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Enhanced Electrochromic Switching in Multilayer Thin Films of Polyaniline-Tethered Silsesquioxane Nanocage

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Polyaniline (PANI)-tethered cubic polyhedral oligomeric silsesquioxane (POSS) in emeraldine base (EB) form is synthesized via oxidative copolymerization of octa(aminophenyl) silsesquioxane and aniline in the presence of HCl followed by the treatment with triethylamine. The chemical structures of POSS-PANI-EB are elucidated by Fourier transform infrared spectroscopy and elemental analysis. POSS-PANI/poly(2-acrylamido-methane-2-propanesulfonic acid) (PAMPS) multilayer thin films are successfully fabricated via layer-by-layer (LBL) assembly. Cyclic voltammetry studies show that the redox reactions in the thin film containing 50 POSS-PANI/PAMPS bilayers ($(\text{POSS-PANI/PAMPS})_{50}$) are close to non-diffusion-controlled processes in the studied scan-rate range of 10−100 mV/s, and the reactions are also more reversible than that in the linear counterpart $(\text{PANI/PAMPS})_{50}$. Under a dynamic switching condition of 40 s per cycle, the electrochromic contrast of $(\text{POSS-PANI/PAMPS})_{50}$ is increased by more than 30% over that of $(\text{PANI/PAMPS})_{50}$ and the switching time of $(\text{POSS-PANI/PAMPS})_{50}$ is also significantly shorter than that of $(\text{PANI/PAMPS})_{50}$. In addition to the better control of film thickness and morphology, the electrochromic performance of the POSS-PANI/PAMPS multilayer films is also superior to the previously studied spin-coated thin films of POSS-PANI/polymeric acid complexes. The improvements can be attributed to the unique morphology brought by the synergistic combination of the starlike structure of POSS-PANI and the LBL assembly method, which allows for more favorable interactions between PANI chains and polymeric dopants as well as faster ion transport during the redox switching.

Introduction

In the past decade, conjugated polymer-based electrochromic materials have attracted great attention because of their low cost, ease of processing, and relatively high optical contrast and response speed,[1−4] which are essential for their applications in electrochromic devices. Conjugated polymers are commonly deposited on electrodes via spin-coating or electropolymerization. An attractive, alternative approach is to fabricate electrochromic thin films using layer-by-layer (LBL) assembly technique. In LBL assembly, a thin film is grown on a substrate by alternating its exposure to aqueous solutions containing species with complementary functionalities.[5,6] The most commonly employed strategy for the LBL assembly is to utilize electrostatic interaction, with which a thin film can be created by combining a polycation with a polyanion.[7] Compared with traditional thin film fabrication methods, the LBL approach is simple and inexpensive, and allows the incorporation of many different functional materials into a single film at a full range of compositions without the issues of phase separation.[8] We have previously employed this technique to create electrochromic thin films of linear poly(ethylene imine) (LPEI)/poly(3,4-ethylenedioxythiophene) (PEDOT), LPEI/Prussian Blue (PB), poly(hexyl viologen) (PXV)/PEDOT, polyaniline (PANI)/poly(2-acrylamido-methane-2-propanesulfonic acid) (PAMPS) and PANI/PB. The high contrast values and fast switching speeds of these thin films along with water-based processing have demonstrated the potentials

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of this technique in enhancing performance of electrochromic devices.[6,9−11]

PANI is the most widely used anodically coloring electrochromic polymer. It possesses good environmental stability and exhibits multicolor electrochromism in visible region as well as electrochromism in infrared region. Many types of electrochromic devices based on PANI, such as PANI/tungsten oxide,[12,13] PANI/PEDOT,[14,15] and PANI/PB[16] dual layer devices, have been reported, which demonstrated the great promise of PANI for electrochromic applications. Recently, we reported that PANI can be tethered onto polyhedral oligomeric silsesquioxane (POSS) nanocage to form star-like POSS−PANI copolymers that exhibit significantly enhanced electrochromic contrasts and electrochemical stability over that of linear PANI.[17,18] Similar starlike PANI copolymers have also been synthesized via attaching PANI chains onto hexa(4-aminophenoxy) cyclotriphosphazene (HACP).[19] For both POSS-PANI and HACP-PANI starlike copolymers, the enhanced electrochromic contrast values were attributed to the loosely packed structure and reduced crystallinity induced by the starlike molecular architecture that facilitate diffusion of ions and hence create more accessible doping sites within the electrochromic layers.

In this work, we demonstrate the first incorporation of a POSS-PANI copolymer into electrochromic thin films via LBL assembly. Here we report the synthesis and characterization of POSS-PANI copolymers in emeraldine base (EB) form (POSS-PANI-EB), the combination of POSS-PANI with linear PAMPS polyanion to form multilayer thin films via LBL assembly, and the electrochemical and electrochromic properties of the resulting thin films. Our results show that under dynamic switching conditions, POSS-PANI/PAMPS multilayer thin films not only exhibit higher optical contrast but also demonstrate faster switching kinetics than their linear PANI/PAMPS counterparts because of the synergistic combination of the starlike molecular architecture and the LBL assembly method. This provides a clear contrast to spin-coated electrochromic thin films of POSS-PANI/polymeric acid complexes where the switching kinetics is similar to their linear PANI counteapart.[18] The synergy between the starlike molecular architecture of POSS-PANI and the LBL assembly method mainly originates from the more effective interactions of POSS-PANI with polymeric dopants in dilute solutions.

Experimental Section

Chemicals. Aniline, acetonitrile (99.5%), *N,N*-dimethylacetamide (DMAc), poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS), lithium perchlorate (≥95.0%), and ferrocene (98%) were purchased from Aldrich. Aniline was purified by vacuum distillation prior to use. Ammonium peroxydisulfate (APS) and triethylamine were purchased from Lancaster. Hydrochloric acid (HCl) was purchased from Honeywell. Octa(aminophenyl) silsesquioxane (OAPS) was purchased from Mayaterials Inc. and purified to reduce the content of octa(nitrophenyl) silsesquioxane prior to use. Other chemicals were obtained from various commercial sources and used as received.

