Cross-Linked, Luminescent Spherical Colloidal and Hollow-Shell Particles

Mi-Kyoung Park, Chuanjun Xia, and Rigoberto C. Advincula*

Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama 35294-1240

Peter Schütz and Frank Caruso*

Max Planck Institute of Colloids and Interfaces, D-14424 Potsdam, Germany

Received July 2, 2001. In Final Form: September 18, 2001

Luminescent core−shell particles were prepared by the layer-by-layer deposition of polystyrenesulfonate (PSS) and water-soluble ionene precursor polymers containing fluorene units (PI) onto spherical colloidal particles. Subsequent cross-linking of the PI in the multilayer shell formed the luminescent conjugated oligo-fluorenes. In a further step, removal of the PI/PSS multilayer coated core yielded luminescent hollow capsules. The formation, characterization, and properties of the PI/PSS-coated colloids and PI/PSS hollow capsules have been investigated by electrophoresis (EPM), single particle light scattering (SPLS), transmission electron microscopy (TEM), atomic force microscopy (AFM), and cyclic voltammetry (CV). EPM and SPLS measurements confirmed the regular deposition of PI/PSS multilayers on the particles, while TEM and AFM demonstrated the formation of hollow capsules composed of PI/PSS multilayers. CV experiments verified cross-linking of the multilayers, which showed an irreversible oxidation process. The procedure employed permits the incorporation of luminescent polymer materials into cross-linked multilayer shells on high surface area colloidal particles and the preparation of luminescent free-standing, three-dimensional hollow capsules after core removal.

Introduction

The fabrication of ultrathin molecular films by the alternate electrostatic adsorption (or layer-by-layer, LbL) of oppositely charged polyelectrolytes from aqueous solution onto solid surfaces was introduced by Decher and co-workers in the early 1990s.[1,2] This process is particularly attractive because it is simple to implement, is versatile, and applies to a broad range of charged species (e.g., polyelectrolytes, nanoparticles, proteins, etc.). The LbL technique has recently been applied to construct multilayer shells on colloid particles: classical polyelectrolyte,[3] protein/polyelectrolyte,[4] and nanoparticle/polyelectrolyte[5,6] multilayers have been prepared.

The LbL molecular-level manipulation of water-soluble conjugated polymers (e.g., polyaniline, sulfonated polyaniline, poly(thiophene-3-acetic acid)) has been utilized to fabricate ultrathin multilayer films.[7] These materials have interesting electrical and optical properties mainly due to their intrinsic π-electron delocalization and charge carrier mobilities.[8] The conjugated and luminescent polymer, poly(*p*-phenylenevinylene) (PPV) has been deposited as LbL films via the polycation precursor route.[9,10] These multilayers have been investigated for use as light-emitting devices and have shown stable and efficient device performance. Ionene polymers are polyelectrolytes with a charge group (commonly positive) at the main chain.[11] The LbL deposition of ionene-type polycations has been investigated more recently by Laschewsky and co-workers.[12] The influence of ionic strength, charge density, and functionality (e.g., the nonlinear dyes) of the polyionene on the formation of LbL films were examined.[12]

Not only would the formation of luminescent multilayers on colloid particles represent an interesting extension to the type of particles prepared using this approach, but also they are expected to be of significant interest in various optical and electronic applications. This includes luminescent colloidal particles for passive matrix displays, light-emitting electrochemical cells, patterned luminescent colloidal particles on surfaces, and so forth. They would also exhibit considerably larger surface areas compared to their planar support counterparts. Furthermore, cross-linked multilayers could potentially display enhanced stability compared with LbL ionically assembled films.[13]

In this paper, we report the preparation of luminescent polyelectrolyte-coated particles and hollow capsules

---

* Corresponding authors.

(1) Decher, G.; Hong, J. D. *Makromol. Chem., Macromol. Symp.* **1991**, *95*, 1430.

(2) Decher, G. *Science* **1997**, *277*, 1232.

(3) (a) Caruso, F.; Donath, E.; Möhwald, H. *J. Phys. Chem. B* **1998**, *102*, 2011. (b) Donath, E.; Sukhorukov, G. B.; Caruso, F.; Davis, S. A.; Möhwald, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2201.

