

Near-infrared and Multicolor Electrochromic Device Based on Polyaniline Derivative^{*}

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Abstract Electroactive conducting copolymers of aniline (ANI) and diphenylamine (DPA) are prepared on indium tin oxide (ITO) surface from 1 mol/L H₂SO₄ aqueous solution with different feed ratios of ANI to DPA by using a potentiostatic method. FTIR spectra and SEM measurements are used to confirm the formation of copolymers. Due to the combination of the *N,N'*-diphenyl benzidine and aniline units in the molecular chain, the copolymer films exhibit improved electrochemical and electrochromic properties, compared to PANI and PDPA. The copolymer [marked as P(ANI9-*co*-DPA1)] film prepared at a ratio of 9:1 (ANI/DPA) exhibits novel transmittance modulation both in visible and near-infrared (NIR) region between −0.8 V and 0.8 V (52% and 67% respectively) and fast response time (3.6 s for coloration and 2.3 s for bleaching at 600 nm). An electrochromic device (ECD) based on P(ANI9-*co*-DPA1) and PEDOT:PSS is also fabricated and shows a multicolor electrochromic performance, with a good optical contrast (29% in visible region and 40% in NIR region), acceptable response time (8.3 s for coloration and 7.5 s for bleaching at 600 nm) and long-term stability. Clear color changes from transparent (−0.8 V), bright green (0 V), seagreen (0.4 V) to dark slate gray (0.8 V) are demonstrated.

Keywords: Conjugated polymer; Spectroelectrochemistry; Electrochromic device; Polyaniline.

INTRODUCTION

Conjugated polymers have received much attention both in science and in industry due to their potential applications in electrochromic devices (ECDs)^[1–3], semiconductors^[4, 5], solar cells^[6, 7] and light emitting diodes (OLEDs)^[8, 9]. Polyaniline (PANI) is a very important conjugated polymer as electrochromic material because of its multicolor electrochromism, ease of synthesis, environmental stability and inexpensive price^[10–12]. A PANI thin film exhibits yellow for the leucoemeraldine base (LB) state, green for emeraldine salt (ES), blue for emeraldine base (EB), and black for pernigraniline salt (PS) during the electrochemical doping process (as shown in Scheme 1). PANI usually is prepared by chemical or electrochemical oxidation of the corresponding monomer, so a significant merit of preparation is the tailor ability of its chemical structure *via* monomer modification and copolymerization to improve its electrochemical and electrochromic properties^[13, 14].

Homopolymerization of aniline (ANI) derivatives, especially the *N*-substituted aniline derivatives has been employed successfully to improve the electrochromic properties of polyaniline^[14]. Diphenylamine (DPA), an *N*-aryl substituted ANI derivative, has been polymerized by pulse potentiostatic^[15] and cyclic voltammetric^[16] method. DPA is polymerized through the 4,4'-phenyl-phenyl coupling^[16], resulting in *N,N'*-diphenyl benzidine

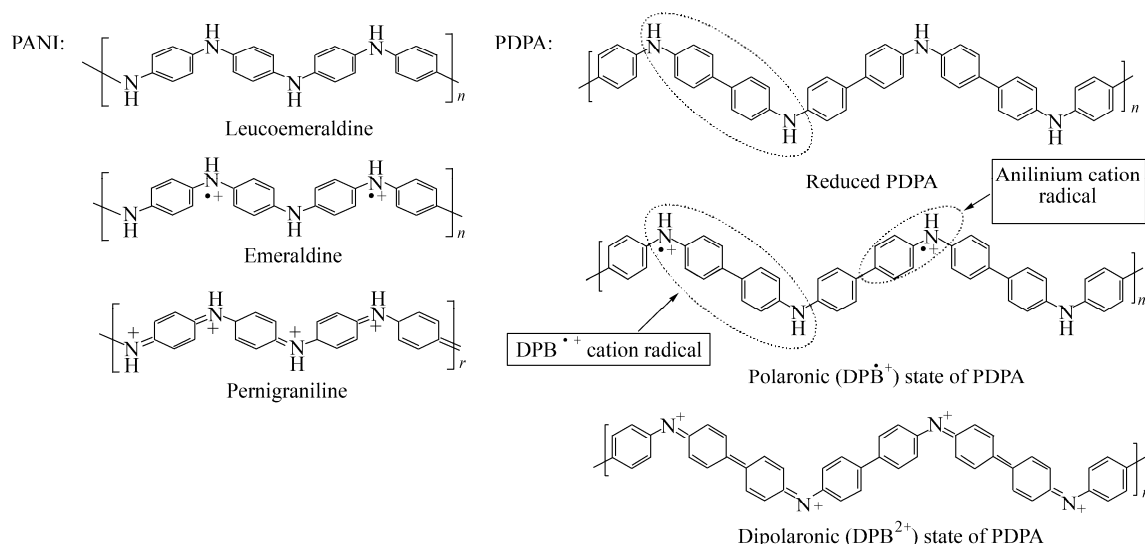
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(DPB) and aniline units in the polymer chains (as shown in Scheme 1), thus poly(diphenylamine) (PDPA) is expected to possess the properties of poly(paraphenylene) and PANI. Previous study demonstrated that the protonation of PANI-type structure in PDPA was different from that of PANI, which led to a higher absorbance contrast in the spectral range from 550 nm to 900 nm than that of PANI^[16–18].



Scheme 1 Molecular structure of PANI and PDPA

Furthermore, copolymerization of aniline with its monomer derivatives is another effective approach to prepare materials with high-quality electrochromic and electrochemical performance, because it can overcome the limitations of a few new conjugated π -bond-containing monomers^[13, 19, 20]. Poly(aniline-*co*-4,4'-diaminodiphenyl sulfone) exhibits three color stages (neutral yellow, dark green and dark blue) under different potentials^[13]. Poly(aniline-*co*-ethyl 4-aminobenzoate) shows multicolor electrochromic behavior (from neutral yellow, green to blue) and can be highly soluble in many polar solvents^[19]. The electrochemical copolymerization of aniline with aniline-2,5-disulfonic acid results in a copolymer with stable conductivity (0.34 S/cm) over a wide pH range (up to pH 9)^[20]. Wen *et al.*^[15] prepared copolymer of ANI and DPA by a pulse potentiostatic method, and found the copolymer films exhibited higher electroactivity than PANI films. Chandrasekhar *et al.*^[21] prepared PANI/PDPA/polymeric dopants ternary composite films for far-infrared electrochromic devices. The composite films presented very high emittance variation (from 0.32 to 0.79) in the spectral region of 0.4 μm to 45 μm , long-term cyclability (up to 10^5 cycles) and fast switching time (< 2 s).