Polymerization. POSS-PANI copolymers were prepared by oxidative copolymerization[20−22] of OAPS and aniline in the presence of HCl with APS as the oxidizing agent. In a typical reaction, aniline (3.72 g, 0.04 mol) and OAPS (0.47 g, 0.40 mmol) were added into 1.2 M HCl (400 mL) in a cooling bath maintained at 0 °C for 4 h. Polymerization was initiated by the addition of APS (9.12 g, 0.04 mol) dissolved in 1.2 M HCl (200 mL) over a period of 30 min. The total polymerization time was 24 h. When the reaction was completed, the precipitated POSS-PANI copolymer in emeraldine salt (ES) form (POSS-PANI-ES) was filtered and washed with 1.2 M HCl, distilled water and methanol. The collected powder was dried at 35 °C for 48 h under dynamic vacuum. POSS-PANI copolymer in emeraldine base (EB) form (POSS-PANI-EB) was obtained by treating the POSS-PANI-ES with triethylamine solution,[23] which was diluted using anhydrous chloroform. The freshly prepared POSS-PANI-EB were suspended with constant stirring in triethylamine solution and stirred for 20 h. After that, the powder was collected and washed with anhydrous chloroform. The washing process was repeated three times. The color of the POSS-PANI-EB obtained is dark brown. The EB form of PANI homopolymer (PANI-EB) was prepared using a procedure similar to that described above.

Structural Analysis. Infrared spectra were obtained on a PerkinElmer Fourier transform infrared (FTIR) spectrophotometer 2000 using KBr method. Elemental analysis was carried out with a PerkinElmer 2400 CHN and CHNS elemental analyzers.

Preparation of Dipping Solutions. 1%POSS-PANI-EB was dissolved in DMAc at a concentration of 10 mg/mL by first stirring the solution overnight and then sonicating it for about 8 h. Some indiscerptible particulates were removed using centrifuge. The dipping solution was prepared by slowly adding one part (by volume) of the centrifuged 1%POSS-PANI-EB solution to nine parts of water that has had its pH adjusted to about 3.0−3.5 with 1 M HCl. The pH was then quickly lowered to 2.5 by adding drops of 1 M HCl solution. The solution was filtered through a 0.45 μm Nylon filter just before use.[24,25] The dipping solution containing PANI was prepared using the same

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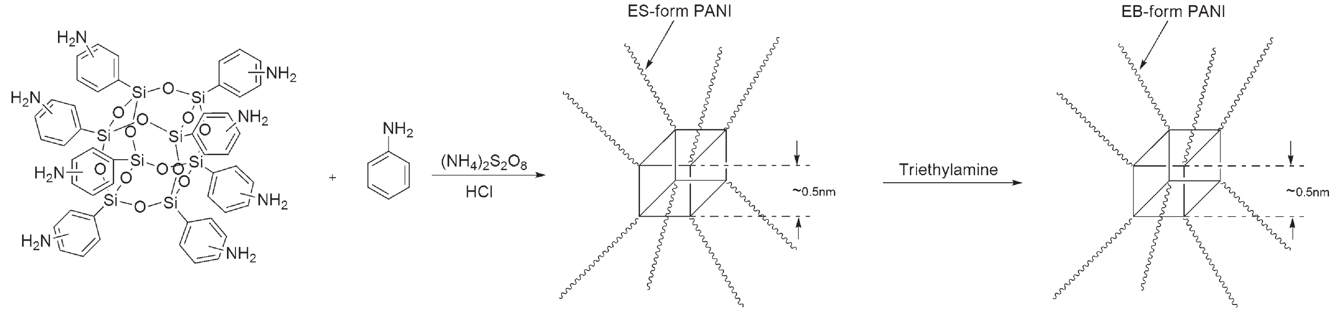
Scheme 1. Oxidative Copolymerization of OAPS and Aniline to Form POSS-PANI-ES, Followed by Conversion to POSS-PANI-EB



procedure. The concentrations of both PANI and 1%POSS-PANI in the dipping solutions were adjusted to 0.04 mg/mL. PAMPS solution (2 mM) were prepared by dissolving the PAMPS in water under stirring and the pH value of the PAMPS aqueous solution was also adjusted to 2.5. The solution was filtered with filter paper before use.

LBL Assembly of Multilayer Thin Films. Multilayer thin films were constructed using a modified Carl Zeiss DS50 programmable slide stainer. Glass coated with indium tin oxide (ITO) (5−15 Ω/□) and uncoated glass substrates, both with the dimensions of 7 × 50 × 0.7 mm (Delta Technologies) were cleaned by ultrasonication in a series of solvents including dichloromethane, acetone, methanol, and Milli-Q water at 15 min each, followed by a 4-min air plasma cleaning (Harrick PDC 32G). Silicon wafers were treated in the plasma cleaner to provide a hydrophilic surface. ITO-glass, uncoated glass and silicon substrates were exposed first to polycation solution for 5−20 min, followed by three consecutive rinsing steps (1.5 min, 1.5 min, 1.5 min) in Milli-Q water, then exposed to polyanion solution for 5−20 min and rinsed. The cycle was repeated to create multilayer thin films of certain thickness.[9] The pH value of all the rinsing solutions was adjusted to 2.5.

