

Preparation of Polyaniline Coated Polystyrene-Poly(styrene-Co-sodium 4-styrenesulfonate) Microparticles and the Further Fabrication of Hollow Polyaniline Microspheres

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ABSTRACT: In this article, the microparticles of polystyrene-poly(styrene-co-sodium 4-styrenesulfonate) (PS-PSS) coated by polyaniline (PANI) were prepared and hollow PANI microspheres were further obtained by dissolving the core. First, surface-sulfonated monodispersed PS was prepared by copolymerization of sodium 4-styrenesulfonate (SSS) and styrene with dispersion polymerization method. Then aniline was polymerized on the surface of the surface-sulfonated PS (PS-PSS) by chemical oxidative polymerization. After purification, we prepared core-shell

(PS-PSS)/PANI particles. Hollow PANI microspheres were prepared by dissolving the plastic PS core of the (PS-PSS)/PANI particles in chloroform. The growth process of PANI on the surface of PS-PSS particles was investigated and the hollow PANI microspheres were characterized. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: core-shell; polyaniline; polystyrene; microparticles; hollow microspheres

INTRODUCTION

In the past few decades, conducting polymers have received considerable attention because of their application in electrostatic dissipation, anticorrosion coatings, batteries, supercapacitors, photovoltaic devices, and sensors.^{1–6} Polyaniline (PANI), an inherently conducting polymer, has been studied extensively among the conducting polymers for its ease of preparation, high conductivity, electric activity, and thermal stability.^{7,8} However, PANI is insoluble in common organic solvents and has poor processability. Various attempts now have been made to improve its solubility and processability. A simple and effective way is to composite PANI with thermoplastic polymers. Liu et al.⁹ prepared core-shell structured semiconducting polymethyl methacrylate/PANI snowman-like anisotropic microparticles and examined its electrorheological characteristics under an applied electric field. Neelgund et al.¹⁰ synthesized submicron poly(vinylidene fluoride)/PANI core-shell latex particles and studied its application in a simple conductometric chemical sensor.

They found that sensor properties of films prepared by the above particles were sensitive in response to varying concentration of NH₃ or HCl vapors. Yang et al.¹¹ fabricated nanostructured PANI films from polystyrene (PS)/PANI core-shell particles and investigated the responses of the resulting nanostructured films to dry gas flow, ethanol vapor, HCl and NH₃. Okubo et al.¹² synthesized electrically conductive, core-shell PS/PANI composite particles by chemical oxidative seeded dispersion polymerization. The pellet of the composite particles had a conductivity of 3.4×10^{-3} S/cm. Kohut-Svelko et al.¹³ prepared core-shell particles PS-PANI by the dispersion process from three types of PS latexes: a noncross-linked core stabilized by a nonylphenoethoxy-late (NP40) and two cross-linked cores stabilized by NP40 and a mixture NP40/surfamid (a surfactant bearing an amide group). They found that a uniform coverage of the core particles was not required to ensure a good conductivity. Niu et al.¹⁴ have reported on the preparation of monodisperse PANI-silica composite capsules and hollow spheres on monodisperse core-gel-shell template particles by an inward growth method and gained the composite capsules and hollow spheres with a mechanical property. Yang et al.¹⁵ successfully used sulfonated PS microspheres as template to produce hollow PANI and hollow polypyrrole. By this method they can readily achieve the appropriate thick and strong PANI or polypyrrole shells. However, most of the researchers

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aforementioned did not investigate the growth process of PANI on the surface of PS-poly(styrene-co-sodium 4-styrenesulfonate) (PS-PSS) particles.

In our previous work, we studied the kinetics of microemulsion copolymerization of styrene and acrylonitrile in the presence of cosurfactant¹⁶ and fabricated PANI-coated poly(styrene-co-styrene sulfonate) nanoparticles in microemulsion media.¹⁷ In this article, we prepared PANI coated PS-PSS micro-particles and hollow PANI microspheres. Monodispersed PS particles were synthesized by dispersion polymerization. Styrene and sodium 4-styrenesulfonate (SSS) were copolymerized on the surface of the PS particles to introduce a functional sulfonic group. During the polymerization of (PS-PSS)/PANI core-shell particles, aniline was absorbed on the surface of the PS because of the functional sulfonic group¹⁸ and was polymerized in the presence of ammonium persulfate (APS). The growth process of PANI on the surface of PS-PSS particles was investigated and the relationship between the morphology of PANI shell and conductivity was characterized. By dissolving the plastic PS of the core-shell (PS-PSS)/PANI particles in chloroform, hollow PANI microspheres were prepared.

