

Self-Assembly and Characterization of Polyaniline and Sulfonated Polystyrene Multilayer-Coated Colloidal Particles and Hollow Shells

Mi-Kyoung Park,[†] Ken Onishi,[†] Jason Locklin,[†] Frank Caruso,^{*,‡} and Rigoberto C. Advincula^{*,†}

Department of Chemistry, University of Houston, Houston, Texas 77063, and Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia

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Conductive core-shell particles were prepared by the deposition of polyaniline (PANI) and poly(sodium 4-styrenesulfonate) (PSS) multilayers onto polystyrene (PS) colloidal particles via the alternate electrostatic layer-by-layer (LbL) assembly technique. PSS was used as a polymeric counterion for multilayer formation as well as a stabilizer and codopant for PANI. Electrophoresis, FT-IR spectroscopy, and transmission electron microscopy (TEM) confirmed the regular growth of PSS/PANI multilayers on PS colloidal particles. It was found that the PSS/PANI-coated particle is oxidatively more stable due to stabilization of the partially oxidized emeraldine salt by PSS. The conductivity of (PSS/PANI)₅-coated PS particles was 0.003 S/cm and increased to 0.1 S/cm after additional dopant exposure with HCl vapor. Furthermore, hollow shells made up of PSS/PANI layers were produced by dissolution of the PS core from PSS/PANI-coated particles. Cyclic voltammetry (CV) showed that PSS/PANI multilayers maintained their oxidative stability and electrochemical properties after removal of the core.

Introduction

In recent years, polyaniline (PANI) has been the focus of intense investigation due to its good electrical conductivity, stability in ambient conditions, and control of the electronic and optical properties by the degree of oxidation and protonation.¹ It has been used in applications such as organic lightweight batteries,² microelectronics,³ electrorheological fluids,⁴ and chemical sensors.^{5,6} However, like many other conducting polymers, unsubstituted PANI is intractable and suffers from poor processability, mainly because of its rigid, highly conjugated backbone. Many methods have been explored to overcome their poor processability.

Recently, several research groups have reported the chemical synthesis of conducting polymer-coated "core-shell" particles where the "core" consists of a nonconducting material.⁷ Wiersma et al. were the first to show that sterically stabilized polyurethane (PU) latex particles could be coated with either polypyrrole (PPy) or PANI in aqueous media to form composite particles with good colloid stability.⁸ Various conducting polymers, such as PPy,^{9,10} PANI,¹¹ and poly(3,4-ethylenedioxythiophene)

(PEDOT),¹² have been extensively studied by the Armes group. They have used poly(*N*-vinylpyrrolidone) (PVP)-stabilized PS latex particles as core templates where the oxidant and monomer were introduced via an aqueous dispersion. A thin overlayer of conducting polymer formed on PS latexes, yielding core-shell morphology. The conducting polymer loading was controlled by varying the latex concentration in the synthesis. This approach demonstrated that better processability and relatively high conductivity can be achieved even with low conducting polymer loading. PANI-coated PS latexes have also been synthesized in the presence of either poly(vinyl alcohol) or sodium dodecyl sulfate.^{13,14}

Another approach to improve processability of PANI is the synthesis of a PANI-poly(4-styrenesulfonic acid) (PSS) composite by polymerization of aniline in the presence of PSS^{15,16} or thermal postpolymerization of *p*-styrenesulfonic acid (SAA) in a PANI-SSA composite.² It has been shown that optically and electrochemically active and stable composites can be prepared where PSS serves the critical function of providing counterions to dope the PANI while maintaining water solubility for processing.^{2,15,16}

[†] University of Houston.

[‡] The University of Melbourne.

* To whom correspondence should be addressed.

