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Synthesis of Monodisperse Hollow Polyaniline Spheres with Nonsulfonated Polystyrene Latex Template

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Monodisperse hollow polyaniline nanospheres with controlled surface smoothness were synthesized by in situ polymerization of aniline monomers adsorbed on a carboxyl-functionalized polystyrene surface through electrostatic interactions.

There has been tremendous interest in hollow nanospheres for their potential applications in artificial cells, controlled delivery systems, catalysis, lightweight fillers, and confined reaction vessels.[1–6] They have been extensively synthesized by using monodisperse colloidal particles as templates, which provide a robust platform for using a specific functional material to construct the shells.[7–12] Among the various polymeric shells, polyaniline (PANi) is of particular interest, because of its associated electrical, electrochemical, and optical properties, coupled with excellent environmental stability.[13–18] As for the colloidal hollow PANi spheres, the most commonly used synthesis method involves in situ polymerization of aniline monomers absorbed on the surface of polystyrene (PS) nanoparticles, followed by selective dissolution of the colloidal template.[19–21] Typically, PS beads have to be pretreated with concentrated sulfuric acid to render their surface with sulfonic acid groups.[10,22–25] This negatively charged functional group can serve as an anchoring site for the adsorption of protonated aniline monomer via electrostatic attraction. However, the sulfonation process is complex and time consuming, and a more simple alternative method is desired.

In this work, a facile approach has been developed for the fabrication of monodisperse hollow PANi nanospheres. As a major deviation from what has been reported, the colloidal PS particles with carboxyl group were synthesized herein, and surface sulfonation prior to deposition of the conducting polymer is not needed. The carboxyl group serves as counter-charged site for adsorption of aniline monomers as well as a chemical dopant for the growing conducting polymer. This process is simple (one-step), environmentally benign, and could provide an opportunity for formation of hollow PANi spheres with uniformity and well-controlled surface morphology.

Figure 1 schematically illustrates the overall synthetic procedure. Methacrylic acid (MAA) was introduced to the emulsion polymerization of PS latex as an inhibitor, bringing carboxyl groups to the as-synthesized particle surface. The PS seed was used without posttreatment. Aniline monomers were converted to cationic anilinium ions in the presence of hydrochloric acid and adsorbed on the negatively charged surface of carboxyl-functionalized PS particles. Polymerization was initiated by the oxidant ammonium peroxydisulfate (APS) and a uniform shell of PANi was formed. After polymerization was complete, the PS core was selectively dissolved by tetrahydrofuran (THF), which does not dissolve PANi but does dissolve PS, and hollow PANi spheres were ultimately obtained.

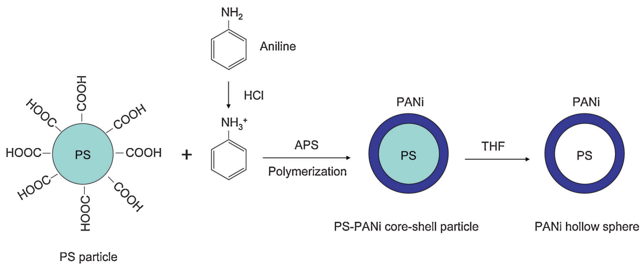

Figure 1. Synthetic procedure of colloidal hollow PANi spheres.

In a typical synthesis, 50 mL of styrene monomer, 400 mL of bidistilled water, and 2 mL of MAA were added into a three-neck flask equipped with a condensator. The mixture was heated to reflux with continuous stirring. After 5 min of boiling, 0.4 g of potassium persulfate powder was added to initiate the polymerization. The whole polymerization lasted 120 min and carboxyl-functionalized PS nanoparticles were obtained. 2 mL of 0.25 M aqueous aniline solution was added to 20 mL of the as-prepared PS latex followed by the addition of hydrochloric acid, also in an equimolar amount relative to aniline. The mixture was stirred with ultrasonic assistance for 150 min at 0 °C to allow sufficient absorption of aniline into the PS seed particles and then was transferred to a three-neck round-bottom flask. Subsequently, 2.5 mL of 0.2 M aqueous APS solution was added dropwise via syringe to initiate the polymerization of aniline. The reaction mixture was kept stirring at 200 rpm for 24 h in an ice bath. The resultant dark-green PANi-coated PS latexes were washed repeatedly by centrifugation until the filtrate became colorless. Finally, the product PS–PANi core–shell particles were dried in a dynamic vacuum for 48 h at room temperature. The extraction of PS core was produced by redispersing the as prepared PS–PANi core–shell particles in 10 mL of THF. The dispersion was kept stirring at 100 rpm at room temperature overnight. The resulting black residue was filtered, washed with THF, and redispersed in water.