(4) Caruso, F.; Möhwald, H. *J. Am. Chem. Soc.* **1999**, *121*, 6039.

(5) (a) Caruso, F.; Caruso, R. A.; Möhwald, H. *Science* **1998**, *282*, 1111. (b) Caruso, F.; Liochtenfeld, H.; Möhwald, H.; Giersig, M. *J. Am. Chem. Soc.* **1998**, *120*, 8523. (c) Caruso, F.; Möhwald, H. *Langmuir* **1999**, *15*, 8276.

(6) Susha, A. S.; Caruso, F.; Rogach, A. L.; Sukhorukov, G. B.; Kornowski, A.; Möhwald, H.; Giersig, M.; Eychmüller; Weller, H. *Colloids Surf., A* **2000**, *163*, 39.

(7) (a) Ferreira, F.; Rubner, M. F. *Macromolecules* **1995**, *28*, 7107. (b) Fou, A. C.; Rubner, M. F. *Macromolecules* **1995**, *28*, 7115. (c) Cheung, J. H.; Stockton, W. B.; Rubner, M. F. *Macromolecules* **1997**, *30*, 2712.

(8) *Conjugated Polymers and Related Materials*; Salaneck, W. R., Lundstrom, I., Ranby, B., Eds.; Oxford University Press: Oxford, 1993.

(9) Lehr, B.; Seufert, M.; Wenz, G.; Decher, G. *Supramol. Sci.* **1995**, *2*, 199.

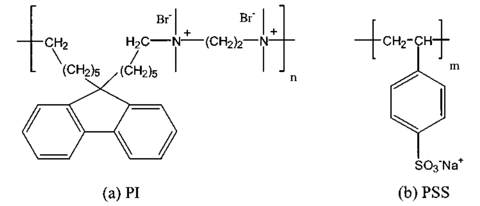
(10) Kirstein, S.; Hong, H.; Steitz, R.; Davidov, D. *Synth. Met.* **1999**, *102*, 1067.

(11) Wang, J.; Meyer, W.; Wegner, G. *Acta Polym.* **1995**, *46*, 233.

(12) (a) Delcorte, S.; Bertrand, P.; Arys, X.; Jonas, A.; Wischerhoff, E.; Mayer, B.; Laschewsky, A. *Surf. Sci.* **1996**, *366*, 149. (b) Laschewsky, A.; Wischerhoff, E.; Kauranen, M.; Persoons, A. *Macromolecules* **1997**, *30*, 8304.

(13) Pastoriza-Santos, I.; Schöler, B.; Caruso, F. *Adv. Functional Mater.* **2001**, *234*, 356.

10.1021/la011006k CCC: $20.00



(a) PI (b) PSS

Figure 1. Chemical structures of PI and PSS polymer materials used for the fabrication.

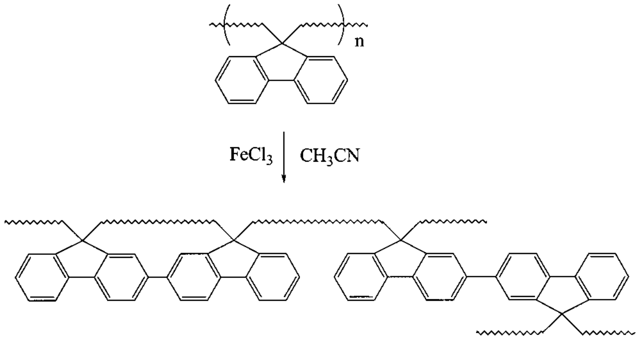


Figure 2. Cross-linking of fluorene in PI showing the formation of oligo-polyfluorene units with higher conjugation length sequences.

through the LbL assembly technique onto colloid particles and subsequent core removal. A suitable system for this purpose was the recently synthesized water-soluble polyionene (PI) "precursor polymer" that contains fluorene units in the side chain (Figure 1).[14] This precursor polymer concept involves the attachment and cross-linking of an electropolymerizable or oxidizable side group with a distinct polymer backbone, in this case, a polyelectrolyte. LbL deposition was achieved by pairing PI with poly(sodium 4-styrenesulfonate) (PSS). The pendant fluorene units of the precursor polymer could be converted to a conjugated oligo-fluorene by oxidation with anhydrous iron(III) chloride (Figure 2). By use of this reaction, the cross-linking of the precursor fluorene layers within the multilayer shells was accomplished. The colloid entities, both solid and hollow, have been characterized by electrophoresis, single particle light scattering, transmission electron microscopy, and atomic force microscopy. The electrochemical behavior of the PI/PSS multilayers has been examined by cyclic voltammetry.