Due to the unique electrochromic properties of PDPA, it is reasonable to introduce the DPB fragments into the molecular chain of PANI to improve the electrochemical and electrochromic properties of PANI. In this work, we report the electropolymerization of ANI and DPA binary monomers in a 1 mol/L H_2SO_4 aqueous solution. The effects of feed ratios of ANI to DPA on the electrochemical and electrochromic properties of copolymer films are studied. Compare to other conjugated polymers with similar molecular structure reported by literatures^[10–12, 14], the P(ANI-*co*-DPA) films have a high optical contrast and a fast response time. In addition, a dual type ECD based on P(ANI-*co*-DPA1) and PEDOT:PSS has been constructed and characterized in detail. The ECD exhibits multicolor and good optical modulation performance between -0.8 V and 0.8 V.

EXPERIMENTAL

Materials

Both aniline (99%) and propylene carbonate (99.5%) were purified by double distillation under reduced pressure before use. Lithium perchlorate was dried under vacuum at 180°C for 15 h. Poly(3, 4-ethylenedioxythiophene):

poly(styrenesulfonate) (PEDOT: PSS, Orgacon EL-P 3040) was purchased from AGFA. Diphenylamine monomer (99%, Shantou Xilong Reagent Co.) was used without further purification. Sulfuric acid and hydrochloric acid were of analytical grade. Indium tin oxide (ITO, $9 \Omega/\text{cm}^2$, Zhuhai Kaivo Co.) coated glasses ($1 \text{ cm} \times 4 \text{ cm}$) were ultrasonically cleaned in acetone, ethanol and distilled water for 20 min, separately.

Preparation of Copolymer Films

Electropolymerization of copolymer films was performed at room temperature from a 1 mol/L H_2SO_4 aqueous solution with fixed 0.005 mol/L DPA and certain ANI concentration at a deposition voltage of 0.8 V using a combination of CHI 660C electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd.). An ITO coated glass as a working electrode, a saturated calomel electrode and a Pt foil were used as the reference electrode and the counter electrode, respectively. To prepare the copolymer films with different ANI units, the concentration of ANI was varied according to the ratio of ANI to DPA. Here the ratios were 1:0, 1:1, 5:1, 9:1, 11:1 and 0:1, and the corresponding copolymer films were abbreviated as PANI, P(ANI1-co-DPA1), P(ANI5-co-DPA1), P(ANI9-co-DPA1), P(ANI11-co-DPA1) and PDPA. To ensure consistent amount of electroactive polymer on the electrode surface during polymerization, the same amount of charge were passed during copolymerization. The thickness of all the prepared films was about 600 nm. After electrodeposition, the copolymer films were washed by 0.1 mol/L HCl aqueous solution and dried in vacuum.

Characterization of Copolymer Films

The morphology was investigated by scanning electron microscopy (SEM, FEI Quanta 200F, 20 kV acceleration voltage). Fourier transform infrared (FTIR) spectra of the materials were recorded by using a Nicolet 510P FTIR spectrometer with KBr pellets.

In situ electrochromic measurements were performed in an experimental cell (similar to the experimental setup in Ref. 22) using a CHI 660C electrochemical workstation. The copolymer films and a Pt wire were used as the working electrode and the counter electrode, respectively. A homemade Ag/Ag^+ electrode, which contained a solution of 0.01 mol/L AgNO_3 and 0.1 mol/L tetrabutylammonium perchlorate in acetonitrile, was used as the reference electrode. A 1 mol/L LiClO_4 in propylene carbonate was used as the electrolyte. The cell was sealed in a glove box before the electrochromic measurements. Optical transmittance spectra of the copolymer films were recorded in the wavelength range of 400–1100 nm using a fiber optic spectrometer (MAYA 2000-Pro, Ocean Optics). The cyclic voltammetry (CV) measurements were performed in a conventional three-electrode electrochemical cell at room temperature.

Fabrication and Characterization of the Electrochromic Device

The copolymer with the highest transmittance variation was chosen for the fabrication of electrochromic device. To protect the copolymer film during device assembly, an epoxy resin ring was coated on the ITO film before the electrochemical synthesis. The copolymer film was used as the working electrode, and the spin-coating (3500 r/min) PEDOT: PSS film (thickness: 300 nm) on ITO glass was used as the counter electrode. A lithium-based transparent and conductive gel electrolyte based on PMMA and LiClO_4 was prepared as follows. PMMA (6 g, M_w : 300000) was dissolved in dry acetonitrile (12 g), followed by adding 5 mL 1 mol/L LiClO_4 /propylene carbonate. Then, the viscous gel electrolyte was kept in the dark for 24 h before use. The conductivity of the gel electrolyte was about $8 \times 10^{-4} \text{ S/cm}^{[10]}$. After spreading the gel electrolyte on the polymer-coated side of the electrode, the two electrodes were placed in a position to make sure the polymer-coated sides face each other and then sandwiched. Finally, an epoxy resin was used to seal the device. This electrochromic device was marked as ITO/P(ANIX-co-DPA1)/gel/PEDOT:PSS/ITO.

Electrochromic measurements of the electrochromic device were performed using a potentiostat-galvanostat (Model 263, EG&G Princeton Applied Research). Optical transmittance spectra were carried out by using the fiber optic spectrometer (MAYA 2000-Pro, Ocean Optics).

