Synthesis and characterization of novel electrochromic devices derived from redox-active polyamide–TiO₂ hybrids†

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Two novel electrochromic (EC) polyamides with functional hydroxyl groups were successfully synthesized for preparing homogeneous hybrid films. The hydroxyl groups in the repeating units of the polymer backbones could serve as active sites in the sol–gel reaction to obtain organic–inorganic nanocomposites comprising titanium dioxide (TiO₂) and anodic EC polyamides (TPPA-OH PA and TPB-OH PA). By using the facile approach of an electron donor–acceptor hybrid system in this report, the EC response capability could be essentially enhanced during the colouring and bleaching process. In addition, the colouring contrast and electrochemical stability of the fabricated EC devices could be further increased by judiciously combining the complementary EC material of heptyl viologen (HV) and TiO₂.

Introduction

Electrochromism is the phenomenon whereby materials exhibit a reversible colour change in transmittance or absorption during electrochemical reduction or oxidation procedures. Electrochromic (EC) materials have been studied for decades, and various representative materials have been reported such as inorganic coordinating complexes (e.g., Prussian blue¹ and Terpyridine complexes²), transition metal oxides (e.g., WO₃³), conjugated polymers (e.g., polyaniline⁴) and organic molecules (e.g., viologen⁵). Inorganic EC materials are well known for their excellent switching stability, while organic EC materials have advantages such as high coloration efficiency, multiple colouring within the same material, and competitive processability. Generally, EC materials have mainly been investigated towards achieving colour changes in the visible light region (e.g., 400–800 nm), and this gave rise to some typical products like optical switching devices, e-paper, camouflage materials, and smart windows.⁶ Since 2002, our group has published reports on novel triphenylamine (TPA)-containing EC polymers that show interesting multicolour transitions and unique EC behaviours both in the visible and near infrared (NIR) regions.⁷ Recently, panchromatic electrochromic devices (ECDs) with high optical contrast have also been successfully prepared;⁸ however, the EC switching response capability and stability remain a challenge. Thus, the crucial issue is how to reduce the response time without sacrificing other EC properties, and the incorporation of a charge-acceptor metal oxide as a charge storage unit into EC polymers to produce polymer hybrid EC materials is one of the most efficient approaches for EC applications.

Polymer hybrids with strong covalent bonds between metal oxide and polymers have been studied in our group by designing and synthesizing various polymers with reactive functional groups (–OH and –COOH).⁹ The sol–gel reaction is a convenient and effective method to combine the organic and inorganic materials that are used in transistor and resistor type memory devices.¹⁰ TiO₂ is an excellent semi-conducting material that has been used in photo-catalysis,¹¹ solar cells,¹² EC devices, etc.¹³ because TiO₂-based hybrid films demonstrate rapid charge transport properties and easy formation of nanostructures with large surface area. EC materials based on conducting polymers/ TiO₂ hybrids have been prepared and investigated, but most of them work just by physical interaction between the two materials.¹⁴ Consequently, replacing with strong covalent bonds within the hybrids could enable a more direct and effective process for the enhancement of EC properties.¹⁵ According to the electrochromism principle, electron-withdrawing TiO₂ nanoparticles play an important role as an electron-storage counterpart in the ambipolar system during the EC process. The colour can be generated by the oxidation or reduction reaction, and the charges produced can be stored by TiO₂ within the donor-acceptor system.

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Thus, in this report, we try to utilize TPA-based polyamides, typically anodic EC materials, to prepare novel redox-active polyamide–TiO₂ hybrids via the sol–gel reaction for studying the donor–acceptor effect on the EC performance. The results demonstrate that the EC response capability could be substantially enhanced during the colouring and bleaching process. In addition, the on/off optical contrast and electrochemical stability of the fabricated EC devices (ECDs) could be further increased by judiciously combining the complementary EC material of heptyl viologen (HV) and TiO₂ because the TPA-based EC polyamides could more effectively release and obtain electrons during oxidation redox switching via the covalent-bonded strong electron withdrawing TiO₂ near the polyamides.