EXPERIMENTAL

Materials and equipments

The water used here was redistilled and deionized. Styrene and aniline (AR, Shanghai Chemical Reagent) were purified by distillation under reduced pressure. Polyvinylpyrrolidone (PVP) (Tianjin Chemical Reagent), with a molecular masses about 40,000, was used without further purification. Azobisisobutyronitrile (AIBN, Beijing Chemical Reagent) initiator was crystallized again before being used. APS was purchased from Beijing Chemical Reagent Company and was used as the oxidant of the polymerization of aniline. Hydrochloric acid and chloroform were purchased from Nanjing Chemical Reagent and was used as received. All other chemicals were of analytical grade and were used without further purification. Samples were analyzed by transmission electron microscopy (TEM, JEM-100CX, Japan), scanning electron microscopy (SEM, Hitachi S-4800, Japan), Fourier transform infrared spectrometer (FTIR, Bruker Vector22, Germany), and Hall effect testing instrument (HMS-3000, Germany).

Preparation of monodispersed PS

PVP (2 g) and water (10 g) were mixed in a three-neck round-bottomed flask and was stirred for half an hour, allowing PVP to solute in the water. Then the mixture of 10 g styrene, 100 g ethanol, and 0.15 g

TABLE I
Reaction Recipes of PS-PSS Particles

Material	Weight (g)
PS	10
PVP	2
Ethanol	100
Water	10
AIBN	0.15

The late period { SSS (Sample H₁: SSS 0.5 g;
Sample H₂: SSS 1.0 g; Sample H₃: SSS 1.5 g)
+ ethanol 20 g
+ water 2 g

AIBN, which was served as initiator, was dropped into the flask. The polymerization occurred in nitrogen atmosphere at 70°C (water bath) for 8 h. During this process, the intense stirring was indispensable.

To purify the PS particles, the mixture was centrifuged at 8000 rpm and the supernatant was removed. The precipitates were dispersed in ethanol by ultrasonic dispersion for 10 min. The centrifugation, decantation, and redispersion cycle was repeated until the supernatant became transparent. Finally, the monodispersed PS particles were dried in a vacuum oven at 50°C over 24 h. In addition, the purification of PS-PSS particles, core-shell (PS-PSS)/PANI particles, and hollow PANI microspheres was the same as that of monodispersed PS particles.

Preparation of PS-PSS

On the basis of the preparation of monodispersed PS, 3 h before the polymerization finished, a mixture of 10 g ethanol, 2 g water, and SSS (its content was alterative and the reaction recipes were summarized in Table I) was continuously dropped into the flask. Potassium persulphate (150 μL, 2 wt %) was added into the mixture to initiate the copolymerization between the SSS and the unreacted styrene. The mixture was stirred (400 rpm) for 3 h in nitrogen atmosphere and the temperature was also kept at 70°C in water bath. The mixture was purified after polymerization and the PS-PSS particles powder was gained.

Preparation of (PS-PSS)/PANI

PS-PSS powder (0.6 g) was diluted in 50 g water. The mixture was stirred for 0.5 h and ultrasonicated for 0.5 h. Meanwhile, 50 g water, 0.25 g HCl (36 wt %), and different amount of aniline (its content was alterative and the reaction recipes were summarized in Table II) were stirred for 0.5 h in a flask. The mixture of diluted PS-PSS powder was dropped into the flask and stirred in icy water bath with the

TABLE II
Reaction Recipes of PS-PSS/PANI Particles

Sample	PS-PSS powder (H ₁) (g)	Aniline (g)	APS (g)
S ₁	0.6	0.20	0.20
S ₂	0.6	0.35	0.35
S ₃	0.6	0.50	0.50

protection of nitrogen for another 2 h. Different amount of APS according to the recipe was diluted in 50 g water and was dropped into the flask (the dropping process was controlled in 0.5 h). The color of the reaction system changed from colorless, light blue, light green to invisible green at last throughout the reaction for 18 h. During this process, the intense stirring (700 rpm) and the protection of nitrogen was indispensable. The mixture was purified after the polymerization and the (PS-PSS)/PANI particles powder was prepared.

