

Next Generation Hybrid Nanofiber Based Electrochromic Devices

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Abstract

This study focuses on the electrochromic device (ECD) applications of poly(3,4-ethylenedioxythiophene)/tungsten oxide (PEDOT/WO₃) hybrid nanofibers prepared via electrospinning method. Nanoporous WO₃ films were initially electrosynthesized on Pt sheet. The PEDOT layer was electropolymerized onto the entire surface of the WO₃ nanoporous host framework in the presence of different ionic liquids: 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (BMIMTFSI), and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide (BMPTFSI). ECDs changed color reversibly from transparent to light brown by switching from +3 V to -3 V. It was found that the highest optical modulation of 47.89% and maximum coloration efficiency of 363.72 cm²/C is achieved for PEDOT/WO₃/BMIMPF₆ based electrochromic device. Hybrid nanofibers exhibited excellent long term stability even after 1000 chronoamperometric cycles.

Key words: tungsten oxide, PEDOT, ionic liquid, hybrid nanofiber , electrochromic device

1. Introduction

Electrochromic devices (ECDs) are of much current interest for a wide range of applications, including color displays, sensors, reflectance mirrors, vehicle sunroofs and smart windows [1,2]. WO₃ is perceived as a prospective candidate for ECDs since it has many advantages such as genuine color switching and good chemical stability and exhibits the most efficient electrochromic properties both in the visible and near infrared regimes [3]. These properties are substantially dependent on the crystal structure, which in turn affects the electronic properties of the ion injection/ejection during electrochemical reactions [4]. The crystal structure of WO₃ can be controlled by synthetic methods or deposition processes. Several methods can be used to fabricate WO₃ electrodes for EC applications, including sputtering [5], thermal evaporation [6], sol-gel coating [7], hydrothermal [8] electrochemical methods [9] and electrospinning [10]. In addition to bulk-type electrodes, nano-structured WO₃ has been increasingly investigated because its morphology provides a high surface area for electron and ion transport [11].

In a recent study, nanobrick-like WO₃ thin films have been synthesized via facile hydrothermal route. The WO₃ film comprised of nanobricks exhibit high crystallinity with large surface area that affects ion insertion kinetics leading to enhance EC performance [12]. In another study, tungsten oxide nanowires grown on the ITO-coated glass substrates were prepared successfully by the thermal evaporation process and an electrochromic device (ECD) was assembled using the tungsten oxide nanowires as the electrochromic layer. Nanowires of tungsten oxide was found to have larger transmittance change in visible light region and better electrochromic effect [13]. Electrochromic films with a stacked structure of two-dimensional crystalline tungsten trioxide

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(WO₃) nanosheets were fabricated on fluorine-doped tin oxide (FTO) coated glass by a layer-by-layer (LBL) technique. Unique electrochromic property and excellent long-term stability was observed during the injection/ejection process of the protons into/from the stacked structure [14]. From such inspiring results that the nanostructures could allow the faster injection/ejection processes with ions leading to improved optical modulations for the electrochromic applications, more efficient materials with an electrochromic active layer are extremely needed [15].

Hybrid materials based on organic conjugated polymers (CP) and inorganic nanostructures have been effectively studied in recent years to outperform the mere addition of the features of the components due to possible synergistic effect [16]. Intensive studies on electrochromic systems composed of WO₃ and conducting polymers have recently been performed, including hybrids of WO₃ NPs and PEDOT:PSS that have been prepared by LBL assembly. The coloration efficiency is remarkably improved to 117.7 cm²/C. With comparable thickness of each film, the optical contrast of the hybrid film (DT=20%) is significantly higher than that of WO₃-NP (DT=7.3%) and PEDOT:PSS (DT=9.6%) films [17]. The polyaniline/WO₃ nanocomposite films have been prepared by electrodeposition of PANI onto WO₃ coated ITO glass. Transmittance modulation of PANI/WO₃ hybrid film was found as 35.3% and coloration efficiency of 98.4 cm²C⁻¹ was obtained [18] whereas 59% optical modulation and coloration efficiency of 86.3 cm²C⁻¹ were achieved for the WO₃/PANI core/shell nanowire array prepared by the combination of solvothermal and electropolymerization methods [19]. Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most successful conducting polymers from a fundamental and practical point of view owing to its unique combination advantages of moderate band gap, low redox potential, high conductivity, optical transparency and stability [20].