Experimental Section

Materials. The polyionene was synthesized using the procedure described elsewhere.[14] 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 of 640 nm) were prepared as previously described.[15] The positively charged, weakly cross-linked melamine formaldehyde (MF) particles (diameter of ca. 2.3 μm) were purchased from Microparticles GmbH, Berlin. Acetonitrile (CH_3CN) and sodium chloride were obtained from Merck, and iron(III) chloride ($FeCl_3$) was purchased from Aldrich. The water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus purification system and had a resistivity higher than 18.2 MΩ cm.

Polymer Multilayer Assembly on Colloids. A precursor polyelectrolyte multilayer film was first deposited on the PS particles as described elsewhere.[5] A 2-layer polyelectrolyte film [PDADMAC/PSS] was deposited on the PS particles, and a 3-layer polyelectrolyte film [PSS/PDADMAC/PSS] was deposited on the MF particles. The PI/PSS multilayers were fabricated by (a) the addition of 1 mL of a 1 mg/mL aqueous PI solution (containing 0.5 M NaCl) to the polyelectrolyte-coated particles, allowing 15 min for PI adsorption, (b) removal of excess PI by four repeated centrifugation (10 000*g*, 15 min for PS latices; 3000*g*, 3 min for MF particles)/water wash/redispersion cycles, and (c) subsequent deposition of PSS (1 mg/mL solution containing 0.5 M NaCl) in identical fashion. The desired number of PI/PSS multilayers was assembled by the repeated consecutive assembly of PI and PSS using this method.

Cross-Linking of the PI Layers. For the cross-linking reaction, water was exchanged for acetonitrile by centrifuging, removing the supernatant, and redispersing the coated particles in 1 mL of acetonitrile. To ensure complete exchange of solvents, this process was repeated five times. The polyelectrolyte-coated particles in acetonitrile were transferred into a round-bottomed flask, followed by the addition of an excess amount (>4-fold) of iron(III) chloride to the solution and stirring at room temperature for 48 h under N_2. The polyelectrolyte-coated particles were then washed with acetonitrile to remove the trace ions.

For electrochemical studies, the cross-linked PI/PSS (9 layers, PI outer layer) colloid particles were deposited onto ITO glass. A negatively charged ITO surface was prepared by coating with 3-aminopropyltrimethoxysilane (Aldrich), followed by PSS adsorption.

Hollow Capsule Production. For the production of hollow capsules from polyelectrolyte-coated MF particles (before and after the cross-linking reaction), 0.2 mL of the coated MF particles were exposed to 1 mL of HCl at pH = 1 for 10 min. The capsules were then centrifuged at 10 000*g* for 15 min and redispersed in water, and the supernatant was exchanged for pure water. The acid treatment and water washing steps were repeated a further two times.

Characterization. Electrophoretic mobilities of the coated PS lattices 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). Single particle light scattering (SPLS) measurements were performed using a home-built instrument. Details of the SPLS experimental system and principle of measurement have been described elsewhere.[16] UV–vis absorption spectra were recorded by using a Perkin-Elmer Lambda 20 spectrophotometer, and photoluminescence spectra were obtained by using a Perkin-Elmer LS50B spectrometer. Transmission electron microscopy (TEM) measurements were performed on a Zeiss EM 912 Omega instrument. 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. AFM was done using a Molecular Imaging Instrument (PicoScan). Cyclic voltammetry measurements were performed with an Amel 2049 potentiostat and Power Lab system with a three-electrode cell in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) in acetonitrile at a scan rate of 100 mV/s. Platinum wire was used as the counter electrode, and Ag/Ag^+ was used as the reference electrode.

