안정한 은 콜로이드 용액을 이용한 나노 복합체 제조

이영호, 신승일, 오성근
한양대학교 화학공학과

Preparation of nano-composites using the stable silver colloid

Young-Ho Lee, Seung-Il Shin, Seong-Geun Oh
Department of Chemical Engineering and CUPS, Hanyang University

1. Introduction

In recent years, metal colloids have been used for optical applications in nanocomposites for centuries. Metal nanoparticles, especially silver, gold, and copper, have been the focus of great interest because of their unique optical properties. By incorporation of metal nanoparticles in glass and polymer, colored materials were obtained in which light was absorbed.

Various techniques were investigated for the preparation of nanocomposites comprising of metal and polymer. Many researcher prepared various polymer films containing silver nanoparticles and considered the influence of the particle size on optical properties of nanocomposites. C. Bastiaansen et al. prepared the various nanocomposite films, such as PVAL-gold, PE-gold, and PE-silver and analyzed their optical properties.(1-5) Yvo Dirix et al. prepared oriented arrays of silver nanoparticles in polyethylene and applied this composite to polarization-dependent color filters.(3) For obtaining colloidal latex spheres coated with uniform thin layers of silver, A. B. R. Mayer et al. introduced polystyrene microspheres coated with silver nanoparticles by several in-situ chemical reduction methods.(6) Q. Luca et al. reported the encapsulation of silver nanoparticles into a polymer shell via emulsion polymerization to produce a chemically stable system. 100 nm silver particles were coated with polystyrene and polystyrene/methcrylate and layers of varying thickness(ranging from 2 nm to about 10 nm) were produced.(7)

In this study, Silver-encapsulated polystyrene nanoparticles was prepared in emulsion system. Aqueous suspensions of unprotected silver and gold particles are easy to irreversible aggregation. This aggregation is traditionally overcome through the spontaneous adsorption on the particle surface of polymeric stabilizers. For dispersing silver nanoparticles into the organic solvent(herein, styrene), thiol-derivatized silver nanoparticles were prepared in one-phase system and these particles were dispersed in styrene.(8-9) And then, PS/Ag composite was synthesized in emulsion system. Existence of silver in samples, was confirmed by TEM pictures and FT-IR. TGA analysis and UV-vis spectroscopy were measured.

2. Experimental

2.1. Materials

Styrene monomer(99%, Aldrich) was distilled at 55°C at reduced pressure. Potassium peroxydisulfate (KPS, 99+%, Aldrich), Sodium dodecylsulfate(SDS, 99%(GC), Sigma), silver nitrate (99%, Kojima Chemical Co., LTD.), sodium borohydride (99+%, Aldrich), decanethiol (96%, Aldrich), and ethanol (99+%(GC), Fluka) were used as received. Water (18.2 MΩ cm) was purified with Rios and Milli-Q system (Millipore).

2.2. Preparation of the silver colloid dispersed in styrene

Thiol-derivatized silver nanoparticles were prepared by one-phase synthetic route( ). 5 mM of $AgNO_3$ was dissolved in ethanol containing 5wt% of water and then 12.5 mM of decanethiol was added dropwise to the solution with vigorous stirring and then after stirring for 30 min. Saturated $NaBH_4$ aqueous solution was added dropwise to the mixture for 1h and then after stirring for 2h. The solution turned brown immediately with vigorous stirring. The obtained suspension was centrifuged at 3000 rpm. Supernatant was removed and the precipitates were washed with ethanol and acetone to remove remaining free thiols. This centrifugation, decantation and redispersion cycle was repeated several times. Finally, obtained precipitates were dried in a incubator at 40°C over 2 days.

Thiol-derivatized silver nanoparticles were dispersed in styrene and 500 ppm of the silver colloid in styrene was obtained.

2.3. Preparation of Ag/PS composite

Two-neck round bottom flask was charged with 8g of styrene containing 500 ppm(w/w) of silver, 2g of SDS, 0.08g of KPS and 90g of water. The reaction mixture was stirred for 30min until it formed stable emulsion at room temperature and then placed into a thermostatted at 45°C. The polymerization proceeded for 24h under nitrogen atmosphere. At the end of the reaction, small amount of diluted hydroquinone solution was added to stop polymerization. Excess amount of methanol was added into the PS dispersion to precipitate PS powder by breaking the hydorphilic-lyphophilic balance of the system. The precipitates were collected with glass filter and washed four times with methanol to remove unreacted chemicals and SDS. Then, precipitate of PS particles was dried in an incubator under the vacuum for 72h at 40°C.