Thin Film Characterization. Thickness measurements were performed with a Tencor P16 surface profiler. X-ray photoelectron spectroscopy (XPS) experiments were performed using a VG ESCALAB 220i-XL instrument equipped with a monochromatic Al Kα X-ray source (1486.7 eV photons). Atomic force microscope (AFM) measurements were performed in the tapping mode using Digital Instruments Nanoscope 3100 AFM. The surface morphology of the thin films was examined using a JSM-6700F field-emission scanning electron microscope (FESEM). In situ spectro-electrochemical properties of the multilayer thin films were characterized using an Autolab PGSTAT30 electrochemical workstation and Cary UV−vis−NIR spectrophotometer 6000i. The electrochromic thin films on ITO-glass were positioned in a quartz cell as working electrodes. The electrolyte is 0.1 M $LiClO_4$ in acetonitrile. Platinum wire (99.99%) and silver wire (99.9%) were used as counter and reference electrode, respectively. The pseudoreference silver wire was calibrated vs. Fc/Fc^+ by dissolving ferrocene in the electrolyte solution and determining the $E_{1/2}$ of the Fc/Fc^+ against the silver wire.

Results and Discussion

Synthesis and Structural Verification. POSS-PANI copolymers were prepared by oxidative copolymerization of OAPS and aniline, as shown in Scheme 1. The feed molar ratios of OAPS to aniline were 1.0/99.0 and 4.0/96.0. For clarity, the values of the POSS feed concentrations are specified in sample names. Because the POSS cage is stable under acidic conditions but may undergo hydrolysis when the pH value is higher than 10, to prevent the breakage of the POSS cage, an organic base, triethylamine, was used to treat the polymerization products to obtain the EB-form POSS-PANI. The base was then washed out using chloroform under anhydrous conditions.

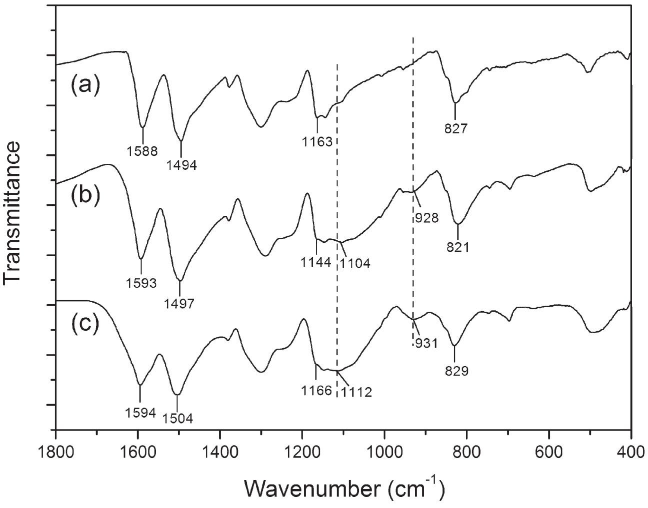


Figure 1. FTIR spectra of (a) PANI-EB, (b) 1%POSS-PANI-EB, and (c) 4%POSS-PANI-EB.

The chemical structures of the PANI-EB homopolymer and POSS-PANI-EB copolymers are characterized using FTIR and elemental analysis. To clearly identify the structural differences between the PANI-EB and POSS-PANI-EB, we used 4%POSS-PANI-EB to elucidate the chemical structure of POSS-PANI-EB. In the FTIR spectrum of 4%POSS-PANI-EB (Figure 1), several characteristic bands associated with the EB form of PANI[26,27] can be clearly observed. The band at 1594 cm^{-1} is attributed to C=N bonds of quinoid units and the band at 1504 cm^{-1} to C−N bonds of benzenoid units. The presence of the quinoid rings is also confirmed by the weak band at 1166 cm^{-1}, which is related to the electronic-like absorption of the N=Q=N vibration. The band corresponding to C−H out-of-plane bending of the 1,4-disubstituted aromatic ring appears at 829 cm^{-1}, which is the evidence for the formation of poly(*p*-aniline). Comparing the FTIR spectra of the 4%POSS-PANI-EB and

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Table 1. Elemental Analysis Data for PANI-EB and 4% POSS-PANI-EB*

		C (%)	H (%)	N (%)	Si (%)
PANI-EB	found	72.8	4.9	3	0
	calcd	79.5	5.0	15.5	0
4%POSS-PANI-EB	found	59.1	4.3	10.5	6.0
	calcd[a]	69.4	4.6	13.5	6.8

[a] The feed molar ratio of OAPS to aniline of 4/96 was used to calculate the elemental weight percentage.

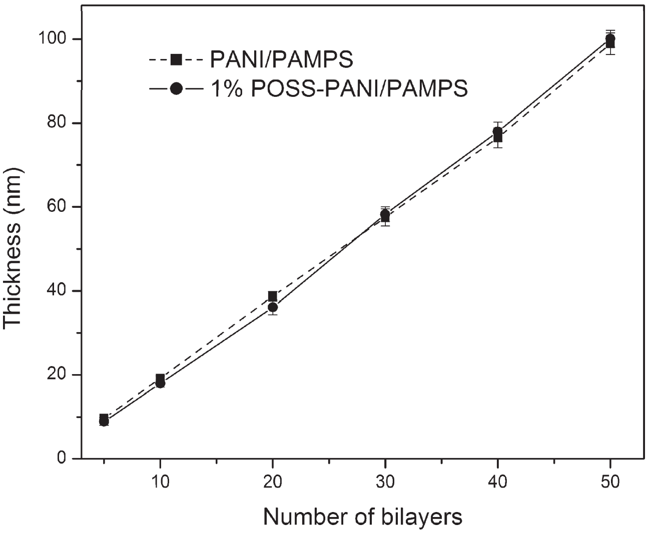

Figure 2. Growth curves for LBL assembled PANI/PAMPS and 1% POSS-PANI/PAMPS thin films on glass.

the linear PANI-EB, there is a strong, broad absorption band at 1112 cm^{-1} and a moderately strong band at 931 cm^{-1} seen only in the former. Both bands can be attributed to the stretching vibration of Si−O−Si. In view of the unreacted OAPS being soluble in the acidic solution and not precipitating out to form a part of the product, the appearance of Si−O−Si stretching band indicates that PANI-EB chains have been successfully tethered onto the POSS cage, which is also supported by the elemental analysis data from 4%POSS-PANI found (Table 1). The FTIR spectrum of 1%POSS-PANI-EB is similar to that of 4%POSS-PANI-EB although the bands corresponding to Si−O−Si stretching are weaker. Because of its low Si content, elemental analysis was not conducted on 1%POSS-PANI.

