



Enhancing the performance of poly(3-methylthiophene)-based electrochromic devices via insertion of a TiO₂ buffer layer

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ABSTRACT

Anatase-titanium dioxide (TiO₂) nanoparticles were spin-coated on indium-tin oxide (ITO) glass substrates to fabricate TiO₂ films through annealing at 450 °C/30 min. 3-Methylthiophene (3MT) was electrochemically deposited onto mesoporous TiO₂ films to form poly(3-methylthiophene) (P3MT/TiO₂) composite electrochromic electrodes. The introduction of TiO₂ mesoporous films enhanced the adhesion of P3MT polymers to the TiO₂/ITO substrate, thereby increasing the long-term stability of the corresponding electrochromic devices. Experimental results reveal that P3MT/TiO₂ composite electrodes retained up to 84% of the maximum optical contrast ($\Delta T\%$), relative to 56% remaining $\Delta T\%$ of pure ITO electrodes. This illustrates the enhanced long-term stability achieved through the introduction of a TiO₂ buffer layer in electrochromic devices. These devices demonstrated excellent response time characteristics and $\Delta T\%$ value of 4 s and ca. of 70%, respectively. This work has shown that conductive polymer/TiO₂ composite electrodes are well suited to electrochromic devices for the promotion of performance and stability.

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1. Introduction

An electrochromic material shows variations in color through the adjustment of applied potential, in which the energy level of the material is influenced by the doping level of electrolytic ions (such as H⁺, Li⁺). Different materials demonstrate different absorption characteristics in the range of visible light, resulting in different colors. In 1969, Deb [1] assembled the first electrochromic devices (ECDs), many of which were fabricated using electrochromic materials, such as conductive polymers (CP). At the same time, the electrochromic display device was also documented in US Patent [2]. Conductive polymers are the result of a material doping state produced through the addition of dopants conjugated along the molecular chains. These materials generate electron or hole pairs, resulting in conductivity and variations in optical absorption. An electrochromic device is a typical electrochemical cell, comprising the following elements: (1) working electrode layer (working electrode), (2) ion electrolyte layer (electrolyte layer), (3) counter electrode layer (counter electrode) and (4) transparent conductive substrate (transparent conductive glass). The optical properties of electrochromic components need to be recognizable, to actuate a strong visual effect and provide display characteristics. In addition,

the reversible process of color change needs to be rapid and stabilized through applied driving potential. Polythiophene [3] has shown excellent electrical conductivity. Yamamoto [4] synthesized long alkyl chains in the β position of 3-alkylthiophene (3AT), to obtain poly-3-alkylthiophene (P3AT) through polymerization, demonstrating good electrical and thermal stability in the doping state. The first electrochemical oxidative polymerization of polythiophene series was conducted in 1983 [5], exhibiting that bonding in the β position of the methyl groups has a higher degree of conductivity (1 S cm⁻¹). Poly (3-alkyl thiophene) exhibits both head-to-tail and head-to-head/tail-to-tail three-dimensional structures. In [6], electrochemical polymerization of polythiophene demonstrated doping/de-doping reversible behavior. Polythiophene film appears bright red in a neutral state however, with a change in oxidation potential, this polymer film is converted to light blue (or gray green). Polythiophene derivatives possess excellent electrochromic properties and scientists have used a series of different side chain groups of thiophene derivatives to study the electrochromic behavior. This modification in side chain groups is capable of change the energy gap of thiophene derivatives, thereby reducing absorption driving potential and achieving a variety of colors. Poly(3-methylthiophene) (P3MT) has good physical performance and chemical nature, producing a clear electrochromic change in color. In [7], ITO was coated with P3MT and fabricated as an electrochromic device, demonstrating a maximum optical contrast of 35% at a wavelength of 530 nm with applied potentials between -0.3 and 2.5 V.

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¹ All student's contributions to this work are the same.

Polythiophene derivatives, using as an electrode assembled into a dual-polymer electrochromic device, exhibited the properties of rapid ion doped polymers, effectively lowering the driving potential. Doping time was significantly reduced at an applied potential over long periods (2000 cycles); whereas the optical contrast declined to 10%, indicating that long-term operating stability must be improved. Ionic electrolytes of boron trifluoride diethyl ether (boron trifluoride ethylether, BFEE) have been used in all kinds of electrochromic thin films produced with polythiophene derivatives [8], and the optical contrast of these single-layer electrochromic films have the highest value of $\Delta T = 46\%$. In [9], poly-(3,4-ethylenedioxythiophene) was coupled with P3MT in a dual-layer device, in which the ionic electrolyte TBABF4 (tetra-butyl ammonium fluoroborate) was used as an electrolyte. Various types of optical testing determined that this kind of device effectively reduces driving potential, despite an increase in optical contrast to $\Delta T = 46\%$ at $\lambda = 655$ nm due to the rapid ionic effects of liquid doping; however, the stability remains an un-solved problem over long periods of time. Conductive polymer electrochromic materials usually produce deterioration with prolonged use, therefore increasing stability over the long term is the most important issue in the application of ECD. Because TiO₂ film is capable of providing a meso-porous layer and moderate electric conductivity, TiO₂ film could be implemented as a buffer matrix to form P3MT electrochromic film using cyclic voltammetry. These layers are then sandwiched with salt (lithium perchlorate) within ECD devices. Improving the performance of electrochromic could be demonstrated by inserting a TiO₂ buffer layer in the P3MT-based electrochromic devices.