Preparation of hollow PANI microspheres

(PS-PSS)/PANI (0.5 g) particles prepared by the above processes were mixed with 150 mL chloroform and stirred intensively for 12 h. The mixture was centrifuged and the supernatant was removed. The precipitate was purified and the hollow PANI particles were fabricated.

RESULTS AND DISCUSSION

Characterization and analysis of monodispersed PS

TEM analysis of monodispersed PS

Particle size and morphology were investigated by TEM. The PS powder prepared above was diluted in ethanol and was ultrasonicated before dropping on the carbon coated copper grid. The carbon coated copper grid coated with PS powder was dried in a

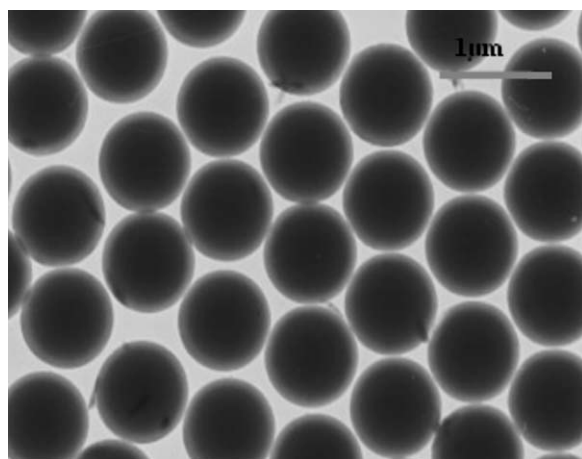


Figure 1 TEM image of monodispersed PS particles produced by dispersion polymerization.

desiccator at room temperature. All other samples were treated like this before the observation of TEM. The TEM image of monodispersed PS is shown in Figure 1. From Figure 1, we can see that the unsulfonated PS particles have a smooth surface and are monodispersed. The diameter of PS particles is about 0.8 μm.

SEM analysis of monodispersed PS

All samples of SEM were sputter coated with a thin layer of gold before imaging. Figure 2 shows the SEM image of monodispersed PS particles. From the image, the PS particles have a uniform diameter and are highly monodispersed. They are spherical with a smooth surface. The diameter is about 0.8 μm, which is consistent with that of TEM image.

Characterization and analysis of PS-PSS particles

SEM analysis of PS-PSS particles

Figure 3 shows the photographs of PS-PSS particles with different amount of SSS. The sample H₁ was synthesized with 0.5 g SSS, which was 5% of the amount of styrene. While the samples H₂ and H₃ were prepared with 1.0 and 1.5 g SSS, respectively. From Figure 3(a), we can observe that the PS-PSS particles are uniformly dispersed and the morphology of them is similar with the monodispersed PS. Some small burr-like protrusions are found after careful observation. That is mainly because of the introduction of functional sulfonic group. With the increase of the amount of SSS, light adhesion appeared in sample H₂ [Fig. 3(b)]. But the spherical morphology is still clear. When the amount of SSS is increased to 1.5 g [Fig. 3(c), sample H₃], the surface of the microparticles become blurred and severe adhesion is occurred. Compared with styrene, SSS is

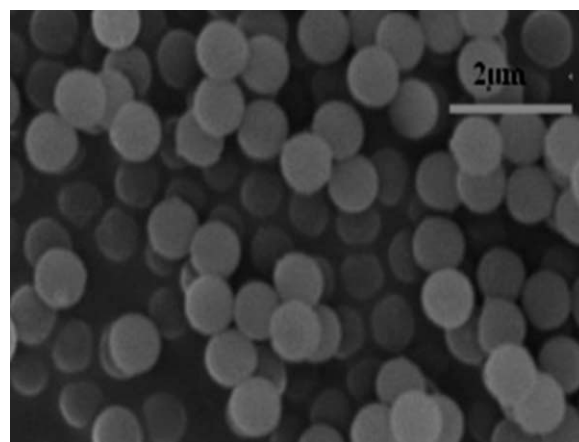


Figure 2 SEM image of monodispersed PS particles produced by dispersion polymerization.

