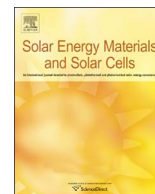




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# High-performance polythiophene film covalently bonded to ITO electrode: Synthesis and electrochromic properties

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## ABSTRACT

Indium tin oxide (ITO) electrode was modified with triethoxy-2-thienylsilane (TETS), and then the polythiophene (PT) film covalently bonded to ITO electrode (PT-ITO) was prepared by the electrochemical polymerization. It was found that the adsorption force of PT on ITO electrode was enhanced, PT-ITO exhibited better stability. Cyclic voltammetry (CV) and UV–vis spectroscopy measurements indicated that the doping/dedoping reproducibility of PT-ITO in electrolyte was good. When the applied potential was 0 V, PT-ITO exhibited red color. While the positive potential was higher enough, PT-ITO exhibited grey-blue color, and the color change of PT-ITO was reversible. Moreover, PT film on ITO substrate chemically modified with TETS (T-ITO) was used to successfully fabricate an electrochromic (EC) device that exhibited stable EC switching as a function of applied potential. This again demonstrated that chemical bonding approach could bring about stronger interactions between the PT and ITO substrate, improving the EC properties.

## 1. Introduction

EC materials have drawn tremendous attentions in virtue of their reversible optical modulation. It has found important applications in smart windows [1], anti-glare rear view mirrors [2], displays of portable and flexible electronic devices including smart cards, re-usable price labels and electronic papers [3–5], protective eyewear [6] and textiles for adaptive camouflage [7–9]. Among the EC materials, electrochromic polymers (ECPs) possess a variety of advantageous properties such as low fabrication cost, processibility, flexibility and color-tunability, and have been widely investigated [6,10–17]. You et al. developed a novel strategy for fabricating poly(3,4-ethylenedioxythiophene) (PEDOT) patterns on various substrates, including hydrogels, via sequential solution procedure. And then they successfully fabricated an electrochromic device that exhibited stable electrochromic switching by using PEDOT patterns on ITO glass or ITO film [18]. Reynolds et al. synthesized three ECPs with repeat units composed of electron-rich dimethoxyphenylene in alternation with dimers of 3,4-dialkoxy- and 3,4-propylenedioxythiophenes, yielding high gap polymers that are vibrant yellow or orange in the charge neutral state. They elucidated the subtle steric and electronic effects that governed bandgap and redox properties in dioxothiophene copolymers [19].

Moreover, they found that increasing the composition of 3,4-ethylenedioxythiophene (EDOT)–2,1,3-benzothiadiazole–EDOT monomer in random copolymers yielded more level and uniform absorption across the visible, reducing hue saturation and giving more muted colors relative to the normally vibrantly colored ECPs with no observable loss in contrast [20]. Recently, Meng et al. synthesized the novel donor-acceptor polymer containing thieno[3,2-*b*]thiophene derivative. This polymer exhibited rapid response times, desirable contrasts in both visible and near-infrared (NIR) regions, favorable efficiencies, and reasonable optical memory and stability, making it a promising candidate for use as a new green electrochromic conjugated polymer [21].

To take advantage of the special properties of these polymers in practical and commercial applications, ECPs are integrated into solid-state electrochromic devices (ECDs) [8]. The ECDs are generally fabricated by using optically-transparent electrodes (in which at least one is covered by EC material) in “sandwich” or lateral configurations, and the electrodes are separated by a suitable solid or liquid electrolyte [2,22–27]. In polymer ECD, electrochromic layer is a kind of conductive polymer film, coated on the ITO substrate by either physical coating or electrochemical polymerization method. The obtained films by above methods have some disadvantages: their mechanical strength is low, and the films are easy broken; the adsorption force between the

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films and ITO substrate is weak (van der Waals interactions), the films are easy to detach from the ITO substrate [28]. Although the ECD with outstanding cycling life (up to 150,000 times) has been successfully fabricated [24], the above disadvantages still restrict the stability of polymer film in liquid electrolyte and their application in high performance ECDs.

In search for improved interfacial contact, a self-assembled monolayer process forming covalently-bonded organic-inorganic materials at ITO electrode has been tried [29–31]. Recently, Riffard et al. characterized the immobilization of an antibody on the ITO electrode via covalent chemical bonds between antibody amino-group and the ring of (3-Glycidioxypropyl)trimethoxysilane, and found that its detection threshold was of lower value compared with those obtained using other immunosensors [32]. So far, relatively little research has been conducted on surface modification of ITO electrode with organosilane in polymer ECD. Herein, in order to improve the adhesion force and stability of PT film on ITO electrode, we apply TETS as the modifier to prepare the PT-ITO and assembly the ECD based on PT film on T-ITO substrate. The PT-ITO is analyzed using X-ray photoelectron spectroscopy (XPS), attenuated total reflection infrared (ATR-IR) spectroscopy, atomic force microscopy (AFM), CV and UV–vis spectroscopy. The results indicate that chemical bonding approach can enhance the adsorption force between PT film and inorganic ITO electrode, and improve the EC stability of PT film.

## 2. Experimental

### 2.1. Materials

ITO-coated glass was received from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. (China), its sheet resistance was 7.9–8.5  $\Omega/\text{sq}$ , and the thickness of ITO film on glass substrate was 188–191 nm. TETS was obtained from J&K Scientific Ltd. (China). Thiophene and lithium perchlorate ( $\text{LiClO}_4$ ) were purchased from Acros Organics and used as received. Propylene carbonate, acetonitrile and boron trifluoride etherate were gained from Alfa-Aesar company. Hydrogen peroxide was obtained from Tianjin Benchmark Chemical Reagent Co., Ltd. (China). Poly (methyl methacrylate) ( $M_w = 120,000 \text{ g/mol}$ ) was received from Sigma-Aldrich. Ammonia water and potassium carbonate ( $\text{K}_2\text{CO}_3$ ) were supplied by Tianjin Jiangtian unified Technology Co., Ltd. (China). Anhydrous methanol, ethanol, toluene and isopropyl alcohol were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. (China). All solvents were of analytical grade and were used as received without further purification or distillation.

