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Enhanced electrochromic performance of WO_3 hybrids using polymer plasma hybridization process

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ABSTRACT

A series of electrochromic hybrid materials were synthesized with in-situ polymerization of aniline, 2-fluoroaniline and *N*-methylaniline onto tungsten trioxide (WO_3) powders using a rotating capacitively coupled radio frequency (rf) plasma process. The materials were characterized by means of scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) and X-ray diffraction analysis (XRD). Thin films of tungsten trioxide/polyaniline (WO_3/PANI), tungsten trioxide/poly(2-fluoroaniline) (WO_3/PFANI) and tungsten trioxide/poly(*n*-methylaniline) (WO_3/PMANI) hybrid powders were obtained by e-beam technique onto flexible conducting polyethylene terephthalate electrodes for electrochromic works. The optical and electrochromic properties of WO_3 hybrids-based ECDs were investigated by optical and electrochemical measurements. It is observed that electrochromic performance of hybrid films has changed as depending on electron acceptor or donor properties of substituent group onto PANI chain. The results of flexible electrochromic devices (ECDs) indicated that WO_3/PMANI hybrid-based ECD has a high optical contrast of 49% at 750 nm, reversible coloration with efficiency of 361 cm^2/C and fast switching times (bleaching time: 1.41 s, coloration time: 0.67 s).

1. Introduction

Electrochromism is a phenomenon including reversible change in their optical properties (transmittance, absorbance and reflectance) of some materials as the result of electrochemical oxidation or reduction at different potentials [1–4]. Electrochromic materials are usually used in diverse fields of technology such as rear-view mirrors for automobiles, military camouflage, smart windows, e-papers and low cost displays [2,5]. Recently, flexible and/or stretchable electrochromic devices have been comprehensively studied due to the escalating demands for flexible, lightweight and mobile electronics that can be used in specific applications including real-time healthcare monitoring, biointegrated therapeutic devices, wearable displays, e-papers, e-books [6–8]. Lin et al. showed a remarkable lithium electrochromic performance of flexible tungsten oxide films via the addition of iron oxide onto flexible substrate using a low temperature plasma polymerization method. They investigated the effect of Fe precursor gas flow ratios on the film properties and the electrochromic performance of the low temperature plasma-polymerized WO_yC_z, $WFe_xO_yC_z$ and FeO_yC_z films [9].

Generally, electrochromic devices (ECDs) possess multilayer structures including transparent conductors, an electrochromic film, an ion conductor and ion storage film [7]. A wide variety of inorganic and organic materials can be used as electrochromic layers, such as transition oxide, conducting polymers, etc [7]. Tungsten trioxide (WO_3) is one of the most successful and frequently used inorganic electrochromic materials [2,10–14]. However, it has single color change, slow switching speed and a limited potential window, which prevent its application [2,15]. In comparison with the transition oxide-based electrochromic materials, conjugated polymers usually reveal faster response speed, higher coloration efficiency as well as easy to optimize their electrochromic features through molecular tailoring [2,16]. Polyaniline (PANI) is one of the most widely used electrochromic conjugated polymer due to high optical contrast, environmental stability, easy synthesis, comparatively low cost [2]. Organic/inorganic hybrid films are an advanced systems with integration of the advantage of conducting polymer and transition-oxide. They exhibit improvement of structural, optical and EC properties [2,5,15,17]. Zhang et al. synthesized PANI–WO_3 hybrid thin films via a self-assembly method and chemical oxidative polymerization. The prepared PANI-WO_3 films indicated faster switching speed, better durability than WO_3 film [18]. Hybrid materials based on WO_3 and poly(3-hexylthiophene) (P3HT)

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exhibited enhanced current densities, improved response speed and three different colorations at specific voltage conditions [19].

To synthesize hybrid materials, various methods have been developed, such as layer-by-layer, self-assembly, vapor-deposition, electrochemical, chemical routes [20]. Among the used methods for preparation of hybrids, plasma nanocoating has been shown to one of most effective ways to provide uniform polymer deposition onto inorganic nanoparticles [15,21]. It has some advantageous properties such as solvent-free, nontoxic and well-controlled deposition [15,21]. To the best of our knowledge, there is no report on synthesize of WO_3/PANI, WO_3/PFANI and WO_3/PMANI hybrids using rf rotating plasma modification method. In this study, we introduce a facile preparation method of hybrid films via the plasma polymerization of aniline and derivatives on the surface of WO_3 nanopowders. The thin films of the WO_3 hybrids were prepared using the electron beam evaporation. The prepared flexible thin films were characterized using scanning electron microscopy (SEM). The electrochromic characteristics of ECDs based on hybrids were comprehensively compared to those which are based on changing substituent groups, i.e., electron-acceptor (X: F) substituent and electron-donor (X: CH_3) substituent.