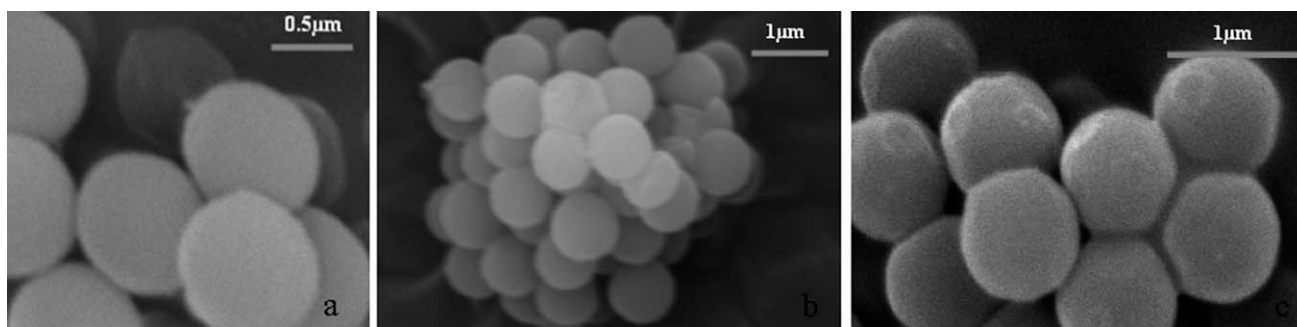


Figure 3 SEM images of PS-PSS particles of (a) sample H₁ : SSS 0.5 g, (b) sample H₂ : SSS 1.0 g, and (c) sample H₃ : SSS 1.5 g.

more hydrophilic and can act as a stabilizer when it is polymerized on the surface of the PS. If the amount of SSS is high, the long chains of sodium PS sulfonate are probably winding with each other. So it is hard for PS-PSS particles to be monodispersed, if the amount of SSS is high.

FTIR spectrum analysis of PS and PS-PSS particles

Figure 4 shows the FTIR spectrum of PS and PS-PSS particles. In Figure 4(A), which was the FTIR spectrum of unsulfonated PS particles, the peak location around 3024 cm⁻¹ is due to the C–H stretching of benzene ring on the PS side chain. The peaks at 1599, 1489, and 1451 cm⁻¹ are the characteristic bands of benzene ring C–C stretching vibration. The peaks at 758 and 700 cm⁻¹ are the bands of aromatic C–H out-of-plane bending vibration. The peak at 2922 cm⁻¹ is due to the C–H stretching vibration of C–H groups on the main PS chain.¹⁹ Compared with the FTIR spectrum of PS, B (sample H₁) and C (sample H₂) are basically identical with A except the peak around 1200 cm⁻¹ at ν(SO₂) in the spectrum, which is attributed to the stretching vibration of the

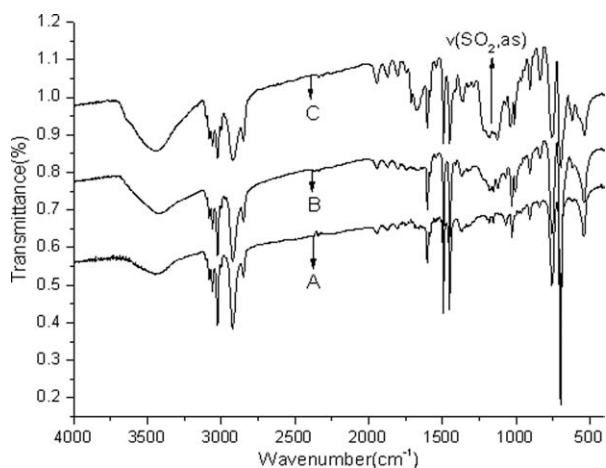


Figure 4 FTIR spectrum analysis of PS-PSS particles. (A: PS particles unsulfonated, B: PS-PSS particles of sample H₁, and C: PS-PSS particles of sample H₂).

