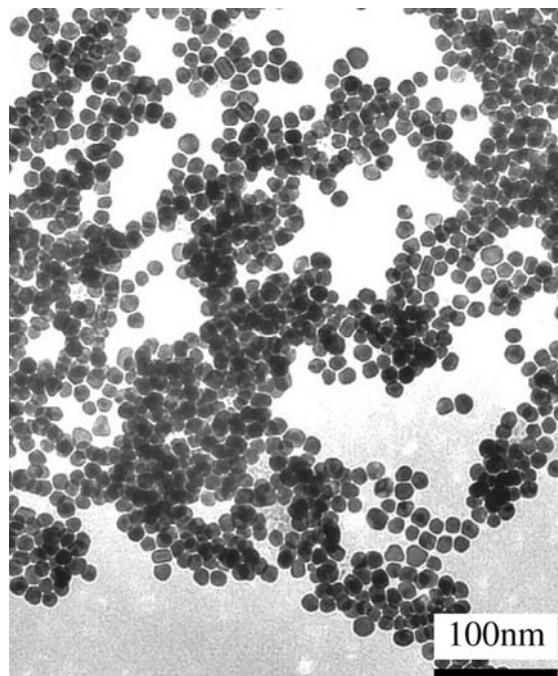


Fig. 2 TEM image of Au nanoparticles when a drop of Au nanoparticles hydrosol is dropped on carbon-coated copper grids

more concentrated gel was used. Maybe the extra ions and decomposing species of citrate were absorbed on the surface of Au nanoparticles and made the nanoparticles adhere each other.

To remove the extra ions and decomposing species, the conventional dialysis method can be used, but it requires several days and a large amount of distilled water (Zhao et al. 2000). On the other hand, phase transfer is an effective method to remove the extra ions. In this study, we try to transfer the Au nanoparticles from water to toluene. Figure 1 shows the UV–vis spectra of water phase and Fig. 3 shows the UV–vis spectra of toluene phase with different concentration of DDAB. In the mixture solution of Au hydrosol with toluene without DDAB, no Au particles were transferred into the toluene phase. The absorption peak of water phase at 520 nm is very high, like that of the original hydrosol. When 6×10^{-6} M DDAB was used, the absorption peak of water phase became smaller than that of original hydrosol as shown in Fig. 1b. This indicates that small portion of the Au particles was transferred from the hydrosol. When the DDAB concentration was increased to 1×10^{-5} M, the absorption peak at

520 nm was decreased further, meaning that more Au particles were transferred out. However, when the DDAB concentration was increased to 3×10^{-5} M, there were some white flocculates in the water phase, and the UV–vis spectrum of water phase could not be obtained. On the other hand, the absorption peak of toluene phase increased when the DDAB concentration increased from 6×10^{-6} to 1×10^{-5} M, as shown in Fig. 3. But as the DDAB concentration increased further to 3×10^{-5} M, no more increase of absorption peak was observed. Possibly, the extra DDAB leads to partial Au nanoparticle aggregation at the interface of water phase and toluene phase, because some colloid Au nanoparticle residue was found at the interface. Thus, the 1×10^{-5} M concentration of DDAB can be assumed as the optimum concentration for the phase transfer of Au nanoparticles. It was valuable to note that the position of absorption peak in toluene phase was 529 nm, which has a red shift of 9 nm comparing with that in hydrosol. This red shift can be contributed to the change of solvent from water to toluene of Au nanoparticles (Liz-Marzan et al. 1996).

In addition to toluene, the Au nanoparticles can also be transferred from hydrosol into other organic solvents such as chloroform, hexane, and cyclohexane under the effect of DDAB. Figure 4 shows the UV–vis spectra of organic solutions of Au nanoparticles obtained by phase transfer when 1×10^{-5} M DDAB was used. The absorption peak at 526 nm means Au nanoparticles have been transferred into the organic phases, and the position of absorption

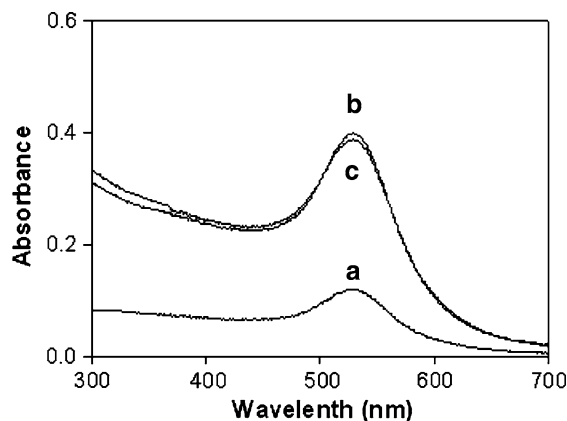


Fig. 3 UV–vis spectra of Au toluene organosol obtained by phase transfer with (a) 6×10^{-6} M DDAB, (b) 1×10^{-5} M DDAB, and (c) 3×10^{-5} M DDAB