Experimental

Materials

\(N,N'-\text{bis}[4\text{-aminophenyl}]\cdot N,N'-\text{di}(4\text{-methoxyphenyl})\cdot 4,4'\text{-biphenyldiamine (TPB)}\) and \(N,N'-\text{bis}[4\text{-aminophenyl}]\cdot N,N'-\text{di}(methoxyphenyl)-1,4\text{-phenylenediamine (TPPA)}\) were synthesized based on previous reports.\(^{16,17}\) Commercially available \(1,4\text{-phenylenediamine (HV)}\), \(N,N\text{-dimethylacetamide (DMAc)}\), \(\text{pyridine (Py)}\), \(\text{triphosphine (TPP)}\), and other reagents were used as received. The cathodic EC material, heptyl viologen tetrafluoroborate \(\text{HV(BF}_4\text{)}_2\) was prepared as follows:\(^{18}\) 4,4’-dipyridyl (3.12 g, 20 mmol) and 1-bromoheptane (31.4 mL, 200 mmol) were added into 30 mL of acetonitrile and refluxed for 6 h, the precipitate was filtered off after cooling down to room temperature and washed with organic solvents such as hot chloroform, acetone, hexane, and then dried in a vacuum to obtain a 96% yield of yellow powder, \(\text{HVBr}_2\) (9.85 g). Afterwards, a solution of \(\text{HVBr}_2\) (5.00 g) in DI water (50.0 mL) was dropwise added to a saturated solution of \(\text{NaBF}_4\) (50.0 mL). After 30 min, the white solid \(\text{HV(BF}_4\text{)}_2\) was obtained after filtration, which was then purified by recrystallization from ethanol.

Preparation of the TPPA-OH and TPB-OH polyamides (PAs)

Two diamine monomers, TPPA and TPB, were respectively used to synthesize the novel hydroxyl-containing polyamides, TPPA-OH and TPB-OH, with \(\text{HV(BF}_4\text{)}_2\) via direct polycondensation\(^{19}\) as shown in Scheme 1. TPPA-OH was as a typical example was prepared as follows: 502.6 mg (1.0 mmol) of the diamine monomer TPPA, 134.1 mg (1.0 mmol) of \(\text{HV(BF}_4\text{)}_2\), 0.2 g of \(\text{CaCl}_2\), 0.5 mL of TPP, 0.5 mL of Py, and 2.0 mL of NMP were heated under stirring at 60 °C for 12 h. After cooling down to room temperature, the polymer solution was poured slowly into 400 mL of a vigorously stirred methanol and water mixture (volume = 3 : 1), giving rise to a fiber-like precipitate that was then collected by filtration. After purification by Soxhlet extraction under reflux with water and methanol for 12 h, it was then dried under vacuum at 100 °C.

Preparation of TPPA-PATiX and TPB-PATiX hybrid films

In this paper, different weight percentages of TiO₂ were added to the polymer films for comparison. Therefore, TPPA-PATiX and TPB-PATiX were used to represent the EC hybrid films with different contents of TiO₂, where X is the wt% value of TiO₂.

Results and discussion

Polymer synthesis

Polyamides can generally be synthesized from dicarboxylic acid and diamine by direct polymerization at temperatures of 100–110 °C for about 3–6 hours.\(^{16}\) However, the above reaction temperature was not appropriate for this work because \(\text{HV(BF}_4\text{)}_2\) possesses a functional hydroxyl group that could also react with the carboxylic group at higher temperature, resulting in a cross-linking structure during the polymerization procedure. Consequently, the modified reaction conditions with a lower temperature (60 °C) and longer reaction time (12 h) were adopted. The FT-IR spectra of the obtained PAs only exhibited the characteristic absorption peaks of the amide functional group at 1670 cm\(^{-1}\) without an ester absorption peak in the range of 1735–1750 cm\(^{-1}\) (as shown in Fig. 1). Thus, the hydroxyl group in \(\text{HV(BF}_4\text{)}_2\) was confirmed to participate in the polymerization.

Basic properties of the PAs

The basic properties of the resulting two new PAs, TPPA-OH and TPB-OH, such as inherent viscosity, molecular weight, and solubility behaviour, are summarized in Tables S1 and S2 (ESI†). These PAs could dissolve in various organic solvents and their excellent solubility demonstrates that these PA films could be easily fabricated for practical application by solution casting. Furthermore, the thermal properties of the PAs were investigated by DSC and TGA (Fig. S1, ESI†), and the data are summarized in Table S3 (ESI†). These partially aromatic PAs also revealed high thermal stability without significant weight loss up to 300 °C both in nitrogen and air atmospheres with the glass-transition temperatures \(T_g\) in the region of 180–195 °C.