S=O. Therefore, the PS-PSS particles are successfully copolymerized. The bands of C at ν(SO₂) are wider than that of B. That is due to the higher amount of SSS in sample H₃. The absorption peak of water is at 3500 cm⁻¹ and C is the widest among the three due to its higher amount of SSS.

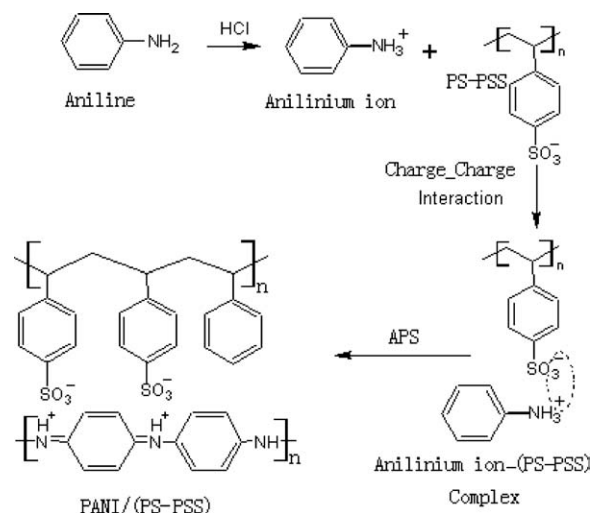
Through the SEM and FTIR analysis of the PS-PSS particles with different amount of SSS, we know that the PS-PSS particles are dispersed well when the amount of SSS is 5% of that of styrene. This lays a good foundation for the fabrication of core-shell (PS-PSS)/PANI and hollow PANI microspheres on the next step.

Characterization and analysis of (PS-PSS)/PANI particles

Mechanism of the synthesis of core-shell (PS-PSS)/PANI particles

The above synthetic procedure of core-shell (PS-PSS)/PANI particles is illustrated in Scheme 1.

At first, aniline was protonated onto positively charged anilinium ions in the presence of HCl, and



Scheme 1 Mechanism of the synthesis of core-shell (PS-PSS)/PANI particles.