Results and Discussion

The assembly of PI/PSS multilayers on the PS particles was first examined by electrophoresis. Figure 3 shows the ζ-potential values as a function of polyelectrolyte layer number for the negatively charged PS particles coated with PI/PSS multilayers. The uncoated PS particles gave a ζ-potential of about −65 mV in water (data not shown). After the formation of precursor layers (2 layers of

---

(14) (a) Advincula, R.; Xia, C.; Inaoka, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41*, 847. Xia, C.; Advincula, R. C. Manuscript in preparation. (b) Xia, C.; Advincula, R. *Chem. Mater.* **2001**, *13*, 1682. (c) Xia, C.; Advincula, R. *ACS-PMSE Prepr.* **2001**, *84*, 697. (d) Inaoka, S.; Roitman, D.; Advincula, R. *ACS-PMSE Prepr.* **2000**, *82*, 340.

(15) Furusawa, K.; Norde, W.; Lyklema, J. *Kolloid-Z. Z. Polym.* **1972**, *250*, 908.

(16) (a) Lichtenfeld, H.; Knapschinsky, L.; Sonntag, H.; Shilov, V. *Colloids Surf., A* **1995**, *104*, 313. (b) Lichtenfeld, H.; Knapschinsky, L.; Dürr, C.; Zastrow, H. *Prog. Colloid Polym. Sci.* **1997**, *104*, 1148.

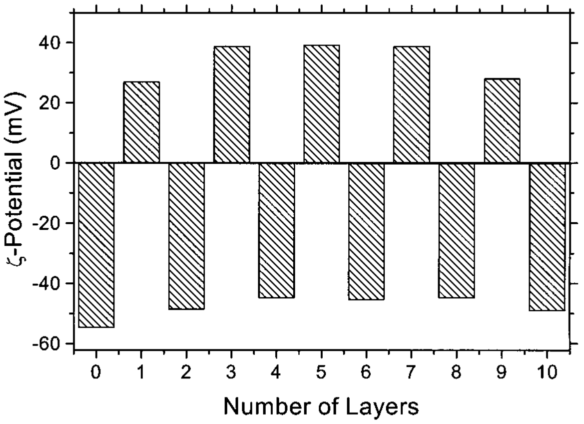


Figure 3. ζ-Potential as a function of polyelectrolyte layer number for (PI/PSS)-coated 640 nm PS spheres. The PS particles were precoated with PDADMAC/PSS layers prior to deposition of the first layer. The even layer numbers correspond to PSS adsorption, and the odd layer numbers to PI deposition.

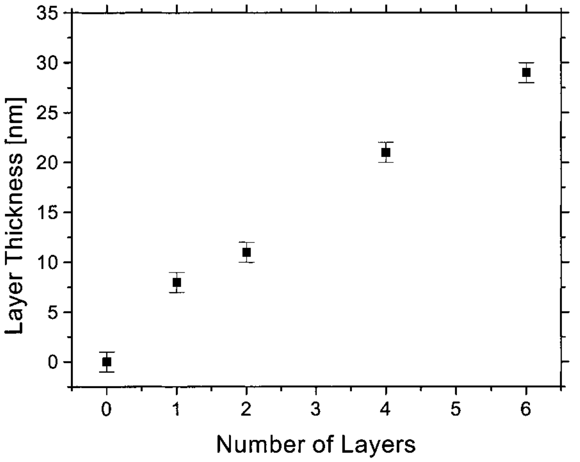


Figure 4. Layer thickness of the PI/PSS-coated PS particles as a function of the number of deposited layers, as determined by SPLS.

[PDADMAC/PSS], marked as layer number 0 in Figure 3) onto PS particles, the measured ζ-potential is -55 mV, a value consistent with the outermost layer being a polyanion. The subsequent alternate assembly of PI and PSS caused a reversal in the sign of the ζ-potential with each deposition up to 10 layers. When PI is the outermost layer, the ζ-potential of the coated particles is about $+30$ to $+40$ mV. This shows that PI acts as a polycation due to the positive charge in the ionene polymer backbone. The alternating negative and positive ζ-potentials suggest stepwise growth of the multilayer films.[3−5]

