Electrochemical preparation and properties of composite films with polypyrrole/poly(styrene sulfonate): polyviologen multilayers

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Abstract

Multilayers consisting of polypyrrole/poly(styrene sulfonate) (PP/PSS) and polyviologen (PV) were electrochemically prepared on Au to enhance long-term and environmental (e.g., pH) stability of PV modified electrodes. PV cationic polyelectrolytes were adsorbed on top of electrochemically synthesized PP/PSS via electrostatic interactions with PSS present at the surface of conducting polymer substrates. By alternating electrochemical synthesis of PP/PSS and PV adsorption in a single medium, multilayers were prepared up to 13 layer-pairs. The electrochemical and electrochromic properties of multilayers produced in this way were quite reproducible, since the film preparation does not require medium changes and the layer thicknesses can be finely controlled using the applied potential and time. Although the redox potential of PP/PSS shifted in the positive direction with increase in the number of layer-pairs, cyclic voltammograms of multilayers indicated that total electroactivity of PP/PSS was retained. PV molecules, sandwiched between reduced PP/PSS layers, were also fully electroactive and quite stable during repeated redox switching processes, indicative of enhanced long-term stability. Multilayers also possessed electrochromic properties which were directly proportional to the number of PV layers.

1. Introduction

Electrochemical and electrochromic properties of viologen (quaternized 4, 4′-bipyridine derivatives) have been widely studied [1–5], mainly due to their deep coloration after one-electron reduction, which is useful as an element of electrochromic displays when combined with anodically colouring materials [6, 7]. Although immobilization of viologen as dialkyl salts onto electrode surfaces is straightforward, strategies to utilize electrostatic interactions between polyviologen (PV) and negatively charged surfaces were also investigated, with a view to obtaining enhanced long-term stability. Kaifer et al. [8] showed that polyviologen can be adsorbed on the surface of carboxylate-terminated self-assembled monolayers and the interaction is pH-dependent. Schlenoff et al. [9, 10] also demonstrated electrochemical and electrochromic properties of multilayers, consisting of polyviologen and poly(styrene sulfonate), prepared by an alternating polyion solution deposition technique.

In this paper, we describe the electrochemical and electrochromic properties of multilayers consisting of PP/PSS and PV. The multilayers were initially produced by potentiostatically synthesizing PP/PSS films on Au and subsequently immobilizing PV on the PP/PSS surface through coulombic interactions. Reynolds et al. [11] claimed that there are three types of PSS anions in PP/PSS films. These are well-entangled PSS chains, mostly employed as dopants within the PP matrix, PSS residing at the surface with only a portion of the chain acting as a dopant, and some PSS chains that are weakly adsorbed or loosely bound by physical interactions. This was proved by examining the interaction between cationic polyelectrolyte, poly(L-lysine hydrochloride) or arginine-rich histone, and PP/PSS using an electrochemical quartz crystal microbalance. It is therefore likely that the latter two PSS chains contribute to the immobilization of PV.

Once a PP/PSS:PV layer-pair was constructed, additional PP/PSS:PV layer–pairs were prepared on top of the underlying PP/PSS:PV by repeating the same procedure until the desired number of layer-pairs was obtained. These processes were performed by controlling the potential in a single-compartment cell, containing the solution of PSS anions and PV cations of judiciously chosen mole ratio to be free from precipitates [12]. It is believed that this strategy can enhance the reproducibility of electrochemical and electrochromic properties and stabilities of multilayers, since the film is not exposed to air during multilayer preparation and the thickness of each layer can be finely controlled. Although electrochemical preparation of viologen-entrapped polypyrrole films from viologen-substituted monomers has been reported [13] and these films are also expected to give excellent reproducibility and stability, the electrochemical method for PP/PSS:PV

multilayers will be more versatile, as it can be easily applied to the immobilization of other cationic species on PP/PSS.