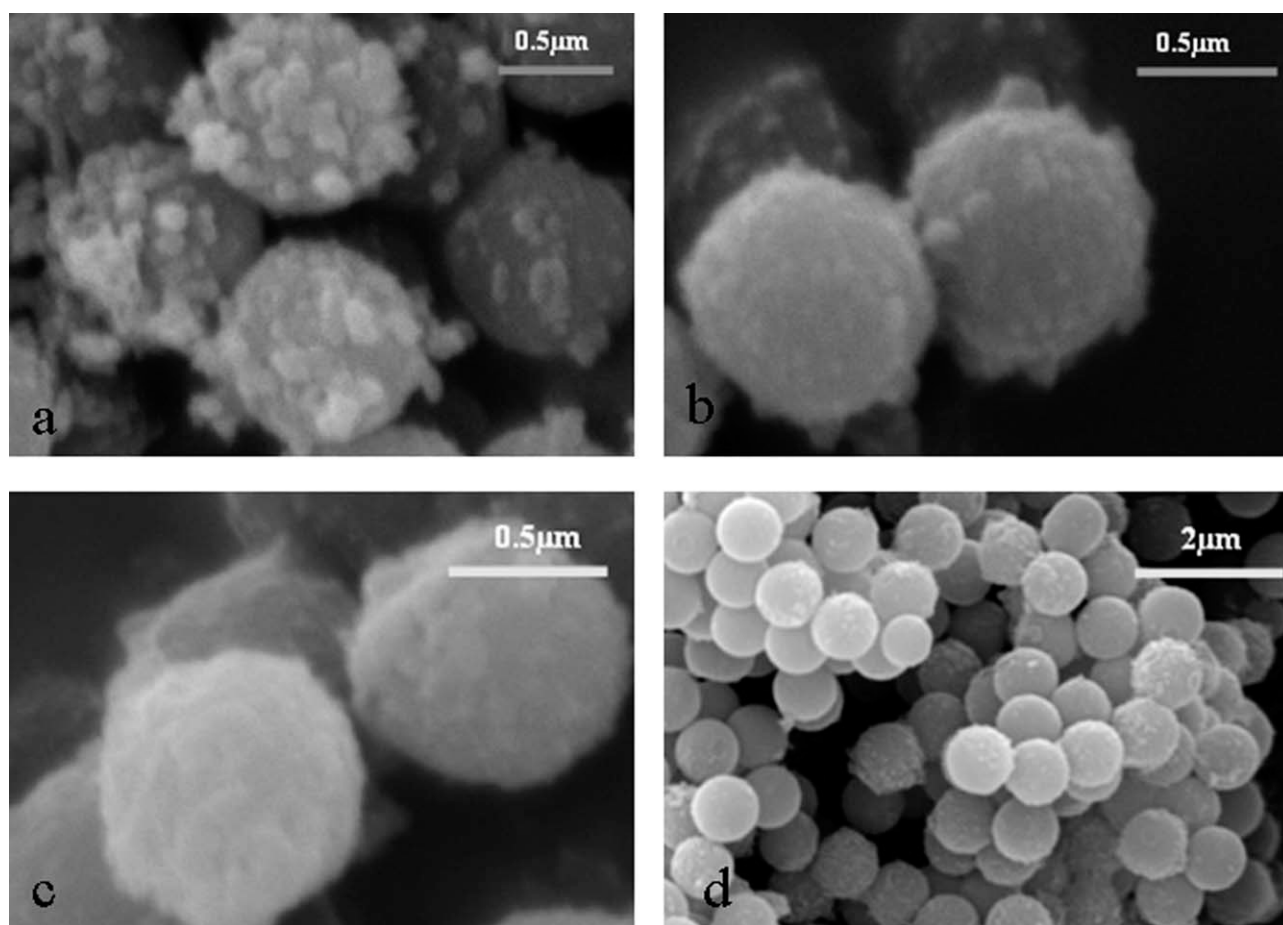


Figure 5 SEM analysis of the core-shell (PS-PSS)/PANI particles. (a) Sample S_1 with 0.20 g aniline and 0.20 g APS, (b) sample S_2 with 0.35 g aniline and 0.35 g APS, and (c, d) sample S_3 with 0.50 g aniline and 0.50 g APS of different magnifications.

subsequently combined with negatively charged sulfonic groups of PS-PSS.²⁰ In other words, the aniline monomer could be attracted on the surface of the PS-PSS particles. Then the polymerization was started under the action of APS. Obviously, the functional sulfonic group could enhance the interaction between the PS-PSS core and the PANI shell because of the electrostatic attraction. That is helpful to improve stability and conductivity of the composite particles.

SEM analysis of the core-shell (PS-PSS)/PANI particles

The SEM images of samples S_1 , S_2 , and S_3 are shown in Figure 5. There are several small protrusions on the surface of the sphere in Figure 5(a) (sample S_1). It indicates that the aniline is not enough to form a uniform shell coating on the surface of the core. With the increase of aniline [sample S_2 , Fig. 5(b)], the PANI shell begins to appear. But the shell is still discontinuous and incomplete. When the aniline is increased to 0.50 g, the shell becomes continuous

and no obvious protrusions are observed [Fig. 5(c), sample S_3]. Therefore, the shell of the composite particles changes from discontinuous protrusions, incomplete coating to complete coating with the increase of aniline. By reducing the magnification of SEM [Fig. 5(d), sample S_3], we can see that the core-shell (PS-PSS)/PANI particles are uniform and have a diameter about 0.9 μm . Coagulations between particles were observed in this image. As the particles are not anymore stabilized by PVP, which was washed away by the purification process and the PSS that helped to stabilize was covered by PANI.

FTIR spectrum analysis of (PS-PSS)/PANI particles

The FTIR spectrum of (PS-PSS)/PANI is shown in Figure 6. Quinoid peak of PANI at 1583 cm^{-1} is observed, and the band at 1305 cm^{-1} is the characteristic absorbing peaks of C–N stretching vibration of PANI, which can confirm the existence of PANI shell [Fig. 6(C)]. The characteristic bands of PS-PSS [Fig. 6(A)] at 700, 754, 1452, 2923, and 3024 cm^{-1} are also found in the spectrum of PS-PSS/PANI

