

STABILITY AND ELECTROCHEMICAL PROPERTIES OF FULL-CONJUGATED SELF-ASSEMBLED FILMS BASED ON POLYANILINE AND ITS ACID-SUBSTITUTED DERIVATES*

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Abstract The stability of full-conjugated self-assembled (SA) multilayer films based on partially doped polyaniline (PANI) as a polycation and poly(*o*-aminobenzoic acid) (PCAN), poly(aniline-2-sulfonic acid) (PSAN) as polyanions is investigated in alkali aqueous solutions. The self-assembled PANI-PCAN films keep their stability within 24 h in 1 mol/L NaOH solution, the PANI-PSAN films, however, maintain the stability for 20 min in the same condition because the solubility of PSAN in alkali solutions is much higher than that of PCAN. The electrochemical properties of the SA films are determined, and the film-CdS composites formed *in situ* are also reported.

Keywords: Polyanilines; Self-assembly multilayer films; Electrochemical Properties; Film-CdS composites.

INTRODUCTION

Much attention has been paid to conducting polymers in view of their multiple potential technological applications such as light-emitting diodes, biosensors and so on^[1–9]. Comparing with the traditional approaches used to fabricate functional ultrathin films, including the Langmuir-Blodgett method, sol-gel synthesis, electrochemical deposition and chemical vapor deposition *etc.*^[10–15], the layer-by-layer (LBL) self-assembly technique^[16–18] has been more widely and successfully used to prepare advanced membranes with desired components such as biomolecules^[19] and electroactive polymers^[20–22]. The full-conjugated self-assembled films fabricated by using this method have attracted more attention because of their potential applications as semitransparent electrodes or as a new type of ultrathin film devices to control the flow of electron and hole carriers^[20–26]. Rubner *et al.*^[21] demonstrated that the facile LBL deposition of a variety of conjugated polyions, such as poly[(*N*-methyl-pyridinium-2-yl)acetylene] and poly(*p*-phenylene vinylene) as polycations, poly(thiophene-3-acetic acid) and sulfonated polyaniline (PAN) as polyanions, can be successfully achieved in dilute aqueous solutions. The typical bilayer thickness ranges from approximately 1 nm to 2.5 nm.

In a previous paper^[27], we only reported the fabrication of full-conjugated self-assembled (SA) films from PANI as a polycation and PCAN and PSAN as a polyanion, and the electrochemical properties of 9-bilayer PANI-PCAN and PANI-PSAN films. Herein, we studied the stability of PANI-PCAN and PANI-PSAN films

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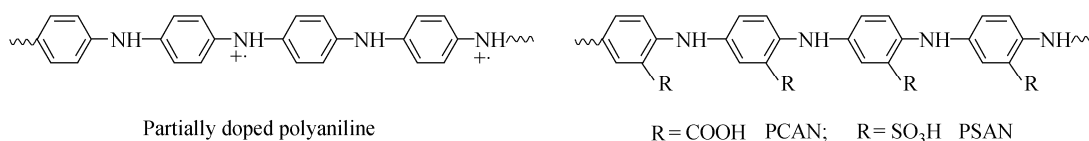
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based on the Coulombic interaction to solvent etching. In addition, the cyclic voltammetry electrochemical behavior of the films was determined to ascertain the relationship between the electrochemical property and the number of bilayers and ionic strength of polyanions. The preparation of the CdS-film composites was also reported.

EXPERIMENTAL

Materials

The syntheses of polyaniline in its emeraldine base form^[28], partially doped polyaniline (PANI)^[29, 30], poly(*o*-aminobenzoic acid) (PCAN)^[31] and poly(aniline-2-sulfonic acid) (PSAN)^[32] were carried out according to the procedure of literatures. The structures of the three polymers used in this work are shown as follows:



Scheme 1 the structures of polymers used in this work

Substrates and Fabrication of Self-assembled Films

The treatment of quartz slides and indium tin oxide (ITO) glass plates and the fabrication of PANI-PCAN and PANI-PSAN self-assembled films were carried out according to the procedure of literature^[27].

UV-Vis Spectroscopy

UV-Vis spectra recorded on a Varian Cary 1E UV-Vis spectrophotometer were used to monitor the layer-by-layer deposition and the photoreaction occurred in the films.

Solvent Etching

Solvent etching was carried out according to a literature method^[33, 34]. A film with 10 bilayers was dipped into an aqueous solution of 1 mol/L NaOH for different times then washed with water, dried in air and was used for determination of UV-Vis spectrum.

Electrochemical Measurements

Cyclic voltammetry (CV) of the SA films was carried out by using a CHI 600A Electrochemical Workstation. ITO glasses modified with 3, 6 and 9 bilayers films were used as the working electrode, the counter electrode was a Pt wire, and a saturated calomel electrode was used as reference. The support electrolyte was an H₂SO₄ solution (0.5 mol/L).