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Synthesis and characterization of the PA hybrids

The compositions of the **TPPA-OH** and **TPB-OH** hybrid films prepared by the sol–gel reaction of the corresponding **TPPA-OH** and **TPB-OH** with titania precursors, respectively, are summarized in Table S4 (ESI†). The hydroxyl groups in these PA backbones could provide reaction sites for organic–inorganic bonding, resulting in homogeneous and transparent hybrid films with a well-dispersed titania domain size of less than 10 nm, as shown in Fig. 2. The excellent thermal stability of the obtained **TPPA-PATiX** and **TPB-PATiX** hybrid films was proved by TGA, and the char yield increased with the increasing titania content, as depicted in Fig. S2 (ESI†). Meanwhile, the TGA measurements under air flow could not only identify the thermal stability but also confirm the inorganic contents in the PA hybrid films by char yields that could be used to demonstrate the successful incorporation of the inorganic nanoparticles into the PAs.

Electrochemical properties of the EC materials

Typical cyclic voltammetry (CV) diagrams of the PAs and their related hybrid films coated on the ITO-coated glass substrates (thickness: 300 ± 50 nm; coated area: 25 mm × 6 mm) were measured in 0.1 M TBABF₄/PC at a scan rate of 50 mV s⁻¹, and the results are summarized in Fig. S3 (ESI†) for comparison. **TPPA-OH** and its hybrids all displayed two obvious oxidation redox peaks, implying that electrons could be removed from the two electroactive nitrogen sites, respectively, with a significant difference of applied voltage (ΔE), while **TPB-OH** only exhibited one broad redox peak comprising the first and second oxidation stages. Meanwhile, these PA hybrid EC materials, the **TPPA-PATiX** and **TPB-PATiX** hybrid films, both showed a lower oxidation potential than their corresponding pristine PAs, and the improvement could be enhanced obviously by increasing the amount of inorganic titania up to 20 wt%, as illustrated in Fig. S3 (ESI†). These EC hybrid films could be oxidized at a
lower driving voltage, implying that the enhancement of EC stability could be expected by this facile approach. Although these new EC PAs both have two oxidation states at the related applied voltages, the first oxidation state should be most valuable for application because of the lower driving energy and the higher EC stability. Therefore, the electrochemical stability of TPPA-OH and its hybrid films with different contents of titania was investigated at the first oxidation state, and the results are depicted in Fig. 3 and Table S5 (ESI†). Comparing with TPPA-PATiX over 1000 redox cycles, the pristine TPPA-OH exhibited the largest $\Delta E (E_{pa} - E_{pc})$, indicating that the response capability for EC switching and bleaching during the oxidation process was worse and slower than the hybrid system. In contrast, there was no obvious oxidation peak in the beginning few cycles for TPPA-PATiX, as shown in the CV diagrams, while the electrolyte can gradually diffuse into the hybrid films after hundreds of scans and the oxidation peak becomes clear. Besides, an enhancement of EC reversibility and stability for the hybrid system could also be observed over 1000 cycle scans in comparison to the pristine PA (Fig. 3). Furthermore, the EC response capability between switching and bleaching during the oxidation redox process for the hybrid system displayed smaller values of $\Delta E (E_{pa} - E_{pc})$, and could be reduced from 0.38 V for TPPA-OH to 0.20 V and 0.17 V for TPPA-PATi10 and TPPA-PATi20 after 1000 cyclic scanning times, respectively (Table S5, ESI†), indicating that the response time could be effectively reduced for both switching and bleaching during the electrochemical and EC redox processes. However, the cross-linking degree of the hybrid films increased with increasing the content of titania, which could also hinder the diffusion of electrolyte into the EC hybrid film, thus the content of TiO2 was limited to 20 wt% within this study.