The chemical components of the products in the polymerization were investigated by Fourier transform infrared (FT-IR) analysis. Figure 2 shows FT-IR spectra of the PS particles, PS–PANi core–shell particle, and hollow PANi spheres. In Figure 2a, typical PS absorption bands at 3025, 2921, 1601, 1492, 754, and 695 cm^{-1} can be seen clearly. Peaks related to carboxyl groups were also observed at 1705 cm^{-1}, indicating the presence of carboxyl component in PS latex. In Figure 2b, additional absorption bands appear at 1302, 1246, and 1145 cm^{-1}. These peaks are attributed to the PANi component. They appear to be relatively intense due to the existence of PS

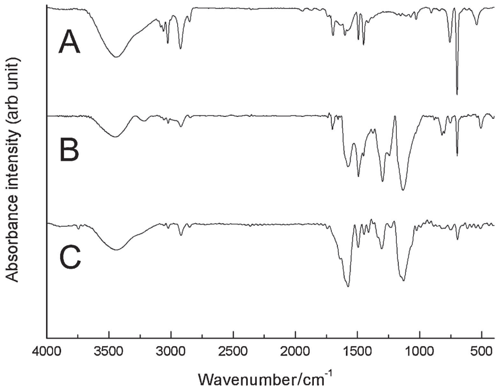

Figure 2. FT-IR spectra of (A) colloidal PS particles, (B) PS–PANi core–shell particles, and (C) hollow PANi spheres.

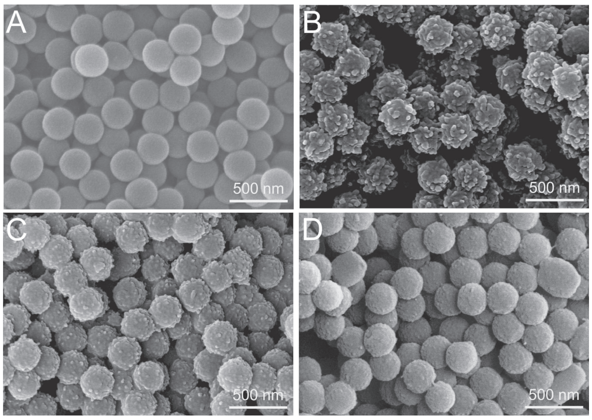

Figure 3. SEM images of (A) colloidal PS particles and PS–PANi core–shell particles, where the PS were synthesized with different MAA/styrene weight ratio: (B) 1:50, (C) 1:25, and (D) 1:12.

component (i.e., the peaks at 1574, 1489, 811, and 698 cm^{-1}). In Figure 2c, a decrease in the intensity of the peaks near 695 and 754 cm^{-1} reflects extinction in the amount of PS and the formation of the hollow PANi sphere.

The morphologies of the PS and PS–PANi core–shell nanoparticles were investigated by scanning electron microscopy (SEM). In comparison with the monodisperse PS seed particles having an average diameter of 260 nm (Figure 3A), the PS–PANi core–shell particles (Figures 3B, 3C, and 3D) had the same spherical shape and good monodispersity. The outline of the core–shell particles exhibited a fine increment in stereoscopic effect compared with the bare PS particles, which are attributed to the increment of surface conductivity derived from the PANi shells. The resultant PANi overlayer was remarkably nonuniform and had a rough outline when a low MAA/styrene weight ratio of 1:50 was used (Figure 3B). This is probably due to inefficient control of the deposition of aniline monomers onto the PS particles. The density of carboxyl groups on the PS particles was relatively low, so the PANi coating tended to take a rough or bumpy morphology. The surface of PANi overlayer gradually became smoother with an increase in the MAA/styrene weight ratio of 1:25 (Figure 3C). As shown in Figure 3D, the PANi coating exhibited good uniformity and perfect surface roughness when the MAA/styrene weight ratio was increased to 1:12. These results indicated that both the uniformity and surface smoothness of the PANi shells could be greatly improved by adding a relatively large amount of MAA to the emulsion polymerization of PS.