In situ Preparation of the Film-CdS Composites

The composite of the SA film and CdS was prepared as follows: The multilayer SA films of PANI-PCAN or PANI-PSAN were first immersed into 1 mol/L NaOH solution for 5 min to increase the ratio of the ionized acid groups of the polyanion available for Cd²⁺ ion binding then immersed into the 0.04 mol/L solution of cadmium acetate for 4 h. After ion exchange, the films were washed in water and dried in air. Cd(II)-containing films were then exposed to hydrogen sulfide (room temperature) for 12 h to form film-CdS composites.

Determination of Surface Morphology

Atom force microscopy (AFM) was used to visualize the surface morphology of the films on mica. AFM measurements were performed in air at ambient temperature with a Nanoscopy IIIA (Digital Instruments, Inc.) in the tapping mode. Commercial silicon probes (model TESP-100) with a typical resonant frequency around 300 kHz were used to obtain the image.

RESULTS AND DISCUSSION

The Stability of the SA Films

The stability of the SA films of PANI-PCAN and PANI-PSAN is easily affected by the concentration of electrolyte, ionic strength, pH value and so on. Since PANI is only dissolved in the pH = 2.5–4.0 aqueous solution^[29] and PCAN and PSAN only dissolves in alkali solutions, the SA PANI-PCAN and PANI-PSAN films should be stable in polar solvents or strong electrolyte solutions, which are very similar with the PANI-PCPA films reported in our previous work^[25].

The stability of a 10 bilayer film was investigated by being immersed in a 1 mol/L NaOH solution. As shown in Fig. 1, the absorbance of the PANI-PCAN film at 617 nm gradually increases in the first 5 h because of the transformation from the emeraldine salt to the emeraldine base. Such a conversion increases the compact degree in the films, blocks the diffusion of alkali ions into multilayer films and imparts high stability to the film. So the absorbance of the films becomes constant between the 5th h and 23rd h in alkali solutions. With gradual diffusion of alkali ions into the multilayer film, more and more PCAN is, however, slowly converted into its water-soluble sodium salt. The PANI-PCAN film begins to dissolve and completely disappears after immersion for 24 h.

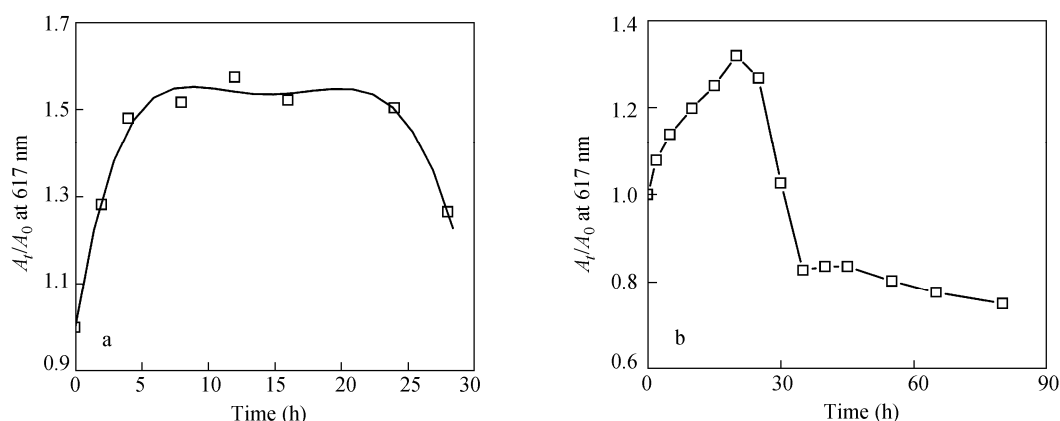


Fig. 1 A_t/A_0 -time plot of PANI-PCAN (a) and PANI-PSAN (b) films at 617 nm in a 1 mol/L NaOH solution

Because of the water solubility of PSAN is superior to PCAN, the stability of the PANI-PSAN films is lower than that of PANI-PCAN films. The experimental results indicated that the absorbance of PANI-PSAN films at 617 nm only increases within first 20 min and then rapidly decreases due to etching (as shown in Fig. 1b).

