

Electroactive Multilayer Films of Polyaniline and Vanadium Pentoxide

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Nanoscale composites of polyaniline (PANI) and vanadium oxide (V_2O_5) were assembled via the electrostatic layer-by-layer (LBL) technique, with a thickness per bilayer of 2.5 nm. Interactions between PANI and V_2O_5 are maximized in comparison to the usual xerogel films due to the nanostructured nature of the LBL films, in which V_2O_5 causes PANI to be oxidized. This has been demonstrated in Raman spectroscopy measurements and is consistent with electrochemical data. These strong interactions make the LBL film to display a color that is different from the colors of the individual materials. Furthermore, they promote a cooperative effect that enhances the charge storage capability of the films, with a total charge of 2.25 mC cm^{-2} for the PANI/ V_2O_5 LBL films, in comparison with 1.86 mC cm^{-2} for the sum of the isolated contributions from PANI and V_2O_5 .

Introduction

The manipulation of novel materials at the molecular level is a target in many applications where high performance is required. In the case of metallic oxides, for example, the interest in such manipulation lies in the possibility of enhancing the energy storage characteristics for batteries and the electrochromic activity.^{1–9} In this context, attempts have been made to produce nanocomposites comprising V_2O_5 and polyaniline^{10–18} basically to increase ion mobility and electronic conductivity of V_2O_5 . One of the most common methods to prepare PANI/ V_2O_5 nanocomposites is the in situ oxidative polymerization/intercalation of aniline in V_2O_5 xerogel. However, this method has been reported to yield V_2O_4 ,¹¹ thus decreasing the charge capability and altering the optical absorption properties of the composite. To minimize the reduction process of the vanadium ions, it is possible to encapsulate the polymer dispersion into the V_2O_5 gel. Nevertheless, with this technique it is not possible to establish an intimate contact between the composite components, which is essential for an appropriate synergistic effect.^{11,19} Another alternative is to fabricate layer-by-layer (LBL) films of PANI and V_2O_5 , as they may be made to possess opposite charges in aqueous solutions.

In a recent communication, we showed that V_2O_5 /PANI nanostructures could be obtained via the LBL technique,¹⁹ in which V_2O_5 and PANI layers were adsorbed alternately on a given solid substrate with a precise thickness control. Adsorption was driven by ionic attraction, because both materials were charged in solution, and probably by H-bonding. The thickness per bilayer of the PANI/ V_2O_5 LBL films was 25 Å. Because of the intimate contact between the components, a stronger

interaction was observed in comparison to the traditional nanocomposites obtained from xerogel.¹⁹ This holds great promise for achieving electroactive nanostructured materials for possible applications in displays, electrochromic windows and lithium microbatteries. In the present work, we focus on the understanding of the specific interactions between PANI and V_2O_5 via spectroscopy and on how these interactions contribute to enhance the electrochemical and electrochromic properties of the PANI/ V_2O_5 LBL films.

Experimental Details

The emeraldine base form of PANI was chemically synthesized using the method proposed by Mattoso et al.²⁰ We followed the procedures by Cheung et al.²¹ to prepare water soluble PANI. Briefly, PANI was dissolved in dimethylacetamide (DMAc) solution and after filtering, HCl was slowly added until the pH was 2.0. $V_2O_5 \cdot nH_2O$ was synthesized via an adaptation of the sol–gel method,^{1,22} with 0.2 mL of vanadyl tris(isopropoxide), $VC_9H_{21}O_4$ (Gelest), being added to 100 mL of water. This solution was heated in a thermal bath at 50°C in a vacuum under stirring for 2 h producing a yellowish solution that eventually became a viscous, red sol–gel liquid. Both PANI and V_2O_5 solutions were used at a concentration of ca. $4 \times 10^{-2} \text{ M}$ and the films were fabricated at room temperature (25 °C) and pH 2.0. This value of pH and concentration allows the formation of V_2O_5 , consistent with the findings of Pelletier et al.²³ and Huguenin et al.^{15,24} PANI/ V_2O_5 films were fabricated by the alternated immersion of the substrate into polycationic (PANI) and anionic (V_2O_5) solutions. After each deposition, the substrates were rinsed for 1 min in an aqueous solution under stirring. The washing solution had the same pH of deposition solutions (pH 2). Films were dried under a nitrogen flow. An immersion time of 3 min was used for adsorption of PANI and V_2O_5 . We observed that adsorption saturates for immersion times shorter than 5 min, with more than 90% of adsorption