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Recently, ultrathin PANI multilayer films have been fabricated by sequential adsorption of doped PANI and a polyanion via the layer-by-layer (LbL) technique.^{17,18} The LbL method permits the fabrication of multilayer thin films assembled on solid supports by the sequential adsorption of oppositely charged species from dilute solutions onto charged substrates.¹⁹ This process is particularly attractive because it is simple to implement and versatile and applies to a broad range of charged species. Cheung et al. first reported that PSS/PANI LbL films could be fabricated from dilute aqueous-based solutions of partially doped PANI, which has sufficient stability to allow multilayer deposition with a polyanion, PSS.^{17a} Ram et al. have investigated the electrochemical response time and diffusion coefficient of these PANI/PSS multilayer films.^{17b} Our group has previously investigated the in-situ optical and electrochemical response of PANI/sulfonated polyaniline (SPANI) films using electrochemical surface plasmon spectroscopy (EC-SPS).¹⁸

The LbL technique has been successfully applied to utilize submicrometer- and micrometer-sized, charged colloidal particles as the adsorbing substrate (template) to produce colloid-supported polyelectrolyte multilayer films.²⁰ Also, it has been shown that novel three-dimensional hollow polymer shells can be fabricated by subsequent removal of the core after the LbL deposition.²¹

This report describes an approach to fabricate conducting polymer-coated "core-shell" particles by alternating self-assembly deposition of a conducting polymer with polyelectrolytes on PS particles. This technique provides several advantages over the conventional method, such as simple processing, the ability to control thickness at the molecular level while maintaining a smooth and uniform morphology with increased conducting polymer loading, and the ability to incorporate a variety of other charged species such as different types of conjugated polymers, polyelectrolytes, nanoparticles, and dyes into the multilayer film. It should be noted that most of these polyelectrolyte or electrolyte combinations are typically unstable complexes in solution but are readily deposited as coatings and films using the LbL method.

In this paper, we report the preparation and investigation of monodispersed PSS/PANI-coated PS particles and hollow capsules through the LbL assembly technique. PSS was used as a polymeric counterion for fabrication of the multilayers as well as a stabilizer and codopant. The colloid entities, both solid and hollow, have been characterized by electrophoresis, FT-IR, and transmission electron microscopy (TEM). The electrochemical behavior of these PSS/PANI multilayers was examined by cyclic voltammetry.

Experimental Section

Materials. The emeraldine base form of polyaniline (PANI), poly(diallyldimethylammonium chloride) (PDADMAC), $M_w < 200\,000$, and poly(sodium 4-styrenesulfonate) (PSS), $M_w 70\,000$, were used without further purification (from Aldrich Chemical

Co.). The negatively charged sulfonate-stabilized polystyrene (PS) particles (diameter 498 nm) were purchased from Micro-particles GmbH, Berlin. Sodium chloride (NaCl), methanesulfonic acid (MeSA), and dimethylacetamide (DMAc) were purchased from Aldrich. The water used in all experiments was prepared in a Milli-Q Academic system equipped with a 0.22 μm Millistack filter at the outlet and had a resistivity higher than 18.2 M Ω cm.

PANI Multilayer (PSS–PANI) Assembly on PS Spheres.

An initial polyelectrolyte multilayer film was first deposited on the PS particles as described elsewhere.²² The three-layer polyelectrolyte film [PDADMAC/PSS/PDADMAC] was deposited on the PS particles to give a higher charge density and a smooth surface. The PANI solution was prepared using a procedure by Cheung et al.¹⁷ The emeraldine base form of polyaniline was dissolved in DMAc at a concentration of 20 mg/mL by first stirring the solution overnight and then sonicating it for about 8–10 h followed by filtering the solution through a 0.7 μm filter. The polyaniline dipping solution was prepared by slowly adding one part (by volume) of the filtered polyaniline solution to nine parts of water that had its pH adjusted to about 3.0–3.5 with MeSA. The pH was then quickly lowered to 2.5–2.6 by adding 1 M MeSA drop wise.

The PSS/PANI multilayers were fabricated as follows: (a) addition of 1 mL of a 1 mg/mL aqueous PSS solution (1 mg/mL solution containing 0.5 M NaCl, pH 2.5) to the polyelectrolyte-coated particles, allowing 15 min for PSS adsorption, (b) removal of excess PSS by four repeated centrifugation (7000 rpm, 20 min)/water wash/redispersion cycles, and (c) subsequent deposition of PANI in identical fashion. The desired number of PSS/PANI multilayers was assembled by repeated consecutive assembly of PSS and PANI using this method. The pH of washing water was adjusted to 2.5.

