Preparation and Characterization of Silica/Polypyrrole Core-Shell Colloidal Particles in the Presence of Ethanol as the Cosolvent

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ABSTRACT: The silica/polypyrrole core-shell composites were fabricated by *in situ* chemical polymerization of pyrrole monomer on the surface of the silica spheres. Silica sol particles with narrow size distributions were prepared by hydrolysis of tetraethoxysilane with sol–gel method. Polypyrrole shell was obtained by chemical polymerization of pyrrole monomer on the surface of the silica spheres in the water–ethanol mixture. It can be seen from the experiment, with the adding of small amount of ethanol cosolvent to the aqueous reaction solution, a uniform coating of polypyrrole appeared on the surface of silica. The core-shell morphology of composite particles prepared with variation ethanol adding amount was analyzed by TEM. Meanwhile, the conductivity of the core-shell composite is found to be enhanced apparently compared with those prepared from pure aqueous system. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3270–3274, 2012

Key words: polypyrroles; silicas; core-shell polymers; ethanol

INTRODUCTION

Conducting polymeric materials have been extensively studied in recent years because of their mixed properties of being an organic polymeric material and having a reasonably high conductivity that can be reversibly modulated over 15 orders of magnitude by controlling the dopant type and level.[1] Among conducting polymers, polypyrrole (PPy) is one of the most extensively studied materials due to its good electrical conductivity, redox properties, environmental stability, and easy preparation by both electrochemical and chemical approaches in various organic solvents and in aqueous solution.[2,3] Potential applications of PPy include electrostatic dissipation, anticorrosion coatings, drug delivery, batteries, and solar control.[4–6] However, like many other conductive polymers, PPy is infusible, insoluble, and suffers from poor processability, mainly because of its strong inter chain interactions and some degree of crosslinking.[7] Preparation of colloidal dispersions has been considered as an important method to improve the processability of PPy. Since 1986, various research groups have reported the preparation of colloidal dispersions of PPy.[8–11] One of the new interests in the generation of stabilized colloidal PPy latices is the preparation of silica/PPy composites.[12–16] In this approach, silica nanoparticles were used preferably because of their simple and well-known method of synthesis, wide range of applications, and the commercial availability. However, the conductivity of this kind of composites was low because of the insulating silica nanoparticles accumulated around the conducting PPy.

To increase the conductivity of the composites, silica should be coated completely with conductive PPy to core-shell silica/PPy composite particles. The present work is an investigation on PPy-coated silica particles synthesized in the presence of ethanol as the cosolvent. Ethanol is supposed to enhance the solubility of pyrrole in the continuous phase and then more pyrrole can polymerize on the surface of silica particles. We synthesized monodisperse silica particles with a diameter about 150 nm by base-catalyzed hydrolysis of tetraethoxysilane (TEOS) at the first step, as described by Stober et al.[17] At the second step, the silica/PPy core-shell composites were fabricated by *in situ* chemical polymerization of pyrrole monomer on the surface of the silica spheres with iron chloride as the oxidant. We studied the effect of adding methanol cosolvent to the aqueous reaction solution on the morphology of the core-shell composites. The conductivity of silica particles coated completely with PPy can reach to 1.2 S/cm.

EXPERIMENTAL

Materials and equipments

Tetraethyl tetraethoxysilane (TEOS, 99%) were purchased from Shanghai Chemical Reagent Co. and

TABLE I
Reaction Recipes of Silica

Samples	Temperature ($^{\circ}$C)	Ethanol (mL)	Water (g)	Ammonia (g)	TEOS (g)
S_1	29	175	10.8	13.60	20.83
S_2	50	175	10.8	13.60	20.83
S_3	29	175	10.8	16.75	20.83

used as received without any purification. Pyrrole (from Aldrich) was purified using a column of activated basic alumina and then stored at -15°C in a refrigerator prior to use. Iron chloride (FeCl$_3$·6H$_2$O, 97%), ethanol, ammonia (25 wt %), and hydrochloric acid (HCl, 36 wt %) were purchased from Tianjin Chemical Reagent Co. and was used as received. Distilled water was used during all the experimental process. Samples were analyzed by transmission electron microscope (JEM-100CX, Japan), Fourier transform infrared spectrometer (Bruck Vector22, Germany), and Hall effect testing instrument (HMS-3000, Germany).