To determine the thickness of the PI/PSS multilayers assembled onto the PS particles, SPLS measurements were performed. The average thickness of the layers was calculated by using the Rayleigh−Debye−Gans theory[17] and a refractive index value of 1.47[18] for the PI/PSS layers. Figure 4 shows the layer thickness as a function of the number of deposited layers (up to 6 layers). The layer thickness increases regularly with the number of layers deposited. The calculated average thickness of the PI/PSS layer pair is 10 ± 1 nm. Furthermore, the first PI layer (about 8 nm) is much thicker than the next PSS layer (about 3 nm). These values are larger than the average thickness (4.4 ± 0.5 nm) of a PI/PSS bilayer based on ellipsometric measurements for PI/PSS multilayer films in air on silicon substrates under the same ionic strength conditions (0.5 M NaCl) (unpublished data). This is consistent with the fact that SPLS measurements were made on solutions, a “wet method” in which swelling of the films by the solvent and ionic interaction can give higher thickness values compared to a flat substrate and “dry method” using ellipsometry. This may also suggest that on the colloid particle surface, the fluorene units of the PI could be aggregated as shown by the fluorescence data (discussed later).[19]

The morphology of the PI/PSS-coated PS particles was examined using TEM. Figure 5a shows the TEM micrograph of [(PI/PSS)$_4$/PI] (9-layer) coated PS particles. A regular coating of the particle surface is seen. The presence of PI/PSS multilayers on PS particles produces an increase in surface roughness as well as an increase in the diameter of the PI/PSS-coated PS spheres compared with uncoated PS particles (data not shown). The average diameter of the PI/PSS 9-layer coated particles is approximately 740 ± 10 nm, corresponding to a thickness of between 40 and 50 nm for the multilayers, or about an average of 10 nm per bilayer. (The diameter of uncoated PS particles with the precursor polymer layer is ∼650 nm.) These data are in agreement with the calculated thickness from the SPLS measurements.

To produce polyelectrolyte hollow capsules, weakly cross-linked MF particles were employed as templates. After deposition of the desired number of layers, the core (MF) was removed by dissolution at pH = 1. The PI/PSS capsules were characterized using TEM and AFM. TEM and AFM images of [(PI/PSS)$_4$/PI] (9-layer) hollow capsules are shown in (b) and (c) of Figure 5. Folds, creases, and flattening of the hollow capsules were observed: these result from the drying procedure prior to the measurements. Some remaining MF can be seen inside the capsules. The height (twice the wall thickness) of the capsule in the AFM image (Figure 5c) ranges from 90 to 200 nm. The former value corresponds to the minimum thickness of the capsule wall, about 45 nm, which is consistent with the SPLS and TEM results, that is, 10 nm per bilayer.

The cross-linking of fluorene within the PI/PSS multilayers on the coated PS particles results in the formation of oligo-fluorene. We chose acetonitrile as the reaction solvent because it is easily exchanged with water. It is also the typical solvent for the oxidation process. After the [(PI/PSS)$_4$/PI] (9-layer) coated PS spheres were repeatedly exposed (at least six times) to acetonitrile, the FeCl$_3$ was added as the oxidizing agent. The reaction was continued for 48 h under nitrogen. Figure 6 shows the photoluminescence spectra of PI/PSS multilayers on PS spheres in water before and after cross-linking of the fluorene unit. Prior to cross-linking, three emission bands were observed. Two peaks at 310 and 320 nm are the normally observed fluorene peaks and correspond to those of PI in solution.[14] The broad emission band at about 350−450 nm is attributed to a lower energy excitonic peak due to aggregation of fluorene in PI.[19] After cross-linking, the peaks at 310 and 320 nm almost completely disappeared while a new broad emission peak was observed between 380 and 500 nm, centered at 422 nm. This spectrum is typical for the emission of oligo-fluorenes and has been studied intensively by the Miller group.[20] According to

---

(17) Kerker, M. *The Scattering of Light and Other Electromagnetic Radiation*; Academic Press: New York, 1969.

(18) Lichtenfeld, H.; Knapschinsky, L.; Sonntag, H.; Shilov, V. *Colloids Surf., A* **1995**, *104*, 313.