2. Experimental

Titanium(IV) oxide, TiO₂, (P25, Degussa), Reagent grade 3-methylthiophene (Alfa), acetonitrile (J.T. Baker), lithium perchlorate (Alfa), propylene carbonate (PC, Fluka), and poly (ethylene oxide) (PEO, MW = 400,000 Aldrich) were used as received.

2.1. Preparation of TiO₂ mesoporous buffer layer

We synthesized hydrothermally processed TiO₂ colloid. In brief, 3 g TiO₂ nanoparticles (P25) were dispersed in 100 mL 10 N NaOH and heated to 130 °C in an autoclave for 1 day. The precipitate was then re-dispersed in 100 mL 1 N HNO₃. This suspension was subjected to autoclaving at 240 °C for 12 h to obtain the TiO₂ colloid. The TiO₂ specimens were baked at 450 °C in air for 30 min. The TiO₂ colloid solution was mixed with polyethylene glycol (PEG-2000) (Fluka) to form a viscous TiO₂ dispersion at a 0.15 of PEG/TiO₂ ratio, which was spin-coated onto an indium-tin oxide (ITO)-coated glass (8 Ω/□, Merck) to form a TiO₂ film with an area of 1.0 cm². The TiO₂ film was controlled at a desire thickness. The film was dried in air at 120 °C for 30 min and calcined at 450 °C for 30 min.

2.2. Electropolymerization of P3MT films

Electrochemical polymerization and characterization were performed on a PGSTAT20 electrochemical analyzer (AUTOLAB Electrochemical Instrument, The Netherlands). A three-electrode cell assembly was utilized using an Ag/AgNO₃ electrode as a reference and a platinum wire was used as a counter electrode. A TiO₂ buffer layer-inserted ITO glass of area 1 cm² was used as working electrode. A luggin capillary, with the tip set at a distance of approximately 1 mm from the surface of the working electrode, was used to minimize errors due to an *iR* drop in electrolytes. All electropolymerization and measurements were performed under

nitrogen atmosphere. The potentials are reported here in terms of the Ag/Ag⁺ reference electrode.

For electrochemical polymerization, 0.1 M 3MT monomer and 0.1 M LiClO₄ supporting electrolyte were dissolved in acetonitrile under N₂ atmosphere. Electro-polymerization was achieved by cycling the potential in the range of –200–800 mV with a sweep rate of 50 mV s^{–1} and cyclic voltammograms (CV) were recorded simultaneously with electropolymerization.

2.3. Spectroelectrochemical studies on P3MT film

The P3MT film was deposited using the method mentioned above regarding cyclic voltammetry (film thickness controlled at the consumption charge of ~40 mC cm^{–2}) using a TiO₂ buffer layer-inserted ITO glass as working electrode. An in situ cyclic spectroamperometric study on P3MT film was carried out for polymer films deposited on this TiO₂ buffer layer-inserted ITO glass plate. In situ UV–visible spectroelectrochemical (spectroamperometric) experiments were performed in a quartz cuvette with a 1 cm path length, by assembling an electrochemical cell with a P3MT film deposited-plate as a working electrode, a platinum wire as a counter electrode, and Ag/Ag⁺ as a reference electrode. UV–visible spectra were continuously recorded while performing spectroamperometric analysis using Microcal origin software. The UV–visible spectra of P3MT films were recorded by maintaining the potential of polymer modified-electrode at different potentials. The above experiments were performed in a nitrogen atmosphere.

2.4. Assembly of electrochromic devices

Gel-type electrolyte was first prepared as follows: 0.1 M LiClO₄ and 1 wt% PEO were dissolved in propylene carbonate (PC) to form a gel-type electrolyte. A P3MT-deposited TiO₂ buffer layer-inserted ITO glass, a bare ITO glass, and the gel-type electrolyte were sandwiched to assemble an electrochromic device structure: ITO|TiO₂|P3MT||LiClO₄-PEO-PC||ITO.

3. Results and discussion

3.1. Preparation of TiO₂ nanoparticles

Fig. 1a shows a TEM image of titanate-derived TiO₂ nanoparticles with an average particle size of ~23 nm. Compared to the JCPDS standard and Raman spectra [10], X-ray diffraction (XRD) patterns of the TiO₂ nanoparticle-film provided evidence of a pure anatase phase (Fig. 1b). The average crystal size was calculated to be approximately 20 nm, according to Scherrer's equation, $L = \lambda K / \beta \cos \theta$, where L is the mean crystallite dimension (Å), K is the shape factor, and β is the line broadening at half the maximum intensity (FWHM) in radians. For instance, the case of (1 0 1) reflection for these TiO₂ nanoparticles: $\beta = 0.45^\circ \times \pi / 180^\circ$, $\lambda = 1.54049$, peak position occurs at $25.2^\circ (2\theta)$; then: $L = (1.54059 \times 1) / [(0.45 \times 3.14 / 180) \times \cos(12.6^\circ)] = 203 \text{ \AA} = 20.3 \text{ nm}$.

3.2. Polymer growth

Cyclic voltammograms (CVs) corresponding to the polymerization of 3-methylthiophene (3MT) are depicted in Fig. 2a, revealing that the first oxidation peak appeared at 350 mV, which corresponds to the transition of reduction to oxidation forms. This peak is responsible for the deposition of P3MT through successive sweeping potentials. The gradually developing waves correspond to the reversible redox process of the polymer (P3MT). This redox process reflects a color change in form from red (reduced) to blue (oxidized). It is noteworthy that the oxidation peaks shift to a

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