RESULTS AND DISCUSSION

FTIR Spectra and Morphology of PANI, PDPA and P(ANI-co-DPA) Films

FTIR spectra of PANI, PDPA and P(ANI-co-DPA) are presented in Fig. 1. The main peaks at 1560 cm^{-1} and 1486 cm^{-1} in the spectrum of PANI correspond to quinone- and benzene-ring stretching deformations respectively^[23, 24]. The absorption band at 1298 cm^{-1} corresponds to the C—N stretching vibration mode of the aromatic secondary amine^[22]. The band characteristic of the conducting protonated form is observed at 1236 cm^{-1} and interpreted as a C—N⁺ stretching vibration in the polaron structure^[23, 24]. The broad absorption band around 1130 cm^{-1} involves overlapping contributions from the vibration mode of —NH⁺= structure at 1150 cm^{-1} ^[23] and the aromatic C—H in plane bending mode at 1116 cm^{-1} ^[25]. The appearance of peak at 1152 cm^{-1} corresponding to stretching of the S=O band indicates that PANI is doped with H₂SO₄^[18]. Because of the *N,N'*-diphenyl benzidine structure in the main chains, the quinone- and benzene-ring stretching deformations of PDPA upshift to 1593 cm^{-1} and 1506 cm^{-1} , respectively. The C—N stretching vibration mode also shifts to 1318 cm^{-1} . In addition, The strong absorption band at 1153 cm^{-1} can be assigned for the C—H bending vibration of diphenoquinoneimine (DPB⁺ polaron or DPB²⁺ dipolaron) units in PDPA^[15]. A very weak absorption shoulder occurring at 1233 cm^{-1} indicates the existence of C—N⁺ structure in the PDPA. The absorption band at 754 cm^{-1} is attributed to C—H out of plane vibrations, indicating the presence of 1, 4-substituted benzene rings. This informs that the monomer units in the polymers (PDPA) are bounded through C—C phenyl-phenyl coupling^[18]. The band at 694 cm^{-1} is assigned for the C—H out-of-plane phase bending vibration of mono-substituted benzene rings at the end of the polymer chains. Only a very weak absorption shoulder corresponding to S=O stretching band occurs at $\sim 1152\text{ cm}^{-1}$.

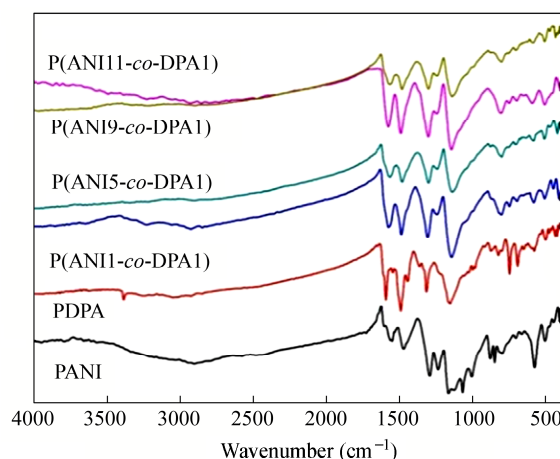


Fig. 1 FTIR spectra of PANI, PDPA, and P(ANI-co-DPA) films

For copolymer films, the absorption peaks in each copolymer are the same, which indicates the molecular structures of copolymers are similar. The bands at 1576 cm^{-1} and 1488 cm^{-1} are due to the quinone- and benzene-ring stretching deformations. The existence of absorption band of 1,4-substituted benzene rings and its shift from 754 cm^{-1} to 801 cm^{-1} indicate that the ANI and DPA monomers are copolymerized. The strength of this peak decreases with the decrease of DPA concentration in the solution, which indicates different amount of DPA unites in the copolymers. Compared to the spectrum of PDPA, the presence of 1243 cm^{-1} band caused by C—N⁺ structures implies the presence of a —C—(NH)—C— link as a result of linking of the —NH₂ group of the aniline with the phenyl C atom of the DPA monomer^[15]. All copolymer films show weak stretching absorption shoulder of S=O, which means the amount of H₂SO₄ in copolymer films is very small.

Figure 2 shows the SEM morphology of PANI, PDPA and P(ANI-co-DPA). It is clear to find the surface of PANI film is covered with nanofibers, and these nanofibers pile up into a loosely bounded open structure. This

nanofiber morphology appears to be intrinsic to PANI^[26–28], and such unique structure character is attributable to the effect of electrophilic substitution reaction during electrodeposition^[27] and 1-dimensional nucleation in the second growth stage^[28]. Compared to the morphology of PANI, the PDPA film shows more compact morphology. The reason may lie behind the polymerization mechanism. Polymerization of DPA is known to proceed through the 4,4'-phenyl-phenyl coupling mechanism^[16, 29]. The increased length of conjugated π -bonding in DPA monomers makes their radicals more stable than the radicals of ANI monomers, relatively high stable radicals may hinder the 1-dimensional nucleation process, leading the PDPA film to be more compact than the PANI film. For the copolymer films, it is found the surfaces of copolymer films are not similar with those of PANI films and PDPA films. Along with the increase of ANI concentration, the surface morphology of copolymer film tends to be less compact. Further, when the ratio of ANI to DPA exceeds 9:1, the surface is covered with loosely bound nanostructure. Because of the increased length of conjugated π -bonding of DPA radicals, the radicals of ANI should be more stable due to their interactions between the DPA radicals, thus the 1D nucleation occurred in the second growth stage of PANI will be hindered. With the decrease of DPA concentration, the stabilizing effect of DPA radicals decreases, which causes the formation of nanostructure.

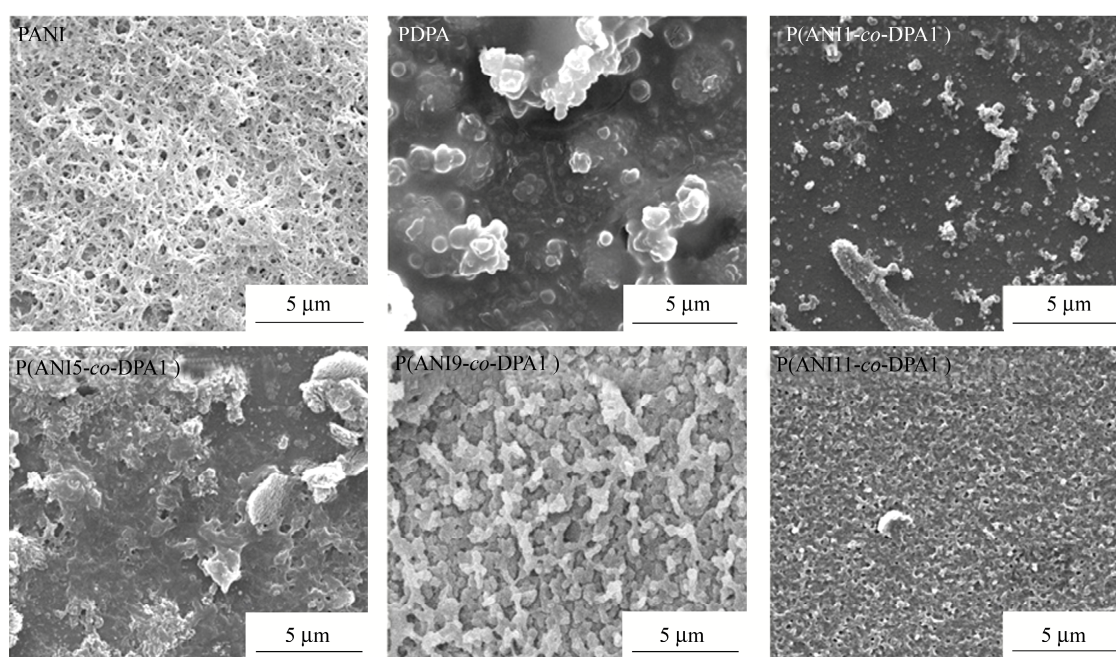
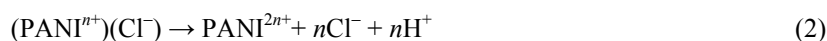
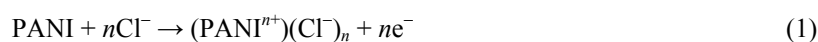


