Fabrication and Characterization of Silica/Polypyrrole Nanocomposites Using Silica Sulfuric Acid as Templates

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ABSTRACT: The sunflower-like silica core-polypyrrole (PPy) shell nanocomposites were prepared by using silica sulfuric acid as templates. The silica sulfuric acid was obtained by treating directly the silica nanoparticles with chlorosulfonic acid. The sulfonic groups ($-SO_3H$) on the surface of silica sulfuric acid not only offered the active sites for formation of polypyrrole particles but also acted as dopant agents in PPy. The nanostructures of sunflower-like silica/PPy nanocomposites and hollow PPy capsules were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The molecular structure and content of PPy were determined by Fourier transform infrared (FTIR) and thermal gravimetric analysis (TGA), respectively. The highest conductivity of nanocomposites is 2.4 S/cm. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1645–1649, 2012

Key words: polypyrrole; silica sulfuric acid; nanocomposite

INTRODUCTION

Over the past years, core-shell conducting polymer nanocomposites have attracted increasing interest because of their wide variety of applications.[1] Template-assisted method is one of the most effective and general methods for generating the core-shell conducting polymer nanocomposites. Since the pioneered works of Khan and Armes on the preparation of the core-shell conducting polymer nanocomposites with polystyrene latex spheres as templates,[2,3] some novel nanocomposites with inorganic or organic material as core and conducting polymer as shell, such as Ag/polypyrrole (PPy),[4,5] Au/PPy,[6] Fe_2O_3/PPy,[7] Fe_3O_4/polyaniline,[8] polystyrene/polyaniline,[9] polystyrene/PPy[10] etc. had been synthesized and relevant synthetic process had been reviewed.[11]

Among conducting polymers, PPy is one of the most extensively studied materials due to its good environmental stability, redox properties, and high conductivity.[12] On the other hand, compared with other templates, the silica template particles reveal some advantages due to its simplicity of synthetic procedure, low cost, and ease of functionalization. Some research groups had devoted much effort towards silica-based conducting polymer nanocomposites.[13–15] However, the hydrophilic surface of silica is not favorable for adsorption of hydrophobic pyrrole monomers. To provide strong interaction between silica particles and the pyrrole monomers, the surface-modified process of the silica is essential. To date, different agents, such as poly(*N*-vinylpyrolidone) (PVP),[16] cetyltrimethylammonium bromide (CTAB),[17] and 3-(trimethoxysilyl)propyl methacrylate[18] had been used to modify the surface of SiO_2 for fabricating SiO_2/PPy core-shell nanocomposites.

However, above modified-agents only provide some "anchoring sites" for pyrrole monomer and less contribution to the properties of the final product. At present, one novel strategy utilizing sulfonic-functionalized silica spheres as templates to prepare SiO_2/PPy nanocomposites has been developed.[19] The hydrophilic sulfonic acid groups on the surface of SiO_2 not only offered the "active sites" to induce the growing of PPy chains but also acted as dopant agents. It is an interesting method, nevertheless, the surface-modified procedure is very complicated and not suitable for bulk-synthesis. To overcome these shortcomings, in the present work, we used silica sulfuric acid as templates to fabricate SiO_2/PPy nanocomposites. The preparation of silica sulfuric acid was very simple: the direct treatment of silica nanoparticles with chlorosulfonic acid. Using sulfonated silica as the core, pyrrole monomers were in suit polymerized on the surface of sulfonated silica to form sunflower-like nanocomposites. When SiO_2
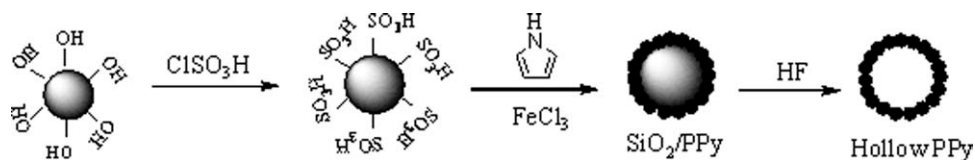
Figure 1 Schematic illustration for the synthetic procedure of silica/PPy nanoparticles and hollow PPy.

was selectively removed by HF (10%) aqueous, hollow PPy capsules were obtained. The method was economical and the product exhibited relatively high electric conductivity.