Electrochemical Properties of the Films

CV was used to investigate the electrochemical properties of the multilayer films deposited on an ITO-coated glass plate. Figure 2(A) presents the cyclic voltammograms of a 9 bilayer PANI-PCAN film during the potential cycling from -0.2 V to $+1.0$ V at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$ in a $0.5 \text{ mol/L H}_2\text{SO}_4$ solution. The first oxidation peak corresponding to the transfer from radical cation to as-reduced state of polyaniline is at 0.26 V and the second oxidation peak corresponding to the transfer from quinone diimine to radical cation appears at 0.82 V, which are very similar to those of the PANI/SPANI films reported by Knoll *et al.*^[35]. The oxidation peak currents of the multilayer films increase as a function of bilayer numbers because of increasing of the amount of PANI and PCAN deposited as shown in Fig. 3(a). Meanwhile, it shows little change in the peak potential values with decreasing bilayer deposition from 9 to 3, which reveals that the oxidation electrochemical response of PANI-PCAN films is independent of the number of bilayers. Compared with PANI-PCAN, the cyclic voltammograms of the PANI-PSAN films are very similar to those of PANI-PCAN films, as shown in Fig. 2(B). The oxidation peak currents of PANI-PSAN multilayer films with the same bilayer number are, however, relatively low

(Fig. 3), which supports the observations in the UV-Vis spectra. That is, the redox peak currents are in direct proportion to the amount of polyelectrolytes deposited on the surface in the same area. The redox potential of PANI-PSAN films is, however, almost equal to that of PANI-PCAN films because the specific conductivity of PSAN and PCAN is 10^{-5} S/cm^[31] and 10^{-8} S/cm^[30], respectively, which are much lower than that of PANI (10^0 S/cm)^[28] and don't affect the redox potential of the films.

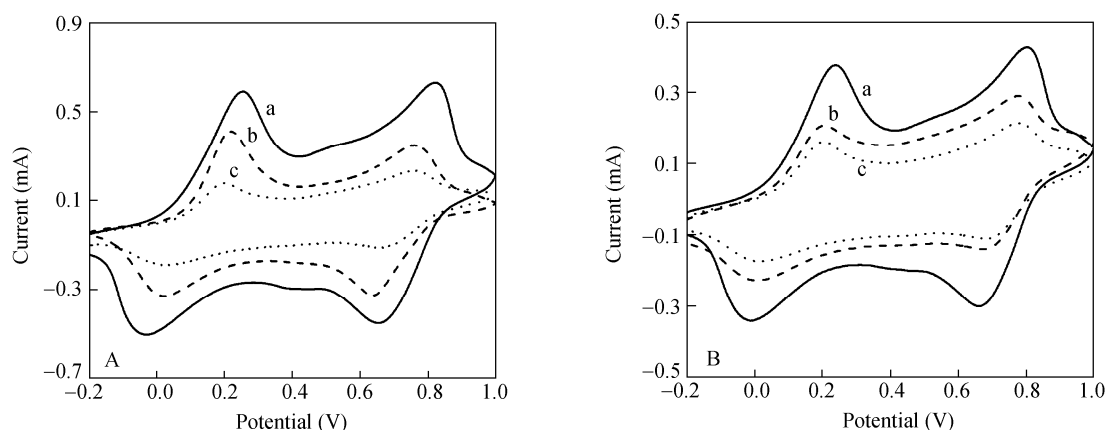


Fig. 2 Cyclic voltammograms of the PANI-PCAN (A) and PANI-PSAN (B) films with different bilayer number: (a) 9, (b) 6 and (c) 3

The measurements were carried out in a 0.5 mol/L H_2SO_4 solution, and the scan rate was at $100 \text{ mV}\cdot\text{s}^{-1}$.

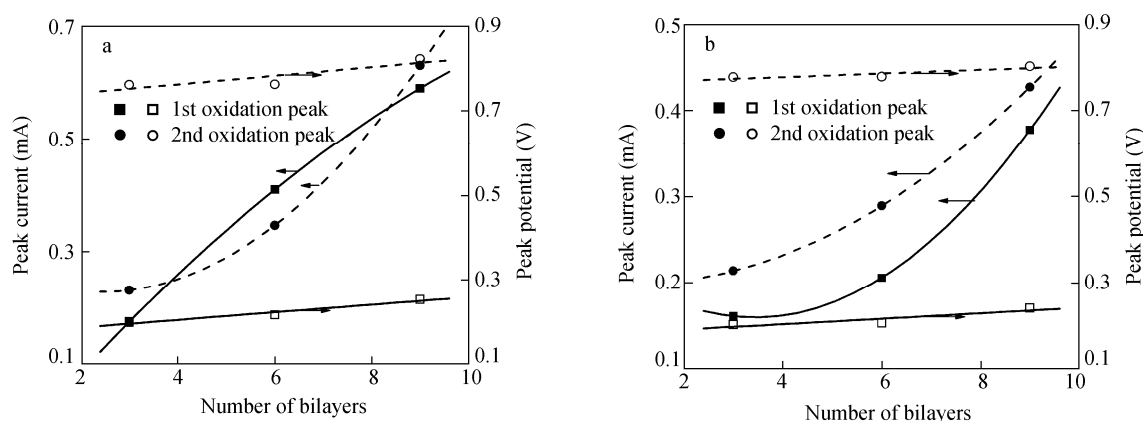


Fig. 3 The two oxidation peaks' currents and potentials of the PANI-PCAN (a) and PANI-PSAN (b) films immersed in a 0.5 mol/L H_2SO_4 solution versus the number of bilayers at the scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$