LBL Assembly of Multilayer Thin Film. As the solubility of 4%POSS-PANI in DMAc is very low, only PANI-EB and 1%POSS-PANI-EB were used to fabricate the multilayer films. According to the time-dependent adsorption behavior of the PANI/PAMPS and 1%POSS-PANI/PAMPS adsorbed onto glass substrates (see the Supporting Information), the dipping time in polycation and polyanion solution is optimized at 15 min. Figure 2 shows that the LBL growth of both PANI/PAMPS and 1%POSS-PANI/PAMPS multilayer thin films are linear with the thickness of each bilayer being about 2.0 nm. The other layer-by-layer assembled starlike polymer system recently published by our group also shows the similar growth characteristics.[28]

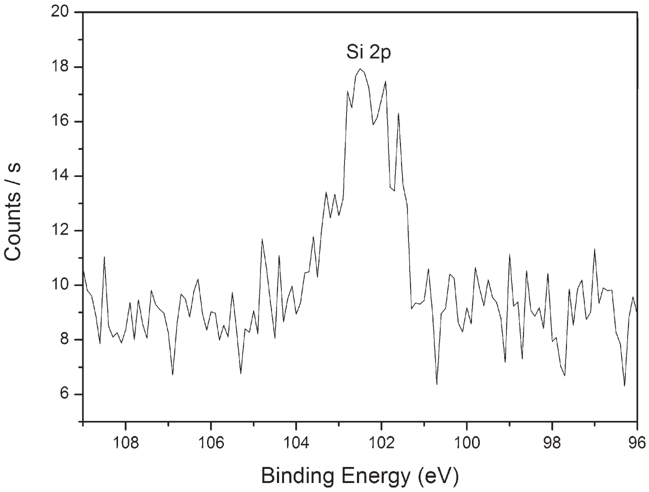

Figure 3. Si 2p XPS spectrum of (1%POSS-PANI/PAMPS)$_{15}$ on silicon wafer. The binding energy (BE) of the core level C 1s peak was set at 285.0 eV to compensate for surface-charging effects.

Figure 3 shows the XPS spectrum[29] of 1%POSS-PANI measured from a (1%POSS-PANI/PAMPS)$_{15}$ thin film on silicon substrate. A characteristic peak of Si 2p is visible in the spectrum. To confirm that the peak is from POSS rather than from the substrate, we have also measured the XPS spectrum of the silicon wafer. There are two Si 2p peaks in the XPS spectrum of the silicon wafer (see the Supporting Information); the strong, sharp one originates from Si and the other from Si−O. In the XPS spectrum of (1%POSS-PANI/PAMPS)$_{15}$, the peak from Si is not observed, which indicates that surface of the wafer is completely covered by the polymers. The Si 2p peak observed thus must be from POSS in the multilayer film, which verifies the successful incorporation of 1% POSS-PANI copolymer into the multilayer film.

Surface Morphology. The surface roughness of the multilayer films with the electrochromic layer on top was examined using AFM. Compared with the multilayer thin film made of linear PANI and PAMPS, it is obvious that the surface roughness of 1%POSS-PANI/PAMPS multilayer thin film is higher (Figure 4). This indicates that the starlike structure of POSS-PANI can provide larger interaction area between PANI and PAMPS layers. The surface morphologies of the multilayer films with the electrochromic layer on top were also examined using FESEM. In Figure 5a, we can see relatively densely packed small islands (bright regions). In contrast, in Figure 5b, it is obvious that the islands are surrounded by dark regions tens of nanometers wide, which again suggests an interdigitated morphology for 1%POSS-PANI/PAMPS multilayer film.

Cyclic Voltammetry (CV). On the basis of the growth curve presented in Figure 2, 50 bilayers of PANI/PAMPS and 1%POSS-PANI/PAMPS are assembled on ITO-coated glass. The two thin films have the same thickness

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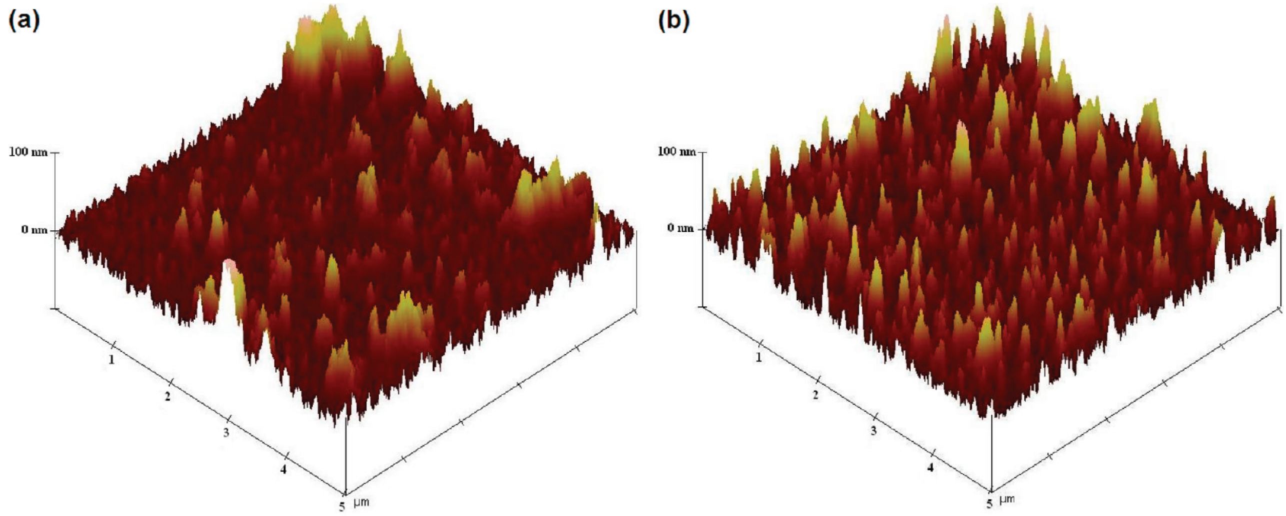

