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An Efficient Route to Prepare Metal Organosols by Phase Transfer Procedure

Ji Kuan ZHAO, Xiao CHEN*, Chun Jie YANG, Zhen Ming SUI,
Yong Cun CHAI, Guo Dong ZHANG, Jie LIU

Key Laboratory of Colloid and Interface Chemistry (Shandong University),
Ministry of Education, Jinan 250100

Abstract: Silver and gold organosols are easily prepared by transferring nanoparticles from aqueous phase into isooctane with high efficiency (>90%). Concentrations of sodium oleate and magnesium chloride have crucial effects on the transfer efficiency. Based on the UV-visible absorption spectra, TEM micrographs of nanoparticles, as well as molecular modeling calculation about the adsorption conformation of sodium oleate molecules, a possible phase transfer mechanism is proposed.

Keywords: Nanoparticles, organosol, phase transfer, sodium oleate.

Because of the simple and facile preparation of hydrophilic nanoparticles, direct phase transfer from metal hydrosol to organosol has become popular[1-3]. However, nanoparticles are easily aggregated at organic solvent/water interface during the transfer process [4, 5], resulting in low production of hydrophobic nanoparticles. Here we report an efficient method for the preparation of metal organosols by transferring silver and gold nanoparticles from water into isooctane in the presence of sodium oleate, using inorganic salts as inducers. The phase transfer efficiency (R) is estimated by the ratio of the maximum absorbance at the plasmon resonance peaks of organosol and hydrosol.

Silver hydrosol is prepared according to the previously described procedures[6]: 25 mL 2×10^{-3} mol/L $AgNO_3$ aqueous solution is added into 25 mL 4×10^{-3} mol/L $NaBH_4$ solution containing 0.5×10^{-3} mol/L sodium oleate under vigorous stirring at an ice-cold temperature. For the gold hydrosol preparation, 2×10^{-3} mol/L tetrachloroauric (III) acid solution is used instead of the silver nitrate.

5 mL isooctane is added to the hydrosol of the same volume and sodium oleate aqueous solution (1.25×10^{-3} mol/L) is used as emulsifying agent. After 1 h vigorous stirring, certain amount of inorganic salts $MgCl_2{\cdot}6H_2O$, NaCl, KCl, $NaH_2PO_4{\cdot}2H_2O$ is added to the emulsion to induce phase transfer independently. The stirring is kept for 3 h and then the mixture separates spontaneously into two liquid layers: upper colored organic phase of nanoparticles dispersion and lower transparent or colorless aqueous

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* E-mail: xchen@sdu.edu.cn

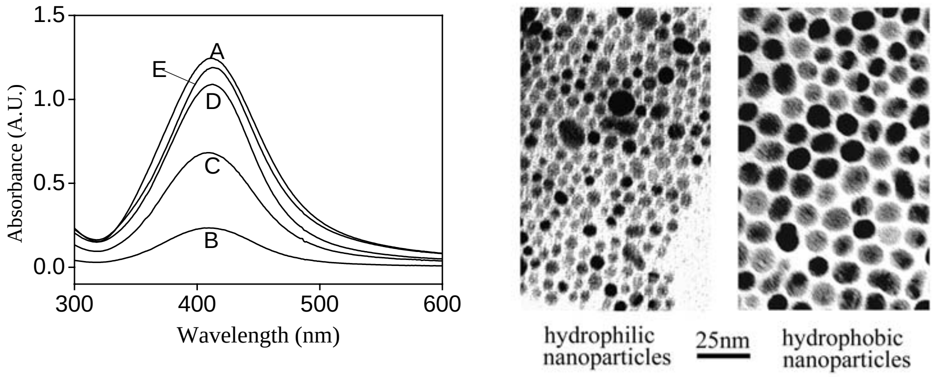
phase. All experiments are carried out at 20 ± 2 °C. UV-visible absorption spectroscopy and transmission electron microscopy (TEM) are utilized to characterize the nanoparticles before and after phase transfer.

Figure 1 shows the UV-visible absorption spectra and TEM micrographs of silver nanoparticles. The hydrosol displays a symmetric surface plasmon band at 411 nm with a maximum absorbance of 1.24 (curve A in **Figure 1**). TEM image shows the hydrophilic nanoparticles are nearly monodispersed, with the average diameter of 6.0 ± 2.3 nm. Fixing the concentration of $MgCl_2{\cdot}6H_2O$ at 0.1 g/mL, different sodium oleate concentrations (C_S) are used to carry out phase transfer. When no surfactant is added ($C_S = 0.25 \times 10^{-3}$ mol/L), there is a lot of brown Ag film deposited at the water/isooctane interface, and the obtained organic phase is pale yellowish with transfer efficiency as low as 28.2% (curve B in **Figure 1**). Increasing C_S to 0.34, 0.48, 0.66 and 0.75×10^{-3} mol/L, much more nanoparticles are transferred into the organic phase; the highest R (91.1%) is obtained at C_S of 0.66×10^{-3} mol/L, when a yellowish silver organosol is prepared. This phenomenon indicates that increasing oleate concentration in the aqueous phase favors the migration of silver nanoparticles from water to isooctane.

The four aforementioned inorganic salts are used to induce phase transfer separately. It is found that there will be no evident nanoparticles migration until the salt is added into the emulsion under vigorous stirring. When the concentrations of sodium oleate and inorganic salts are selected as 0.75×10^{-3} mol/L and 0.1 g/mL, the R values of 55.6%, 66.1%, 84.7% and 87.1% are obtained corresponding to $NaH_2PO_4{\cdot}2H_2O$ (curve C in **Figure 1**), KCl, NaCl and $MgCl_2{\cdot}6H_2O$ (curve D in **Figure 1**) respectively, suggesting the strongest inducing power perhaps due to the divalent nature of Mg^{2+}.

