Research paper

The trade-off between electrochromic stability and contrast of a thiophene−Quinoxaline copolymer

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ABSTRACT

The stability of organic electrochromic devices is a crucial issue for their applications. However, until now the degradation mechanism of electrochromic materials are still not fully understood especially for electrochromic conjugated polymers (ECPs). To improve device stability, intensive investigation on the degradation mechanism of ECPs is urgently needed. Here we report our study on the electrochromic degradation in a thiophene–quinoxaline copolymer: poly [2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1). The results of X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectra (UPS) and UV–vis transmission spectra reveal that there are three main factors during the electrochromic degradation of TQ1. The first one is anion (ClO_4^-) irreversibly deep trapped, while the second is peroxidation of the thiophene group in TQ1. Both factors reduce the conductivity and electrochromism of TQ1. The third is structural relaxation resulting lager conjugated system of TQ1 molecules in film, which is gradually developed during 400 cycling of CV at a narrow potential range (0–1 V). When a potential range 0–0.7 V is applied, all three factors are prohibited, no electrochromism degradation is observed anymore, although the contrast becomes smaller. Our investigation systematically discloses the degradation mechanism during the electrochemistry processing of a ECP (TQ1), demonstrating the significance of trade-off between the electrochromic stability and contrast of the ECP.

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1. Introduction

Electrochromic device can reversibly change its transmittance when the electrochromic material is oxidized or reduced driven by an electric field. Electrochromism can be applied to smart windows in energy-saving buildings [1], display [2], and color variable clothes, etc.

Most inorganic electrochromic materials include transition metal oxide, need expensive processing and show slow switching [3,4]. While electrochromic conjugated polymers (ECPs), as electrochromic active layers, possess many superior properties, such as all solution processing, higher coloration efficiency, faster switching, flexibility and ease of color control by molecular structure modification, etc [5,6]. Therefore, ECPs are promising candidates for applications. However, the stability of some ECPs is a big challenge since its degradation mechanism is still not fully understood [7,8].

The degradation mechanism of inorganic electrochromic materials has been controversial until recent years although they have already been commercialized [4,8,9]. Ion irreversible insertion and extraction is supposed as the main deterioration mechanism of their electrochromism, which is well proved by Wen et al. in WO_3, the most commonly investigated inorganic electrochromic material [8]. Recently, irreversible ion trapping is also found in ECPs [10]. Actually ECPs have different molecular structure, elements and film composition with inorganic electrochromic materials. Therefore besides irreversible ion trapping, there must be other factors involving in the electrochromic degradation process of ECPs.

For an electrochromic device which includes electrochromic layer, electrolyte, charge storage layer and two electrodes. Besides, there are some interfaces between different layers. The whole degradation origins from all the layers and interfaces. Investigating those layers and interfaces separately is the only way to clearly

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understand the degradation mechanism of an electrochromic device. Our work focus on the most important functional part, that is, electrochromic layer and reveal the degradation mechanism. In this paper, we investigated the electrochromic characteristics of poly [2,3-bis-(3-octyloxyphenyl) quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1), a thiophene–quinoxaline copolymer, which is commonly used as an electron donor in the active layers of organic solar cells [11,12]. Distinct electrochromic degradation mechanisms in TQ1 were revealed through different processing settings in electrochemistry system via cyclic voltammetry (CV). Along with cycles by CV, the current and UV–vis transmission were recorded to show the electrochromic stability of TQ1. After CV processing, X-ray photoelectron spectroscopy (XPS) was employed to detect the elements composition, ultraviolet photoelectron spectra (UPS) and UV–vis transmission spectra of different samples was used to explore the evolution of electrochromism degradation.

We observed three main factors involved in the degradation of TQ1 during the electrochromic process. The first factor is anion (ClO_4^-) irreversible trapping, the second one is peroxidation of thiophene group in TQ1. Both factors affect conductivity and electrochromism of TQ1. The third one is structural relaxation resulting lager conjugated system of TQ1 during CV sweeping (0–1 V) for 400 cycles. When a potential range 0–0.7 V is applied, all the three factors prohibited, no electrochromism degradation is observed anymore, which shows the importance to balance the stability and the contrast of TQ1. Therefore, using an appropriate potential to operate ECPs is essential for prolonging the lifetime of electrochromic devices.

2. Experimental Section

2.1. Materials and methods

TQ1, with weight average-molecular weight Mw = 45 kDa, and polydispersity index (PDI) = 2.7, was synthesized in Chalmers University of technology, Sweden. The synthesis of TQ1 is described in detail elsewhere [13]. Solutions of TQ1 was prepared at a concentration of 20 mg/ml in o-xylene. TQ1 films used in electrochemistry system and XPS measurements were prepared by spin-coating TQ1 solutions on cleaned ITO substrates at the speed of 2000 rpm/min.