EXPERIMENTAL

Materials

Tetraethyl orthosilicate (TEOS) was purchased from Aldrich. Pyrrole, ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), chlorosulfonic acid (HSO_3Cl), ammonia aqueous (25%), hydrofluoric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Shanghai, China. Pyrrole was distilled under reduced pressure before use. Other reagents were used without further purification.

Preparation of silica sulfuric acid

Monodisperse silica spheres were synthesized using a modified Stöber method.[20] The silica sulfuric acid was obtained according to the reference.[21] Generally, 5.0 g silica spheres were charged into 50-mL suction flask. The flask was equipped with a constant-pressure dropping funnel containing different amount of chlorosulfonic acid and gas inlet tube for conducting HCl gas over an adsorbing solution, i.e., water. After addition of chlorosulfonic acid, the mixture was shaken for 1 h at room temperature (RT). A white solid (silica sulfuric acid) was obtained and the product was dried in vacuum for 12 h at RT. In our experiment, 1, 2, and 5 mL of chlorosulfonic acid were added and resulting silica sulfonic acid were S1, S2, and S3, respectively.

Preparation of PPy/SiO$_2$ and hollow PPy capsules

One gram sulfonated silica spheres was dispersed in 100 mL of deionized water. Subsequently, 0.5 mL of pyrrole was added and stirred for 3 h. Ten milliliters of $1M$ HCl aqueous solution of $FeCl_3$ as the oxidant were dropped into above mixture (the molar ratio of pyrrole to $FeCl_3$ was 1 : 2.33). The reaction was allowed for 24 h at RT. The precipitate was washed with methanol and deionized water consecutively, followed drying in vacuum oven at 50°C. Hollow PPy capsules were obtained by removing the SiO_2 core with HF aqueous solution (10%).

Characterization

Transmission electron microscope (TEM, H-7650) and scanning electron microscope (SEM, S-4800) were used to observe the morphologies of nanocomposites. Fourier transform infrared (FTIR) spectroscopy measurements were performed on Varian Scimitar1000 Fourier transform IR spectrophotometer using KBr pressed discs. Thermogravimetric analysis was conducted using a Perkin-Elmer thermogravimetric analyzer (TG-DTA, SSC-5200) at a heating rate of 10 °C/min in air.

RESULTS AND DISCUSSION

The mechanism of the formation of sunflower-like silica/PPy nanocomposites and hollow PPy capsules is shown in Figure 1. Firstly, —SO_3H groups were introduced onto the surfaces of silica spheres by sulfonation reaction. Subsequently, pyrrole monomers were added and attached to the surface of silica spheres via hydrogen-bonding interaction between the —SO_3H groups and pyrrole monomer. After the addition of $FeCl_3$, pyrrole monomers were polymerized to form PPy shell on the surfaces of silica spheres. The PPy hollow capsules could be obtained by removing the silica.

The SEM and TEM images of S1/PPy nanocomposites and PPy obtained by removing silica are shown in Figure 2. Figure 2(A,B) show that a few smaller PPy nanoparticles with diameter of about 100 nm attach on the surfaces of the silica spheres. In addition, it was found that the smaller PPy nanoparticles infirmly attached to the silica surfaces and some PPy nanoparticles fell from the surfaces of the silica. After removal of silica, the SEM and TEM images of resulting product are shown in Figure 2(C,D), respectively.

The SEM image of S2/PPy nanocomposites is shown in Figure 3(A). Compared with Figure 2(A), the silica surfaces were enwrapped by more PPy nanoparticles. However, the silica spheres were still not surrounded completely, which are further confirmed by Figure 3(B). The nanobowl-like PPy nanostructures were obtained by removing silica, as shown in Figure 3(C,D).