Figure 4. Tapping mode AFM images of (a) $(PANI/PAMPS)_{15}$ with PANI on top and (b) $(1\%POSS\text{-}PANI/PAMPS)_{15}$ with 1%POSS-PANI on top.

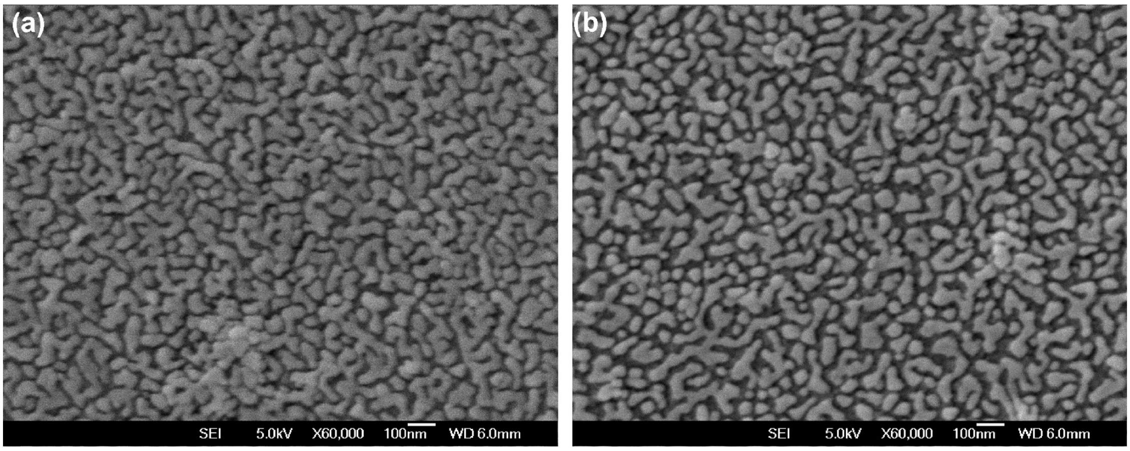

Figure 5. FESEM images of (a) $(PANI/PAMPS)_{15}$ with PANI on top and (b) $(1\%POSS\text{-}PANI/PAMPS)_{15}$ with 1%POSS-PANI on top.

of 100 nm, which allows a fair comparison of the electrochromic properties. The two thin films are named as $(PANI/PAMPS)_{50}$ and $(1\%POSS\text{-}PANI/PAMPS)_{50}$, respectively. The CV curves of both $(PANI/PAMPS)_{50}$ (Figure 6a) and $(1\%POSS{-}PANI/PAMPS)_{50}$ (Figure 6b) show two oxidation and reduction peaks. The first oxidation peak at lower potentials can be assigned to the leucoemeraldine to emeraldine transition, and the second oxidation peak at higher potentials is due to the transition from the emeraldine to pernigraniline state.[14,30] Despite the similarity in the oxidation process, the reduction (dedoping) peaks of POSS−PANI, especially the ones at higher potentials corresponding to the transition from the pernigraniline to emeraldine state, are much more distinctive than those of PANI, which implies the dedoping process in the $(1\%POSS{-}PANI/PAMPS)_{50}$ multilayer thin film benefits from the structure of POSS-PANI. When the anodic and cathodic peak current densities for the peaks at higher potentials are plotted against the scan rate, ν (Figure 6c), approximate linear relationships are obtained for $(1\%POSS{-}PANI/PAMPS)_{50}$, whereas for $(PANI/PAMPS)_{50}$, the cathodic current density shows an approximate linear relationship with the square root of the scan rate, $\nu^{1/2}$ (Figure 6d), instead. This signifies that the reduction process in $(PANI/PAMPS)_{50}$ is largely diffusion controlled,[18,31] whereas the redox reactions in $(1\%POSS{-}PANI/PAMPS)_{50}$ are close to non-diffusion-controlled processes in the studied scan-rate range.

It is important to note that the redox behaviors of the spin-coated films of POSS-PANI/polymeric acid complexes are very different from that of the LBL-assembled POSS-PANI/PAMPS multilayer film.[18] Given the same film thickness (~100 nm) and testing conditions, the reduction peaks at higher potentials are indistinctive in the CV curves of the spin-coated film of 1%POSS-PANI doped with poly(4-styrene sulfonic acid) (PSS) (see the Supporting Information), especially at high scan rates. The key difference between the spin-coated and LBL-assembled systems is probably the conformation of the polymer chains in solutions. The LBL-assembled multilayer films were fabricated via alternatively dipping the substrate in extremely dilute aqueous solutions of POSS-PANI-EB and the polymeric dopant (PAMPS