2.2. Measurements

Electrochemistry experiments were performed with an Autolab Potentiostat. CV measurements were carried out in a three-electrode cell configuration with ITO substrate covered by TQ1 film, Pt wire, and Ag/Ag$^+$ (0.01 M AgNO$_3$ and 0.1 M TBAPF$_6$ in acetonitrile) as the working, counter, and reference electrodes, respectively. 1 M LiClO$_4$/Propylene carbonate electrolyte was used in all electrochemistry experiments. All measurements were recorded at 50 mV s^{-1}. The potential window chosen in this paper are 0–1 V and 0–1.5 V. Detailed information on the potential window is in Fig. S1, which prove both potential windows are reliable to show the electrochromic and electrochemistry characteristics of TQ1.

Two pictures of TQ1 films shown in Fig. 1(a) were taken with an iPhone 7 Plus without any modification.

XPS experiments was carried out by a Scienta SES 200 spectrometer with a monochromatized Al (Kα) source (hν = 1486.6 eV) and UPS was done in a dedicated home designed and built spectrometer using He I radiation (hν = 21.2 eV), respectively under a base pressure of 2×10^{-10} mbar. The spectrum was calibrated with Au 4f peak on a clean Au foil. All XPS spectra were collected at normal emission and at room temperature. There is no X-ray beam damage observed during XPS measurements. High-resolution core level spectra of Cl 2p, S 2p, and C 1s were recorded in different samples for comparison. The binding energies in UPS were obtained referenced to the Fermi level with an error bar of ±0.1 eV.

UV-vis transmission spectra were recorded by using an UV–vis spectrophotometer (LAMBDA 950, Perkin Elmer) with a cubic quartz cuvette. Spectro-electrochemistry vs. time at the wavelength of 620 nm was carried out during CV processing.

3. Results and Discussion

TQ1 is an easily synthesized and processed conjugated polymer, which employs electron donor (thiophene)-acceptor (quinoxaline) in chain, resulting intramolecular and intermolecular charge transfer. TQ1 displays deep blue color at its neutral or reduced state, transparent at its oxidized state [14]. The molecular structure of TQ1 and its colored/bleached state are shown in Fig. 1(a). The electrochemical oxidation process is followed by anion ClO_4^- insertion into TQ1 film from electrolyte. The electrochemical reduction comes along with extraction of ClO_4^- from TQ1 film into electrolyte. Both reactions are reversible which can be controlled by the applied potential. The UV–vis transmission spectra of neutral TQ1 film in Fig. 1(b), shows that it obtains its lowest transparency at the wavelength (λ_{min}) of 620 nm. When the potential increases gradually to 1 V, the transparency around λ_{min} becomes higher, while it gets lower in near infrared (NIR) range. This characteristics makes TQ1 especially suitable for application
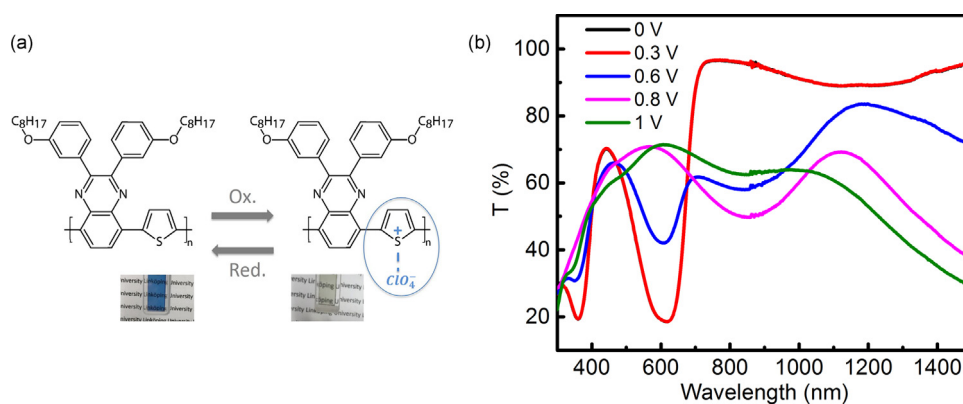
Fig 1. (a) Neutral TQ1 is oxidized to form a conducting polycation in the presence of charge-balancing anions. The pictures display the appearance of colored state and bleached state of TQ1 films. (b) UV–vis transmission spectra of TQ1 films at the voltage of 0 V, 0.3 V, 0.6 V, 0.8 V and 1 V (vs. Ag/Ag$^+$) applied in three electrode electrochemistry system. ITO substrate with spin-coated TQ1 film, Pt wire, and Ag/Ag$^+$ (0.01 M AgNO$_3$ and 0.1 M TBAPF$_6$ in acetonitrile) as the working, counter, and reference electrodes, respectively. Supporting electrolyte: 1 M LiClO$_4$ in propylene carbonate.