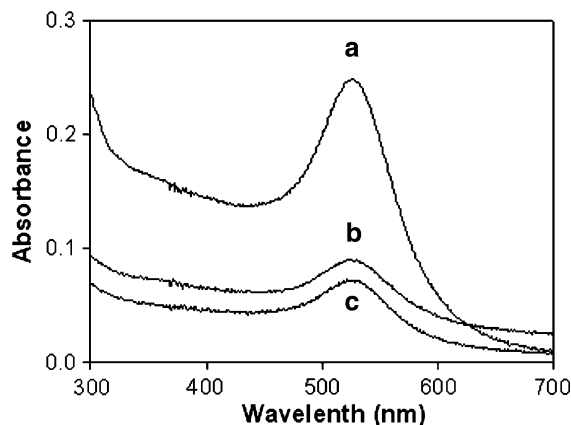


Fig. 4 UV–vis spectra of Au organosol obtained by phase transfer with 1×10^{-5} M DDAB (a) chloroform, (b) hexane, and (c) cyclohexane

peak is a little blue shift compared to that in toluene solution.

The transfer efficiency to organic phases is nice to be discussed. Table 1 shows the transfer efficiency from aqueous phase to organic phases that were calculated according to the height of absorption peak in Figs. 1, 3, and 4. The transfer efficiency was given by the rate of the absorption peak heights of organic phase after phase transfer and aqueous phase before phase transfer. It is clear that the highest transfer efficiency is arrived at 63% in toluene solution with 1×10^{-5} M DDAB. However, lower transfer efficiency was got in other solvents, such as chloroform, hexane, and cyclohexane. For example, transfer efficiency is only 5% in cyclohexane. So the effect of DDAB concentration will be investigated in detail for various organic solvents in the future.

After vacuum evaporation of the toluene solution of Au nanoparticles, a dry powder is obtained. The powder can be redispersed in organic solvents such as toluene, chloroform, hexane, and cyclohexane easily, meaning that the Au nanoparticles still retain their integrity. This is further supported by the TEM observation of self-assembled monolayer of Au nanoparticles from chloroform solution obtained by redispersion of dry powder, as shown in Fig. 5a. The self-assembled monolayer was formed as ordered domains, and particles in the domains were densely packed structures. A few voids were found, which could be attributed to the evaporation of solvent. The size distributions of the particles were measured from the enlarged photograph of the transmission electron

Table 1 Transfer efficiency of Au nanoparticle in various solvents

Organic phase	Concentration of DDAB	Transfer efficiency (%)
Toluene	6×10^{-6}	18
Toluene	1×10^{-5}	63
Toluene	3×10^{-5}	62
Chloroform	1×10^{-5}	40
Hexane	1×10^{-5}	14
Cyclohexane	1×10^{-5}	5

microscope image. The mean diameter of the Au particles is 12.5 nm, and the size deviation is 14.2%. The histogram of the size distribution is shown in the insertion of Fig. 5a. After phase transfer, the size distribution of nanoparticles is narrowed; especially the bigger particles were not transferred to the aqueous phase. This can be seen by comparing the TEM images of Au nanoparticles before and after the phase transfer (Figs. 2, 5a). We have tried to transfer Au particles with other sizes, and the preliminary results indicated that for the size range of gold nanoparticles in 4–20 nm, our method was worked out. For larger particles (>20 nm), which are difficult to stabilize in organic solvent due to the increasing van der Waals forces, further work is in progress to make sure the applicability of this method.

Energy dispersive spectroscopy confirmed the formation of Au nanoparticles. A randomly selected nanoparticle on the copper grid was analyzed as shown in Fig. 5b. The peaks attributed to Cu were caused by copper grid. Electron diffraction (ED) pattern of the Au nanoparticle is shown in Fig. 5c. It revealed dense ring patterns with d spacings of 2.34, 2.08, 1.43, 1.22 Å, which match the standard body centered cubic gold lines (JCPDS card, no. 04-0784).