2.4. Characterizations

The size and morphology of the obtained particles were investigated by Transmission Electron Microscopy(JEOL model, JEM2000-EX II). Samples were prepared by dropping highly diluted latexes on the carbon coated copper grid and dried in a desiccator at room temperature. UV-vis spectroscopy (UNICAM8700 SERIES UV-Vis spectrophotometer) and FT-IR spectra (Nicolet, Magna-IR 760) were recorded. TGA thermograms were recorded using Universal V2.6D TA Instruments. The programmed heating rate and N_2 flow rate were 10°C min^{-1}, 80 ml min^{-1}, respectively.

3. Results and Discussions

3.1. Thiol-derivatized silver nanoparticles

As shown in Figure 1, distinct peak is observed at 425 nm in the UV-vis spectra of thiol-derivatized silver nanoparticles dispersed in cyclohexane. Particle size is below 10 nm. Figure 2 shows stable silver colloid in styrene. In Figure 2-(A), upper phase is dispersion of silver nanoparticles in styrene and lower phase is pure water. After vigorous stirring, silver particles were not detected in water.

3.2. PS/Ag nanocomposite

Silver nanparticles in PS sphere was detected by TEM image and FT-IR. Samples were compared with bare PS in TGA thermodiagrams.

4. Acknowledgement

This reaserch was funded by Center for Ultramicrochemical Process Systems.

5. Reference

(1) Heffels W., Friedrich J., Darribère C., Teisen J., Interewicz K., Bastiaansen C., Caseri W., Smith P., *Recent Res. Devel., Macromol. Res.* **2**, 143 (1997)
(2) Bastiaansen C., Caseri W., Darribère C., Dellsperger S., Heffels W., Montali A., Sarwa C., Smith P., Weder C., *Chimia* **52**, 591 (1998)
(3) Dirix Y., Bastiaansen C., Caseri W., Smith P., *Adv. Mater* **11**, 223 (1999)
(4) Dirix Y., Bastiaansen C., Caseri W., Smith P., *J. Mater. Sci.* **34**, 3859 (1999)
(5) Dirix Y., Bastiaansen C., Caseri W., Smith P., *Mater. Res. Soc. Symp. Proc.* **559**, 147 (1999)
(6) Mayer, A. B. R.; Grebner, W.; Wannemacher, R. J. *Phys. Chem. B.* **101**, 189 (1997)
(7) Luca Q., George C. *J. Am. Chem. Soc.* **121**(45), 10642 (1999)
(8) Brust M., Fink J., Bethell D., Schiffrin D.J., and Kiely C. *J. Chem. Soc., Chem. Commun.* 1655 (1995)
(9) So Young K. and Kwan K. *Langmuir* **14**, 226 (1998)

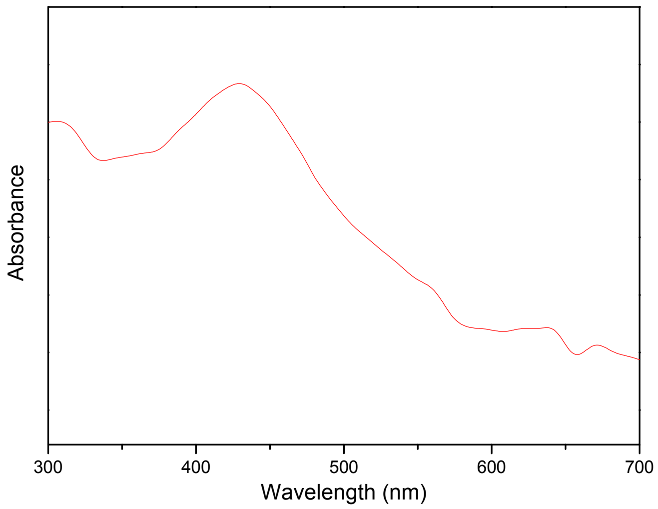

Figure 1. UV-vis absorption spectra of decanethiolate-derivatized silver nanoparticles in cyclohexane

Figure 2. Pictures of silver colloids in styrene
(A) upper : silver colloid in styrene; lower : water
(B) Silver colloid in styrene