Fig. 2 SEM images of PANI, PDPA and P(ANIX-co-DPA1) films

Comparison of the Electrochemical and Electrochromic Performance of PANI, PDPA and P(ANI-co-DPA) Films

The electrochemical/electrochromic characteristics are the important properties of electrochromic materials. The CV curves of PANI, PDPA and P(ANI-co-DPA) films are compared in Fig. 3. All polymer film electrodes are scanned from -0.8 V to 0.8 V at a scan rate of 10 mV/s, and the first five circles are recorded. The color changes of polymer films at different voltages are shown in Fig. 4. From Fig. 3(a), two anodic peaks and a cathodic peak are found. The first anodic peak at ~ -0.03 V corresponds to the reaction between LB state (transparent at -0.3 V in Fig. 4a) and ES state (green at 0.3 V in Fig. 4a). The redox reaction can be expressed as Eq. (1)^[10]. The second anodic peak at ~ 0.45 V is attributed to the change from ES state to EB state (blue at 0.7 V in Fig. 4a) as Eq. (2) expressed^[10]. The cathodic peak at ~ -0.15 V represents the transition from ES state to LB state.



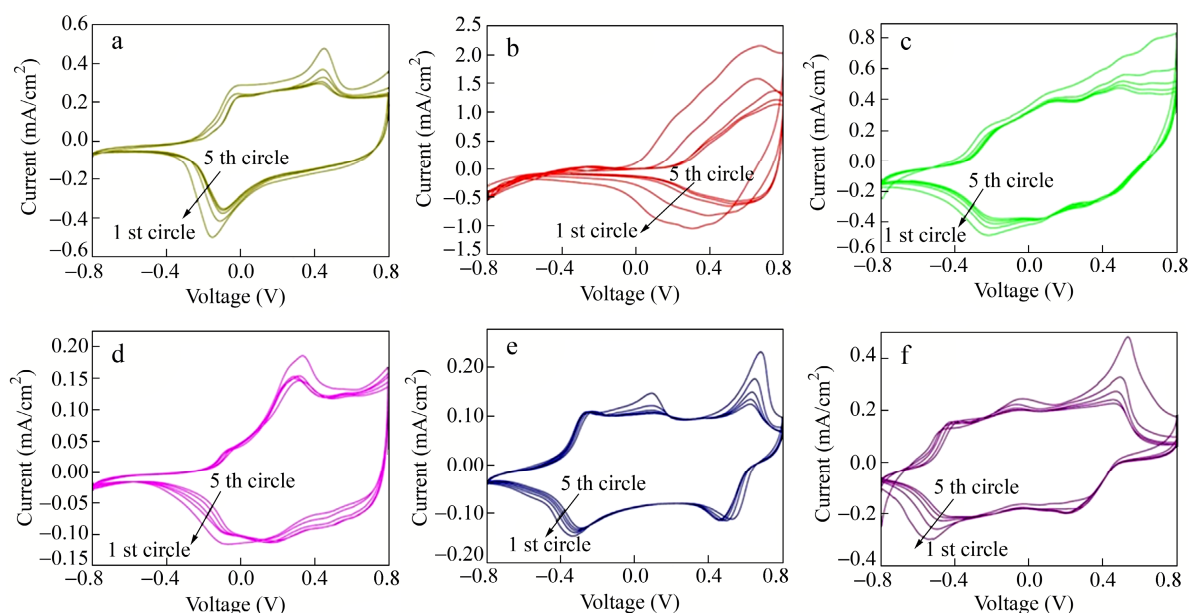


Fig. 3 Cyclic voltammograms of PANI (a), PDPA (b), P(ANI1-co-DPA1) (c), P(ANI5-co-DPA1) (d), P(ANI9-co-DPA1) (e) and P(ANI11-co-DPA1) (f) films at a scan rate of 10 mV/s

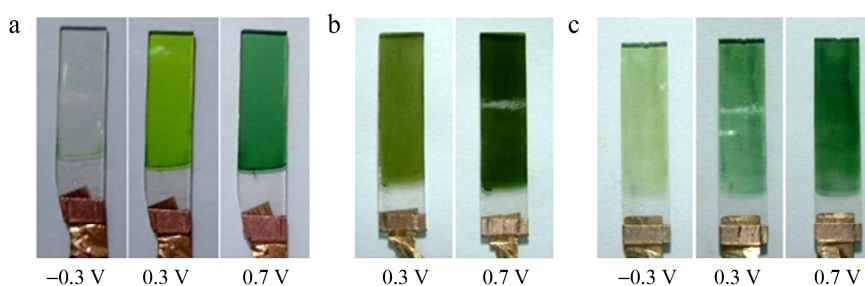


Fig. 4 Digital photographs of PANI (a), PDPA (b) and P(ANI9-co-DPA1) (c) at different potentials

In Fig. 3(b), the PDPA film exhibits only one couple of redox peaks and shows unstable electrochemical properties. By making a comparison with the results of Wen^[30] and Fehér^[31], the anodic peak at ~ 0.66 V corresponds to the reaction between DPB (olive drab at 0.3 V in Fig. 4b) and $DPB^{+\cdot}$ (dark olive green at 0.7 V in Fig. 4b). The reaction can be expressed as Eq. (3). The cathodic peak at ~ 0.31 V represents the change from $DPB^{+\cdot}$ to DPB. The reaction between anilinium cation type radicals and anilinium type units in PDPA is not found.



