Preparation of SiO₂@polystyrene@polypyrrole sandwich composites and hollow polypyrrole capsules with movable SiO₂ spheres inside

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Abstract

In this paper, we describe a flexible method for preparing conducting building blocks: SiO₂@polystyrene@polypyrrole (PPy) sandwich multilayer composites and hollow PPy capsules with movable SiO₂ spheres inside. First, SiO₂@polystyrene (PS) core/shell composites were synthesized, and then SiO₂@PS@PPy sandwich multilayer composites were prepared by chemical polymerization of pyrrole monomer on the surface of SiO₂@PS composites. Furthermore, hollow PPy capsules with movable SiO₂ spheres inside were obtained after removal of the middle PS layer. The diameter of sandwich multilayer composites could easily be controlled by adjusting the dosage of pyrrole monomer. The conductivities of composites increased with the increase of PPy content. After the insulating PS layer was selectively etched, the conductivities of hollow capsules with movable SiO₂ spheres inside were much higher than those of the corresponding sandwich multilayer composites.

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Keywords: Polypyrrole (PPy); Sandwich multilayer composite; SiO₂; Polystyrene (PS); Building block

1. Introduction

Self-assembled colloid crystals stand out as ideal templates for creating highly ordered three-dimensional (3D) or two-dimensional (2D) structures. They have remarkable potential applications in the fields of microelectronics, chemical sensors, engineering, and biomedicine due to their special periodical dielectric structures and unique optical properties [1–6]. Various methods have been successfully established to create colloidal crystals with lattice constants of micrometers or nanometers, and many perfect structures have been fabricated [7–14]. As is well known, building blocks play an important role in self-assembly methods. 3D or 2D structures with different building blocks display different properties. For example, packed magnetic nanoparticles with regular arrays can be used in data storage [15,16]. The incorporation of metal nanoparticles into ordered structures may find applications in catalysis and photonic crystals [17–20]. Although many functional materials have been used as building blocks, little attention has been paid to conducting polymers. Once conducting polymers are used as building blocks to form ordered structures, it will enlarge their applications in electronic devices, light-emitting diodes, electrochromic devices, and transparent electrode materials [21–24].

It is well known that polypyrrole (PPy) is an outstanding conducting polymer. It can easily be synthesized by various approaches—for example, oxidative polymerization and electrochemical polymerization. In addition, PPy presents several advantages such as environmental stability, good redox properties, and the ability to give high electrical conductivities [25–28]. One of the most widely studied and applied techniques in this respect is to form core/shell composites using conducting polymers as the shells and organic or inorganic particles as the cores [29–36]. In this paper, we synthesized SiO₂@polystyrene@polypyrrole sandwich multilayer composites and hollow PPy capsules with movable SiO₂ spheres inside. First, SiO₂ nanoparticles grafted with 3-(trimethoxysilyl)propyl methacrylate (MPS) were employed as cores in styrene emulsion polymerization to synthesize SiO₂@polystyrene (PS) core/shell composites. Then steric...
agent poly(N-vinylpyrrolidone) (PVP) was adsorbed onto the surface of SiO$_2$@PS by ultrasound as an anchor molecule and the polymerization of pyrrole monomers was performed around SiO$_2$@PS composites to form SiO$_2$@PS@PPy sandwich multilayer composites. Finally, the middle PS layer was selectively etched by tetrahydrofuran (THF) and hollow PPy capsules with movable SiO$_2$ spheres inside were obtained.

2. Experimental

2.1. Materials

Pyrrole and divinylbenzene (DVB) were purchased from Fluka. PVP with molecular weight of 3.6 × 10$^5$ was obtained from Sigma and used without further purification. 3-(Trimethoxysilyl)propyl methacrylate (MPS), styrene, and pyrrole were distilled under reduced pressure before being used. Tetraethyl orthosilicate (TEOS), absolute ethanol, ammonium hydroxide, sodium dodecyl benzene sulfonate (SDBS), potassium persulfate (KPS), FeCl$_3$·6H$_2$O, and THF were analytical grade and used as received.

2.2. Preparation of SiO$_2$@PS@PPy sandwich multilayer composites

SiO$_2$@PS core/shell composites with different sizes were synthesized according to the references [37,38].