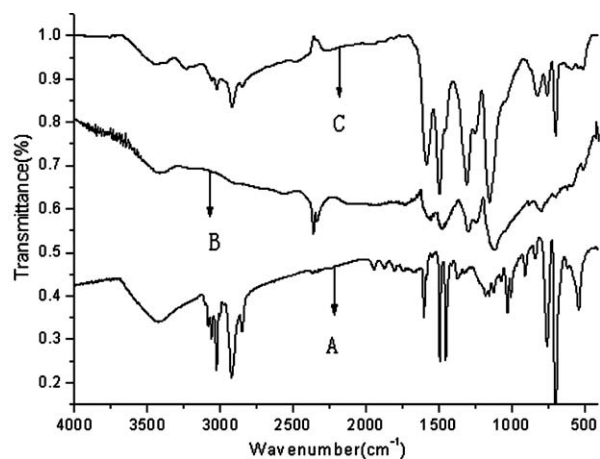


Figure 6 The FTIR spectrum of (PS-PSS)/PANI particles. (A: PS-PSS, sample H₁, B: PANI, and C: (PS-PSS), sample S₃).

particles, which can confirm the existence of PS-PSS core. But these characteristic bands of PS-PSS in the spectrum of PS-PSS/PANI particles are weaker than that in Figure 6(A) (PS-PSS, sample H₁). It is prob-

ably due to the coating shell, which covers the characteristic bands of the PS-PSS core.

Characterization and analysis of hollow PANI microspheres

From the above discussion, we know that samples S₂ and S₃ have a relatively complete core/shell structure. We prepared hollow microspheres through the samples S₂ and S₃ and labeled them with K₁ and K₂, respectively.

SEM analysis of hollow PANI microspheres

Figure 7 shows the SEM photographs of the hollow PANI microspheres. In Figure 7(a) (sample K₁), the hollow microspheres are collapsed and broken. That is because the PANI shell is very thin and is discontinuous in some places. Therefore, it could not keep its spherical morphology. While in Figure 7(b,c) (sample K₂), the shell is complete and thick. The PANI shell is durable enough to keep its spherical morphology.

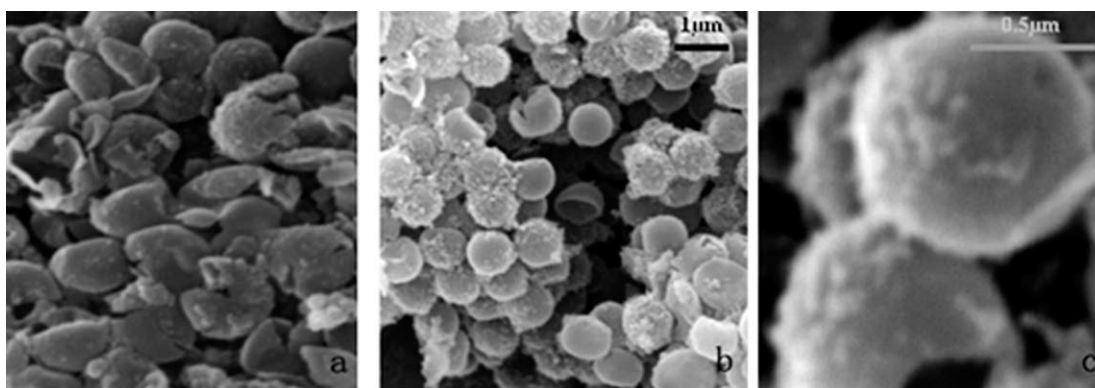


Figure 7 SEM analysis of hollow PANI microspheres. (a) Sample K₁ and (b,c) sample K₂ with different magnification.