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occurring within the first minute. Such a fast adsorption process denotes high affinity between V_2O_5 and PANI. The buildup of multilayers was monitored by UV-vis absorption spectroscopy (HITACHI U-2001 spectrophotometer). Glass slides were partially rendered hydrophilic and used as substrates. ITO (indium-tin oxide, $In_2[Sn_x]O_{3-y}$, one side coated on glass by Delta Technologies, sheet resistance $\leq 20\Omega$) was also used as substrates for electrochemical experiments. For the sake of comparison, we prepared LBL films of PANI/poly(vinyl sulfonic acid) (PANI/PVS) and poly(allylamine hydrochloride)/ V_2O_5 (PAH/ V_2O_5). Because PVS and PAH are electrochemically inert and transparent in the region investigated, the electrochemical response for PANI and V_2O_5 could be studied separately.

LBL films containing up to 20 bilayers were characterized by micro-Raman spectroscopy and electrochemical measurements. The Raman spectra were collected with the 632.8 nm laser line (He-Ne laser, Spectra Physics, mod 127) using a Renishaw Raman Imaging (system 3000) equipped with an Olympus metallurgic microscope and a CCD detector. For electrochemical experiments, the counter electrode was a platinum sheet with an area of 1 cm^2 . The reference electrodes were Ag/NO_3 (100 mM) for nonaqueous medium and saturated calomel electrode (SCE) for aqueous medium. The working electrode was an ITO conducting glass with a geometric area of 1 cm^2 . An electrolytic solution of 0.5 M $LiClO_4$ (Aldrich) in propylene carbonate (Aldrich) and 0.1 M HCl were used. Chromogenic analysis was made simultaneously with voltammetric experiments using a microprocessor-controlled solid-state light source (WPI, Inc). Plastic fiber optic cables up to 1 mm in diameter were used to deliver red light (660 nm) from the instrument to a PDA1 photodiode amplifier (WPI, Inc.) and the analogue signal proportional to the transmittance was sent to an Autolab PGSTAT30. In subsidiary experiments with cyclic voltammetry, electrochemically synthesized PANI was used following the procedures described in ref 25.

Results and Discussion

An idealized structure for the PANI/ V_2O_5 LBL film is suggested in Figure 1. Adsorption of the first PANI layer on the hydrophilic glass is expected to occur via H-bonding and/or ionic interactions between PANI and the surface charges of the glass slides.²⁶ Because PANI is in its charged state (pH of the solution = 2.0), assembling the multilayer is primarily driven by ionic interactions between PANI positive sites and the negative charge of V_2O_5 , but some degree of H-bonding is also expected.^{11,15} Figure 2 shows that the UV spectra of the LBL films depend on which material is at the topmost layer. When the top layer is V_2O_5 , an absorption band at ca. 600 nm appears, which is characteristic of emeraldine base PANI and/or PANI in the pernigraniline form. When the top layer is PANI, the absorption maximum shifts to ca. 800 nm, which is characteristic of emeraldine salt PANI. The spectrum of doped PANI in solution is not shown here, but the band at 800 nm is considerably narrower than for the PANI/ V_2O_5 /PANI films.²⁰ A broader band for the LBL film is due to H-bonding between PANI and V_2O_5 . A more detailed report concerning the buildup of the films can be found in ref 19. The growth of the PANI/ V_2O_5 multilayers is illustrated by the increase in absorption with the number of bilayers in the inset of Figure 2.

Figure 3 shows the Raman spectra obtained at different deposition steps, corresponding to the letters marking the layers in the schematic structure of Figure 1. Thus, Figure 3a corresponds to the Raman spectrum taken after the deposition of a PANI/ V_2O_5 bilayer, the oxide being the top layer. Because