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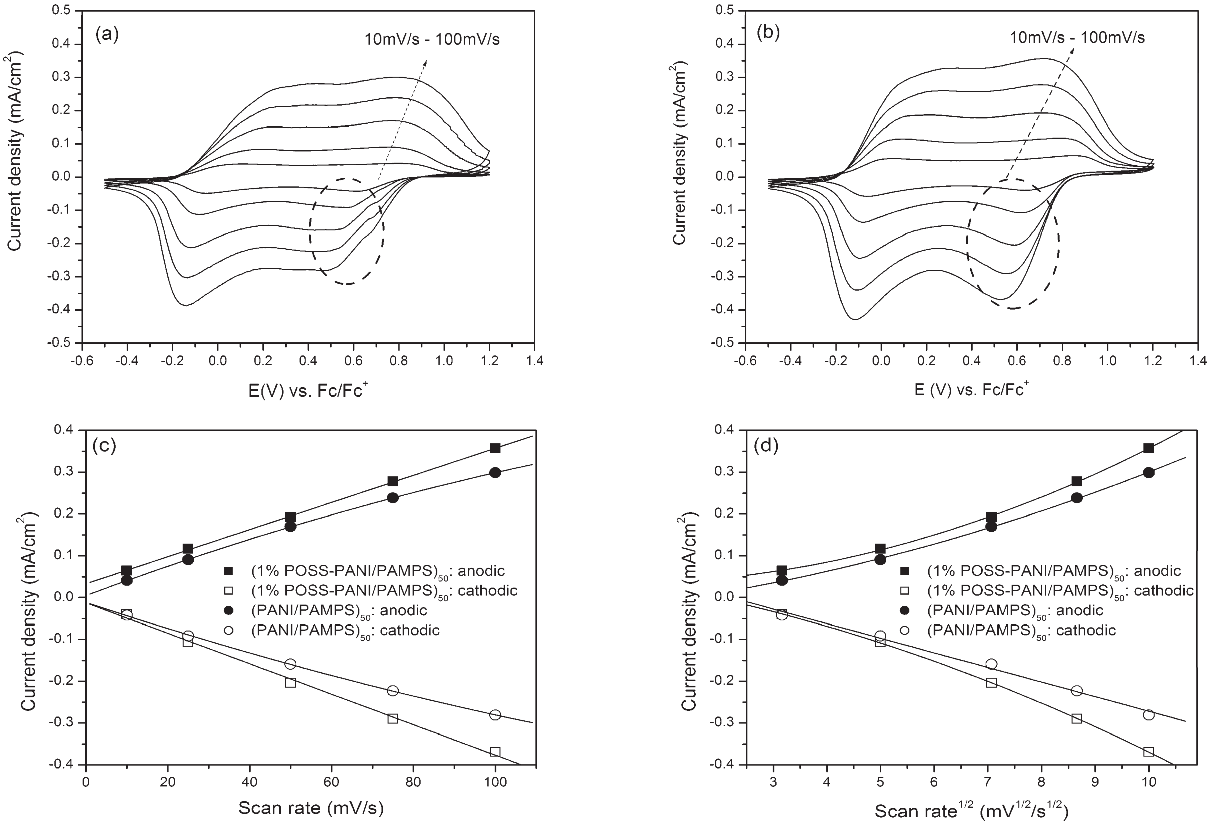

Figure 6. CV curves of (a) (PANI/PAMPS)$_{50}$ and (b) (1.0%POSS-PANI/PAMPS)$_{50}$ measured in a 0.1 M LiClO$_4$/acetonitrile solution with scan rate of 10, 25, 50, 75, and 100 mV/s using silver wire as the reference electrode. (c) Plots of peak current densities vs scan rate. (d) Plots of peak current densities vs square root of scan rate.

Table 2. Composition of the Multilayer Films Obtained from XPS Analysis of (1%POSS-PANI/PAMPS)$_{15}$

name	peak BE	at %	N/S ratio	molar ratio of PANI unit/PAMPS unit
N 1s	400.33	74.87	2.98/1.00	1.99/1
S 2p	168.27	25.13		

conc. = 0.4 mg/mL). In dilute solutions, the polymer molecules exhibit extended chain conformation. Thus, the polymeric dopants are able to interact with POSS-PANI effectively via electrostatic forces. The dopant molecules that are absorbed onto the thin film via van der Waals interactions are mostly washed out in the rinse steps. XPS analysis of the composition of the multilayer thin films verifies that the 1%POSS–PANI/PAMPS multilayer film indeed has a fairly low PANI/dopant molar ratio (Table 2). In contrast, the POSS-PANI copolymer used in the spin-coated thin film was made by in situ polymerization, which was conducted in a concentrated solution (PSS conc. = 12.7 mg/mL).[18] Under such a condition the polymer chains have smaller radius of gyration and interactions between dopant molecules may also be possible. Thus many acid groups may be entrapped in highly coiled dopant chains or chain clusters. To have a greater number of active PANI units, we have to use an excess amount of dopant molecules, which fill up the space among the arms of the starlike PANI and hence slow down the ion diffusion. This explains why at high scan rates the reduction peaks at higher potentials are indistinctive for the spin-coated film. The comparison between the LBL-assembled and spin-coated POSS-PANI thin films demonstrates that the synergy between the star-like molecular architecture of POSS-PANI and LBL assembly method enables faster kinetics for ion transportation.

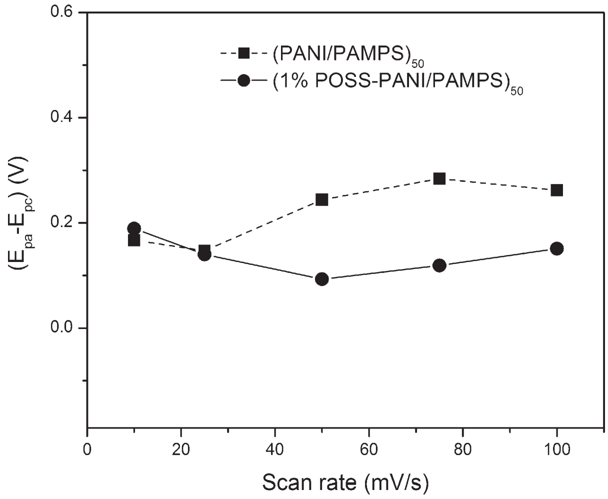

Figure 7. Anodic–cathodic peak separation of (PANI/PAMPS)$_{50}$ and (1%POSS-PANI/PAMPS)$_{50}$.