2. Experimental

2.1. Materials

WO_3 powder (Sigma Aldrich, 99.9%), Aniline (ANI, Sigma Aldrich), 2-fluoroaniline (FANI, Sigma Aldrich), *N*-methylaniline (MANI, Sigma Aldrich), lithium perchlorate ($LiClO_4$, Sigma-Aldrich), poly(methyl methacrylate) (PMMA, Sigma-Aldrich), propylene carbonate (PC, Sigma-Aldrich), acetonitrile (ACN, Sigma-Aldrich) were used as received. ITO-coated PET substrates (sheet resistance of 80–100 Ω/sq, 25 μm thickness) were purchased from Teknoma Company/Turkey and were cleaned with ethanol prior to use.

2.2. Preparation of WO_3/PANI, WO_3/PMANI, WO_3/PFANI hybrid powders

The reactor used for plasma coating is a capacitively coupled, 13.56 MHz radio-frequency (RF) rotating plasma installation (Fig. 1). Dry WO_3 powders were regularly spread into a cylindrical chamber. The vacuum pressure was achieved to drop 150 mTorr using a vacuum pump. The monomer vapors were sent into the rotating chamber, plasma is ignited and sustained for reaction time. The experimental parameters employed during the plasma treatment are as follows: RF-power, 40 W and deposition time, 2 h. The proposed mechanism of coordination of PANI or its substitute derivatives with WO_3 powders is shown in Fig. 2. Polyaniline (R_1, R_2: H), Poly(2-fluoroaniline) (R_1:F, R_2:H), Poly(*N*-methylaniline) (R_1:H, R_2:CH_3) were abbreviated as PANI, PFANI, PMANI, respectively.

2.3. Thin film deposition and construction of ECDs

Both WO_3 and hybrid films were deposited onto indium tin oxide (ITO) coated PET electrodes via the electron beam evaporation technique. The pelletized hybrid powders and WO_3 targets were used as evaporation material and were heated using an electron beam that was collimated from the dc heated cathode, a tungsten filament. The distance between the target area and the rotating panel substrate was 60 cm. The optimized experimental parameters used in this study are as follows: filament current, 33 A; voltage, 6 kV; base pressure, 7×10^{-6} Torr. The electrochromic film thicknesses onto PET film were controlled using Inficon SQM-160 model thin film deposition monitor during deposition. The QCM film thickness was calibrated with cross-sectional SEM images.

For flexible electrochromic device (ECD) fabrication, the gel electrolyte was prepared according to literature [11]. The ECD was built via arranging the ITO films coated with electrochromic film and the ITO films facing each other separated via a gel electrolyte. Active area of ECD was 3.5 cm^2.

2.4. Characterization

Gamry PCl4/300 model potentiostat was used for electrochemical studies. Electrochemical experiments were carried out using a conventional three-electrode cell, electrochromic film, a Pt wire and an Ag/AgCl with 3 M KCl were used as working, counter and reference electrodes, respectively. A computer-controlled setup of HR4000 (Ocean Optics, Dunedin, FL, USA) spectrophotometer was employed from 400 to 900 nm wavelength range for transmission measurements of solid-state devices. Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) and cross-sectional images were acquired using FEI Quanta FEG 250. X-ray diffraction (XRD) analyses were performed on Bruker D8 Advance diffractometer with CuKα radiation (λ: 1.54 Å). The diffraction data was recorded for 2θ angles between 10° and 90°. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range of 0.01 Hz–100 kHz, by use of an ac voltage amplitude of 10 mV and CHI760E electrochemical workstation.

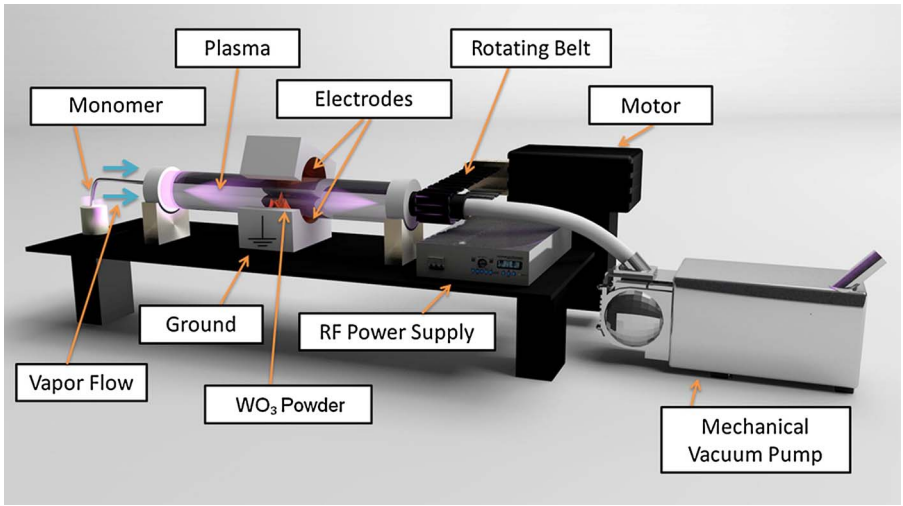

Fig. 1. A schematic diagram of RF Rotating Plasma.