Hollow Capsule Production. For the production of hollow capsules from polyelectrolyte-coated PS particles, 0.2 mL of the coated PS particles were exposed to 1 mL of THF for 12 h. The capsules were then centrifuged at 10 000g for 15 min and redispersed in THF, and the supernatant was exchanged for THF. To ensure complete core removal, the THF treatment and washing steps were repeated a further two times.

Characterization. Electrophoretic mobilities of the coated PS latexes were measured using a Malvern Zetasizer 4. The mobility u was converted into a ζ -potential by using the Smoluchowski relation $\zeta = u\eta/\epsilon$, where η and ϵ are the viscosity and permittivity of the solution, respectively. All ζ -potential measurements were performed on coated PS particles redispersed in air-equilibrated pure water (pH \approx 5.6). TEM images were obtained using a Hitachi transmission electron microscope (H-7000). Samples for TEM were prepared by depositing an aqueous solution of the coated PS particles on a carbon-coated copper grid. The solution was then allowed to air-dry for 1 min, and the extra solution was blotted off. FT-IR spectra of PSS- and PANI-coated PS particles were obtained using a Nicolet NEXUS 470 FT-IR system. The dispersion of conducting polymer-coated PS particles was dried under vacuum. The samples of each bilayer of PSS and PANI coated particles were prepared by grinding powdery samples with KBr powder and then pressing the mixtures into pellets. Cyclic voltammetry measurements were performed with an Amel 2049 potentiostat and Power Lab system with a three-electrode cell in a solution of 1 M HCl aqueous solution at a scan rate of 50 mV/s. Platinum wire was used as the counter electrode, and Ag/AgCl was used as the reference electrode. The conductivities of compressed pellets of the PSS/PANI-coated PS powder were determined using a Keithley 2700 multimeter equipped with disk type electrodes at room temperature. It is estimated that the random error associated with such measurements is approximately 10%. In some cases, the pellets were additionally doped by exposing to HCl vapor (vapor from concentrated HCl) for 1 h under controlled atmospheric conditions in a sealed glass chamber.

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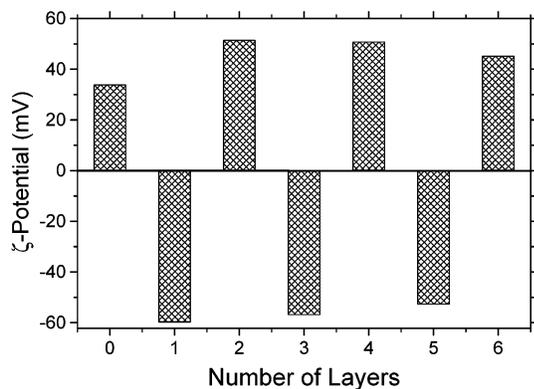


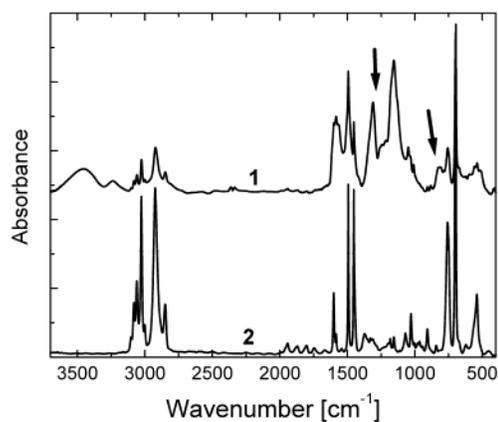
Figure 1. ζ -potential as a function of polyelectrolyte layer number for PSS/PANI-coated 498 nm PS spheres. The PS particles were precoated with PDADMAC/PSS/PDADMAC layers (0 layer in the figure) prior to deposition of the first layer. The even layer numbers correspond to PANI adsorption and the odd layer numbers to PSS deposition.