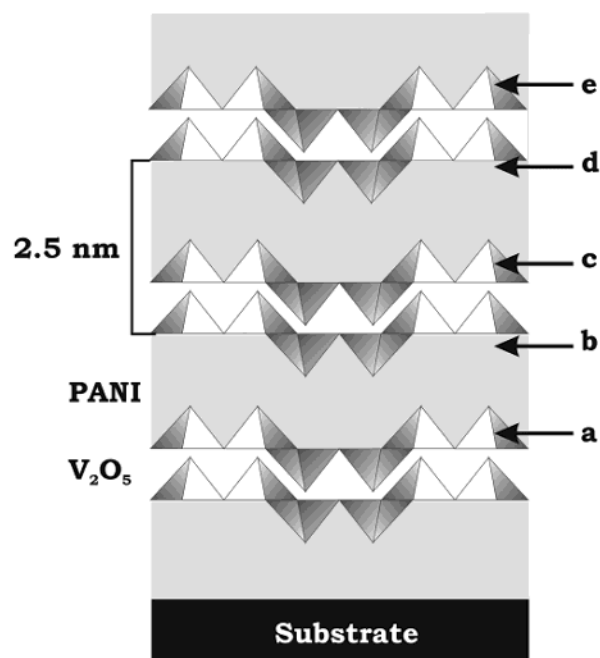


Figure 1. Idealized structure of V_2O_5 /PANI LBL films. Subsidiary X-ray diffraction experiments (2θ varying from 5 to 50°) showed no Bragg peaks, indicating the lack of long-range order in the plane of the layers.

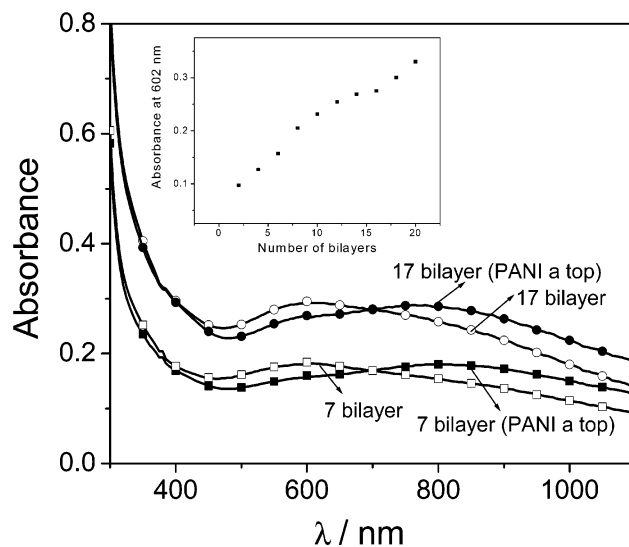


Figure 2. UV-vis absorption spectra of a 7- and 17-bilayer PANI/ V_2O_5 and PANI/ V_2O_5 /PANI LBL film. The inset shows the maximum absorbance as a function of the number of deposited bilayers for a 20-bilayer PANI/ V_2O_5 film.

of the resonant effect, all bands observed in the spectrum correspond to polyaniline in the emeraldine salt state. The bands due to V_2O_5 do not appear. This spectrum is characteristic of the conducting form of PANI^{27,28} with a prominent band at 1330 cm^{-1} assigned to polaronic species ($\nu C-N^{+}$), which was confirmed in subsidiary experiments as follows. An electrochemically synthesized PANI film was polarized at 0.3 V in a HCl solution, conditions under which PANI is known to adopt the emeraldine state. Figure 4a shows the Raman spectrum for such film, and as expected, the intensity of the 1330 cm^{-1} band is higher than that of the 1470 cm^{-1} band (quinoid segments, $\nu C=N$), which is consistent with the Raman spectrum of Figure 3a for PANI/ V_2O_5 .

The spectra shown in Figure 3, parts b and c, were taken after the deposition of one additional layer of PANI and of V_2O_5 ,

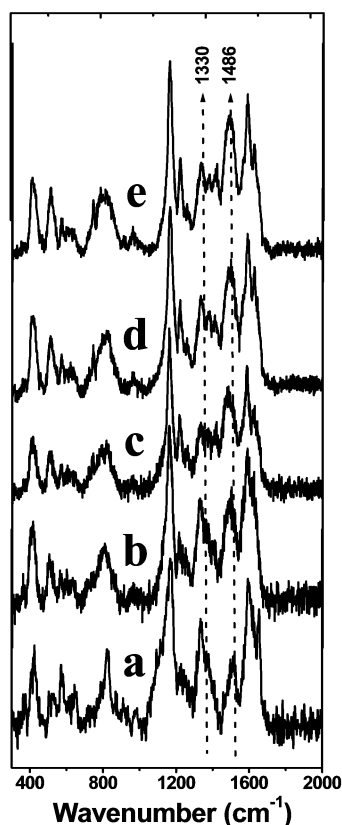


Figure 3. Raman spectra at different deposition steps for a PANI/ V_2O_5 LBL film: (a), (c), and (e): V_2O_5 atop, (b) and (d) PANI atop.