From Figs. 3(c)–3(f), it is clear to find the copolymer films show different electrochemical properties with those of PANI and PDPA films. The anodic peaks (LB $\rightarrow$ ES and ES $\rightarrow$ EB) and cathodic peak (ES $\rightarrow$ LB) can be found in the CV curves. In addition, compared with the redox peaks of PANI and PDPA, the improved current intensity of reduction wave around 0.4 V can be assigned for the reaction from $DPB^{+\cdot}$ to DPB. Moreover, when the ratio of ANI concentration to DPA concentration comes to 9:1 and 11:1, three anodic peaks and two cathodic peaks are found clearly. It means the films prepared under these two concentration ratios have better electrochemical properties than other copolymer films. Moreover, compared with the stability of CV curve of P(ANI11-co-DPA1) film, the P(ANI9-co-DPA1) film shows more stable electrochemical properties. The color changes of P(ANI9-co-DPA1) are shown in Fig. 4(c). It changes from very light green at -0.3 V to light

seagreen at 0.3 V, and comes dark seagreen at 0.7 V finally.

To demonstrate different electrochromic behaviors of PANI, PDPA and P(ANI-co-DPA) films, *in situ* transmittance spectra (from 400 nm to 1100 nm) of these films were measured in the sealed experimental cell under the same conditions. Figure 5 shows the transmittance spectra of the films from -0.8 V to 0.8 V, and the transmittance spectra are recorded for every 0.2 V. With varied potentials, all films show electrochromic activity with transmittance variations. It is obvious that the PDPA film showed higher transmittance contrast (ΔT) than PANI film. The integrated transmittance variations of PDPA in the visible and NIR region are 38% and 52%, respectively, which are higher than those of PANI film ($\Delta T_{\text{vis}} = 28\%$, and $\Delta T_{\text{NIR}} = 33\%$). It is also interesting to note that the PDPA film shows significantly higher transmittance contrast at low wavelengths (from 400 nm to 500 nm), the PDPA film presents improvement of integrated transmittance contrast in this spectral region by a factor of 3. By combining with the results of CV measurements, it is reasonable to deduce that the copolymerization between ANI and DPA can significantly improve the electrochemical and electrochromic properties of PANI.

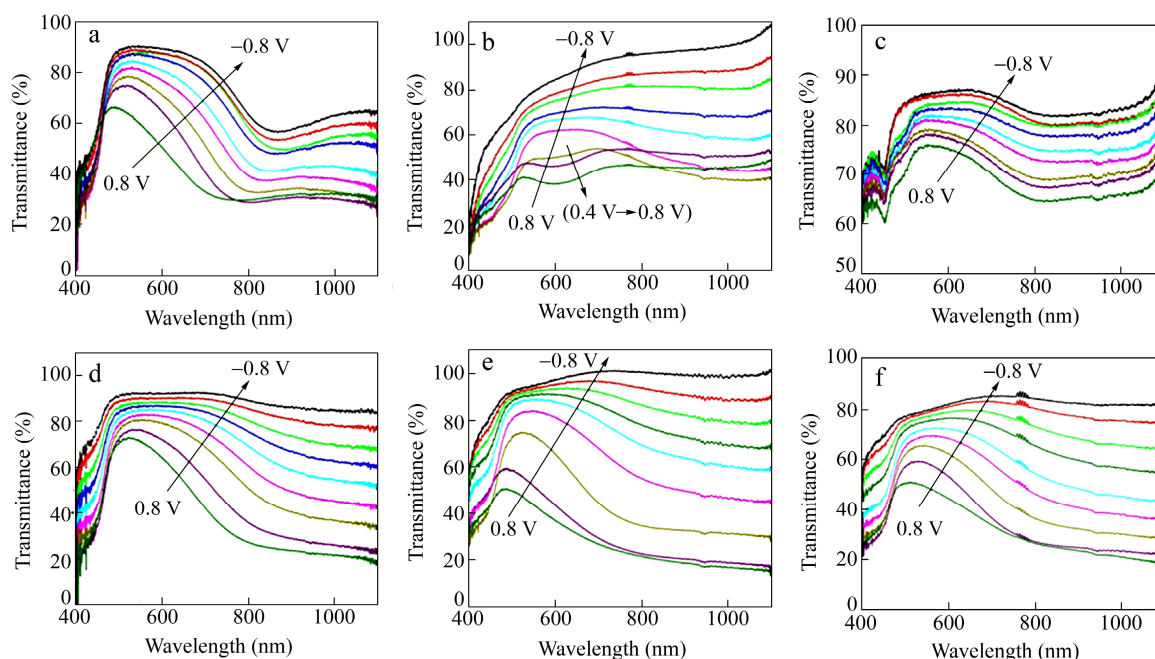


Fig. 5 Transmittance spectra of PANI (a), PDPA (b), P(ANI1-co-DPA1) (c), P(ANI5-co-DPA1) (d), P(ANI9-co-DPA1) (e), and P(ANI11-co-DPA1) (f) films from -0.8 V to 0.8 V (The transmittance spectra were recorded for every 0.2 V.)

From Figs. 5(c)–5(f), it is apparent to find that the copolymer films show electrochromic properties different from those of PANI and PDPA films. All copolymer films present apparent transmittance modulations in the spectral range between 400 nm and 500 nm. In addition, the concentration ratio of ANI to DPA has a significant effect on the electrochromic properties of copolymer films. Before decreasing to 35% [P(ANI11-co-DPA1)], the transmittance contrast of copolymer films increases from 12% [P(ANI1-co-DPA1)] up to 52% [P(ANI9-co-DPA1)] in the visible spectral region, and the transmittance contrast of P(ANI9-co-DPA1) film is almost 2 times higher than that of PANI film. At the NIR wavelength side, the copolymer film also gets its integrated maximum transmittance contrast when the concentration ratio of ANI to DPA arrives at 9:1 (67%), and this value is much larger than that of PANI film (28%). The maximum transmittance contrast of P(ANI9-co-DPA1) in the NIR region occurs at 1100 nm (70%), which is also higher than the maximum transmittance contrasts of PANI (42% at 800 nm) and PDPA (58% at 1100 nm) in the NIR region. At the wavelength of