Preparation of monodisperse silica

Different amount of ethanol, water, ammonia (the reaction recipes were summarized in Table I) were introduced in a three neck round flask of 250 mL equipped with a refrigerating system. The system was stirred to homogenize. TEOS (20.83 g) was introduced continuously and slowly into the flask. Reaction occurred at room temperature (29°C) or a higher temperature (50°C) under continuous stirring and lasted for 12 h. Silica suspensions gained above were centrifuged and washed with water and methanol until the super supernatant became transparent. Finally, the white silica particles were dried in a vacuum oven at 60°C for 12 h.

Preparation of silica/PPy core-shell composite particles

Different amount of ethanol and water with a total mass of 40g (the mass ratio of ethanol and water was alterative and was summarized in Table II) were introduced into a conical flask of 100 mL. Silica particles (0.5 g) prepared above and 0.1 g pyrrole was introduced into the flask. The mixture was stirred for 30 min at 0°C to allow sufficient swell of pyrrole into silica particles. Hydrochloric acid

TABLE II
The Mass Ratio of Ethanol and Water of Preparation of Silica/PPy Core-Shell Composite Particles

Samples	K_1	K_2	K_3	K_4
The mass ratio of ethanol and water ethanol/water	0/40	2/38	5/35	10/30

(1 mol/L) was added to the mixture to adjust the pH to 2. FeCl$_3$ · 6H$_2$O (0.9 g) was dissolved in 10 g water and was dropped slowly and continuously into the flask at 0°C. The mixture was stirred with a magnetic stirrer at 0°C for 12 h. The product, after precipitation in acetone to remove un-reacted monomers, was dispersed in distilled water and then separated by centrifugation. The latter process was repeated for several times. The final product was obtained after drying in a vacuum oven at 60°C for 12 h.

RESULTS AND DISCUSSION

Characterization and analysis of the silica particles

TEM analysis of silica particles

Particle size and morphology were investigated by TEM in this article. The silica powder prepared above was diluted in ethanol and was sonicated before dropping on the carbon coated copper grid. The carbon coated copper grid coated with silica powder was dried in a desiccator at room temperature. All other samples were treated like this before the observation of TEM.

Figure 1 shows the TEM images of silica particles. Sample S_1 are monodisperse and are uniform in size with a diameter about 150 nm [Fig. 1(a)]. When the reaction temperature is kept at 50°C, silica particles still keep a spherical morphology [sample S_2, Fig. 1(b)]. But the diameter is reached to 300 nm and some partially coalesce is observed. At higher temperature, the viscosity of silica sol is low and molecular motion becomes violent. The opportunity of -OC$_2$H$_5$ groups of TEOS and -OH groups of silica to meet and react with each other becomes large. Coalesce between particles appears at this situation. When the amount of ammonia increases, the particles' diameter becomes inhomogenous in the range of 130–200 nm [sample S_3, Fig. 1(c)]. Ammonia can affect the hydrolysis of TEOS but can also promote the growth of nucleation.[18] The former makes the diameter smaller, while the latter makes the diameter larger.
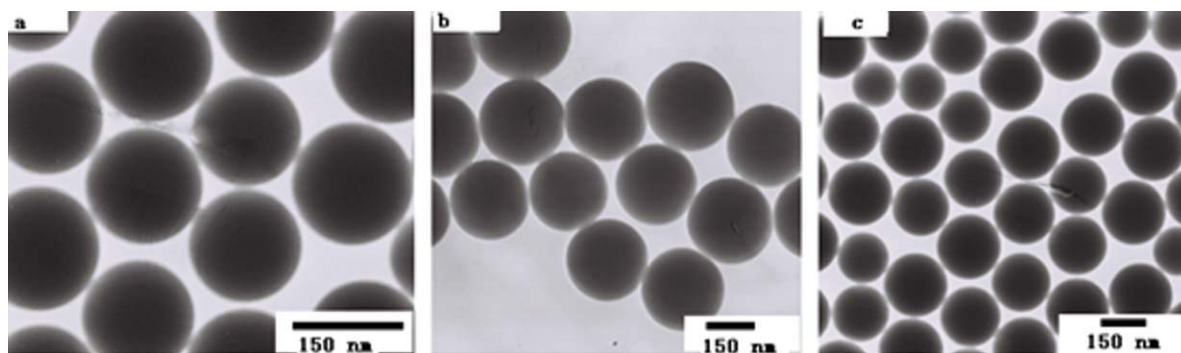
FTIR analysis of silica particles