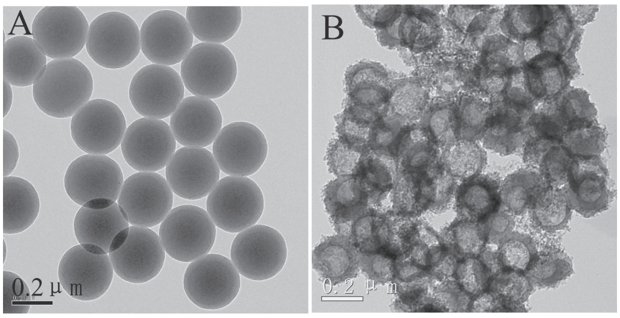

Figure 4. TEM images of (A) PS–PANi core–shell particles and (B) hollow PANi spheres.

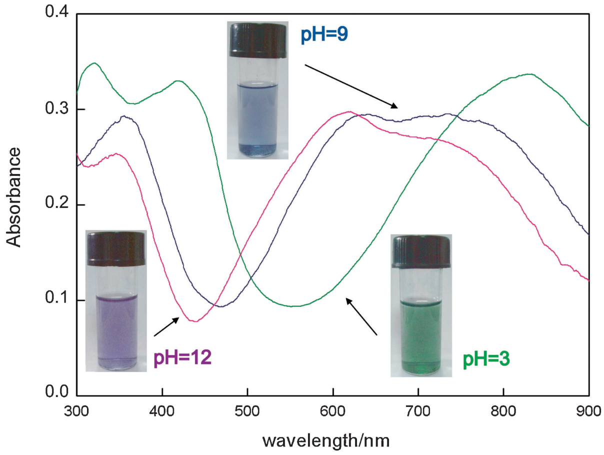

Figure 5. UV–vis spectra and photographs of the aqueous hollow PANi sphere dispersion solution for different pH values.

Transmission electron microscopy (TEM) images of the hollow PANi spheres, as well as the intermediate product of PS–PANi core–shell particles are presented in Figure 4. A uniform pale ring around the dark core can be observed in Figure 4A, which provides direct evidence for the core–shell morphology. Figure 4B demonstrates the PANi residue after immersing the original core–shell particle in THF overnight. In contrast, it reveals a pale center and dark edge of the sphere, confirming that they were all hollow inside. Evidently, all of the hollow spheres still maintained their perfect spherical outline. Compared with conventional methods,[10,20] nonuniform, incomplete shells and irregular outlines were not observed here, due to efficient control of the deposition of PANi onto the PS particles and sufficient mechanical strength to retain its structural integrity.

UV–vis absorption analysis was employed to investigate the dedoping behavior of the dispersion solution of hollow PANi nanospheres. Figure 5 shows the change in the UV–vis absorption spectrum of the resulting hollow PANi nanospheres with varying pH value of 3, 9, and 12. At pH 3, the spectrum of the resulting product exhibits three absorption bands. The absorption at 310 nm is assigned to a π–π^* transition of the benzenoid rings, and the characteristic band ascribable to the polaron transition is observed at around 420 and 800 nm, indicating that the PANi was in the doped state or in the form of emeraldine salt. On the other hand, when the pH of the solution increased up to 12, the PANi was transformed from the emeraldine salt to the emeraldine base form, as reflected in the spectrum by the disappearance of polaron bands at around 420 and 800 nm and emergence of a strong absorption band at 600 nm. This band is assigned to the electron transer between the benzenoid ring and the quinoid ring. Note that the π–π^* transition band shifts to the red by around 40 nm after increasing pH. Such a shift may also be attributed to the deprotonation of PANi. The pictures of the hollow PANi spheres dispersed in ethanol at different pH conditions are also given in Figure 5. Consistent with the band shift in the UV–vis spectrum, different colors were observed, which varied from green to blue and to violet with increased pH from 3 to 9 and to 12, indicating that PANi has been fully dedoped. This behavior is similar to that of materials previously reported.[12]

In conclusion, we have demonstrated a simple approach to fabricate monodisperse colloidal hollow PANi spheres by templating of nonsulfonated PS seed particles. Instead of sulfonation, the carboxyl-functionalized PS particles were synthesized by adding a proper amount of MAA to the common emulsion polymerization of the PS latex. Sufficient MAA is required to generate enough negatively charged carboxyl groups to promote surface adsorption of the protonated and thus positively charged aniline monomers via electrostatic attraction. As a result, suface smoothness of the PANi shells could be well controlled by simply changing the MAA/styrene weight ratio in the preceding synthesis procedure of colloidal PS particles. In addition, these colloidal hollow PANi spheres also showed good pH-responsive dedoping behavior. As the functionalized PS seed particles can be manufactured conveniently for high-volume production of hollow PANi spheres, wide applications in encapsulation, targeted delivery and controlled release are anticipated.

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