### Electrochemical behaviors of the electrochromic devices (ECDs)

The electrochemical properties and operation parameters such as driving potential of the ECDs were investigated. The respective CV diagrams for the devices derived from these PAs and their hybrids are depicted in Fig. S4 (ESI†). The oxidation potentials at the first stage that are needed to generate a cationic radical of the triarylamine moieties from the neutral state in a gel electrolyte system for the ECDs with a size of 20 mm $\times$ 20 mm derived from the pristine PAs of TPPA-OH and TPB-OH were 1.85 V and 2.1 V, respectively. In order to ameliorate the presence of defects owing to the gel type ECDs, a facile approach is just to incorporate TiO2 into the redox-active...
PAs via the sol–gel reaction and introduce the cathodic EC material HV into the gel electrolyte layer of the ECDs to solve this problem. This representative CV diagrams of the TPPA-PATix and TPB-PATix ECDs are also depicted in Fig. S4 (ESI†); the first oxidation potential could be gradually decreased from TPPA-OH: 1.85 V to TPPA-PATi5: 1.75 V, TPPA-PATi10: 1.63 V, and then TPPA-PATi20: 1.53 V. The TPB-OH hybrids also exhibited a similar tendency to the TPPA-OH hybrids, and the driving voltage decreased from 2.00 V to TPB-PATi20: 1.85 V because TiO2 could accept the electrons from the PA moieties, making it easier for the electroactive TPA unit to lose an electron during the oxidation process and then for TPA\textsuperscript{+} to gain an electron during the reduction process. Meanwhile, HV reveals a similar working principle in the ECDs, and it can effectively decrease the first oxidation potential to 1.05–1.10 V for TPPA-OH/HV and 1.35 V for TPB-OH/HV, as shown in Fig. S5 (ESI†). Consequently, by combining these two additional effects, the resulting ECDs with the lowest oxidation potential could be achieved for the TPPA-PATi20/HV: 0.98 V (TPPA-PATi5: 1.05 V and TPPA-PATi10: 1.02) and TPB-PATi20/HV: 1.25 V, as illustrated in Fig. 4.

Spectroelectrochemistry

Spectroelectrochemical measurements were performed to evaluate the optical behaviour of these PAs during the oxidation redox process. The characteristic absorption patterns of these two EC polymer films correlated to the applied potentials are depicted in Fig. S6 (ESI†). All the electroactive PAs are highly transparent and colourless at the neutral state (0.0 V). During oxidation (increasing applied voltage), the characteristic absorption in the visible light region could be greatly enhanced with peaks at around 435 nm and 600 nm in the visible region, associated with an intense green colour owing to the structural absorption peak at 500 nm with a reddish colour; then, each PA would change from PA to PA\textsuperscript{+}. With the potential increasing to the oxidation stages. The first oxidative form of PA1+ revealed a strong absorption peak at 500 nm with a reddish colour; then, TPP-based PA\textsuperscript{+} generated in the second oxidation stage displayed a new broad band with a peak at around 954 nm accompanying the colour change from red to blue. The difference between these two chromogenic moieties was mainly attributed to the longer conjugation length of the biphenyl unit of TPPA-OH compared to the phenyl unit of TPPA-OH, resulting in red-shifted absorption for TPB-OH. Furthermore, a series of ECDs was prepared from the two PAs (TPPA-OH and TPB-OH) and their corresponding ambipolar system combining the PAs and HV (TPPA-OH/HV and TPB-OH/HV), respectively, and its spectroelectrochemical behaviours were also studied and are summarized in Fig. S7 (ESI†).

Response behavior of electrochromic switching

The electrochromic switching of the devices with the ambipolar EC materials was studied to evaluate the transmittance changes of the characteristic absorption as a function of time and to obtain the response time by stepping potential repeatedly between the neutral and coloured states. The response time was determined as the time at 90% of the full switch in transmittance because it is difficult to perceive any further colour change beyond this point with the naked eye. As depicted in Fig. 5 and Fig. S8 (ESI†), the ECDs derived from TPPA-OH/HV exhibited a switching time of 8.0 s at 1.1 V for the colouring process at 435 nm and 30.5 s at −1.15 V for the bleaching process; the device based on TPPA-PATi5/HV showed a switching time of 5.2 s for colouring at 1.05 V and 22.5 s for bleaching at −1.1 V; the device based on TPPA-PATi10/HV showed a switching time of 5.0 s for colouring at 1.0 V and 18.0 s for bleaching at −1.05 V, and device based on TPPA-PATi20/HV showed a switching time of 5.0 s for colouring at 1.0 V and 17 s for bleaching at −1.05 V, respectively. In addition, the devices derived from TPB-OH/HV and TPB-PATi20/HV showed a similar tendency. According to these results, it is noteworthy that

![Fig. 4](image-url) Partial magnification of the cyclic voltammetry diagrams of (a) TPPA-OH and TPPA-PATi5 hybrids, and (b) TPB-OH and TPB-PATi5 hybrids (thickness: 300 ± 50 nm on the ITO-coated glass substrate (coated area: 2 cm × 2 cm) in 0.1 M TBABF4/PC electrolyte with 0.015 M HV.