Figure 2 shows the FTIR spectra of the KBr pellets of the silica particles (sample S_1). In the spectrum,

Figure 1 TEM morphologies of silica particles [(a): sample S_1, (b): sample S_2, (c): sample S_3].

the low-frequency mode, near 468 cm^{-1} involves primarily a rocking motion of the bridging oxygen atoms perpendicular to the Si—O—Si plan, but includes some silicon cation motion. The intermediate-frequency band, at 799 cm^{-1}, involves the motion of the oxygen atoms along the bisector of the Si—O—Si bridging angle, with simultaneous symmetric motion of the Si atoms. The strong and wide peak in the range of 1035–1246 cm^{-1} is assigned to the in-phase motion of adjacent oxygen atoms along a line parallel to the Si—Si direction. All the above peaks are consistent with the characteristic peaks of silica.[19]
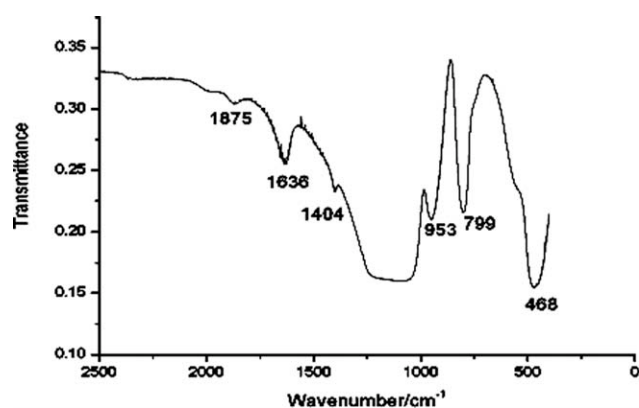
Characterization and analysis of silica/PPy core-shell composite particles

TEM analysis of silica/PPy core-shell composite particles

From the above discussion, sample S_1 is monodisperse and is uniform in size. Therefore, sample S_1 was used as the core in preparation of silica/PPy core-shell composite particles, which were labeled as K_1, K_2, K_3, and K_4, respectively.

Figure 3 shows the TEM images of silica/PPy core-shell composite particles. In Figure 3(a), some