Results and Discussion

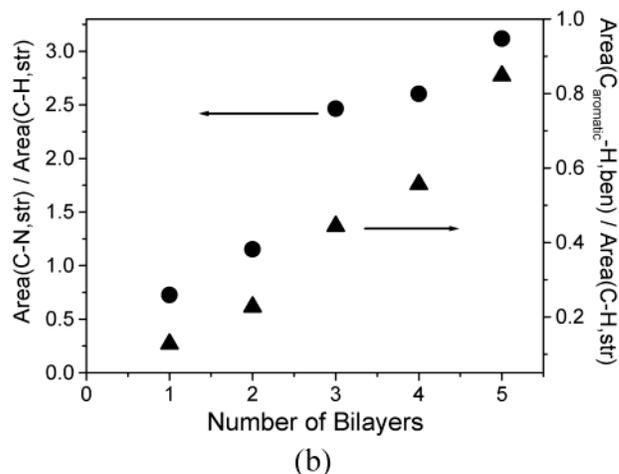
PSS–PANI Multilayer Assembly on PS Spheres.

The assembly of PSS/PANI multilayers on the PS particles was first examined by electrophoresis. Figure 1 shows the ζ -potential values as a function of polyelectrolyte layer number for the negatively charged PS particles coated with PSS/PANI multilayers. The uncoated PS particles gave a ζ -potential of about -65 mV in water (data not shown). After the formation of precursor layers (a three-layer of [PDADMAC/PSS/PDADMAC], marked as layer number 0 in Figure 1a) onto PS particles, the ζ -potential is $+34$ mV, which is consistent with the outermost layer being a polycation. The subsequent alternate assembly of PSS and PANI caused a reversal in the sign of the ζ -potential with each deposition up to six layers. Odd numbers correspond to the PSS layer and have negative values (-50 to -60 mV). Even numbers correspond to the PANI layer and have positive values ($+45$ to $+55$ mV) due to the positive charge in acidic-doped PANI. Small variations between the measured ζ -potentials may be due to a slight drift in pH. The alternating negative and positive ζ -potentials suggest stepwise growth of the multilayer films.^{20–22}

The assembly of PSS/PANI multilayers on the PS particles was examined by FT-IR spectroscopy. The FT-IR spectra of sulfonated-PS colloidal particles (1) and (PSS/PANI)₃-coated PS colloidal particles (2) are shown in Figure 2a. The spectrum was obtained from a mixture of sample with KBr in pellet form. In the spectrum of PSS/PANI-coated PS particles, the peaks related to PANI, the N–H stretching band at 3432 , 3234 cm^{-1} , the C=C (quinoid, Q) stretching band at 1570 cm^{-1} , the aromatic C–N stretching band at 1309 cm^{-1} , the N=Q=N at 1153 cm^{-1} , and the aromatic C–H band at 821 cm^{-1} appeared.²³ To study the PSS/PANI multilayer growth on the PS colloidal particles, two peaks (1570 and 821 cm^{-1}) of PANI were chosen that did not overlap with the peaks of PS and methylene C–H stretching band peaks (2848 and 2921 cm^{-1}) and integrated the area under each peak. The ratio of the area of PANI to that of the C–H peak of PS was obtained for up to (PSS/PANI)₅-coated PS particles. It is critical to obtain the ratio of PANI to PS peak because it is very difficult to maintain a constant concentration of coated particles in each sample. Figure 2b shows the ratio



(a)



(b)

Figure 2. (a) FT-IR spectra of sulfonated PS colloidal particles (1) and (PSS/PANI)₃-coated PS colloidal particles (2). The spectrum was obtained from a mixture of sample with KBr in pellet form. (b) Plot of the ratio of the integrated area under the peak at 1309 cm^{-1} (C–N stretch) over the area under the peak at 2848 and 2921 cm^{-1} (C–H stretch) (left) and the ratio of the integrated area under the peak at 821 cm^{-1} (C–H bend) over the area under the peak at 2848 and 2921 cm^{-1} (C–H stretch) (right) as a function of the number of PSS/PANI bilayers deposited.