(19) (a) Troxler, T.; Pryor, B.; Top, M. *Chem. Phys. Lett.* **1995**, *239*, 44. (b) Boo, B.; Choi, Y.; Kim, T.; Kang, S.; Kang, Y.; Lee, S. *J. Mol. Struct.* **1996**, *377*, 129. (c) Porzio, W.; Botta, C.; Destri, S.; Pasini, M. *Synth. Met.* **2001**, *122*, 7.

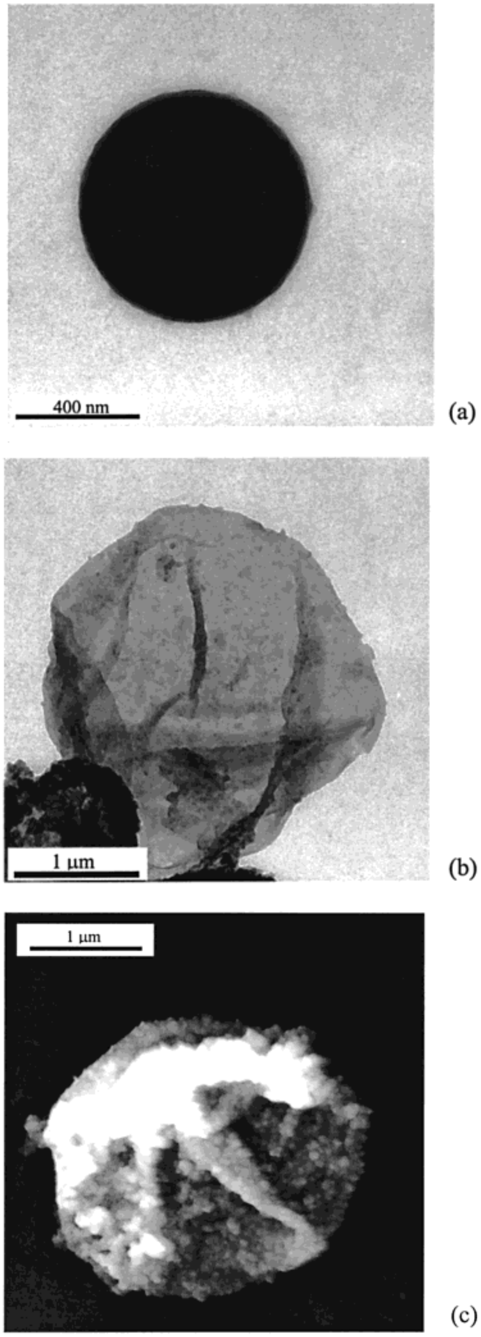


Figure 5. (a) TEM image of a [(PI/PSS)$_4$/PI]-coated PS particle. The PS particles used as templates have a diameter of 640 nm. (b) TEM and (c) AFM images of hollow [(PI/PSS)$_4$/PI] capsules, obtained after decomposition of the MF template (diameter of 2.3 μm). The outermost layer is PI.

their study, the conjugation length of oligo-fluorene after cross-linking can be determined with a peak at 422 nm corresponding to four oligomer units. The fact that a wide band was obtained indicates the varying degrees of cross-linking or distribution of oligofluorene units within the particle surface.

After the cross-linking, some aggregation of the PI/PSS-coated PS particles was observed by TEM. This may be due to the *inter-cross-linking* of the coated particles with each other and the effect of exchanging solvent for the cross-linking reaction (water−acetonitrile−water). However, no significant changes in the morphology of the hollow capsules, as examined by TEM and AFM, were

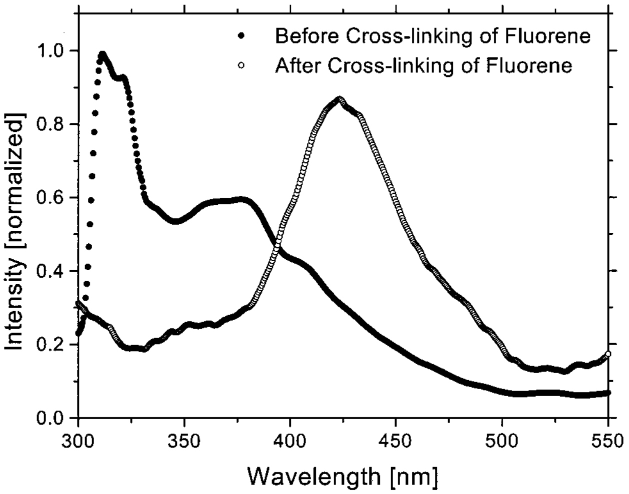


Figure 6. Photoluminescence spectra of PI/PSS multilayers (the outer layer is PI) on PS spheres of 640 nm diameter in water before (dotted spectrum) and after cross-linking of the fluorene (solid spectrum). The excitation wavelength was 290 nm.