It is known that as well as coating techniques and using different organic structures, hybrid materials synthesis media and electrolytes affect electrochromic properties in hybrid electrochromic devices. Significant results demonstrated that RTILs can be the superior solvents for the synthesis nanostructured materials because of their unique characteristics, such as the wide electrochemical window, high thermal and chemical stability and good ionic conductivity [21]. Electrochromic device of PEDOT/TiO₂ nanocomposite electrode synthesized in BMIMBF₄ was reported to have enhanced long-term stability [22]. Solid state devices of PEDOT/WO₃ and PPy/WO₃ composite films prepared in ionic liquids such as BMIMPF₆, BMIMTFSI and BMPTFSI as electrolyte media were found to have high chromatic contrast, reasonable switching time, high coloration efficiency and electrochromic properties changed depending on characteristic of ionic liquids [23,24].

As an important one dimensional nanomaterial, nanofibers have extremely high specific surface area because of their small diameters, and a porous structure with excellent pore-interconnectivity. These unique characteristics plus the functionalities from the materials themselves impart nanofibers with desirable properties for a range of advanced applications in areas as various as sensors, optics, photocatalysts, biomedical engineering, wound healing, drug delivery and release control, catalyst and enzyme carriers, filtration, environment protection, composite reinforcement, energy conversion and storage and many others [25].

As is well known, electrochromic performance mainly relies on the diffusion of ions in the electrochromic material. Ultrathin nanofibers with open 1D permeable channels could maximize the utilization ratio of the active materials and reduce diffusion paths of the ions significantly, resulting in faster color-switching speed and higher coloration efficiency. Moreover, the 1D configuration with large surface area allows for high interfacial contact area with the electrolyte

and intimate contact with the substrate facilitating fast interfacial charge transfer in devices. In a word, ultrathin 1D nanofibers could provide an ideal platform for fabricating electrochromic devices with enhanced performance [26].

In our attempts to synthesize hybrid nanofibers, electrochemical polymerization of PEDOT onto nanoporous WO_3 was made and subsequent electrospinning was performed. According to the best of our knowledge, there is no precedence in the literature for nanofibers of WO_3 with PEDOT prepared through electrochemical method in ionic liquid media and it is the first time that this novel and convenient strategy to fabricate hybrid nanofibers by electrospinning for the assembly of electrochromic devices is proposed. Our aim was to study the feasibility of electrochromic device applications of PEDOT/ WO_3 hybrid nanofibers. The electrochemical, electrochromic and morphological characterization of the hybrid nanofibers are presented in this contribution.

2. Materials and Method

2.1. Chemicals and Materials

All chemicals were from commercial sources and were of the highest purity available. Deionized water was used in all cases for making solutions. The monomer 3,4-ethylenedioxythiophene (EDOT) and ionic liquids BMIMBF₄, BMIMPF₆, BMIMTFSI and BMPTFSI were supplied from Sigma Aldrich. W nanopowder was procured from SkySpring Nanomaterials. The as-purchased poly(methyl methacrylate) (PMMA) (Alfa Aesar), propylenecarbonate (PC) (Sigma Aldrich), lithium perchlorate (LiClO₄) (Fluka) and acetonitrile (ACN) (Merck) were used as received. N-methylpyrrolidone (NMP) (Merck) was used to dissolve the PEDOT/ WO_3 hybrid film. Dimethylformamide (DMF) (Merck) was utilized as a solvent to prepare the electrospinning solution.

2.2. Preparation of WO_3 film

Electrodeposition solution were prepared by dissolving W powder in aqueous 30% H_2O_2 solution. After the exothermic reaction ended, the cathodic electrodeposition was performed at a fixed potential (-0.45 V vs. Ag/AgCl) for 6 h in a 30% ethanol and 70% water solution containing 50 mmol/l tungsten at room temperature. A typical three-electrode configuration was used with an platinum sheet with dimensions 1.5 × 2 cm as the working electrode, an Ag/AgCl/3M KCl reference electrode and a Pt wire as counter electrode.

2.3. Electrosynthesis of PEDOT/ WO_3 Hybrid

Electrochemical synthesis of PEDOT/ WO_3 hybrid was carried out potentiostatically in a three-electrode electrochemical cell with WO_3 coated Pt sheet as working electrode, Ag/AgCl/3M KCl reference electrode and a Pt wire as counter electrode. PEDOT was electropolymerized in 10 ml ionic liquid (BMIMBF₄, BMIMPF₆, BMIMTFSI and BMPTFSI) containing 1M EDOT monomer at a constant potential of 1.4V for 1 h.