2. Experimental details

Pyrrole was passed over aluminum oxide until colorless before use. 1,6-dibromohexane, 4,4′-bipyridine, sodium poly(styrene sulfonate) (NaPSS), sodium chloride, and acetonitrile were purchased from Aldrich and used as received, unless otherwise mentioned. Water was double distilled, having a resistance of 18 MΩ cm or higher. Polyviologen (PV) was synthesized by refluxing an equimolar mixture of 1,6-dibromohexane and 4,4′-bipyridine in dry acetonitrile for 24 h [14]. The precipitate was filtered, washed with acetonitrile to remove unreacted materials, and dried. PV and NaPSS were dialyzed against distilled water, using membrane tubing of 6000 to 8000 molecular weight cutoff. A mixed solution of PV and PSS (1:10 ratio based on total number of cationic to anionic charges) was prepared by dropping 10 mM PV into a NaPSS solution to achieve 9 mM PV and 0.09 M PSS. The initial cloudiness disappeared after gently shaking for a few minutes.

The electrochemical experiments were performed using BAS CV-50W and Elchema PS-705, with a conventional three electrode configuration. A Au button (electrochemical area 0.019 cm^2) and indium–tin oxide (ITO) (geometrical area 1.00 cm^2, from Samsung Corning) were used as working electrodes. For electrochemical measurements, Ag/AgCl and Pt were used as reference and counter electrodes, respectively. Electrochromic studies were performed by placing multilayers, prepared on ITO, in a cuvette equipped with Ag wire and Pt as quasi-reference and counter electrodes, respectively. Visible spectra (Hitachi U-3210) were obtained at −0.7 V (vs Ag/AgCl) for multilayers of various number of layer-pairs.

The multilayers were made in aqueous solution of PV and PSS containing 0.1 M pyrrole by controlling the potential and time. The PP/PSS layer was electrochemically synthesized at +0.8 V (vs Ag/AgCl). All further potentials are reported relative to this reference electrode. After the desired thickness of PP/PSS was obtained, the potential was immediately stepped to −0.7 V and held for 10 s to deposit PV radical cations on the PP/PSS surface. The film was then subjected to 0.0 V for 30 s to allow reoxidized PV to diffuse out of the PP/PSS surface. It should be noted that PV molecules electrostatically bound to PSS chains remain at the surface during this step. Potential application longer than 30 s does not alter the PV redox peak heights during subsequent potential cycling of multilayers, indicating that PV concentrations at the electrode surface become identical to the bulk concentration within 30 s and electrostatically bound PV resides at the PP/PSS surface for extended periods of time. Spontaneous adsorption of PV at open circuit is also possible, but takes much longer to reach equilibrium. For example, PP/PSS in 5 mM PV solutions required more than 1200 s to show similar electrochemical results. This three-step potential program (Figure 1) was repeated until multilayers of desired layer-pairs were obtained. The outmost layers were always PP/PSS, so that a multilayer of *n* layer-pairs means n PP/PSS:PV pairs plus an outmost PP/PSS layer. The PP/PSS film thicknesses were calculated from the charge passed during synthesis, using a conversion factor of $2.5 \ \mu\text{m C}^{-1} \text{ cm}^2$ [15].