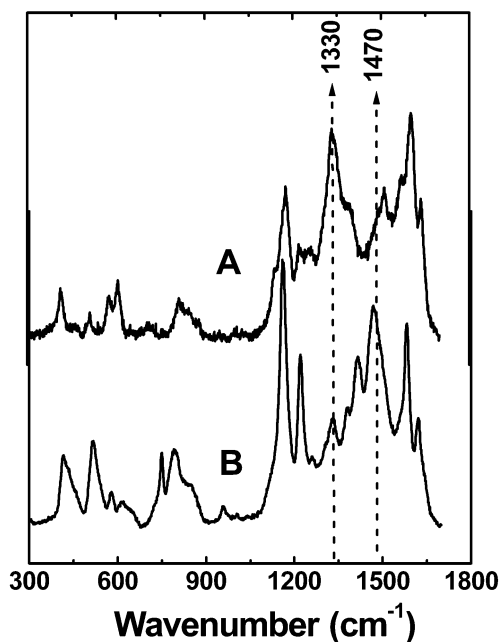


Figure 4. (a) Raman spectrum of an electrochemically synthesized PANI film polarized at 0.3 V in a HCl solution. (b) Raman spectrum of a PANI layer oxidized at 0.75 V up to the pernigraniline state in a HCl solution.

respectively. An increase in the quinoid character can be noted, especially in spectrum in Figure 3c when the V_2O_5 layer is at the top. This prominence of the quinoid character is attributed to oxidation of PANI caused by V_2O_5 . To confirm this finding, we obtained the Raman spectrum of an electrochemically synthesized PANI layer, oxidized at 0.75 V up to the pernigraniline state (oxidized) in a HCl solution. Figure 4b shows the

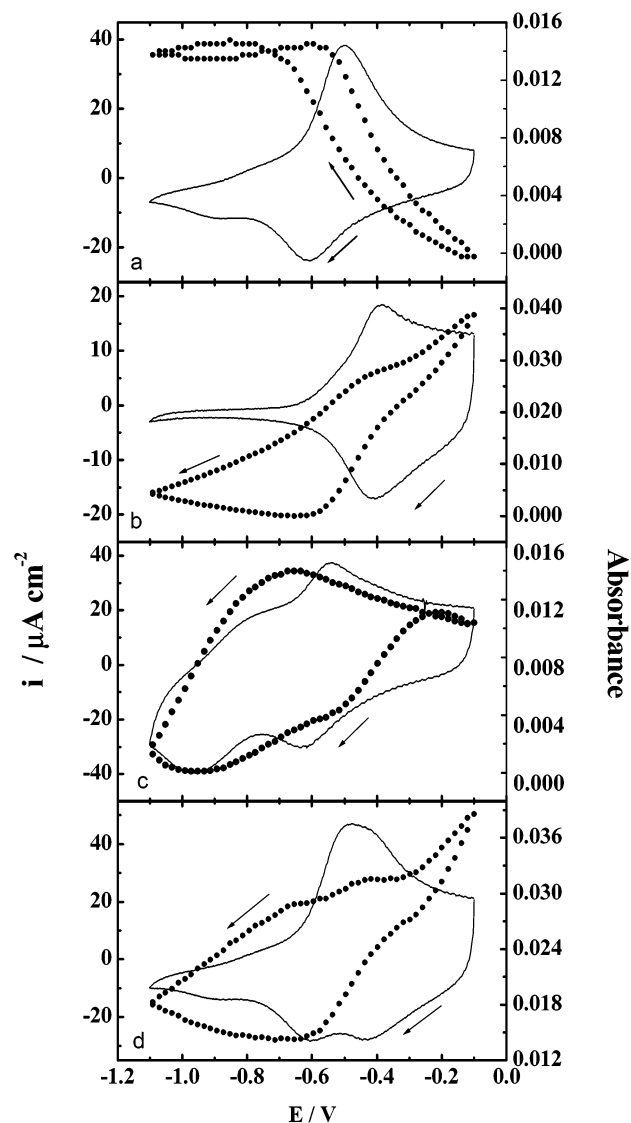


Figure 5. Cyclic voltammograms (solid line) and the in situ absorbance (660 nm) for 20 bilayers of (a) V_2O_5 /PAH LBL film, (b) PANI/PVS LBL film, and (c) PANI/ V_2O_5 film. (d) Arithmetic sum of absorbance and current values from Figure 5, parts a and b, corresponding to the sums of the signals from V_2O_5 and PANI. An electrolytic solution of 0.5 M $LiClO_4$ in propylene carbonate was used. Scan rate = 10 $mV s^{-1}$.

spectrum for this oxidized PANI, consistent with Figure 3c. The deposition of a further PANI/ V_2O_5 bilayer causes the Raman spectra to change, as shown in Figure 3, parts d and e. The relative intensity of the bands at 1330 and 1486 cm^{-1} (polaronic and quinoid segments respectively) changes depending on the film architecture. When V_2O_5 is at the top layer, the spectrum resembles that of oxidized PANI; that is, V_2O_5 causes the PANI underneath to be oxidized. In summary, in the PANI/ V_2O_5 LBL films, strong interactions occur between PANI and V_2O_5 layers, leading to overoxidation of PANI to the pernigraniline form.