little PPy particles are observed around the surface of silica particles (at the arrow mark). The inset image of Figure 3(a) is a single particle of silica/PPy core-shell composite particles. The silica particle is about 150 nm in diameter with a PPy shell about 15 nm. After careful observation, we find that some PPy particles are polymerized in the continuous phase, rather than on the surface of silica particles. This may be due to the poor solubility of pyrrole in water. Pyrrole monomer cannot effectively gather together around the silica particles. When ethanol was used as the cosolvent (the mass ratio of ethanol and water is 2/38), in Figure 3(b), the PPy shell of the composite particles becomes thicker and compacter with a diameter about 20 nm. A broken PPy shell, which still maintains a certain hemispherical morphology, is observed in the picture. This indicates that the PPy shell is thick and possesses a certain mechanical strength. When the mass ratio of ethanol and water further increases, the diameter of PPy shell reduces to about 15 nm and 10 nm in Figure 3(c) (sample K_3) and (d) (sample K_4), respectively. No protrusions are observed in Figure 3(d). Higher concentration of ethanol increases the solubility of pyrrole in solvent and results in a smooth surface of silica/PPy core-shell particles. But the higher solubility can also cause the self-polymerization of pyrrole in solvent, which makes the diameter to reduce.
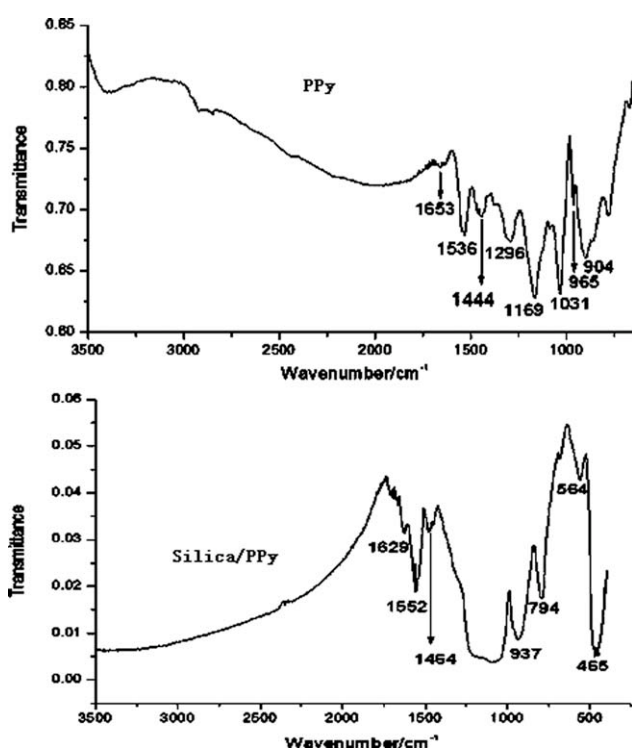
FTIR analysis of silica/PPy core-shell composite particles

Figure 4 shows the FTIR spectra of the KBr pellets of the PPy particles and silica/PPy core-shell composite particles. The characteristic peaks of silica in the spectrum of silica/PPy particles at 465 cm^{-1}, 794 cm^{-1}, and the wide absorption peaks around 1100 cm^{-1} indicates the existence of silica in the composite particles. In the spectrum of PPy, the pyrrole ring fundamental vibration at 1536 cm^{-1}, C—N stretching vibration in the ring at 1444 cm^{-1}, the =C—H in-plane vibration at 1031 cm^{-1}, the N—H in-plane

Figure 2 FTIR analysis of silica particles.
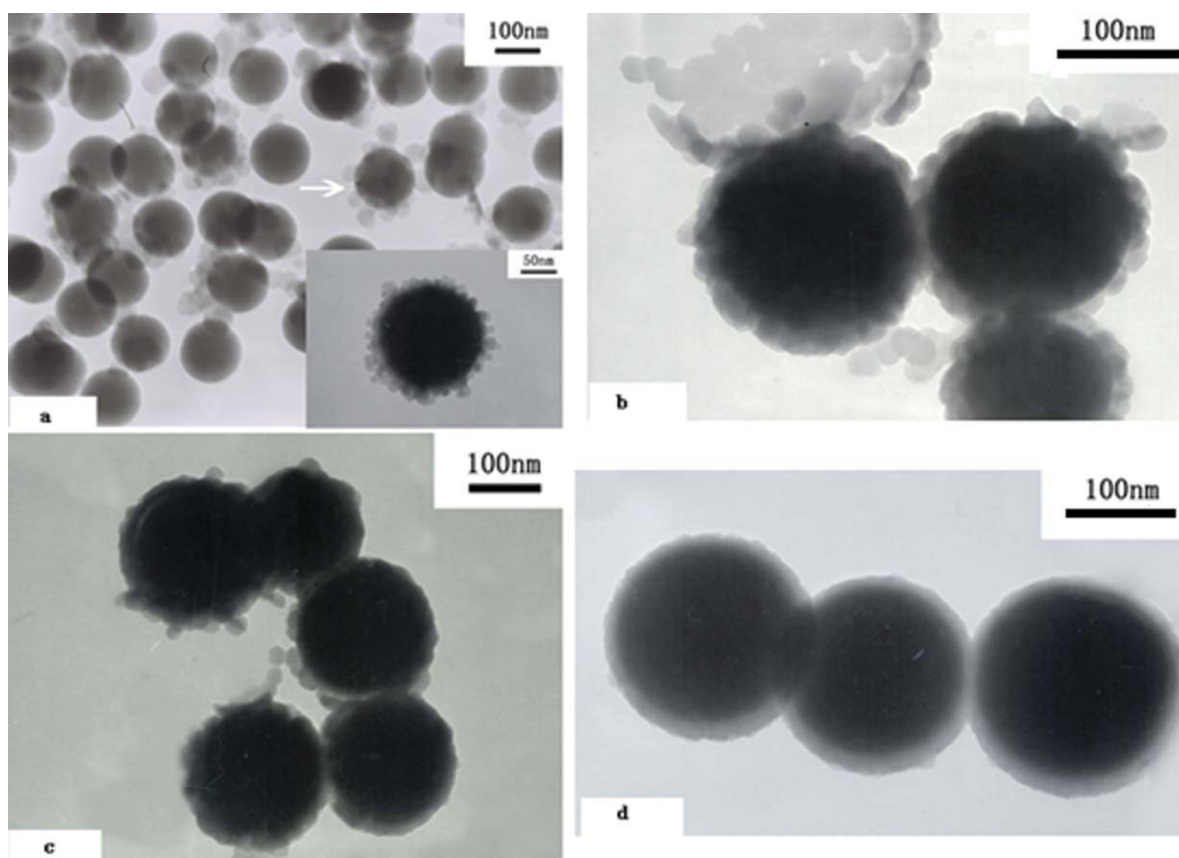
Figure 3 TEM morphologies of silica/PPy core-shell composite particles [(a): sample K_1, (b): sample K_2, (c): sample K_3, (d): sample K_4]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4 FTIR analysis of silica/PPy core-shell composite particles.