### 2.2. Preparation of PT-ITO

First, ITO-coated glass was cut into 10 mm  $\times$  20 mm coupons, which were cleaned according to our previous procedure [11]. After drying, the bare ITO substrates (B-ITO) were hydroxylated according to the literature [11]. The hydroxylated ITO-coated glass (H-ITO) substrate was held vertically in a solution of TETS (0.33 M in toluene) in a 15 ml sealed bottle for 24 h. The treated ITO coupon was then removed from the bottle and was heated at 140  $^\circ\text{C}$  in a degassed reaction tube for 24 h to bond the TETS to ITO surface. The ITO substrate chemically modified with TETS (T-ITO) was sonicated in 0.5 M  $\text{K}_2\text{CO}_3$  in 2:1 ethanol/water for 20 min, followed by copious rinsing with deionized water and ethanol [33]. After that, the T-ITO substrate was inserted vertically into boron trifluoride etherate solution (0.15 M) containing thiophene. Electrochemical polymerization was then carried out by T-ITO as working electrode, respectively using Ag/AgCl (3 M KCl) reference electrode and Pt counter electrode. A voltage of 1.5 V was applied across the cell to induce potentiostatic polymerization, and PT-ITO was obtained after 3 min. Scheme 1 shows the schematic representation of synthetic route of PT-ITO. Moreover, H-ITO was held vertically in a solution of TETS (0.33 M in toluene) for 24 h, and then

taken out. After the volatilization of toluene, TETS physically adsorbed on ITO (P-ITO) was obtained.

### 2.3. Fabrication of electrochromic device

The gel electrolyte was prepared by dissolving poly (methyl methacrylate) ( $M_w = 120,000 \text{ g/mol}$ , 2.8 g) and lithium perchlorate (0.512 g) in 6.65 ml of propylene carbonate and 28 ml of dry acetonitrile. The mixture was stirred overnight at room temperature under an argon atmosphere. And then the sandwich structured device (ITO//polymer active layer//gel electrolyte layer//ITO) was fabricated by assembling the two ITO/glass substrates (PT film on T-ITO substrate and another piece of ITO glass) together with gel electrolyte in contact according to the methods [34–38]. The counter electrode is the ITO glass alone without any secondary electrochromic material coated for simplifying the device structure and gaining accurate electrochromic performance of the active layer [36]. External potentials of + 2.0 and – 2.0 V were applied to the EC device to achieve switchable color changes [18].

### 2.4. Characterization

XPS (Axis-Ultra) was performed using monochromatic Al K $\alpha$  (150 W, 15 kV) X-ray irradiation at a photon energy of 1486.71 eV, and the vacuum in the spectrometer was  $10^{-9}$  Torr. Binding energies were calibrated relatively to C 1s hydrocarbon peak at 284.8 eV. ATR-IR spectra were collected by using a VERTEX 70 Fourier transform infrared spectrometer. The morphologies of substrates were evaluated by using a SPA-400 scanning probe microscope. The CV experiments were carried out on a Autolab PGSTAT 302 N potentiostat-galvanostat using PT-ITO, Pt (99.99%) plate and Ag/AgCl (3 M KCl) as the working, counter and reference electrodes, respectively, in a 0.1 M lithium perchlorate/acetonitrile electrolyte solution. The spectroelectrochemical properties of PT-ITO were recorded using an Autolab PGSTAT 302 N potentiostat with a UV–vis spectrometer (Shimadzu 2550).

## 3. Results and discussion

### 3.1. XPS spectra of T-ITO and PT-ITO

Fig. 1a shows XPS spectra of B-ITO, H-ITO, T-ITO and PT-ITO surface. It can be seen that compared with H-ITO, the C 1s, S 2p and Si 2p peak intensities of T-ITO increase, confirming the formation of a TETS layer. Moreover, the C 1s and S 2p peak intensities further increase after chemical bonding of PT to T-ITO surface. This indicates that PT is probably combined with TETS on ITO surface by covalent bond [11,29]. XPS spectra of O(1s) peak region of B-ITO are presented in Fig. 1b. It is seen that the three main components of the fit are at 529.4 eV (ITO), 531.1 eV (surface In-OH), and 532.7 eV (Si-O), they well agree with those reported in the literatures [39–43]. Moreover, it can be observed from Fig. 1c that the three main components of the fit are located at 529.1 eV (ITO), 531.4 eV (surface In-OH) and 532.9 eV (Si-O), respectively. Compared with the O(1s) lines of B-ITO and H-ITO surface, the intensity of O(1s) peak (surface In-OH) for H-ITO increases significantly, indicating that the number of In-OH groups on ITO surface increases after hydroxylation. Fig. 1d displays XPS spectra of S(2p) peak region of B-ITO, H-ITO, T-ITO and PT-ITO surface. High-resolution scans of the S(2p) region show the presence of nitrogen on the T-ITO and PT-ITO surface. There is no obvious S(2p) peak on B-ITO and H-ITO, this confirms the formation of TETS layer by chemical modification [44,45]. Additionally, it is also seen that the intensity of S(2p) peak of PT-ITO is much higher than that of T-ITO.

### 3.2. ATR-IR spectra of T-ITO and PT-ITO

Fig. 2a shows ATR-IR spectra of P-ITO. It is found that the C=C

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