PVP was dissolved in ethanol by ultrasound in the presence of SiO$_2$@PS composites for 1 h; then the suspension was stirred for 24 h to ensure that the surface of the composites was adequately covered by PVP. Unadsorbed PVP was removed by centrifugation. Subsequently, the composites were redispersed into deionized water, which was directly used for the pyrrole-coating step.

A quantity of 1.0 g FeCl$_3$·6H$_2$O was added into 30 ml of the above solution (containing 0.24 g SiO$_2$@PS composites covered by PVP) under magnetic stirring at ambient temperature. After half an hour, the pyrrole monomer was added into the system using a syringe. The suspension color turned from yellow to dark green; at last it became black. After stirring for 16 h, black SiO$_2$@PS@PPy sandwich composites were obtained.

2.3. Preparation of hollow PPy capsules with movable SiO$_2$ spheres inside

SiO$_2$@PS@PPy composites were soaked in THF solution under magnetic stirring for 12 h; the PS layer between the PPy shell and the SiO$_2$ core was selectively etched. After being washed with deionized water and ethanol several times, the black sediments were dried in vacuum overnight. Hollow PPy capsules with movable SiO$_2$ spheres inside were obtained.

2.4. Characterization

A JEOL JSM-6700F scanning electron microscope (SEM) was employed to observe the surface morphologies. The mean diameter of composites was estimated by counting all particles in SEM images. The structure and shell thickness of the composites were determined by a JEOL-2010 transmission electron microscope (TEM). The FT-IR spectrum was measured at wavenumbers ranging from 500 to 4000 cm$^{-1}$ using a Nicolet Avatar 360 FT-IR spectrophotometer. Thermogravimetric analysis (TGA) was conducted with a Netzschsta 449C thermogravimetric analyzer at a heating rate of 10°C per min in N$_2$ from room temperature up to 700°C. (The temperature of SiO$_2$@PS composites was up to 480°C.)

3. Results and discussion

3.1. Morphology and structure

The overall procedure for forming SiO$_2$@PS@PPy composites and hollow PPy capsules with movable SiO$_2$ spheres inside is illustrated in Fig. 1.

MPS was critical during the preparation of SiO$_2$@PS composites. Only pure SiO$_2$ nanoparticles and pure PS nanoparticles were obtained in the reactor when the surface of the SiO$_2$ spheres was not grafted with MPS. Fig. 2 shows SEM and TEM images of the SiO$_2$@PS composites, which display good dispersity. The mean diameters of the SiO$_2$ cores and the composites are 80 and 230 nm, respectively. It is seen that most of the core/shell composites contain only one SiO$_2$ core, but in
Fig. 2. SEM and TEM (inset) images of SiO$_2$@PS composites.

Fig. 3. FT-IR spectra of (a) SiO$_2$, (b) PS, (c) bare SiO$_2$@PS composite, and (d) SiO$_2$@PS composite with adsorbed PVP.

Table 1

<table>
<thead>
<tr>
<th>PPy content (wt%)</th>
<th>Diameter (nm)</th>
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<tr>
<td>60</td>
<td>445</td>
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<tr>
<td>55</td>
<td>420</td>
</tr>
<tr>
<td>50</td>
<td>400</td>
</tr>
<tr>
<td>45</td>
<td>370</td>
</tr>
</tbody>
</table>

several composites two SiO$_2$ cores appear. The reason is that the SiO$_2$ nanoparticles we used were small. Composites with more than one cores could be observed due to the aggregation of small particles when the diameter of SiO$_2$ cores was less than 100 nm [37].

FT-IR spectra of (a) SiO$_2$ nanoparticles, (b) PS nanoparticles, and (c) bare SiO$_2$@PS composites are shown in Fig. 3. In spectrum a the characteristic peak of SiO$_2$ at 1097 cm$^{-1}$ corresponds to the Si–O–Si stretching vibration. PS main peaks at 3025, 2923, 1492, 1452, and 698 cm$^{-1}$ are shown in spectrum b. In spectrum c, all the PS main peaks appear and the SiO$_2$ characteristic peak shifts from 1097 to 1106 cm$^{-1}$. SEM, TEM images and FT-IR spectra have proved that the SiO$_2$@PS composites were successfully prepared.

