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Polyaniline electrochromic devices with transparent graphene electrodes

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ABSTRACT

Transparent, conductive and uniform graphene films have been prepared and used as electrodes of the electrochromic devices of polyaniline. Polyaniline films on both graphene and the widely used indium tin oxide (ITO) electrodes showed similar electrochemical and spectroelectrochemical properties. However, graphene electrodes exhibited much higher electrochemical stability than ITO in aqueous acidic electrolytes. The performances of the electrochromic devices with graphene electrodes exhibited slight decrease upon voltage switching while those of the devices with ITO electrodes decreased dramatically. After 300 cycles, the electrochromic devices with graphene electrodes showed much larger optical contrast and shorter switching time than those of the devices with ITO electrodes.

1. Introduction

Electrochromic devices (ECs) change light transmission or reflection properties during electrochemical redox processes [1–5] and they can be used as large area displays, smart mirrors and windows. Conducting polymer films have been widely used as active layers of ECs since they can reversibly change colors upon electrochemical doping and de-doping treatments. Furthermore, these polymers can be easily synthesized and processed into thin films, and their optical properties can be adjusted through structural modifications [6–16]. Among various conducting polymers, polyaniline is particularly attractive due to its unique optical properties and high environmental stability. It has four redox states with distinct colors, which are leucoemeraldine base (LB, yellow), emeraldine salt (ES, green), emeraldine base (EB, blue) and pernigraniline base (PB, purple) [17–24]. The LB to ES transformation is highly repetitive under low driving potential, and its color contrast is high in visible light region. The main barrier to the commercial use of polyaniline as an electrochromic material is that this polymer has electroactivity only in aqueous solutions with low pH values [25]. However, indium tin oxide (ITO), the most widely used transparent conducting electrode (TCE), is unstable in an acidic medium. Up to date, various techniques including using an organic solvent [26–31], synthesis of self-doped or polymer acid doped polyaniline [32–35], and using carbon nanotube thin films for replacing ITO [36,37] have been developed to overcome this problem.

Graphene, a two-dimensional (2D) sheet of covalently bonded carbon atoms, has attracted great attention recently due to its unique optical, mechanical, thermal and electronic properties [38–50]. With high conductivity, good transmittance and low cost, graphene is suitable for fabricating TCEs [51–57]. Compared with electrodes of carbon nanotubes, graphene electrodes are cheaper and have smoother surfaces. Graphene TCEs have been made by various methods and used as electrodes in both dye-sensitized and polymer solar cells [58–62]. In this paper, we report polyaniline ECs with graphene electrodes working in acidic aqueous media. These devices showed significantly improved performances comparing those of the devices with ITO electrodes.

2. Experimental

2.1. Materials

Aniline (Changping Shiying Chem. Eng. Plant, Beijing, China) was purified by refluxing with iron powder for 1 h and then distilled at 182 °C before use. It was further purified by distillation under reduced pressure with nitrogen protection after being dried with sodium hydroxide for 12 h. N-methyl pyrrolidinone (NMP) and $(NH_4)_2S_2O_8$ were purchased from Beijing Chem. Fact. (Beijing, China) and used as received.

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2.2. Synthesis of PANI

PANI was synthesized by chemical oxidation of aniline with ammonium persulfate at 0 °C [63]. The procedures are described as follows. 4.7 g aniline was dissolved in 1 mol L^{-1} aqueous solution of HCl (50 mL). Then, a few drops of 1 mol L^{-1} HCl aqueous solution were added to the mixture to adjust its pH value to be 1.0. The mixture was then cooled to 0 °C under stirring. Successively, 26 mL aqueous solution containing 12.9 g $(NH_4)_2S_2O_8$ was dropped into the reaction mixture. Then, polymerization was carried out at 0 °C under stirring. After 20 h of reaction, the product was collected by filtration and washed with deionized water. The green powder was deprotonated by stirring in NH_3 aqueous solution (100 mL, 33 wt%) for 24 h. Finally, the neutralized product was filtrated, washed twice with water and then dried under vacuum at 60 °C. 4.0 g PANI in emeraldine base state (brown powder) was obtained.

2.3. Fabrication of electrochromic electrodes

Transparent conductive graphene electrodes were prepared referred to the reference [60]. Briefly, aqueous dispersion of GO was produced by the Hummers' method [64] and purified through dialysis and centrifugation. GO sheets were deposited on pretreated hydrophilic quartz substrates by dip-coating method. The thermo reduction of the thin films was performed at 1000 °C under Ar atmosphere.