Based on the obtained results, different amounts of $MgCl_2{\cdot}6H_2O$ are utilized to further increase phase transfer efficiency, with oleate concentration of 0.66×10^{-3} mol/L. In the experiment, R reaches as high as 96.0% when $MgCl_2{\cdot}6H_2O$ is used at the

Figure 1 UV-Vis spectra of silver hydrosol (A) and organosols (B-E) and typical TEM micrographs of hydrophilic and hydrophobic nanoparticles



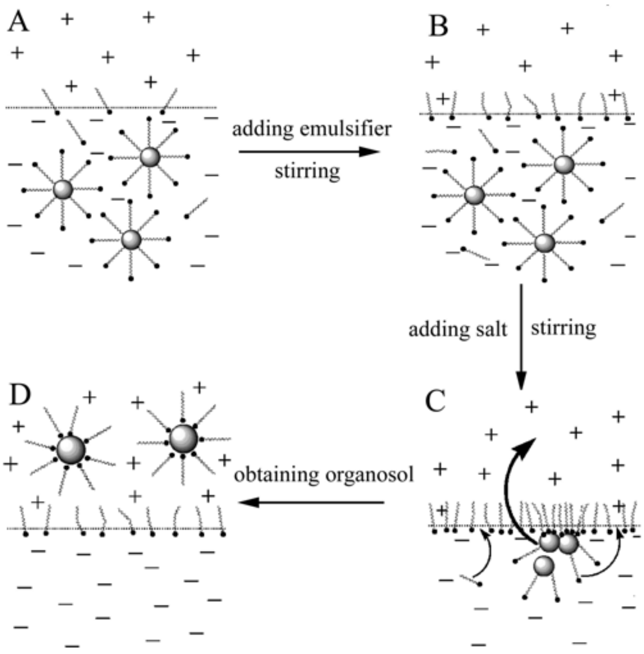
Organosols prepared respectively at (B) C_S of 0.25×10^{-3} mol/L, $MgCl_2{\cdot}6H_2O$ 0.1 g/mL; (C) C_S of 0.75×10^{-3} mol/L, $NaH_2PO_4{\cdot}2H_2O$ 0.1 g/mL; (D) C_S 0.75×10^{-3} mol/L, $MgCl_2{\cdot}6H_2O$ 0.1 g/mL; (E) C_S of 0.66×10^{-3} mol/L, $MgCl_2{\cdot}6H_2O$ 0.15 g/mL.

concentration of 0.15 g/mL (curve E in **Figure 1**), the corresponding wavelength of the plasmon peak is 413 nm. The average diameter of the prepared hydrophobic silver nanoparticles is 9.0 ± 1.7 nm, as shown in **Figure 1**. Compared with the hydrophilic nanoparticles, the hydrophobic ones exhibit increased diameter and a narrower size distribution, indicating some coalescence of small nanoparticles during the phase transfer process. The described method can be extended to transfer gold nanoparticles from water phase to isooctane with the highest efficiency of 97.8%. All prepared metal organosols are stable for at least one month with no evident changing.

In order to describe the phase transfer mechanism, molecular modeling calculations are performed with the software package CERIUS-2 (Accelrys), and polymer consistent force field is applied to model interactions among oleate, silver nanoparticles and solvent. The calculated adsorption energy results suggest that in aqueous solution double bonds serve as anchor for sodium oleate molecules to adsorb on the surface of silver nanoparticles, while carboxylate groups are preferred to adsorb on the nanoparticle surface in isooctane. This result is consistent with the infrared experimental data depicted in reference 4. A possible phase transfer mechanism of nanoparticles is therefore proposed as follows.

Oleate surfactant molecules will spontaneously adsorb at the water/isooctane interface to emulsify the two immiscible liquids. Higher surfactant concentrations in

Figure 2 Schematic map of the phase transfer of nanoparticles from water phase (-) into the isooctane (+)



(A) Mixture of isooctane and hydrosol; (B) Status after adding sodium oleate; (C) Status after adding inorganic salt; (D) Nanoparticles are pulled into isooctane.

aqueous phase will promote more oleate molecules to be arranged at the interface with hydrophobic tails extending to isooctane. Inorganic salt will decrease the critical micelle concentration (CMC) of surfactant solution and reduce the surface tension greatly[7]. So, adding magnesium chloride into the emulsion will decrease the solubility of sodium oleate in aqueous phase and prompt them to transfer to the interface. Some of the adsorbed molecules will also desorb from the particle surface. At the same time, nanoparticles will aggregate due to the screening charge effect of the counter ions. Under vigorous stirring circumstance and in the presence of inorganic salt, the oleate molecules distributed at the interface have great tendency to adsorb on the nanoparticles by carboxylate groups, which renders nanoparticles hydrophobic. When there are adequate oleate molecules arranged at the interface, nanoparticles will eventually be pulled into the isooctane by such adsorbing, as shown on the schematic map in **Figure 2**.

In conclusion, a simple and efficient method for transferring metal nanoparticles from aqueous phase into isooctane is established with sodium oleate as emulsifier. The concentrations of added surfactant and inorganic salts play an important roles to increase transfer efficiency. The addition of inorganic salts into the emulsion will decrease the CMC and solubility of the surfactant in aqueous phase, and promote oleate molecules to transfer to the interface. As a result, nanoparticles will be pulled into organic phase by the adsorption of sodium oleate *via* carboxylate groups.

Acknowledgments

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