600 nm, the P(ANI9-co-DPA1) film exhibits 63% transmittance modulation, which is nearly 2 times of the modulation of PANI film. The transmittance modulation of P(ANI9-co-DPA1) at 600 nm is comparable with that of the PANI-PEDOT hybrid film (66%)^[32], the multilayer polyaniline/poly(aniline sulfonic acid) film deposited *via* layer-by-layer approaches (~60%)^[12], and the highly porous PANI film prepared in ionic liquid (62%)^[25], but higher than that of the porous PANI film (~40%) prepared from aqueous solutions^[33]. Further, this result is coincident with the experimental results of Tsai *et al.*^[17]. Tsai *et al.* prepared PANI and P(ANI-co-DPA) films and tested their optical sensing properties as pH sensors. It was found that P(ANI-co-DPA) films showed higher optical variation than PANI films during interacting with hydrogen ions. It is also worthy to mention that the copolymerization eliminates an electrochromic drawback of both PANI and PDPA. In spectral range between 780 nm and 1100 nm, the transmittance variation of PANI film reaches its highest value at 0.6 V, and then decreases along with the increase of potential to 0.8 V. For PDPA films in the spectral range between 720 nm and 1100 nm, the transmittance variation reaches the highest value at 0.4 V, and then declines with the increase of voltage. In contrast, all copolymer films show the increase of transmittance variations with the increase of the applied potentials.

Coloration efficiency (CE, η) is also an important characteristic for the electrochromic materials, because it considers the energy consumption. CE can be calculated using the following equation^[24, 34]:

$$\eta(\lambda) = \Delta OD(\lambda) / Q_{in} \quad (4)$$

where $\Delta OD(\lambda) = \lg[T_b/T_c]$. ΔOD is the change of the optical density. T_b and T_c are the transmittances before and after coloration, respectively. Q_{in} is the amount of injected charge per unit sample area. The CE of PANI, PDPA and P(ANI-co-DPA) films is presented in Fig. 6. The integrated values of transmission modulation and coloration efficiency over the visible- and NIR-regions for PANI, PDPA and P(ANI-co-DPA) are also summarized in Table 1.

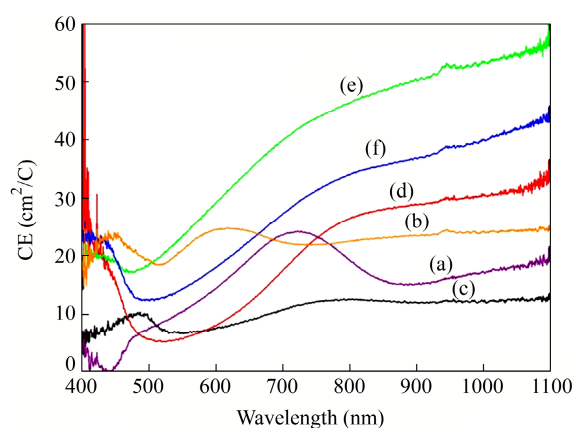


Fig. 6 Coloration efficiency of PANI (a), PDPA (b), P(ANI1-co-DPA1) (c), P(ANI5-co-DPA1) (d), P(ANI9-co-DPA1) (e) and P(ANI11-co-DPA1) (f) films

From Table 1, the PDPA film shows higher CE in almost all spectral range than the PANI film, except for the very small spectral range around 730 nm. Further, as discussed above, the DPB structural fragments introduced by DPA monomers make copolymer films exhibit different CE properties with respect to the PANI film or PDPA film. Compared with PANI, PDPA and other copolymer films, the P(ANI9-co-DPA1) film demonstrates the highest effective energy consumption. The P(ANI9-co-DPA1) exhibits 25.7 cm²/C in the visible range and 51.4 cm²/C in the NIR range. The PDPA film shows 22.1 cm²/C in visible region and 24.0 cm²/C in the NIR range. The CE of PANI film is even smaller in the visible- and NIR-regions. Finally, it is reasonable to conclude that the P(ANI9-co-DPA1) is a more promising candidate material for electrochromic device, compared to PANI film and PDPA film.

Table 1. Electrochromic characteristics of PANI, PDPA and P(ANI-co-DPA1) films

Electrochromic property	PANI	PDPA	P(ANI1-co-DPA1)	P(ANI5-co-DPA1)	P(ANI9-co-DPA1)	P(ANI11-co-DPA1)
ΔT_{VIS} (%)	28	38	12	32	52	35
ΔT_{NIR} (%)	28	44	14	52	67	62
$\Delta T_{600 \text{ nm}}$ (%)	40	46	12	27	61	38
CE_{VIS} (cm^2/C)	11.1	22.1	8	11.3	25.7	18.5
CE_{NIR} (cm^2/C)	18.9	24.0	10.3	29.1	51.4	43.2

Electrochromic Switching Response and Stability of P(ANI9-co-DPA1) Film

Response time is also an important characteristic for the electrochromic materials and defined as the time needed to perform switching between the oxidized (coloration) state and reduced (bleaching) state. For a more detailed analysis of electrochromic properties of P(ANI9-co-DPA1) film, response time is evaluated. *In situ* response time performance of P(ANI9-co-DPA1) film was measured in the as mentioned sealed cell. The transmittance response versus time at wavelength of 600 nm is shown in Fig. 7(a). Response time is defined as the time required for attaining 95% of total transmittance variation. It is found to be 3.6 s from the reduced to the oxidized state, while from the oxidized to the reduced state, the time is 2.3 s. In majority of conjugated polymers, the reduction step proceeds more quickly than the oxidation step because of the difference in charge transport rates between the oxidized states and reduced state^[35]. In this study, P(ANI9-co-DPA1) can be rapidly switched to the reduced state due to the ease of charge transport in the film when it is oxidized. The response time of P(ANI9-co-DPA1) film is much higher than the response time of PANI film and PDPA film, which was more than 5 s^[24, 34, 36].