3. Results and discussion

Films were prepared by controlling the potential in the multilayer-preparation medium consisting of 0.1 M pyrrole, 0.09 M NaPSS, and 9 mM PV. First, a PP/PSS single layer (8 nm thick) was potentiostatically synthesized on a Au button at +0.8 V and placed in a 0.1 M NaCl aqueous solution after thorough washing. Figure 2(a) shows that the redox potential of PP/PSS is about −400 mV and peak separation is relatively small.
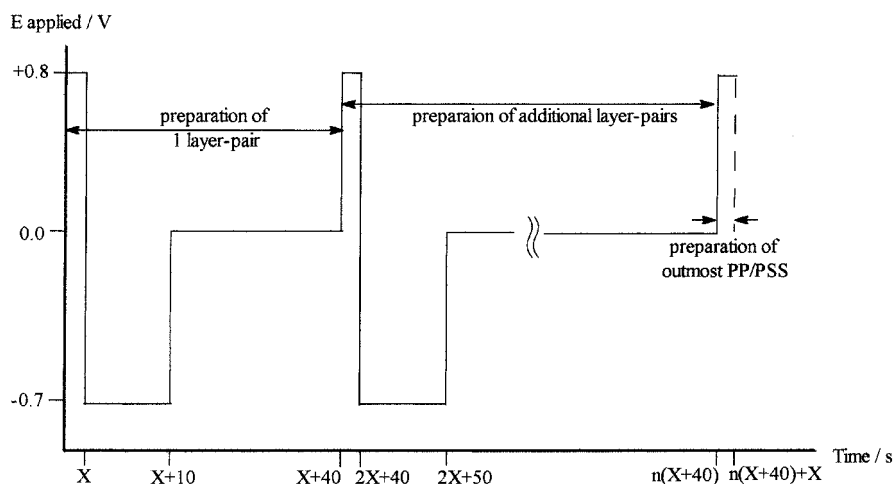

Fig. 1. Potential program used for electrochemical preparation of multilayers.
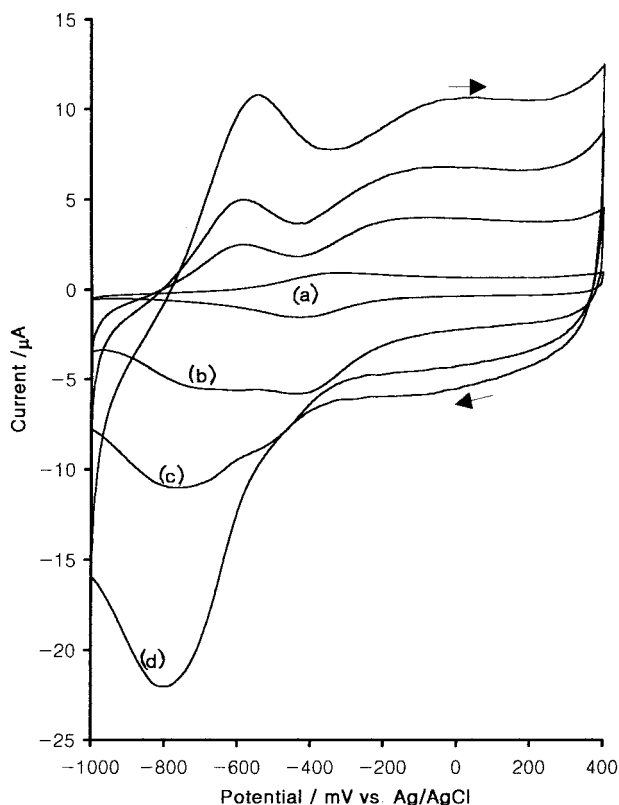
Fig. 2. Cyclic voltammograms of (a) PP/PSS and multilayers consisting of (b) 3, (c) 5 and (d) 9 layer-pairs. Each PP/PSS thickness was 8 nm. Films were cycled in 0.1 M NaCl at 100 mV s^{-1}.

The absence of a redox peak of PV at potentials lower than -500 mV also indicates that PV is not incorporated into, or spontaneously adsorbed on, the surface of a PP/PSS matrix during electrochemical synthesis.

Multilayers composed of various numbers of layer-pairs were prepared without removing electrodes from the film-preparation medium. After a PP/PSS single layer was synthesized, the potential was stepped to -0.7 V to deposit PV radical cations on the PP/PSS surface. After 10 s at -0.7 V, the films were subjected to 0.0 V for 30 s and subsequently to $+0.8$ V to electrochemically polymerize PP/PSS on the underlying PP/PSS:PV layer-pair. These potential steps were repeated until 13 layer-pairs were produced. Cyclic voltammograms of multilayers consisting of 3, 5, 9 layer-pairs are shown in Figure 2(b)–(d). Both anodic and cathodic peak heights resulting from PV redox processes increase with the number of layer-pairs, indicating that the electroactivity of PV is not reduced in PP/PSS:PV multilayers. Peak separations also gradually increase with the number of layer-pairs, suggesting that the redox process of PV, although fully electroactive, is slightly hampered by the presence of reduced PP/PSS.