2.4. Fabrication of PEDOT/ WO_3 /PMMA Composite Nanofibers

PMMA was selected as co-spinning polymer. PMMA was dissolved in DMF at a concentration of 7.3 % (w/w). To fabricate hybrid nanofibers, firstly the as-prepared PEDOT/ WO_3 hybrid was taken from Pt sheet electrode surface and dissolved in N-methylpyrrolidone (NMP) for 5 days to form a homogenous solution. Then, the solution was added into the PMMA/DMF solution to

yield the optimized volume ratio of 1:1 (PEDOT/WO₃-PMMA/DMF). The mixture was stirred for 2 h to form homogeneous solution for electrospinning. Briefly, 4 ml of resulting solution was loaded in a 4 ml syringe, equipped with a 21-gauge, stainless steel, a flat tip needle connected to a high-voltage supply (EMCO 4300) attached to a syringe pump (New Era Pump System Inc., USA) which provided a steady solution flow rate of 15 μ l/h during electrospinning. The hybrid solution was electrospun at room temperature at driving voltage of 15 kV. The electrospun nanofibers were collected onto ITO coated glasses which were horizontally placed 5 cm away from the spinneret.

2.5. Preparation of the gel electrolyte and electrochromic device assembly

The gel electrolyte was used as ion conducting layer between working and counter electrodes in electrochromic device. The electrolyte was prepared by using LiClO₄:ACN:PMMA:PC in the ratio of 3:70:7:20 by weight. As soon as the dissolution of LiClO₄ in acetonitrile (ACN), poly(methyl methacrylate) (PMMA) was plasticized by propylenecarbonate (PC) in order to form a highly transparent and conductive gel [27]. ECDs were built by arranging two ITO glasses (PEDOT/WO₃ nanofiber coated ITO and bare ITO) facing each other and separated by a gel electrolyte. To provide the ion exchange between two layers, ITOs were positioned so that the conducting sides faced each other. The electrochromic device had the resulting structure: ITO|WO₃/PEDOT nanofiber || ACN:PC:PMMA:LiClO₄ ||ITO.

2.6. Characterization Methodology

The morphologies of the WO₃/PEDOT nanofiber hybrid samples were studied using a Phillips XL-30S FEG model scanning electron microscope. All electrochemical measurements were performed on a Gamry 300 Model potentiostat instrument, in a classical one-compartment, three-electrode electrochemical cell. Cyclic voltammograms of the WO₃/PEDOT nanofiber hybrids synthesized in different ionic liquids were registered in 1 M LiClO₄-PC solution at a scan rate of 100 mVs⁻¹. Optical transmittance spectra of solid state devices were measured using a spectrophotometer (Ocean optics HR 4000, Mikropack Halogen Light Source HL-2000- FHSA in the 400–900 nm wavelength range).

3. Results

In order to acquire further information on the electrochemical activity of the hybrid materials, cyclic voltammograms were recorded in 1 M LiClO₄-PC. The cyclic voltammograms in Figure 1 below suggest that the WO₃/PEDOT nanofibers synthesized in different ionic liquids exhibit good electroactivity within the potential range studied. Cycling in this electrolyte is indeed advantageous, since both WO₃ and PEDOT are known as Li⁺ exchangers, thus showing a quasi-reversible electroactivity in this media. Figure 1(a-b-c-d) bear out the fact that both the WO₃ support and PEDOT exhibit well-defined and reversible electroactivity in the hybrid configuration. Although electrochemical behaviours are similar, the PEDOT/WO₃ nanofiber synthesized in BMIMPF₆ medium has the highest current values in cyclic voltammograms [28].