of (a) (C–N stretch, 1309 cm^{-1})/area (C–H stretch, 2848 and 2921 cm^{-1}) and (b) (C–H bend, 821 cm^{-1})/area (C–H stretch, 2848 and 2921 cm^{-1}) as a function of the number of bilayers deposited. The ratio values increase with the number of bilayers, confirming the growth of PSS/PANI bilayers on the PS colloidal particles.²⁴

Direct observation of the multilayer growth process and morphology of the PSS/PANI-coated PS particles were examined using TEM. Figure 3 shows the TEM micrograph of the uncoated latex (inset in (a)), (PSS/PANI)₁-coated PS particles (a), and (PSS/PANI)₃-coated PS particles (b). The uncoated PS particle has a smooth surface while the coated particles exhibited increased surface roughness. Deposition of the PSS/PANI layers also resulted in an increase in the overall diameter of the particles. The average diameter of the (PSS/PANI)₁- and (PSS/PANI)₃-coated particles is approximately 510 ± 5 and 550 ± 10 nm, respectively. For three bilayers of PSS/PANI-coated PS particle, the diameter increases to about 40 nm from a one-bilayer-coated PS particle, corresponding to an average layer thickness of about 10

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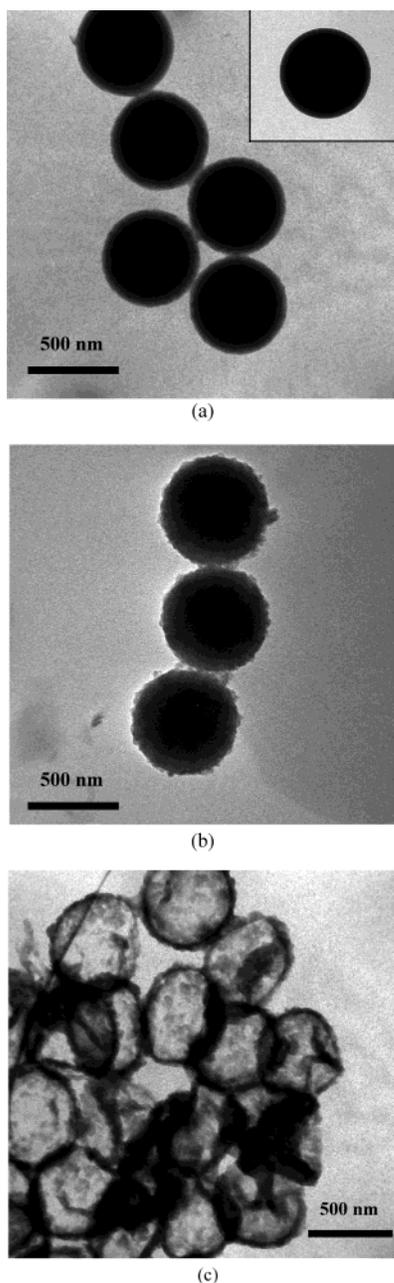


Figure 3. TEM images of (a) (PSS/PANI)₁-coated PS particles. The PS particles used as templates have a diameter of 498 nm (inset). TEM images of (b) (PSS/PANI)₃-coated PS particles and (c) hollow (PSS/PANI)₅ capsules, obtained after decomposition of the PS template.

nm for the PSS–PANI layer pair. (The diameter of the precursor layer PDADMAC/PSS/PDADMAC-coated PS particles is 506 ± 5 nm.) However, the layer thickness for the first PSS/PANI bilayers is only about 2 nm. Such behavior has often been observed, with a few polyelectrolyte layers required prior to regular multilayer growth of films assembled by the LbL technique.²⁵

We observed that the increase in surface roughness is mainly due to PANI. This may have resulted from the formation of PANI aggregates in solution that are subsequently adsorbed on the surface of the spheres. Ram et al. have reported that the surface of PSS/PANI LbL multilayer on flat glass substrates is covered by particles

with a diameter of 16 ± 2 nm and that the PSS/PANI grain size increases with the number of layers.^{17b} The obtained thickness and size are greater than those attributed to true polyaniline monolayers and are most likely due to the propensity of PANI to aggregate. Furthermore, we also note that the aggregation of PSS/PANI-coated colloidal particles occurred after the deposition of five bilayers. As the number of bilayers increases, the surface becomes rougher; therefore, interparticle entanglement occurs and leads to aggregation.²⁶