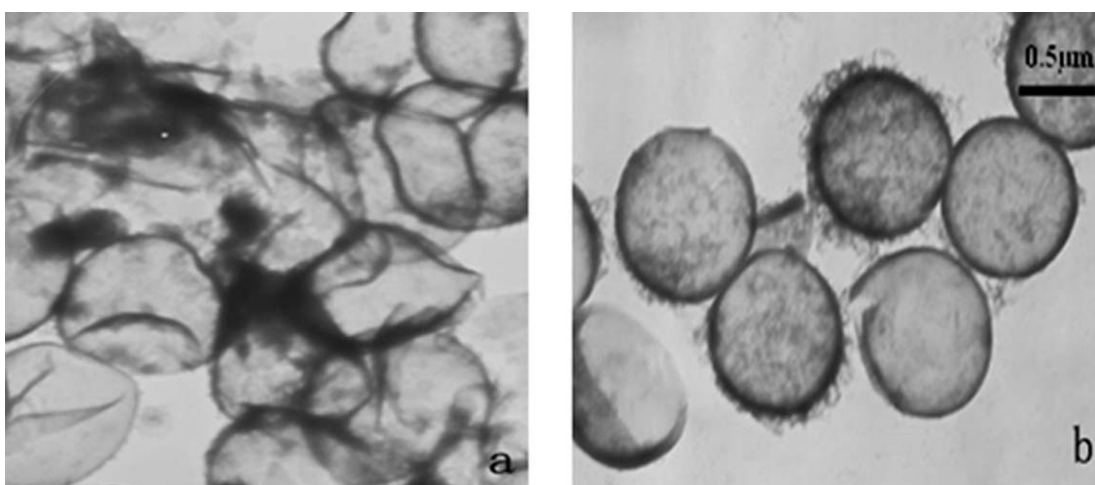


Figure 8 TEM analysis of hollow PANI microspheres. (a) Sample K₁ and (b) sample K₂.

TABLE III
Conductivity Analysis of Core-Shell (PS-PSS)/PANI
Particles and Hollow PANI Microspheres

Samples	Morphology of the PANI shell	Conductivity (S/cm)
S ₁	Mainly protrusions	1.7×10^{-1}
S ₂	Incomplete coating shell	1.43
S ₃	Complete coating shell	2.11
K ₁	Collapsed hollow spheres	2.18
K ₂	Complete hollow spheres	2.17
A	Pure PANI particles	2.20

TEM analysis of hollow PANI microspheres

The TEM images of hollow PANI microspheres are shown in Figure 8. The collapsed and deformed microspheres can be seen clearly [Fig. 8(a), sample K₁]. While in Figure 8(b), the microspheres are uniform and hollow. The diameter of the hollow microspheres is about 0.9 μm .

Conductivity analysis of core-shell (PS-PSS)/PANI particles and hollow PANI microspheres

The conductivity of core-shell (PS-PSS)/PANI particles and hollow PANI microspheres is measured by four point probe. Table III shows the relationship between the morphology of PANI shell and conductivity. Compared with samples S₁, S₂, and S₃, the conductivity enhances with the increase of PANI coating. The surface of sample S₁ is only coated with some protrusions of PANI and the protrusions could not connect with each other. Therefore, its conductivity is the lowest. With the increase of PANI coating, the PANI shell begins to form. Although the shell is still thin and incomplete, the conductivity of sample S₂ can reach to 1.43 S/cm. The shell of sample S₃ is complete and thick and can form a good conductive path. The conductivity of sample S₃ is 2.11 S/cm, which is close to the pure PANI particles (the pure PANI was synthesized by the method similar with the preparation of (PS-PSS)/PANI particles without the addition of PS-PSS powder solution). As the hollow PANI (samples K₁, K₂) is compacted before measurement, the conductivity of hollow PANI is approximately equal to the pure PANI particles.

CONCLUSIONS

In this article, we prepared PANI coated PS-PSS microparticles and hollow PANI microspheres.

Monodispersed PS microparticles were prepared by dispersion polymerization. Through the copolymerization of styrene and SSS on the surface of PS, the PS-PSS particles were prepared with a diameter of 0.8 μm . When SSS was 5% of the amount of styrene, the PS-PSS particles were uniform and monodispersed. These as-prepared PS-PSS particles were successfully coated with a conductive polymer PANI by chemical oxidative polymerization, and the core-shell (PS-PSS)/PANI particles were prepared. The shell of the composite particles was complete and continuous when the ratio is [m(PS-PSS):m(aniline) = 0.6 : 0.5]. The conductivity of the core/shell (PS-PSS)/PANI particles was 2.11 S/cm. Further dissolving the core, we obtained hollow PANI microspheres. The conductivity experiments showed that the hollow PANI microspheres possessed a conductivity of 2.17 S/cm.

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