To cover SiO$_2$@PS core/shell composites with PPy, PVP was used as a steric agent. Because of highly polar amide groups in the pyrrolidone ring and nonpolar methylene groups along its backbone, PVP adsorbed strongly onto the PS surface through hydrophobic interaction [39]. In Fig. 3, spectrum d is the FT-IR spectrum of SiO$_2$@PS composites adsorbed with PVP. Compared with spectrum (c), an additional characteristic peak appears at 1652 cm$^{-1}$ corresponding to the pyrrolidone carbonyl group of the steric agent. PVP could provide active sites for pyrrole monomer loading [40,41]. Pyrrole monomers could polymerize both on the surfaces of SiO$_2$@PS composites and in solution. As PVP adsorbed onto the surfaces of composites, pyrrole monomers preferred to polymerize on the surface with possible formation of hydrogen bonds between the amino groups on pyrrole rings and the carbonyl groups on PVP backbones, so the process of coating PPy shells onto the composites’ surfaces was considered to be a physical course. PVP could not effectively prevent the PPy from aggregating when the hydrodynamic diameter of PVP was shorter than the thickness of the PPy shell [29]. The experimental results show when the content of PPy exceeds 60 wt% in sandwich composites, the PPy shell is too thick to form hydrogen bonds between the carbonyl groups on the PVP backbones and the amino groups on pyrrole rings, which leads to the formation of pure PPy nanoparticles originating from the polymerization of pyrrole monomers in the solution.

The FT-IR spectrum of the SiO$_2$@PS@PPy sandwich composites (not shown in this paper) reveals that the pyrrole monomer is successfully polymerized onto the surfaces of the SiO$_2$@PS composites. The characteristic peaks of pyrrole ring are at 1651, 1538, and 1462 cm$^{-1}$. The peaks at 1104 and 897 cm$^{-1}$ are attributed to $\equiv$C–H group in-plane vibrations and out-of-plane vibrations.

When pyrrole monomers are polymerized onto the surfaces of 230 nm SiO$_2$@PS composites, the relationship between the content of PPy and the diameter of the sandwich multilayer composites is listed in Table 1. This indicates that we can control the size of the composites ranging from 370 to 445 nm by adjusting the content of PPy.

After SiO$_2$@PS@PPy sandwich composites were synthesized, the middle PS layer could be etched by THF and hollow PPy capsules with movable SiO$_2$ spheres inside were successfully prepared. Fig. 4 shows SEM and TEM images of hollow PPy capsules with movable SiO$_2$ spheres inside, and its diameter is about 370 nm. In this case, the middle PS layer almost vanishes, which also demonstrates that the PPy shell is not quite compact and is permeable to the dilute THF for the dissolution of PS.

Sandwich composites of different sizes were prepared by adjusting the diameters of SiO$_2$ nanoparticles and SiO$_2$@PS core/shell composites. In Fig. 5, the mean diameters of SiO$_2$ spheres, SiO$_2$@PS composites, and SiO$_2$@PS@PPy sandwich composites are 260, 520, and 650 nm, respectively. The PPy layer is not tightly attached to the surface of the PS layer and...
Fig. 4. SEM and TEM (inset) images of movable SiO$_2$ spheres in hollow PPy capsules; the arrow indicates the SiO$_2$ sphere.

Fig. 5. SEM and TEM (inset) images of the SiO$_2$@PS@PPy composites with diameter 650 nm. The arrows indicate the (a) PPy layer, (b) PS layer, and (c) SiO$_2$ sphere, respectively. We inferred that the PS and PPy layer shrank about 25 nm from the TEM image.

The interspace between them is about 25 nm, measured from the TEM image. A possible explanation of the phenomenon was that two polymer layers swelled in the solvent, and after the composites were dried in a vacuum oven to remove organic solvent and water, both the PS layer and the PPy layer shrank, which made them separate from each other. However, the separation did not appear between the PS layer and the SiO$_2$ sphere, because the interaction between them was covalent bond, which was much stronger than the hydrogen bond between the PVP and PPy layer or the hydrophobic interaction between the PVP and PS layer. The phenomenon of the PS layer separating from the PPy layer also revealed that both the PPy shell coated on the outer of the PS layer and the PVP adsorbed on the surface of the PS layer were physical courses.