Figure 6a is the FT-IR spectrum of solid sodium citrate. Two strong absorption peaks were observed at 1,394 and 1,575 cm^{-1} , characteristic of the RCO_2 symmetric and asymmetric stretches, which were clearly imposed on the FT-IR spectrum of Au nanoparticles (Fig. 6b). Figure 6d is the FT-IR spectrum of Au nanoparticle recorded when two drops of Au nanoparticles chloroform solution obtained by redispersion of dry powder was placed on the ZnSe plate and dried in air. FT-IR spectrum of DDAB is shown in Fig. 6c. The characteristic CH_2 vibration

peaks at 718, 1470, 2849, 2915 cm^{-1} as well as that of CH_3 at 2,956 cm^{-1} of DDAB were clearly observed in Fig. 6c. The surface-coated Au nanoparticle spectrum shows two peaks around 1,219 and 1,733 cm^{-1} , and the absorption peak around 1,470 cm^{-1} is weak compared to DDAB. Also, the peak of sodium citrate at 1,394 cm^{-1} becomes weaker and the peak at 1,575 cm^{-1} disappeared. This is interpreted as the complexation between the dimethyldioctadecylammonium cation and citrate anions on Au particle surfaces. Particularly, the peak contributed to methylene rocking around 718 cm^{-1} disappeared and a strong absorption peak appeared around 772 cm^{-1} . The peak values for the symmetric (d+) and antisymmetric (d-) CH_2 stretching vibrations can be used as a sensitive indicator of the ordering of the alkyl chain (Chen et al. 2001; Kumar et al. 2000; Nuzzo et al. 1987, 1990; Hosteler et al. 1996). The two peaks at 2,915 and 2,849 cm^{-1} in Fig. 6c imply that the number of gauche defects in the methylene chains is few. However, for DDAB-coated Au nanoparticles, the d- and d+ peaks at 2,920 and 2,851 cm^{-1} , respectively, indicate that the ordering of the alkyl chain at the surface of Au nanoparticle is a little worse than in solid DDAB.

Kimura et al. (Yao et al. 2001; Chen et al. 2001) used TOAB as phase transfer agent to transfer MSA-modified and GTR-modified Au nanoparticles from hydrosol to toluene. They reported that 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. In our case, no special stabilizer was used, so it is likely that citrate anions (Giersig and Mulvaney 1993) were absorbed on the surface of Au nanoparticle and prevented Au nanoparticles against aggregation in hydrosol. The ion-pair will be formed between citrate anions and dimethyldioctadecylammonium cations (DDA^+). By ion-pair formation, the phase transfer reagent, DDAB, makes the Au nanoparticles to have a smaller solubility in water and a larger solubility in chloroform and causes the phase transfer of the Au nanoparticles from aqueous medium to organic solution. In order to examine the effect of molecular structure of quaternary ammonium salt to the phase transfer of nanoparticles, other cationic surfactants including decyltrimethylammonium bromide ($\text{C}_{10}\text{H}_{21}\text{N}(\text{CH}_3)_3\text{Br}$), dodecyltrimethylammonium bromide