The sunflower-like SiO_2/PPy nanocomposites are shown in Figure 4(A,B). The silica spheres were almost completely surrounded by smaller PPy
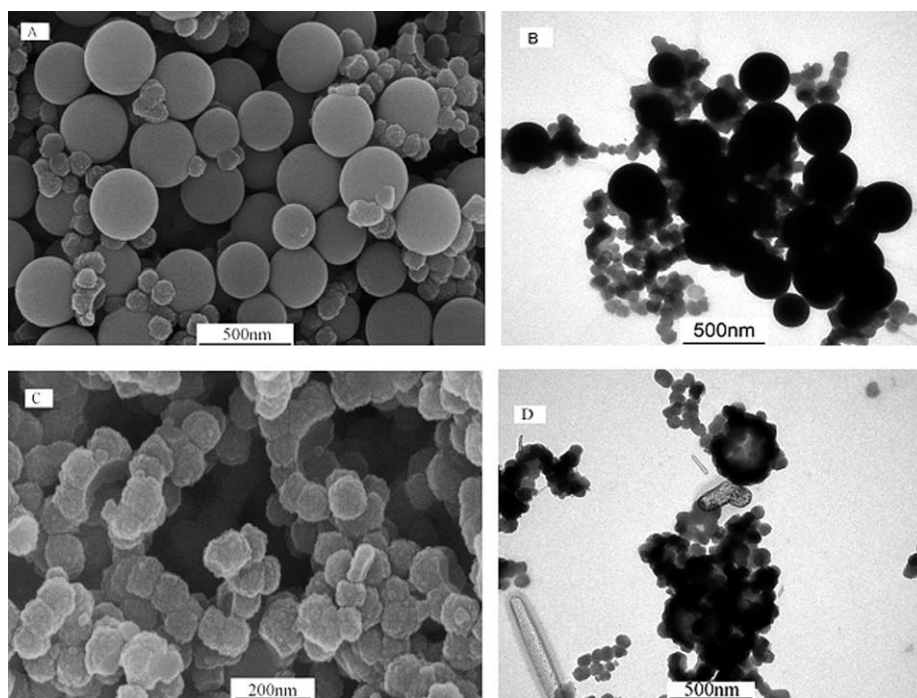
Figure 2 (A) SEM and (B) TEM images of S1/PPy composites particles, (C) SEM and (D) TEM images of PPy obtained by etching S1/PPy composites using HF.

nanoparticles. The hollow PPy could be confirmed via some broken PPy capsule [Fig. 4(C,D)], which clearly showed that PPy shell composited with PPy nanoparticles and shell thickness was about 100 nm.

The various nanostructures of the SiO$_2$/PPy can be attributed to the different contents of sulfonic acid groups of SiO$_2$. The lower content of sulfonic acid groups of S1 offers fewer active sites for growing the PPy.
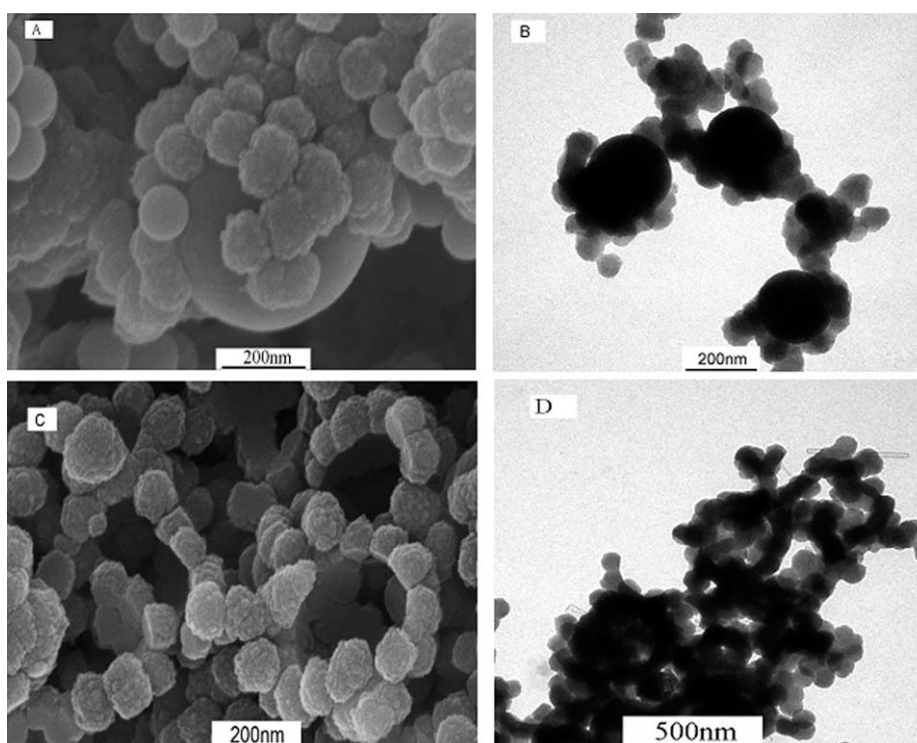