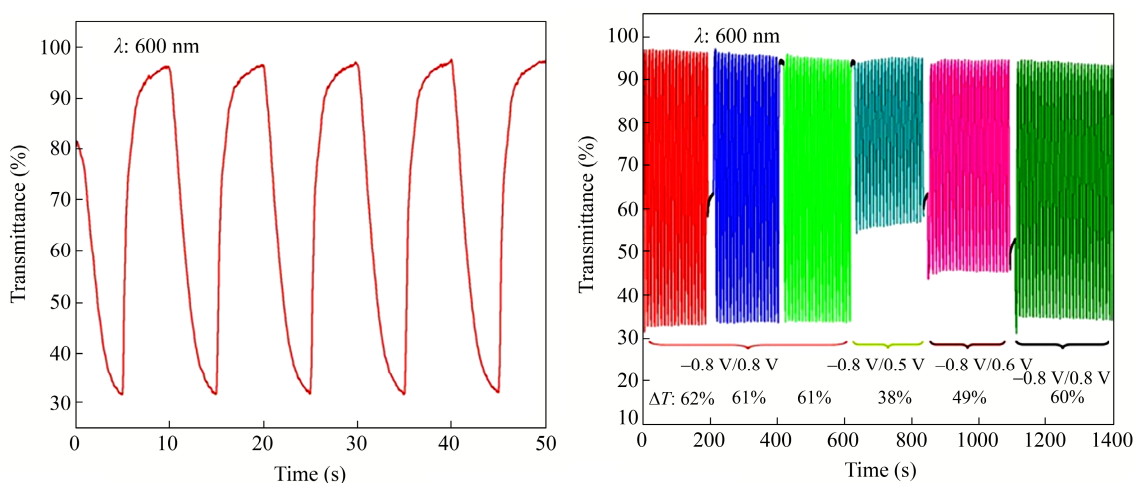


Fig. 7 Switching curves (a) and optical switching stability (b) of P(ANI9-co-DPA1) film between -0.8 V and 0.8 V at 600 nm

Figure 7(b) presents the optical switching stability with irregular time intervals and different switching potential ranges (-0.8 V to 0.8 V , -0.8 V to 0.6 V and -0.8 V to 0.5 V) with a residence time of 5 s. Each time interval sustains a period between 12 s and 14 s (the dark parts in Fig. 8). And the transmittance contrast (ΔT) here is the average value. Under the same switching potential range (-0.8 V to 0.8 V), the first time interval occurs when the film is being oxidized (under 0.8 V), followed by a reverse polarized potential (-0.8 V), and the second time interval occurs when the film is almost fully reduced. The impact of these two time intervals on the transmittance contrast is negligible, which indicates that the electrochemically active sites for redox reaction in P(ANI9-co-DPA1) film are very stable. It is also notable that the transmittance contrast between -0.8 V and 0.8 V recovers after switching under different potential ranges (-0.8 V to 0.5 V and -0.8 V to 0.6 V). This result further indicates the stability of electrochromic active sites. Besides the stability, another important aspect is the

adjustability. Under different potential ranges, the film exhibits different and stable transmittance contrasts. Thus, the P(ANI9-co-DPA1) film shows an excellent stability, adjustability and a sharp transmittance contrast without the performance deterioration inside the LiClO₄/propylene carbonate electrolyte.

Electrochromic Properties of ITO/P(ANI9-co-DPA1)/Gel/PEDOT:PSS/ITO ECD

A simple double-layer ECD consisting of P(ANI9-co-DPA1) and PEDOT:PSS is fabricated as shown in Fig. 8(b). Its electrochromic properties are investigated. In this device, the P(ANI9-co-DPA1) film acts as an anodically coloring part, and the PEDOT:PSS film is cathodically colored^[37, 38]. Before testing, the potential on the two electrodes is slowly alternated between -0.8 V and $+0.8$ V at a rate of 0.01 V/s for 3 times, and the initial voltage on the P(ANI9-co-DPA1) film was set at -0.8 V. *In situ* transmittance measurements are performed by increasing potentials from -0.8 V to $+0.8$ V by an increment of 0.2 V between the two electrodes. Figure 8(a) illustrates the color changes. Figure 8(c) shows the corresponding transmittance spectra between -0.8 V and 0.8 V. At the potential of -0.8 V, the P(ANI9-co-DPA1) film is in the reduced state and transparent, and, the PEDOT:PSS film is almost colorless and transparent at this potential^[37, 38], thus the device is colorless and transparent (Fig. 8a). With the increase of potential on the P(ANI9-co-DPA1) film but blow 0.4 V, the device exhibits bright green at 0 V and seagreen at 0.4 V (Fig. 8a). During this potential range, the device exhibits similar color changes with the P(ANI9-co-DPA1) film, and the reason is due to the electrochromic properties of PEDOT. Between 0 V and -0.4 V, there is no obvious color change in PEDOT film^[37, 38]. When the potential on the P(ANI9-co-DPA1) film increases beyond 0.4 V, the PEDOT:PSS film starts to become blue because a reduced reaction occurs^[37, 38]. Meanwhile, the color of P(ANI9-co-DPA1) film goes deeper due to the further oxidation. This simultaneous color changes make the color of device become even deeper. At the potential of 0.8 V, the color of the device gets to dark slate gray (Fig. 8a). Therefore, there is a synergetic electrochromic effect between P(ANI9-co-DPA1) film and PEDOT:PSS film, which makes the device show multicolor performance. The transmittance measurement results also exhibit the synergetic electrochromic effect. From Fig. 8(c), it is clear to find that the transmittance variation of the device shows similarity with that of the P(ANI9-co-DPA1) film in 1 mol/L LiClO₄/propylene carbonate electrolyte between -0.8 V to 0.4 V (Fig. 5e). However, when the potential on the P(ANI9-co-DPA1) film is beyond 0.4 V, the relative transmittance variations both in visible- and NIR-regions become lower than those of the P(ANI9-co-DPA1) film in 1 mol/L LiClO₄/propylene carbonate electrolyte, due to the reduced reaction of PEDOT:PSS film. Further, it is worthy to notice that the ECD device exhibits the same behaviors of visible versus NIR electrochromism. Between applied voltages from -0.8 V to 0.8 V, the visible- and NIR-region transmittances vary in tandem, *i.e.*, they both decrease. This allows the device to be more effective on solar energy control when it is used as the smart window under cold climate conditions^[39]. In the cold climate areas, an electrochromic smart window should be transparent in the NIR region due to the need of heating. The NIR part of the solar radiation—carrying large part of the solar energy—should be admitted when the devices are in their bright state. Moreover, for the ITO/P(ANI9-co-DPA1)/gel/PEDOT:PSS/ITO ECD, integrated transmittance variation exhibits 29% in visible region and 40% in NIR region, in contrast, PET/ITO/PANI/gel/ITO/PET ECD just shows 18% transmittance variation at 780 nm^[10] and $\sim 25\%$ transmittance variation occurs in the FTO/PANI/gel/PEDOT/FTO ECD at the wavelength of 600 nm^[40].