On the other hand, while the peak heights of PP/PSS increase, the redox potentials shift in the positive direction with increase in the number of layer-pairs. The reason is not clear at this time, but it appears that the presence of cationic polyelectrolytes in the proximity of PP/PSS change the ion transport mechanism from cation dominant to anion dominant. It is well known that the redox potential of anion dominant PP is about 300 mV higher than that of cation dominant PP [16, 17]. This may be the case since the interface between layers is not distinct due to interpenetration of polymer chains.

The shift of PP/PSS redox potentials with the number of layer-pairs was further confirmed by using $Ru(NH_3)_6^{3+}$ as an electrochemical probe. A multilayer of three layer-pairs was redox-switched in an aqueous solution of 10 mM $Ru(NH_3)_6Cl_3$ and 0.1 M NaCl. The cyclic voltammogram was compared with that obtained on bare Au (Figure 3(a)–(b)). Explicit differences of peak heights at about -250 mV clearly indicate that direct electron transfer between $Ru(NH_3)_6^{3+}$ and Au is substantially suppressed in multilayers. Since blocked access of $Ru(NH_3)_6^{3+}$ is possible when PP/PSS is in a reduced state, the voltammetric result reveals that the redox potentials of PP/PSS of multilayers become higher than that of $Ru(NH_3)_6^{3+}$ due to positive shifts in the peak potentials of PP/PSS. The electron transfer reaction between $Ru(NH_3)_6^{3+}$ and Au, however, can be activated through PV within a multilayer. When compared with the cyclic voltammogram obtained in $Ru(NH_3)_6^{3+}$-free 0.1 M NaCl (Figure 3(c)), Figure 3(b) shows that cathodic processes of PV are greatly enhanced and anodic processes of PV occur between PV radical cations and $Ru(NH_3)_6^{3+}$, indicative of PV mediated electron transfer reaction (Figure 4). It should be mentioned that blocked access of $Ru(NH_3)_6^{3+}$ is not complete, since the total charges during the anodic and
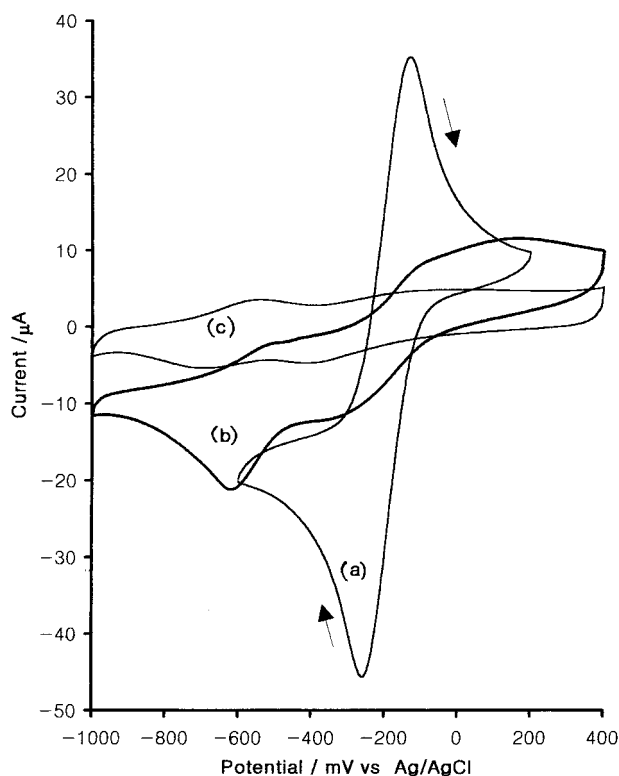