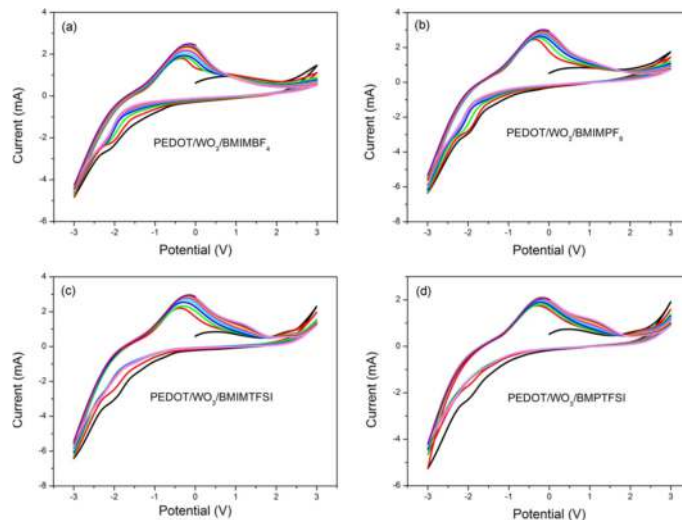


Figure 1. Cyclic voltammograms of (a) PEDOT/WO₃/BMIMBF₄ hybrid nanofibers, (b) PEDOT/WO₃/BMIMPF₆ hybrid nanofibers, (c) PEDOT/WO₃/BMIMTFSI hybrid nanofibers, (d) PEDOT/WO₃/BMPTFSI hybrid nanofibers in 1 M Li-PC during 10 cycles, respectively.

Electrochromic materials change their color when an electrical voltage is applied. It is well-known that the insertion–extraction cycle of protons and electrons accounts for the coloring–bleaching reactions. The change in redox state can be correlated quantitatively with changes in optical properties [29]. The transmittances of PEDOT/WO₃ hybrid nanofibers based ECDs were recorded at constant potentials of 0, +3V and -3V. The optical transmittances against the wavelength of BMIMBF₄, BMIMPF₆, BMIMTFSI and BMPTFSI based fibers are shown in Figs. 2(a-d), respectively. All the four fibers exhibited maximum transmittance differences (DT) between the bleached and colored states at wavelength of around 510 nm, which is defined as optical contrast. Optical contrasts of BMIMTFSI and BMPTFSI based fibers were determined as 33.71 and 18.57. However, BMIMBF₄ and BMIMPF₆ based fibers reached contrast values of 40.58 and 47.89, respectively. Electrochromic parameters of all nanofiber based devices are shown in Table 1.

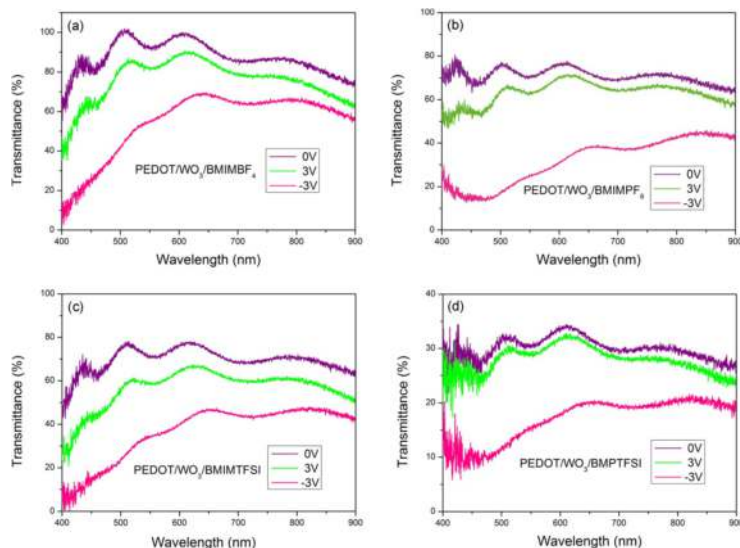


Figure 2. Visible transmittance spectra of (a) PEDOT/WO₃/BMIMBF₄ nanofiber based ECD, (b) PEDOT/WO₃/BMIMPF₆ nanofiber based ECD, (c) PEDOT/WO₃/BMIMTFSI nanofiber based ECD, (d) PEDOT/WO₃/BMPTFSI nanofiber based ECD for applied potentials of 0, +3 V -3V, respectively.