PANI (0.5 g) was dissolved in 25 mL NMP to form a dark blue solution. The solution was centrifuged at 6000 rpm for 20 min to remove the sediment. Then, PANI films were spin-coated onto graphene electrodes by using the NMP solution of PANI to fabricate electrochromic electrodes (named as PANI-G electrodes here). The spin-coating process was firstly 550 rpm for 5 s and then 1300 rpm for 50 s. For comparison, PANI films were spin-coated on ITO (14 Ω sq^{-1}, Xiamen ITO Corp., China) electrodes through the same procedures as described above. ITO glass slides were carefully washed by ethanol/acetone mixture (1:1), NaOH solution (5%), detergent and deionized water in sequence before use. The resulting electrochromic electrodes were named as PANI-ITO electrodes. Before electrochromic measurements thin Au strips (50 nm thick and 1 mm wide) had been sputtered onto the edges of PANI-G or PANI-ITO electrodes to reduce the contact resistance between EC electrode and the electrode clamp of potentiostat.

2.4. Characterization

The electrochromic measurements were performed at room temperature in a 1 cm × 1 cm colorimetric cell controlled by a

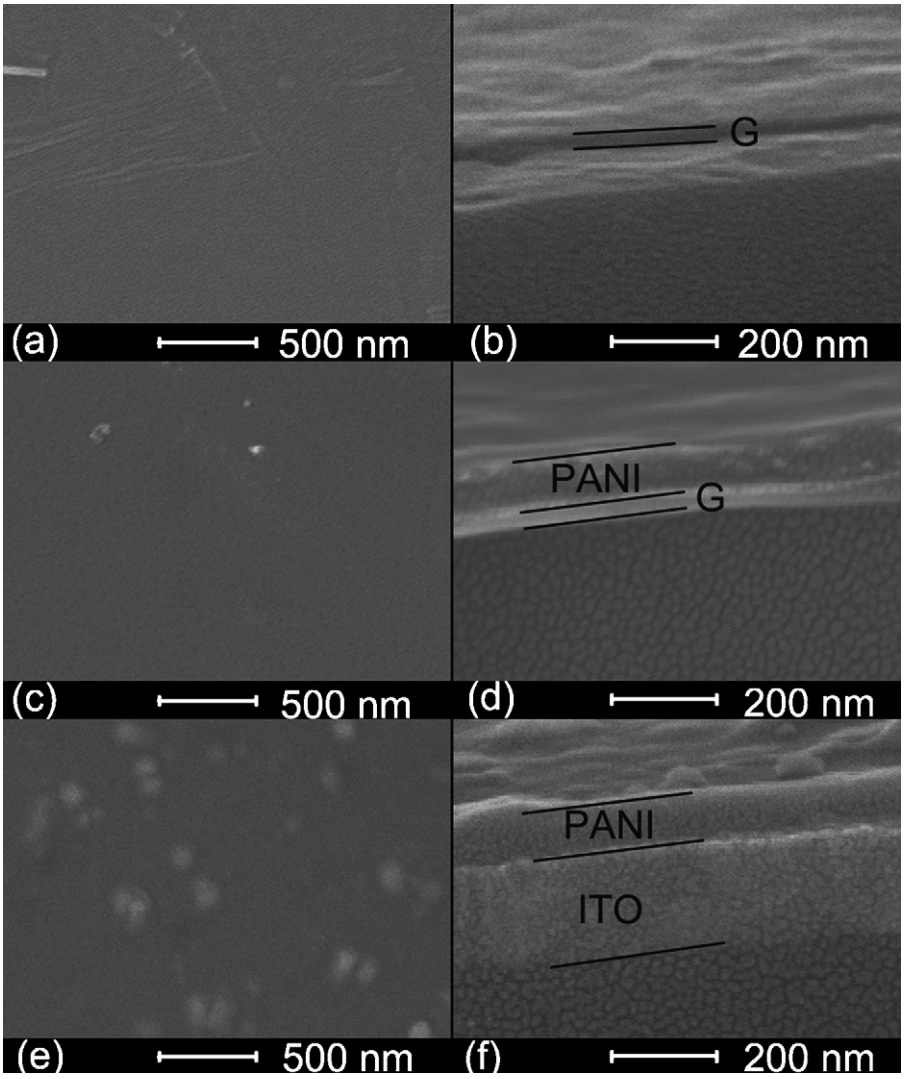

Fig. 1. SEM images of the surfaces (a, c, and e) and cross sections (b, d, and f) of graphene (a and b), PANI-G (c and d) and PANI-ITO (e and f) electrodes.