PSS/PANI Hollow Shells. For the production of hollow capsules from PSS/PANI-coated particles, the core (PS) was removed by dissolution in THF after depositing the desired number of layers. The PSS/PANI capsules were characterized using TEM. A TEM image of (PSS/PANI)₅ hollow capsules is shown in Figure 3c. Folds, creases, and flattening of the hollow capsules were observed, which were a result of the drying procedure prior to the measurements.²¹ From the image, it can be seen that complete, hollow spheres are produced, which indicates that by exposing the PSS/PANI-coated particles to THF, the PS core can be successfully dissolved and extracted from the core via permeation through the semipermeable PSS/PANI multilayer walls.²⁷ The 10–50 nm sized aggregates of PANI are clearly seen. The thickness of (PSS/PANI)₅ hollow capsules is about 40 ± 10 nm, corresponding to a layer thickness of about 7 nm for the PSS–PANI layer pair.

Electrochemical Investigation. The electrochemistry of the PSS/PANI-coated PS particles and hollow shells was investigated using cyclic voltammetry. The suspension was cast onto a gold substrate and dried to yield a green film. The cyclic voltammogram (CV) of (PSS/PANI)₃-coated PS particles in a 1 M HCl acidic medium at a scan rate of 50 mV/s is shown in Figure 4a. Platinum wire was used as the counter electrode, and Ag/AgCl was used as the reference electrode. Three sets of redox peaks are observed with the $E_{1/2}$ at 0.33, 0.53, and 0.69 V. Two characteristic peaks of PANI (0.33 and 0.69 V) correspond to the redox transitions between the fully reduced, insulating form (leucoemeraldine) and the partially oxidized, conducting form (emeraldine) and between emeraldine and the fully oxidized, insulating form (pernigraniline), respectively.²⁸ The middle peak at 0.53 V has been identified as belonging to the water-soluble degradation products. The CVs as a function of bilayers (data not shown) also have been investigated and showed similar peak positions and shape, which suggests that the oxidation electrochemical response of PSS/PANI is practically independent of the number of bilayers.^{17b} Two important points to be noted from the CV are that the second redox peak of PANI is significantly smaller than the first peak, and the first redox peak is seen at higher potential than that of the electrochemically synthesized PANI (typically, $E_{1/2} < 0.2$ V vs Ag/AgCl). Liu and co-workers have reported that the enzymatically synthesized PANI/PSS complex showed only one set of redox peaks at $E_{1/2} = 0.43$ V (vs Ag/AgCl).¹⁵ Also, Chan and co-workers have showed that poly(*o*-aminobenzylphosphonic acid) had only one redox peak at $E_{1/2} = 0.39$ V (vs Ag/AgCl).²⁹ They suggested that the absence of the second redox process is due to the

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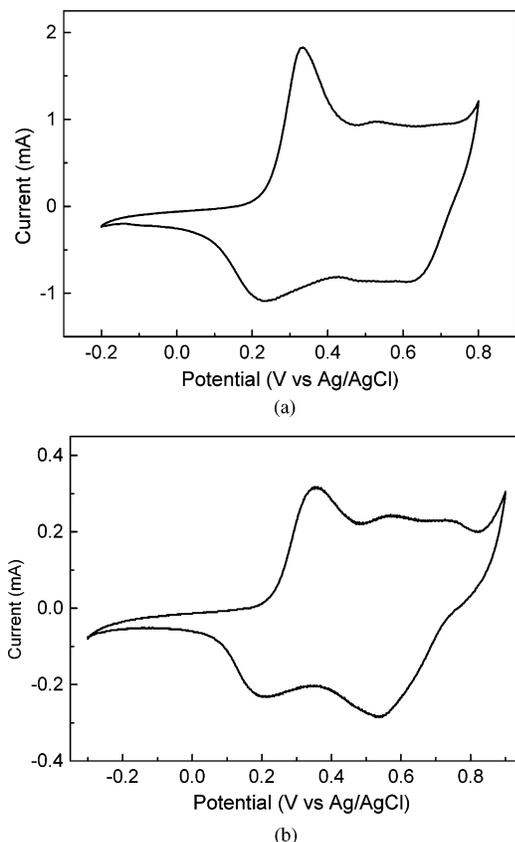