Fig. 3. Cyclic voltammograms of (a) bare Au in 10 mM $Ru(NH_3)_6^{3+}$/0.1 M NaCl and multilayers of three layer-pairs in (b) 10 mM $Ru(NH_3)_6^{3+}$/0.1 M NaCl and (c) 0.1 M NaCl at 100 mV s^{-1}.
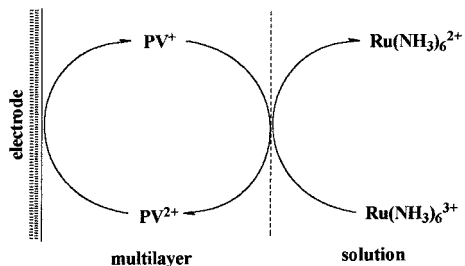
Fig. 4. Schematic diagram showing PV-mediated $Ru(NH_3)_6^{3+}$ reduction.

cathodic processes of PP/PSS in Figure 3(b) are higher than those in Figure 3(c). This is likely due to the presence of PP/PSS domains which are unaffected by the presence of PV chains and have a lower redox potential than that of $Ru(NH_3)_6^{3+}$.

The effects of PP/PSS film thicknesses were also investigated. Multilayers of three layer-pairs with various film thicknesses were prepared by simply controlling the polymerization time, as shown in Figure 1. Figure 5 shows cyclic voltammograms of multilayers of 8, 16, 32 and 59 nm thick PP/PSS. On the one hand, the increase in PP/PSS thicknesses results in enhanced PP redox peak heights, as expected. On the other hand, the total charges due to PV redox processes appear to be similar, as the area under the anodic peaks is invariant. This is quite likely since the electrostatic interaction between PV and PSS is limited to the PP/PSS surface
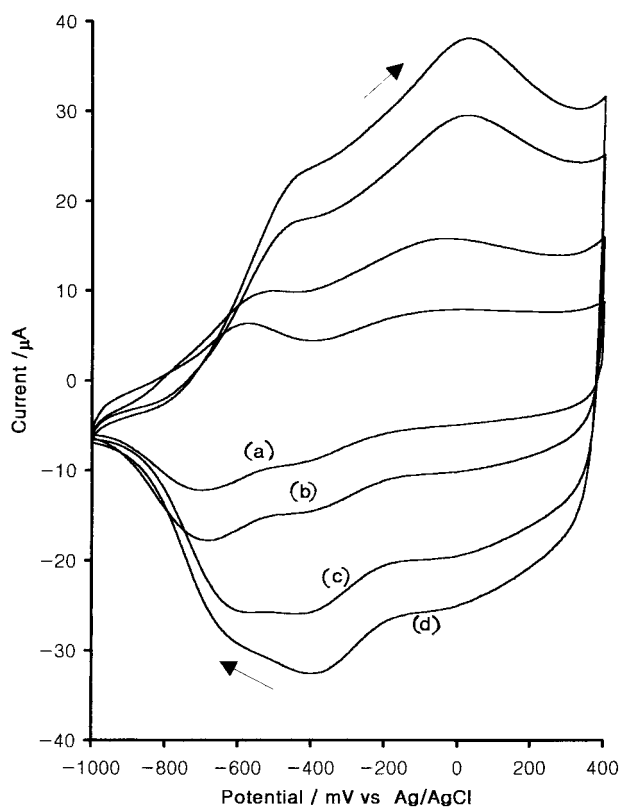
and the surface roughness effect is negligible in the range of PP/PSS thicknesses examined.

The other feature of the cyclic voltammograms of Figure 5 is that the cathodic peaks at about −400 mV become obvious with increase in PP/PSS thicknesses. As mentioned above, the presence of PV in the proximity of PP/PSS gives a shift in the redox potential of PP/PSS in the positive direction. For thick PP/PSS layers, however, a relatively high portion of the PP/PSS domain, which is not affected by cationic polyelectrolytes, should exist. This makes the cation dominant ion transport process of PP/PSS a major ion transport mechanism in multilayers of thick PP/PSS, leading to distinct cathodic peaks at about −400 mV. In the same context, cyclic voltammograms of multilayers with thick PP/PSS do not show enhanced cathodic peaks of PV, as explained in Figure 3.