In situ Preparation of the Film-CdS Composites

Nanodisperse heterojunctions based on semiconductor nanoparticles (NPs) and conjugated polymers are subject of intense studies for fundamental research and applications ranging from light emitting diodes to solar cells^[36–38]. Figure 4 shows that the CdS particles are in-situ prepared within PANI-PCAN and PANI-PSAN films. It is explained that most of the ionized acid groups end up forming ion pairs with the cationic groups of PANI when a PCAN or PSAN chain is adsorbed onto a surface containing an oppositely charged PANI, the remaining free acid and anionic groups are only available for subsequent reactor chemistry^[38, 39]. For increasing the ratio of the ionized acid groups available for Cd^{2+} ion binding, the multilayer films were first immersed into a 1 mol/L NaOH solution for 5 min under the presupposition of non-destroying the structure of films. The base-pretreated films were then immersed into the 0.04 mol/L solution of cadmium acetate for 4 h and employed the ionized acid group of PCAN or PSAN to bind Cd^{2+} from an aqueous solution. Following the sulfidation, CdS particles are produced *in situ* within the films^[38, 39]. Otherwise, the yield and diameters of CdS nanoparticles

prepared in the PANI-PSAN film is obviously higher than that in the PANI-PCAN film. According to the above-mentioned analysis, though sulfonic groups in PSAN have higher electro-negativity than carboxylic groups in PCAN, which induce that the deposition amount of PANI-PSAN in every dipping cycle is less than that of PANI-PCAN under the same condition, the ability of sulfonic groups in PANI-PSAN films to bind Cd^{2+} is more stronger than that of carboxylate groups in PANI-PCAN films. The more Cd^{2+} ions are bound into the PANI-PSAN self-assembled films.

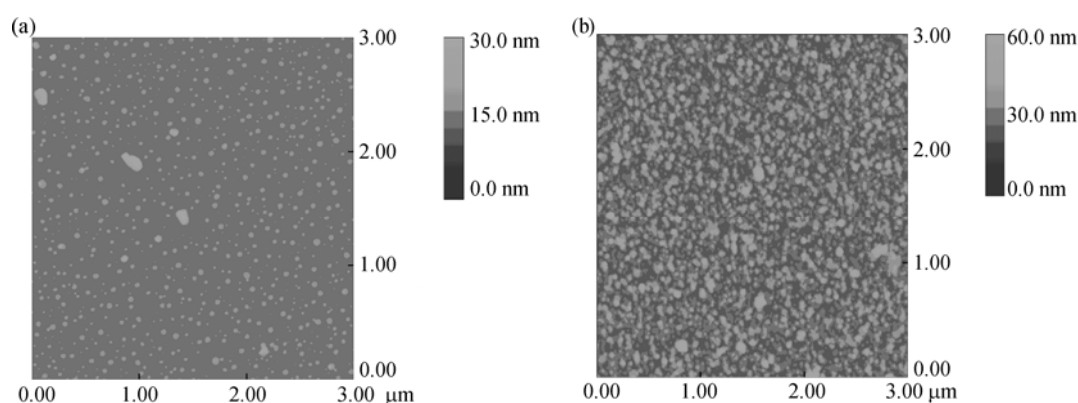


Fig. 4 Surface morphology of the nanocomposites of CdS particles embedded within the 3-bilayer self-assembled films of PANI-PCAN (a) and PANI-PSAN (b), respectively

CONCLUSIONS

The full-conjugated PANI-PSAN and PANI-PCAN SA films are uniform and stable in polar organic solvents, strong electrolytes and acid aqueous solutions. A 10 bilayer PANI-PCAN film keeps stable within 24 h in a 1 mol/L NaOH aqueous solution, however, the stability of the PANI-PSAN film is relatively low. The oxidation peak current of the film increases as a function of bilayer numbers because of increasing the amount of PANI deposited. The electrochemical property of the PANI-PSAN SA films is inferior to that of PANI-PCAN films due to the effect of deposition amount of PCAN and PSAN. Because the ability of sulfonic groups in PANI-PSAN films to bind Cd^{2+} is stronger than that of carboxylate groups in PANI-PCAN films, more Cd^{2+} ions are bound into the PANI-PSAN self-assembled films.

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