Figure 3 (A) SEM and (B) TEM images of S2/PPy composites particles, (C) SEM and (D) TEM images of product obtained by etching S2/PPy composites using HF.
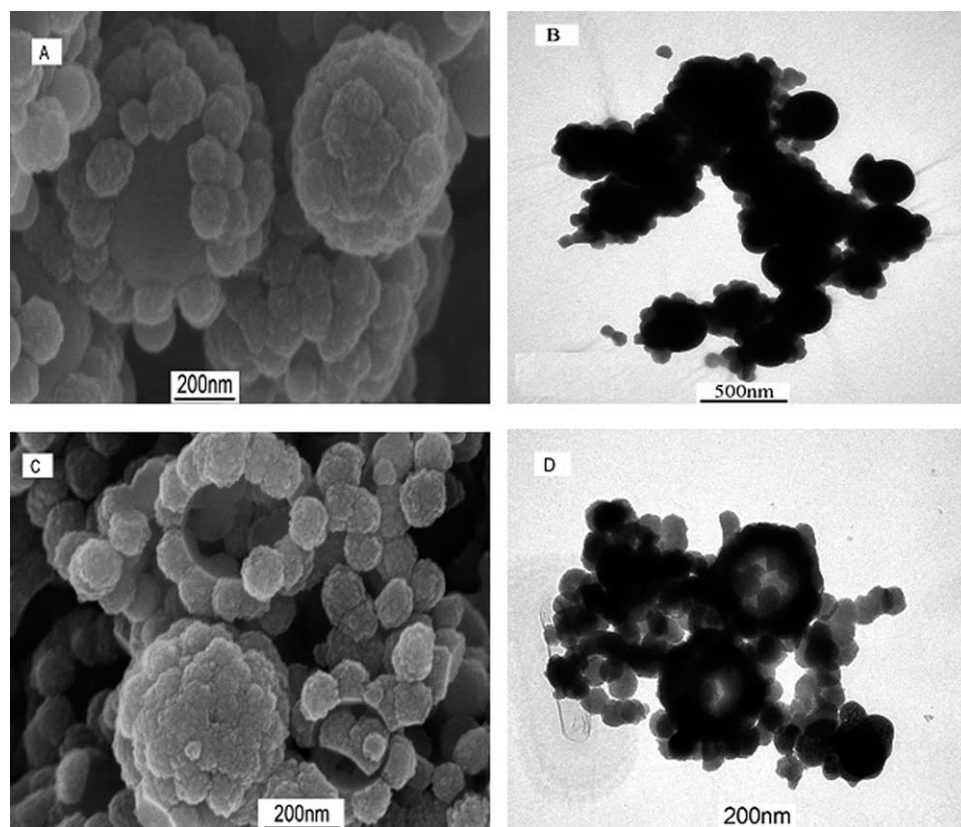
Figure 4 (A) SEM and (B) TEM images of S3/PPy composites particles, (C) SEM and (D) TEM images of product obtained by etching S3/PPy composites using HF.

The higher density of $-SO_3H$ groups of S2 or S3 is in favor of forming more pyrrole nuclei,[22] which result in formation PPy layer on the SiO_2.