It is also useful to compare the anodic–cathodic peak separation as a measure of reversibility in the switching process.[32] In Figure 7, at a constant scan rate of 50 mV/s,

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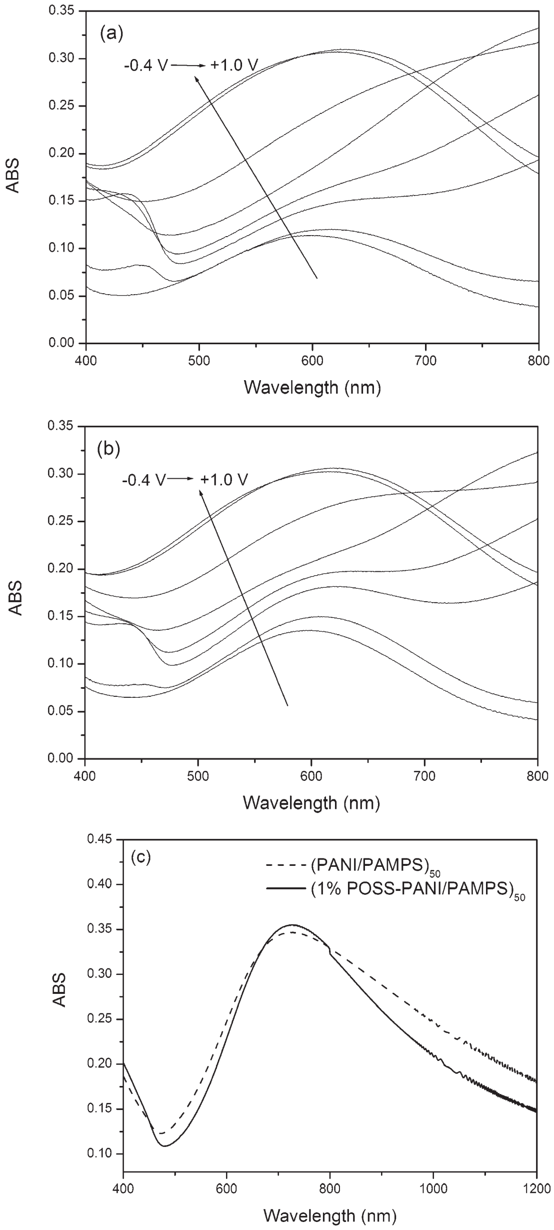

Figure 8. Visible spectra of (a) $(PANI/PAMPS)_{50}$ and (b) $(1\%POSS\text{-}PANI/PAMPS)_{50}$ under different potentials (−0.4, −0.1, +0.1, +0.2, +0.4, +0.6, +0.8, +1.0 V). (c) UV−vis−NIR spectra of $(PANI/PAMPS)_{50}$ and $(1\%POSS\text{-}PANI/PAMPS)_{50}$.

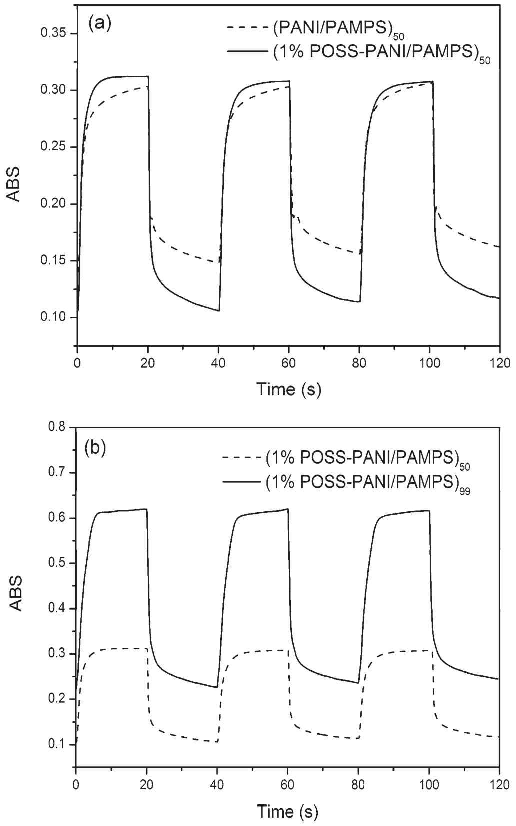

Figure 9. (a) Potential step absorptometry of $(PANI/PAMPS)_{50}$ and $(1\%POSS\text{-}PANI/PAMPS)_{50}$ with 100 nm thickness, and (b) potential step absorptometry of $(1\%POSS\text{-}PANI/PAMPS)_{50}$ and $(1\%POSS\text{-}PANI/PAMPS)_{99}$.

the peak separation value for the transition from the pernigraniline to emeraldine state is 244 mV for $(PANI/PAMPS)_{50}$ while that for $(1\%POSS\text{-}PANI/PAMPS)_{50}$ is 93 mV. It indicates that the electrochemical reactions in POSS-PANI are more reversible than those in linear PANI.