For the application of ECD, response time and stability are two important characteristics. The double potential step chronoamperometry is also used to estimate the response time and its switching stability. Potentials were between -0.8 V and 0.8 V with a residence time of 10 s. Figure 8(d) demonstrates the transmittance response versus time profile of the ECD at 600 nm over 2500 s (*i.e.*, 125 times). At wavelength of 600 nm, it takes 50 switching times to make the coloration state stable with a transmittance variation (ΔT) loss of 6%, and 60 switching times to make the bleaching state stable with a transmittance variation (ΔT) loss of 4%. The initial transmittance variation was 41%, and the response time required to attain 95% of total transmittance variation is found to be 5.0 s from the reduced state to the oxidized state, while 6.8 s from the oxidized to the reduced state. After 60 switching times, the transmittance variation between the oxidized state and reduced state

becomes stable, the response time was found to be 8.3 s from the reduced to the oxidized state, and 7.5 s from the oxidized to the reduced state. Compared with the response time of P(ANI9-co-DPA1) film (Fig. 7) in 1 mol/L LiClO₄/propylene carbonate electrolyte, the low response time of device is due to the slow Li ion mobility in the solid gel electrolyte. The conductivity of this solid gel electrolyte is just 8×10^{-4} S/cm, compared to 6×10^{-2} S/cm in the 1 mol/L LiClO₄/propylene carbonate electrolyte^[41].

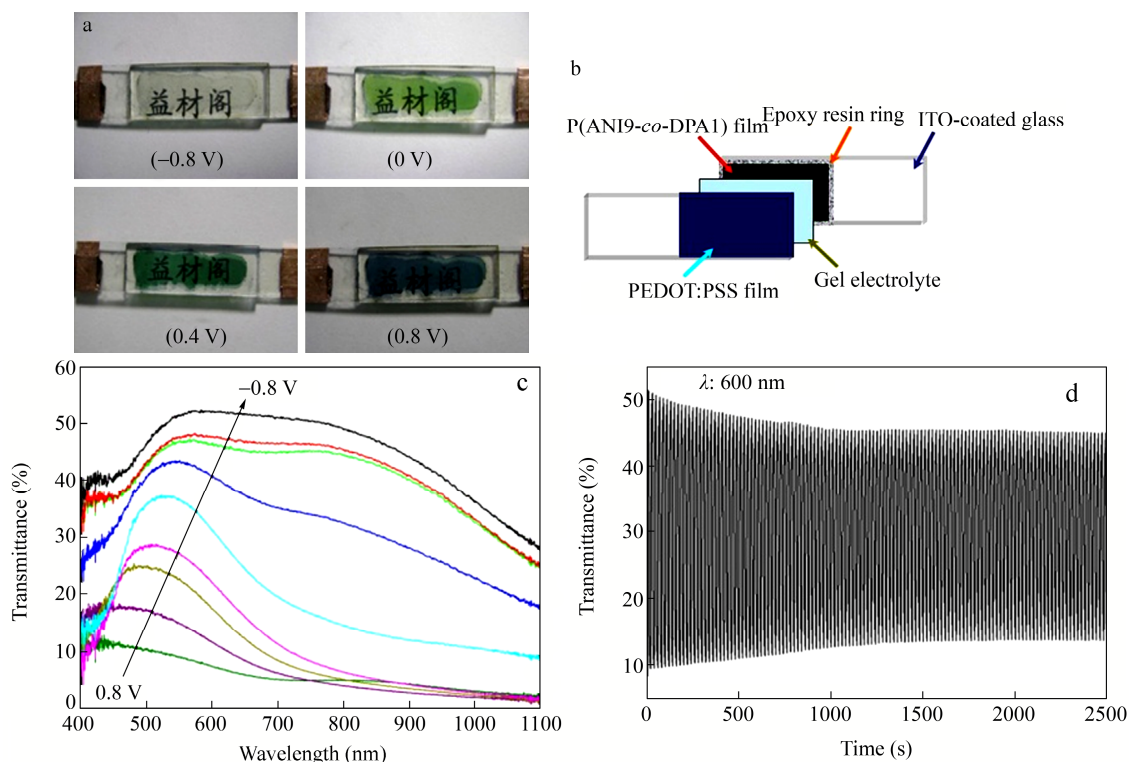


Fig. 8 (a) Digital photographs of ECD at different potentials; (b) schematic diagram of ECD; (c) transmittance spectra of ECD at different potentials (The transmittance spectra were recorded every 0.2 V.) and (d) switching curves of ECD film with -0.8 V and 0.8 V for 2500 s at 600 nm

CONCLUSIONS

Copolymers of aniline and diphenylamine have been prepared on ITO surfaces by potentiostatic method in an aqueous solution consisting of 0.005 mol/L diphenylamine, 1 mol/L H₂SO₄, and different concentrations of aniline. The formation of copolymers, poly(ANI-co-DPA), is ascertained from the FTIR and SEM data. The copolymer films prepared with different feed concentrations of diphenylamine exhibit different cyclic voltammetric behaviors and electrochromic properties. The copolymer film formed from 0.005 mol/L diphenylamine and 0.045 mol/L aniline solution [marked as P(ANI9-co-DPA1)] exhibits novel optical contrast both in visible region (52%) and NIR region (67%) between -0.8 V and 0.8 V, fast response time (3.6 s for coloration and 2.3 s for bleaching at 600 nm) and long-term stability. The ECD constructed by P(ANI9-co-DPA1) and PEDOT also presents multicolor electrochromic performance with high optical modulation in the visible- and NIR-regions (29% in visible region and 40% in NIR region), acceptable response time and long-term stability. The corresponding color changes from transparent state (-0.8 V) to bright green (0 V), seagreen (0.4 V), very light green (-0.3 V), light seagreen (0.3 V) and dark slate gray (0.8 V). Considering these results, the P(ANI9-co-DPA1) is a promising candidate material for electrochromic devices.

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