![Fig. 5](image-url) ECD switching (a) between 1.1 V and −1.15 V for TPPA-OH and (b) 1.0 V and −1.05 V for TPPA-PATi20 at 435 nm; (c) between 1.35 and 1.40 V for TPB-OH and (d) 1.25 and −1.3 V for TPB-PATi20 at 500 nm (thickness: 300 ± 50 nm) on the ITO-coated glass substrate (coated area: 2 cm × 2 cm) in 0.1 M TBABF4/PC electrolyte with 0.015 M HV.
by combining the electron acceptors of TiO₂ and HV into the EC devices, a synergetic effect could be observed both in lowering the oxidation potential and enhancing the response capability, especially for the bleaching process. After merging TiO₂/HV into the ECDs, the bleaching time could be significantly reduced to almost half the values of the pristine ones. TiO₂ bonded to the nearby backbone of the PAs plays an important role in temporarily storing electrons released from the anodic EC PAs, and the received electrons remained in the TiO₂ hybrid film adhered on the surface of the anode electrode. Therefore, the electrons could return much faster back to the redox-active triarylamine units of the PAs, resulting in a dramatic enhancement of response capability in the bleaching process compared to just the ambipolar HV system. Consequently, these TiO₂/HV ECDs demonstrate that not only an obvious effect on the reduction of working response time but also long-term electrochemical stability could be achieved simultaneously. Thus, the change of ΔT was only 2% after 300 continuous switching cycles, as shown in Fig. S9 (ESI†). Furthermore, the EC coloration efficiency (η = ΔOD/ΔQ) and injected charge (Q) after various switching steps were also monitored and are summarized in Table S6 (ESI†).

Electrochromic behaviors of panchromatic hybrid ECDs

Based on the spectroelectrochemical results we have discussed in the previous section, we can easily prepare ECDs that can switch between the transparent state and a black color state by just combining TPPA-PA, TPB-PA and HV in one system. In order to obtain panchromatic ECDs with a higher response capability during the switching process, the characteristic optical absorption behaviours of TPPA-PATi20 and TPB-PATi20 based on spectroelectrochemical measurements were merged together and the blended system was used to prepare the ECDs. According to our previous study, an extremely high optical contrast over the whole visible light region was lower than 6% at an applied potential of 1.4 V and ΔL was close to 80, as depicted in Fig. 6, demonstrating that a similar contrast to the previous study could be attained under a lower driving voltage. Furthermore, the colouring and bleaching time based on the characteristic absorption peaks of TPPA and TPB could also be significantly shortened, as illustrated in Fig. 7. Besides, the switching stability revealed an obvious amelioration during the 40 cycles of testing, as shown in Fig. S10 (ESI†).

Conclusions

Novel redox-active polyamides with a hydroxyl group and their TiO₂ hybrids obtained by the sol-gel reaction have been successfully synthesized for the fabrication of novel ECDs with enhanced electrochemical response capability and stability. TiO₂ in the hybrid system played a crucial role as charge storage units connected to the polymer backbone via covalent bonding that could effectively deliver electrons back and forth between the triarylamine moieties and during the oxidation redox process at the anode electrode. Consequently, response time could be substantially reduced both in switching and bleaching procedures. Furthermore, the ECD comprising both HV and TiO₂ exhibited excellent EC performance, especially for bleaching time.
A response time of more than 30 s for the devices based on TPPA-PA/HV or TPB-PA/HV is necessary for the bleaching process, while with the help of TiO₂, in the cases of TPPA-PATi20/HV and TPB-PATi20/HV, only half the time of those system containing only HV is needed. These results demonstrate the synergetic effect on the improvement of EC performance. Therefore, the panchromatic ECDs with enhanced response capability could be obtained by integrating TPPA-PATi20/HV and TPB-PATi20/HV, and they displayed excellent EC performance such as transmittance over the whole visible light region reaching less than 6% with an extremely high ΔL close to 80. Thus, by this facile approach of utilizing redox-active polyamide–TiO₂ hybrids, the most crucial issue of working response time could be effectively improved in addition to long-term electrochemical stability that could be achieved simultaneously.

Conflicts of interest

There are no conflicts to declare.

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Notes and references