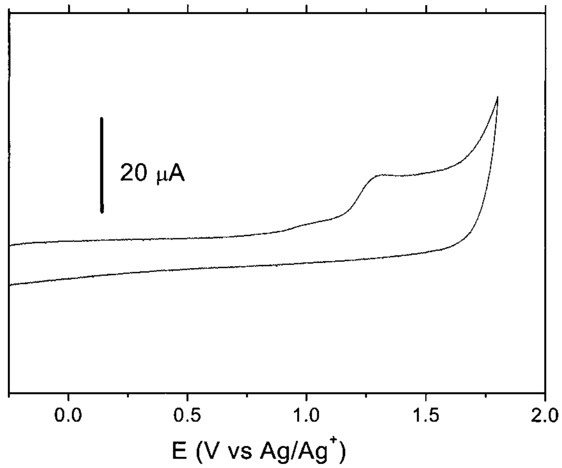


Figure 7. Cyclic voltammogram of [(PI/PSS)$_4$/PI]-coated PS particles on an ITO substrate. The potential scan rate was 100 mV/s.

observed as a result of cross-linking. The hollow capsules could also be successfully produced when the core was removed after cross-linking of PI/PSS multilayer coated PS particles. Studies are being made to compare the differences in the order of core removal and cross-linking.

Cyclic voltammetry (CV) was employed to obtain further evidence of the cross-linked PI/PSS multilayers on the PS particles as well as to investigate the electrochemical behavior of the multilayers. A negatively charged ITO-coated glass slide, used as the substrate, was dipped into a PI/PSS coated particle dispersion for 15 min and then dried with nitrogen. The substrate was additionally dried in a 100 °C conventional oven to remove excess water. As the reference, the CV was measured with Ag/Ag$^+$ in a solution of TBAH (0.1 M) in acetonitrile at a scan rate of 100 mV/s. Figure 7 shows CV of [(PI/PSS)$_4$/PI]-coated PS particles in acetonitrile. The measured oxidation onset potential is 1.1 V versus Ag/Ag$^+$. This corresponds to the oxidation of the polyfluorene unit and is consistent with our results using chemical oxidation.[21] The PI/PSS multilayer coated PS particles showed an irreversible oxida-

---

[20] Klaerner, G.; Miller, R. D. *Macromolecules* **1998**, *31*, 2007.

[21] (a) Troxler, T.; Pryor, B.; Top, M. *Chem. Phys. Lett.* **1995**, *239*, 44. (b) Boo, B.; Choi, Y.; Kim, T.; Kang, S.; Kang, Y.; Lee, S. *J. Mol. Struct.* **1996**, *377*, 129.

tion process indicating the consumption of the fluorene units to form oligo-fluorenes.

Conclusions

Luminescent core–shell particles have been fabricated by the layer-by-layer deposition of PSS and an ionene polymer containing fluorene units onto colloid particles. It has been demonstrated that the water-soluble ionene polymer that has fluorene side groups can be deposited and subsequently cross-linked into luminescent conjugated oligo-fluorene. Photoluminescence spectra confirmed the formation of luminescent particles. Furthermore, hollow capsules comprising PI/PSS multilayers could also be produced by decomposition of the core from PI/PSS-coated MF particles before and after the cross-linking. Further studies will focus on the quantum efficiency, cross-linking efficiency, and luminescent properties of the particles.

Acknowledgment. We thank Christine Pilz and Heinz Lichtenfeld for assistance with the ζ-potential and SPLS measurements, respectively. R.C.A. acknowledges partial support from a NSF-CAREER grant, NSF DMR-99-82010. F.C. acknowledges support from the BMBF.

LA011006K