vibration at 1653 cm^{-1}, and the C=C stretching vibration at 1169 cm^{-1} is observed.[14] Compared with the spectrum of PPy, both the C—N stretching vibration in the ring at 1444 cm^{-1} and the pyrrole ring fundamental vibration at 1536 cm^{-1} shift to higher wavenumber: 1464 cm^{-1} and 1552 cm^{-1} in the spectrum of silica/PPy core-shell particles. Meanwhile, the characteristic peak of the N—H in-plane vibration at 1653 cm^{-1} shifts to a lower wavenumber (1629 cm^{-1}) in the composite particles. These findings reveal that hydrogen bonding exists between the silica core and the PPy shell.

Conductivity analysis of silica/PPy core-shell composite particles

We measured the conductivity of silica/PPy core-shell composite particles using Hall effect testing instrument by four-point probe, and the results were summarized in Table III. Sample K_2 had a conductivity of 1.2 S/cm, which was the highest among the four samples. As we discussed above, sample K_2 possessed a thicker and compacter PPy shell than the other samples. The addition of ethanol increases the solubility of pyrrole in solvent and makes the

TABLE III
Conductivity of Silica/PPy Core-Shell Composite Particles

Samples	K_1	K_2	K_3	K_4
Conductivity (S/cm)	$(1.4 \pm 0.12) \times 10^{-3}$	1.2 ± 0.18	$(9.9 \pm 0.09) \times 10^{-1}$	$(2.8 \pm 0.16) \times 10^{-3}$

polymerization of pyrrole on the surface of silica easier. So the conductivity increases. But when the concentration of ethanol is too high, much pyrrole monomer is polymerized in the solvent. Therefore, there is an extreme value of conductivity with the increase of ethanol in solvent in the preparation of silica/PPy composite particles. The result is in good agreement with the TEM analysis of silica/PPy core-shell composite particles.

CONCLUSIONS

Silica/PPy core-shell composites were successfully fabricated by *in situ* chemical polymerization of pyrrole monomer on the surface of the silica spheres. We discussed the effect of reaction temperature and the using amount of ammonia on the base-catalyzed hydrolysis of TEOS to prepare the monodisperse silica particles with a uniform diameter. Ethanol was used as a cosolvent in preparation of silica/PPy core-shell particles. We measured the composite particles by TEM, FTIR, and Hall effect testing instrument and found that there was an extreme value of the adding amount of ethanol (ethanol/water: 2/38). When the mass ratio of ethanol and water was kept at 2/38, the PPy shell was thick and compacter. The conductivity of the composite particles was highest at 1.2 S/cm.

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