The FTIR spectra of the PPy and PPy/SiO$_2$ nanocomposites are shown in Figure 5. The characteristic bands of the PPy were the pyrrole ring's fundamental vibration at 1597 cm^{-1}, C$-$H in-plane vibration at 1375 and 1040 cm^{-1}.[15] The peaks at 1298 cm^{-1} and 1462 cm^{-1} corresponded to the C$-$N stretching vibrations and the symmetric ring stretching modes of pyrrole rings, respectively.[17] The peaks at 1167 and 1040 cm^{-1} were attributed to $=$C$-$H in-plane deformation vibrations.[22] Compared with Figure 5(a), there was a strong peak at 1106 cm^{-1} in Figure 5(b), which was the characteristic peak of silica.[23] In addition, we also found that the absorption peaks of
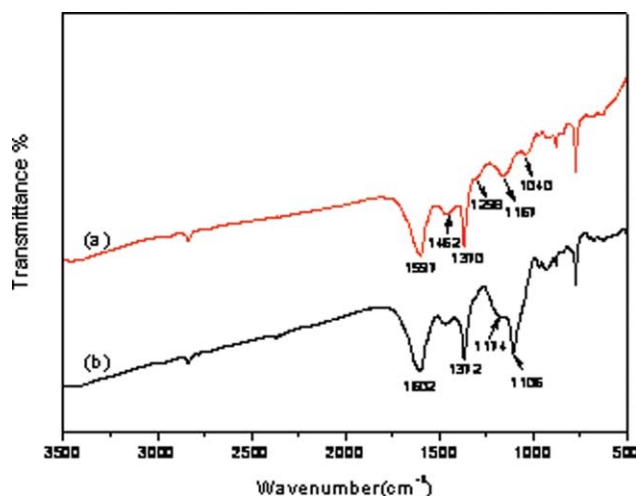

Figure 5 FT-IR spectra of PPy (a) and PPy/SiO$_2$ nanocomposite (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
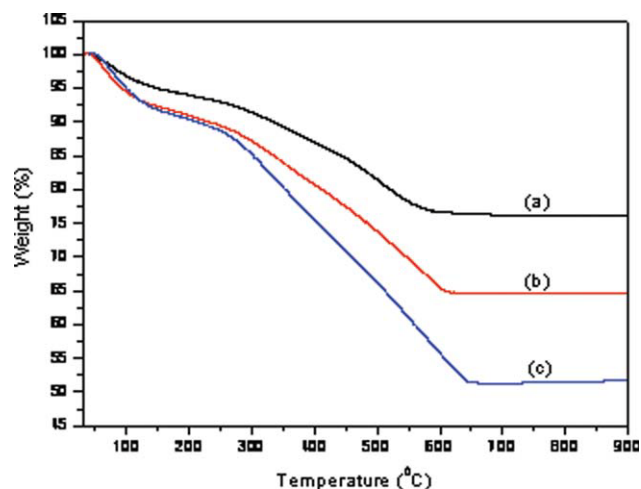

Figure 6 TGA curves of (a) S1/PPy, (b) S2/PPy, and (c) S3/PPy composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Conductivities of the SiO$_2$/PPy Nanocomposites

Sample code	PPy content in composites (wt %)	Conductivity (10^{-2} S/cm)
S1/PPy	23.3	5.2
S2/PPy	35.1	1.7
S3/PPy	48.5	240.0

PPy/SiO$_2$ had some shift, compared to those of pure PPy. This is an indication of a strong interaction between PPy and sulfonted-silica.

Figure 6 illustrates the results of thermogravimetric analysis of S1/PPy, S2/PPy, and S2/PPy. The TGA curves of silica/PPy composites showed a two-step weight loss. The weight loss in the first step below 200°C was attributed to the loss of residual moisture and residual organic solvent. The second step starting around 260°C corresponded to the PPy degradation. Residual sample mass after 700°C belongs to silica.[22] From Figure 6, it was found that the contents of PPy in S1/PPy, S2/PPy, and S3/PPy composites were 23.3, 35.1, and 48.5 wt %, respectively.

The sample was pressed into disks at room temperature and the conductivity of samples was determined using standard four-point probe techniques. The conductivities of samples are listed in Table I. When PPy content increased from 23.3 to 48.1 wt %, the conductivity of the samples improved from 5.2×10^{-2} S/cm to 2.4 S/cm. The conductivities of the S1/PPy and S2/PPy were lower, since silica particles were not completely covered by PPy shell. Interparticle charge carrier transport occurs via the surface of the composites, and insulating SiO$_2$ hampers the electron transport, which cause a reduction of conductivity.[24]

CONCLUSIONS

In summary, we provided a simple procedure for preparation of SiO$_2$/PPy nanocomposites. Using silica sulfuric acid as templates, sunflower-like PPy/SiO$_2$ nanocomposites were successfully obtained. The morphologies and properties of the nanocomposites could be easily modified. The conductivity of nanocomposites increased with the increase of PPy content and the highest conductivity was 2.4 S/cm.

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