A method for synthesizing the core (Ag)/shell (PSt) composite nanoparticles

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Abstract

Core–shell composite materials have been widely used in many fields. In this paper, the core (Ag)–shell (PSt) composite nanoparticles have been successfully fabricated in microemulsions at ambient pressure. Firstly, Ag nanoparticles with about 60–100 nm in diameters were synthesized by reducing silver nitrate by ascorbic acid, and then, styrene polymerized at the surface of Ag nanoparticles by K2S2O4 initiator in microemulsion solutions. The Ag/PSt core-shell composite nanoparticles were identified by transmission electron microscopy (TEM), X-ray powder diffraction (XRD) and infrared spectra (IR). Results show that Ag-core nanoparticles were coated with ultra thin PSt shell with thickness of about 3–6 nm.

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1. Introduction

Core/shell composite materials are consisted of a core structural domain covered by a shell domain [1], which may be composed of a variety of materials including polymers, inorganic solids, and metals [2,3]. Such materials have been widely used in some fields because the integrated properties of such materials are better than those in single-component counterparts [4].

Silver (Ag) is a promising candidate in the application for optics [5], electronics [6], catalysis [7], and surface enhanced Raman scattering [8,9]. The core (Ag) has been prepared with the shells of polymer to protect the noble metal silver, which is hoped to be widely used as antibacterial materials, self-depuration materials, and activator etc. For example, as a promising conductor, silver with large size (~100 nm) is widely used as fillers to fabricate percolative composite capacitors [10]. The coated polymer shells not only prevent the segregation of Ag particles, but also produce excellent compatibility between the fillers and the polymer matrix [10]. So far, the various silver core-shell composite materials have been successfully synthesized, for example, polystyrene (PSt) spheres coated with Ag [11,12], Ag/C core-shell-structured nanoparticles [13], and Ag/PSt core-shell nanoparticles [14]. However, few reports about silver nanoparticles coated by ultra thin polymers have been found.

In the present paper, we will report a new method for synthesis of the core (Ag)/shell (PSt) composite nanoparticles in microemulsions at ambient pressure.

2. Experiments

2.1. Preparation of core (Ag)–shell (PSt) nanoparticles

Ammonia was added to AgNO3 solution to form ammoniac silver solution. Water-soluble polymer poly (N-vinylpyrrolidone) (PVP) was used as a stabilizer. The mixture was filled in a flask with ethanol. Ascorbic acid was then added as a reduction. Thus, the Ag nanoparticles can form at different temperatures.

Ag nanoparticles were collected and re-dispersed into fresh water, then the aqueous solution was added into a cyclohexane solution of n-butanol and stearic glyceride to form microemulsion solutions. Styrene monomer and K2S2O4 were added to the microemulsion solutions. The reaction temperature was fixed at 80 °C. Then Ag nanoparticles coated by PSt can be obtained after stirring for about 2 h.

2.2. Characterization

XRD measurement was performed on X'pert PRO X-ray diffractometer of Panalytical using Cu Kα radiation (λ = 0.1541 nm). The sample for XRD analysis was prepared by centrifuging the mixture and finally drying the obtained precipitates. The transmission electron microscopy (TEM) was performed on a Tecnai F30 transmission electron microscope with an accelerating voltage of 20 kV. The sample for TEM observation analysis was obtained by sonicating the synthesized sample in ethanol for 10 min and placing a drop of the dispersed solution onto a carbon-covered copper grid and then evaporating in air at room temperature. The infrared spectra (IR) were recorded in the range of 500–4000 cm⁻¹ on an Alpha Centauri FT/IR spectrophotometer using KBr pellets.

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3. Results and discussion

Fig. 1 shows TEM image of core (Ag)/shell (PSt) composite nanoparticles obtained by the present method. It can be seen that the nanospheres show the uniform core-shell structure with the particle size of about 60–100 nm in diameter, where the dark core is surrounded by the bright shell with thickness of about 3–6 nm. For the electronic density of silver is much larger than that of polystyrene, therefore, the bright edge of the particles is ascribed to the polystyrene shell. However, the size control of Ag particles in our experiment is not so good. The average size of the particles is from 60 nm to 100 nm. The reason may be due to the inhomogeneity of the concentration during adding the reducer. Further work on the controlling of size distributions, such as microemulsion techniques, will be submitted in a separated paper.

The as-prepared pure Ag nanoparticles and core (Ag)/shell (PSt) composite nanoparticles were identified by XRD, as shown in Fig. 2, where all the five broad peaks at $2\theta = 38.2, 44.4, 64.6, 77.6,$ and $81.6$ correspond to the (111), (200), (220), (311), and (222) reflections of cubic structure of metallic Ag, respectively. The broader weak diffraction peak in small diffraction angle in Fig. 2b may arise from the amorphous polymer of PSt.

The IR spectrums of pure Ag and Ag/PSt nanoparticles were given in Fig. 3 to confirm the structure of the composite nanoparticles. Fig. 3(a) shows the IR spectrum of the pure Ag nanoparticles, where the band may originate from the stabilizer (PVP) and the impurity of KBr. By comparing Fig. 3(a) with (b), the band in Fig. 3(b) at 690 and 760 cm$^{-1}$ ascribe to the bending vibration of monosubstituted benzene, and the band at 3030 cm$^{-1}$ represents to the C–H stretching vibration at the phenyl, which confirms the existence of polystyrene.

4. Conclusion

The core (Ag)/shell (PSt) composite nanoparticles have been successfully fabricated. The size of nanospheres is respectively about 60–100 nm in diameter and about 3–6 nm in shell thickness. This general procedure is expected to apply in different metal polymer core-shell hybrid composite nanoparticle.

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