Figure 4. Cyclic voltammogram of (a) (PSS/PANI)₃-coated PS particles on a gold substrate and (b) hollow (PSS/PANI)₅ capsules on gold substrates in a 1 M HCl acid medium at a scan rate of 50 mV/s. Platinum wire was used as the counter electrode, and Ag/AgCl was used as the reference electrode.

exceptional resistance of the PANI to oxidation to the pernigraniline state. In our case, the redox peak shifts to higher potential as well as to significantly lower currents of the second redox peak, suggesting that the PSS/PANI-coated colloidal particles have higher oxidative stability. We believe that this is mainly due to stabilization of the partially oxidized emeraldine salt PANI with PSS.¹⁵

The cyclic voltammogram of (PSS/PANI)₃ hollow shells in a 1 M HCl acid medium at a scan rate of 50 mV/s is shown in Figure 4b. Three sets of redox peaks are also seen at $E_{1/2} = 0.37, 0.55,$ and 0.74 V, which are identical with those of PSS/PANI-coated PS particles within the experimental error range. The first redox peak potential and lower second redox current likewise suggest that the PSS/PANI multilayer shell maintained their oxidative stability and electrochemical properties even after removal of the core. This means that both core-shell and hollow-shell particles maintain a relatively high oxidative stability. This is in contrast to chemically synthesized PANI, which has oxidative stability directly related to anion transport and degree of dopant incorporation.¹ Again, the values were found to be comparable to the electrochemical behavior in PSS/PANI ultrathin films.^{17b}

Conductivity Measurements. The electrical conductivities of compressed pellets of the PSS/PANI-coated PS particles were measured. The PANI films produced by the LbL technique were in partially doped states due to the acidic condition during the procedure as well as because of the presence of the polymeric dopant, PSS. The conductivity of (PSS/PANI)₅-coated PS particles is 0.002–0.003 S/cm and is comparable to that of the bulk PANI/PSS complex, which is chemically synthesized.¹⁵ The conductivity increases to 0.1 S/cm after additional doping by exposure to HCl vapor. Similar conductivities have been reported for typical PANI LbL multilayer on flat substrates.¹⁷ The conductivity of (PSS/PANI)₃-coated PS particles is 1×10^{-4} S/cm after the additional doping, which suggests that the electrical conductivity percolation threshold is in the range of 3–5 bilayers of PSS/PANI. Thus, it is possible to prepare processable colloidal particles of PANI with similar electrical conductivities to bulk and thin film samples.

Conclusions

We have demonstrated that conductive and oxidatively stable core-shell and hollow-shell particles can be fabricated by the layer-by-layer deposition of PSS and PANI onto PS colloidal particles. The LbL multilayers of the PSS/PANI have been characterized by electrophoresis and FT-IR spectroscopy, and the results showed regular growth of PSS/PANI multilayers. Cyclic voltammetry studies showed a significantly larger first redox peak, which suggests that the PSS/PANI-coated particles are oxidatively more stable due to the stabilization of the partially oxidized emeraldine salt with PSS. Furthermore, hollow capsules comprising PSS/PANI multilayers can be prepared by dissolution of the PS core from PSS/PANI-coated particles. TEM images showed the increase in surface roughness as the number of bilayers increased, which may be due to the formation of PANI aggregates in solution that are subsequently adsorbed on the surface of the spheres. The conductivity of (PSS/PANI)₅-coated PS particles is 0.1 S/cm and is comparable to that of the bulk PANI/PSS complex¹⁵ and PANI/PSS multilayers on a planar surface.^{17b} What is unique about this approach is that it should be possible to prepare core-shell and hollow-shell particles with different conducting polymer or polyelectrolyte combinations that do not normally form stable complexes in solution. Research is underway to investigate approaches to higher conductivity and controlled permeability of multilayer films through electrochemical methods.

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