The electrochromic properties of multilayers were also investigated. The multilayers with 8 nm thick PP/PSS were prepared on ITO, as described above, and placed in NaCl. Figure 6 shows visible spectra of multilayers after fully reducing the films at −0.7 V for 60 s. Although no absorption is seen at 570 nm in Figure 6(a), the absorption peaks increase due to reduced PV, with increase in the number of layer-pairs (Figure 6(b)–(e)). It has been confirmed that while the absorption maximum for monoradical cations is at 600 nm, λ_{max}

Fig. 5. Cyclic voltammograms of multilayers of 5 layer-pairs redox-switched in 0.1 M NaCl at 100 mV s^{-1}. PP/PSS thicknesses were (a) 8, (b) 16, (c) 32 and (d) 59 nm.
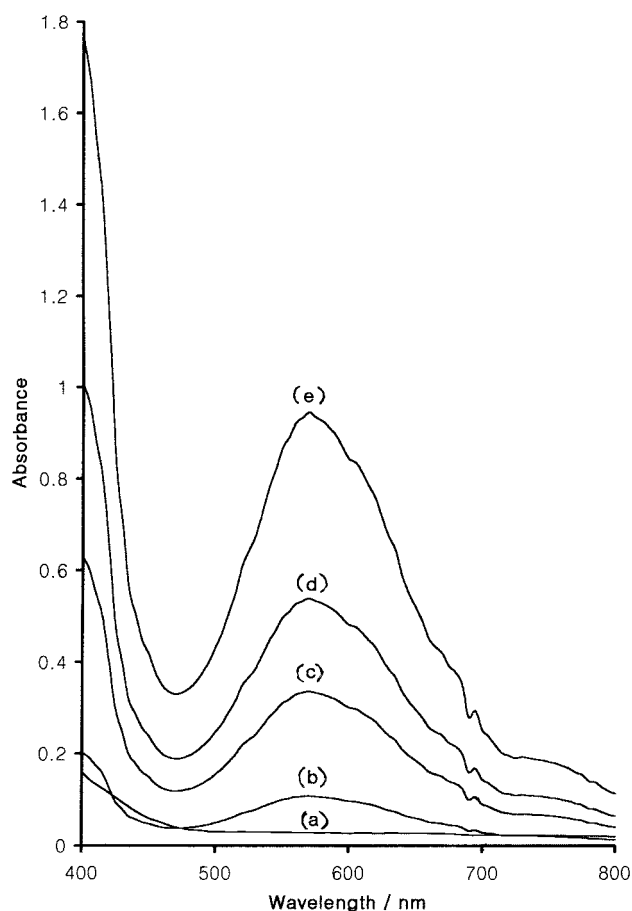

Fig. 6. Visible spectra of (a) PP/PSS and multilayers consisting of (b) 1, (c) 3, (d) 5 and (e) 9 layer-pairs. Each PP/PSS thickness was 8 nm thick.

moves to 550–560 nm for spin-paired radical cation dimers [18, 19]. It is likely, therefore, that the electrochromic behavior results from the π-dimers. The linear dependence between the absorbance and the number of layer-pairs is obvious up to nine layer-pairs, indicating that PP/PSS:PV multilayers, possessing electrochromic properties, can be constructed by simply adjusting the potential and time without changing media. A slight deviation from linearity above nine layer-pairs is observed, most likely due to incomplete reduction of PV.

4. Conclusions

Multilayers consisting of PP/PSS and PV were prepared in a single medium. The three-step potential (0.8 to −0.7 to 0.0 V) program was employed and repeated to obtain multilayers possessing highly reproducible electrochemical and electrochromic properties. PV in multilayers was fully electroactive and showed electrochromic properties even between insulating PP/PSS. While the total electroactivity PP/PSS of multilayers was retained, the redox potential of PP/PSS shifted in the positive direction due to the influence of surface-adsorbed PV.

Acknowledgement

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