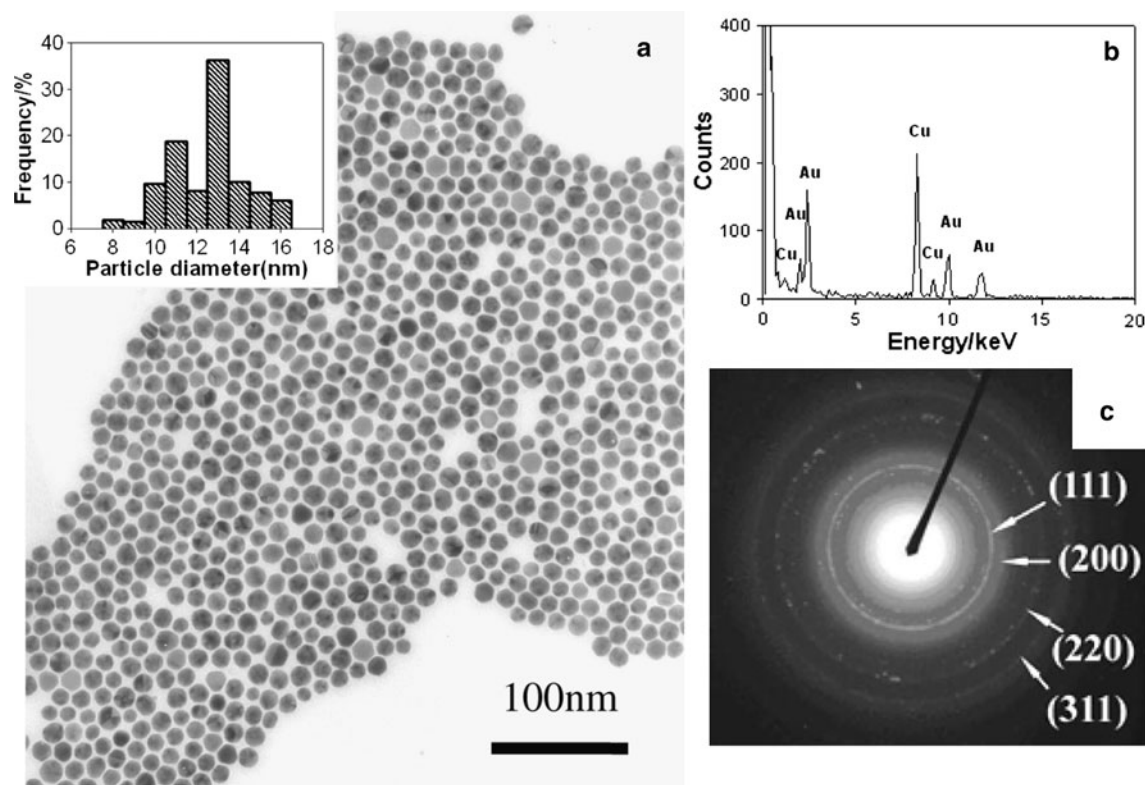


Fig. 5 **a** TEM of self-assembled monolayer of Au nanoparticles from chloroform solution obtained by redispersed of dry powder. **Insertion:** the size distribution of Au nanoparticles as

$d = 12.5$ nm and $\sigma = 14.2\%$. **b** EDS of an Au nanoparticle after phase transfer. **c** ED of an Au nanoparticle after phase transfer

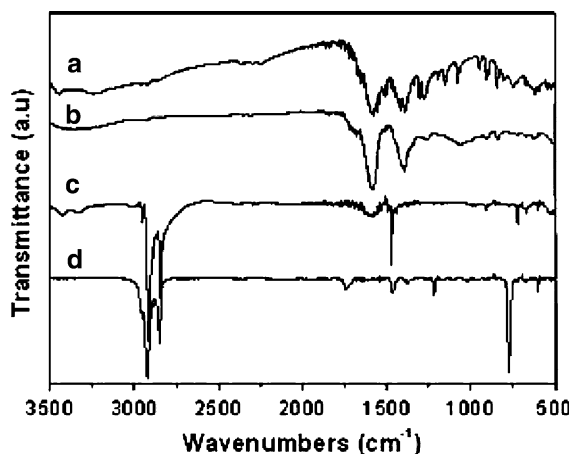
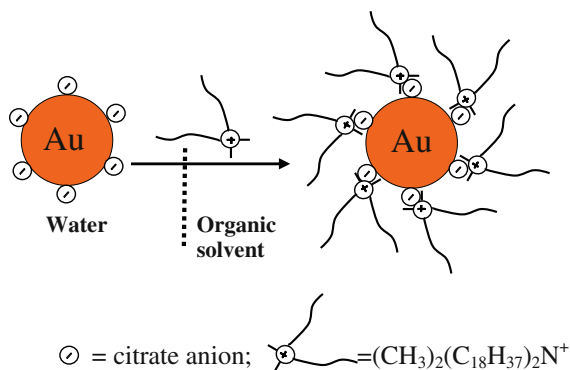


Fig. 6 FT-IR spectra of (a) sodium citrate; (b) Au nanoparticles before phase transfer; (c) DDAB; and (d) Au nanoparticles after phase transfer

($C_{12}H_{25}N(CH_3)_3Br$), cecyltrimethylammonium bromide ($C_{16}H_{33}N(CH_3)_3Br$, CTAB), and tetraoctylammonium bromide ($(C_8H_{17})_3NBr$, TOAB) were used as

phase transfer reagent instead of DDAB. In these cases, no transference of Au nanoparticles from hydrosol to toluene was observed. When their concentrations increased to 1×10^{-4} M, Au nanoparticles were found to aggregate on the wall of the flask. In the case of TOAB, the four octyl chains made it difficult to form ion-pair with anions adsorbed on the surface of nanoparticles because of the big steric hindrance. So the nanoparticles cannot be transferred. In the other cases of CTAB and other surfactants, although the three methyls made it easy to form ion-pair with anions adsorbed on the surface of nanoparticles, the only one long chain (cecyl, dodecyl, and decyl) cannot provide enough hydrophobic forces for phase transfer of nanoparticles. The best result is met in the case of DDAB, because there are two long alkane chains and two short alkane chains in one DDAB molecule. The two short methyls make it easy to form ion-pair with anions adsorbed on the surface of nanoparticles, while the two long octadecyls provide enough hydrophobic forces for phase transfer (Scheme 1).



Scheme 1 A schematic drawing on the phase transfer of Au nanoparticle between aqueous and organic phases with DDAB

Conclusion

Au nanoparticles in aqueous medium were transferred to organic solution, such as toluene, chloroform, hexane, and cyclohexane via a remarkably simple one-step route under the effect of DDAB using as a phase transfer inducer. No special stabilizer was needed; only one reagent (DDAB) was added purposely for the phase transfer. The DDAB concentration is a critical factor affecting the phase transfer, and 1×10^{-5} M of DDAB was found to be the optimum concentration for phase transfer of Au nanoparticles. The molecular structure with two long alkane chains and two short alkane chains of DDAB was used to explain the unique effect of DDAB to the phase transfer of nanoparticles.

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