The intimate contact between V_2O_5 and PANI in the LBL films is manifested in the electrochemical properties of the films. This conclusion is drawn by comparing cyclic voltammograms and in situ absorbance at 660 nm for 3 types of LBL films: V_2O_5 /PAH, PANI/PVS, and PANI/ V_2O_5 , shown in Figure 5a–c, respectively. Because both PAH and PVS are inert electrochemically and do not absorb at 660 nm, Figure 5, parts a and b, display, respectively, the behavior of V_2O_5 and PANI on their own. The solid line in Figure 5a is a typical voltammogram for

V_2O_5 . The increase in absorbance (dotted line) as the potential, E , is scanned toward negative values in Figure 5a is attributed to the intervalence transition from $V^{IV} \rightarrow V^V$.^{5,29} At $E < -0.85$ V, the absorbance tends to saturate or even decrease due to an excess of V^{IV} sites in comparison to the electrochemically active V^V sites. For the PANI/PVS film, the solid line in Figure 5b is a typical voltammogram for PANI in which redox peaks are assigned to interconversion between emeraldine and leucoemeraldine forms.^{30–31} The absorbance decreases monotonically as the potential becomes increasingly negative, which is attributed to a decrease in the number of polarons as PANI is reduced from emeraldine salt to leucoemeraldine salt.³² If there were no molecular-level interaction between PANI and V_2O_5 , the signals for the PANI/ V_2O_5 LBL film in Figure 5c should be the arithmetic sums of the signals in Figure 5, parts a and b. However, the differences between parts c and d of Figure 5 show clearly that interaction occurs, as the signals for the PANI/ V_2O_5 LBL film in Figure 5c are not the sum of the individual signals depicted in Figure 5d. For instance, the absorbance increases when the potential is varied from -0.1 to -0.65 V in Figure 5c, whereas according to the arithmetic sum in Figure 5d, it should decrease. This also means that PANI contribution to the global redox process in the PANI/ V_2O_5 LBL film is small compared to that in Figure 5b. The redox process of PANI is observed from -0.65 to -1.10 V in the PANI/ V_2O_5 LBL film, which leads to a decrease in the absorbance in Figure 5c in this region. The incomplete reduction of PANI in the PANI/ V_2O_5 LBL film in comparison to the PANI/PVS system for $E > -0.65$ V is probably associated with highly resistive paths such as those provided by V_2O_5 and pernigraniline PANI form,^{1,33} as suggested in the Raman results of Figure 3. The total charge in Figure 5c involved in the redox reactions of the PANI/ V_2O_5 LBL film are greater than the arithmetic sum of the individual contributions (Figure 5d). Indeed, the total charge is 2.25 mC cm^{-2} for the PANI/ V_2O_5 LBL films, contrasted to 1.86 mC cm^{-2} for the sum of the isolated contributions. This cooperative effect is attributed to an intimate contact between the conducting phase (PANI) and V_2O_5 . Therefore, in the PANI/ V_2O_5 LBL films, the storage capability of V_2O_5 was not only maintained but also increased. This is due to the molecular-level interaction between the components, as evidenced by the UV-vis and Raman spectroscopy results from Figures 2 and 3.

Conclusions

Ultrathin films comprising PANI and V_2O_5 were fabricated employing the LBL technique. In comparison to the usual PANI/ V_2O_5 films produced by in situ oxidative polymerization/intercalation of aniline in V_2O_5 xerogel, the interactions between PANI and V_2O_5 can be maximized in the LBL films because of the nanostructured nature of the films. Such intimate contact between PANI/ V_2O_5 layers is believed to promote the over-oxidation of PANI (to the pernigraniline form) as revealed by Raman spectroscopy. In addition, these interactions seem to promote a cooperative effect that enhances the charge storage capability of the films in comparison to their separate components. This indicates that PANI/ V_2O_5 LBL films are promising to be used as cathodes in lithium microbatteries and displays. Another important advantage of the LBL technique is the

possibility of obtaining homogeneous films, with precise control of thickness and maximized interaction between the components, which may also be important for producing electrochromic windows and devices.

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