Spectroelectrochemical Characterization. Spectroelectrochemistry plays a key role in examining the optical changes that occur upon doping or dedoping of an electrochromic film. Figure 8 show series of UV−vis absorbance spectra of $(PANI/PAMPS)_{50}$ and $(1\%POSS\text{-}PANI/PAMPS)_{50}$ under various applied potentials varying from −0.4 V to +1.0 V vs Fc/Fc$^+$. Both PANI and 1%POSS-PANI switch between a relatively transmissive reduced state (yellowish green) and an absorbing oxidized state (blue). The maximum change in absorbance (ΔA) of $(PANI/PAMPS)_{50}$ (ΔA = 0.196 at 620 nm) (Figure 8a) is similar to that of $(1\%POSS\text{-}PANI/PAMPS)_{50}$ (ΔA= 0.180 at 626 nm) (Figure 8b). Prior to applying potential, the absorption bands for PANI and 1%POSS-PANI are centered at about 724 and 729 nm, respectively, with almost equal intensity (Figure 8c), which implies that the content of the active units in 1% POSS-PANI is nearly the same as that in PANI. The LBL assembled thin films are fairly homogeneous as demonstrated by their uniform color (see the Supporting Information).

Electrochromic Switching. The optical switching behaviors of the multilayer films are examined at wavelengths corresponding to their maximum change in absorbance (λ_{max}) using a UV−vis spectrophotometer with the applied potential stepped between −0.4 V and +0.9 V at 40 s per cycle. It is striking to see that the contrast of POSS-PANI (ΔA = 0.203) is significantly higher than that of PANI (ΔA = 0.154) (Figure 9a). To understand why the contrast of $(PANI/PAMPS)_{50}$ is approximately the same as that of $(1\%POSS\text{-}PANI/PAMPS)_{50}$ in steady-state measurements while they are very different under the dynamic switching condition, it is necessary to compare panels a and b in Figure 8 with Figure 9a. The absorbance maximum of PANI measured using the chrono amperometric method (A = 0.309) is almost equal to that measured under the dynamic condition (A = 0.303), whereas the absorbance minimum of PANI (A = 0.149) on the dynamic switching curve is significantly higher than that measured using the chrono amperometric method ($A = 0.113$), which causes the relatively low contrast of PANI under the dynamic switching condition. Because the reduction process in (PANI/PAMPS)$_{50}$ is diffusion-controlled, as shown in Figure 6, obviously during chrono amperometric measurements there is enough time for the doping ions to diffuse out of the (PANI/PAMPS)$_{50}$ so that the reduction process can finish completely. Under the dynamic condition with cycle time fixed at 40 s, there is not enough time for the doping ions to move out of the (PANI/PAMPS)$_{50}$ multilayer film. Thus, the reduction process in (PANI/PAMPS)$_{50}$ cannot finish, which leads to the decrease in contrast of (PANI/PAMPS)$_{50}$. For POSS-PANI, the maximum change in absorbance (ΔA) measured using the chrono amperometric method is approximately the same as the contrast obtained from the dynamic switching curve due to the faster ion transportation in (1%POSS-PANI/PAMPS)$_{50}$ compared with that in (PANI/PAMPS)$_{50}$. The relatively high contrast achieved with the 1%POSS-PANI/PAMPS multilayer thin film of only 100 nm thickness can hence be attributed to the unique morphology brought by the synergistic combination of the LBL assembly method with the starlike molecular architecture of POSS-PANI, which allows facile ion motion during the redox switching.

In addition to the improved contrast, the coloration time of the multilayer film, i.e., the time needed for achieving 90% of the total absorbance change, is shortened from 6.3 s for (PANI/PAMPS)$_{50}$ to 4.0 s for (1% POSS-PANI/PAMPS)$_{50}$. This is also an enormous improvement over that of the spin-coated thin film of the same thickness made of in situ polymerized POSS-PANI/polymeric acid complex (see the Supporting Information). It again shows the synergy between the unique material system and the LBL assembly method.

When the number of 1%POSS-PANI/PAMPS bilayers is increased from 50 to 99, the thickness of the POSS-PANI multilayer films is increased from 100 to 200 nm. The optical contrast of (1%POSS-PANI/PAMPS)$_{99}$ is about 0.4, as shown in Figure 9b, which is about twice of that of (1%POSS-PANI/PAMPS)$_{50}$. This demonstrated the potential of the LBL assembled POSS-PANI/PAMPS thin films for enhancing the performance of electrochromic devices.

Conclusions

In summary, POSS-PANI-EB copolymers have been readily synthesized and their chemical structures are verified by FTIR and elemental analysis. 1%POSS-PANI/PAMPS multilayer thin films have been successfully fabricated via LBL assembly technique. CV studies show that both the oxidation and reduction processes in the (1%POSS-PANI/PAMPS)$_{50}$ multilayer thin film are close to nondiffusion-controlled processes in the studied scan-rate range. Under the dynamic switching condition, the electrochromic contrast of (1%POSS-PANI/PAMPS)$_{50}$ is increased by more than 30% over that of (PANI/PAMPS)$_{50}$ and the switching time of (1%POSS-PANI/PAMPS)$_{50}$ is also significantly shorter than that of (PANI/PAMPS)$_{50}$. The switching kinetics of the POSS-PANI/PAMPS multilayer films is also much faster than that of spin-coated thin films of POSS-PANI/polymeric acid complexes. The improvements can be attributed to the unique morphology brought by the synergistic combination of the starlike structure of POSS-PANI and the LBL assembly method.

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Supporting Information Available: Si 2p XPS spectrum of silicon wafer, plots of absorbance of the PANI/PAMPS and 1% POSS-PANI/PAMPS multilayer films (5 bilayers) adsorbed on glass substrates as a function of dipping time, a photograph of (1%POSS-PANI/PAMPS)$_{50}$, CV curves of a spin-coated 1% POSS-PANI/PSS film of 100 nm thickness measured in a 0.1 M $LiClO_4$/acetonitrile solution, and the potential step absorptometry of the spin-coated thin film (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.