3.2. Thermogravimetric analysis

The thermogravimetric analysis results are shown in Fig. 6. Curves a, b, and c correspond to the sample SiO$_2$@PPy composites (they are not hollow PPy capsules with movable SiO$_2$ spheres inside—we coated PPy onto the surface of SiO$_2$ directly, according to Ref. [40]), SiO$_2$@PS composites, and SiO$_2$@PS@PPy sandwich composites.

The weight loss below 200 $^\circ$C is attributed to the evaporation of water and residual organic solvent. In curve a, composites begin decomposing at 300 $^\circ$C, which corresponds to the decomposed temperature of PPy, and its content is about 45 wt%. Similarly, from curve b, PS begins decomposing at 330 $^\circ$C. When the temperature reaches about 480 $^\circ$C, the PS shell completely vanishes, and the residuals are SiO$_2$ nanoparticles, the content of which is about 2.4 wt%. Comparing curve c with curves a and b, the SiO$_2$@PS@PPy composites begin decomposing at 316 $^\circ$C; when the temperature is up to 340 $^\circ$C, the decomposition rate increases, which is caused by degradation of the PS layer. At last, 1.3 wt% SiO$_2$ residues are left behind.

From curve c, it can be confirmed that there are three different substances in composites, and this is also evidence that the sandwich composites were prepared. From the thermogravimetric analysis, we obtained thermodynamical information on the composites and the content of each layer. The PPy content in composites was used in conductivity analysis.

3.3. Conductivity

As a conducting polymer, the conductivity of PPy composites is an important issue. The samples were dried in a vacuum oven overnight and then pressed into disks at room temperature. The conductivity of SiO$_2$@PS@PPy sandwich composites was determined using standard four-point probe techniques.

The research on conductivity of composites with low PPy content had been done by other researchers. For example, Armes’ group loaded 1 wt% PPy onto the PS surface [29]. The conductivity of the composite was less than $10^{-6}$ S/cm, since PS particles were not completely covered by PPy shells and were exposed to the air. Interparticle charge carrier transport occurred via the surface of the composites, and insulating PS
hampered the electron transport, which caused a reduction of conductivity.

We investigated the conductivity of composites with high PPy content (obtained from TGA). Various amounts of PPy were loaded onto the surfaces of 230-nm SiO$_2$@PS composites. Conductivities of sandwich multilayer composites before or after the middle PS layers were etched are listed in Table 2. When PPy content increased from 35.7 to 50.6 wt%, the conductivity of sandwich multilayer composites improved from 1.20 to 4.90 S/cm. After the PS layer was etched, the conductivities of the corresponding composites increase from 18.09 to 27.41 S/cm. Because the content of insulating materials is less than before, the conductivity of hollow PPy capsules with movable SiO$_2$ spheres inside is efficiently improved compared with that of the corresponding sandwich multilayer composites. It can be inferred the conductivities of the SiO$_2$@PS@PPy composites and hollow PPy capsules with movable SiO$_2$ spheres inside increase with increased PPy content. So the content of PPy in composites is a main factor affecting the conductivity of the composites.

4. Conclusions

We successfully synthesized SiO$_2$@PS@PPy sandwich composites and hollow PPy capsules with movable SiO$_2$ spheres inside. The diameters of the sandwich multilayer composites ranged from 370 to 445 nm by adjustment of the content of PPy coated onto 230-nm SiO$_2$@PS core/shell composites. The conductivity increased obviously from 1.20 to 4.90 S/cm when the PPy content in composites increased from 35.7 to 50.6 wt%. After the PS middle layer was selectively etched, the conductivity of corresponding hollow capsules with movable SiO$_2$ spheres inside ranged from 18.09 to 27.41 S/cm. It is expected that SiO$_2$@PS@PPy sandwich composites and hollow PPy capsules with movable SiO$_2$ spheres inside would have potential applications as conducting building blocks in self-assembly.

Acknowledgments

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Table 2

<table>
<thead>
<tr>
<th>PPy content in sandwich composites (wt%)</th>
<th>Conductivity of sandwich composites (S/cm)</th>
<th>Conductivity after PS layer etched (S/cm)</th>
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<tbody>
<tr>
<td>37.5%</td>
<td>1.29</td>
<td>18.09</td>
</tr>
<tr>
<td>44.2%</td>
<td>3.28</td>
<td>24.07</td>
</tr>
<tr>
<td>50.6%</td>
<td>4.90</td>
<td>27.41</td>
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References