Table 1. Electrochromic parameters of all nanofiber-based devices

	T _{bleached} (%)	T _{colored} (%)	ΔT	ΔOD	$\eta(\text{cm}^2\text{C}^{-1})$	t _b (s)	t _c (s)
PEDOT/WO ₃ /BMIMBF ₄	85.54	44.96	40.58	0.279	322.08	2.5	4.2
PEDOT/WO ₃ /BMIMPF ₆	66.28	18.39	47.89	0.556	363.72	11.0	11.8
PEDOT/WO ₃ /BMIMTFSI	59.43	25.72	33.71	0.363	264.55	1.5	2.0
PEDOT/WO ₃ /BMPTFSI	30.52	11.95	18.57	0.407	169.58	3.6	11.6

It is vital to confirm that electrospinning of the polymer solutions resulted in fibrous formation, based on the selected processing parameters. Figure 3(a-d) illustrates the morphological characteristics of electrospun PEDOT/WO₃ nanofibers, which are long, continuously cylindrically shaped, and randomly distributed. The images demonstrate that bead-free fiber formation was achieved in BMIMPF₆ (Fig 3b), BMIMTFSI (Fig 3c) and BMPTFSI (Fig 3d) based fibers. In the SEM images of BMIMBF₄ based fibers shown in Figure 3a, one can observe that the fibers have a roughened surface with the noticeable presence of beads [30]. The resulting PEDOT/WO₃ based PMMA non-woven mats were analyzed (10–12 individual nanofiber diameters were measured) to calculate the average nanofiber diameter and standard deviation. The average diameters of PEDOT/WO₃/BMIMBF₄, PEDOT/WO₃/BMIMPF₆, PEDOT/WO₃/BMIMTFSI and PEDOT/WO₃/BMPTFSI nanofibers with standard deviations were 316.7± 234.2 nm, 348.9± 115.8 nm, 882.4± 343.5 nm and 681.3± 168.2 nm, respectively [31]. Electrochromic efficiency and optical modulation strongly depends on the amount of material synthesized; thinner and dense fibers decrease the probability of extinction of polarons due to the shorter diffusion pathlength [32]. This effect is evidenced by higher electrochromic efficiency and optical modulation as seen in BMIMBF₄ and BMIMPF₆ based fibers.

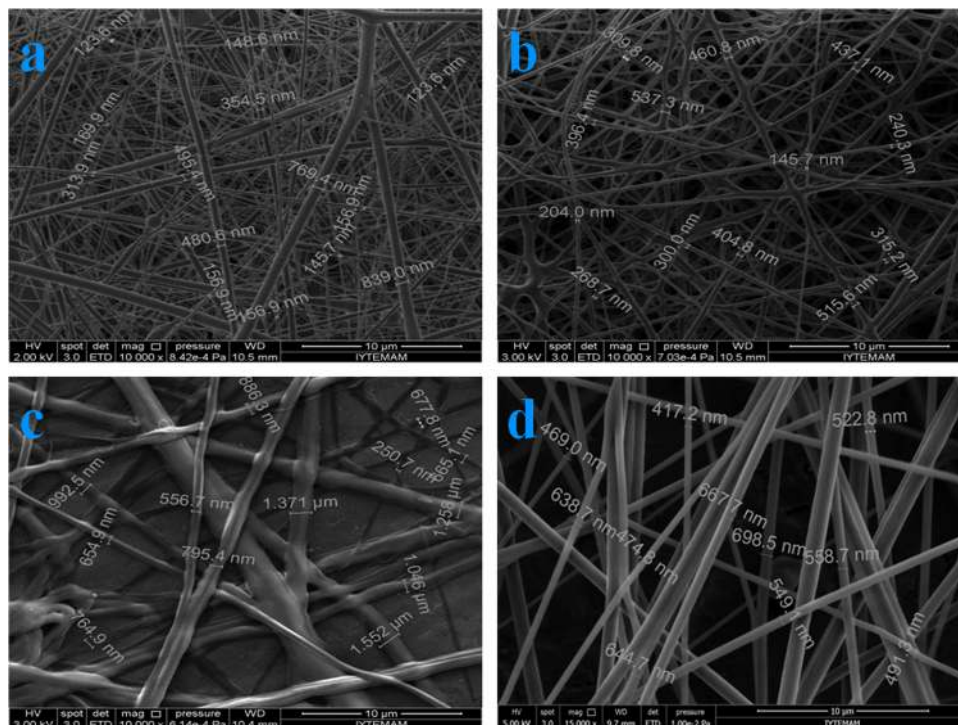


Figure 3. SEM micrographs of as electrospun hybrid nanofibers (a) PEDOT/WO₃/BMIMBF₄ (b) PEDOT/WO₃/BMIMPF₆ (c) PEDOT/WO₃/BMIMTFSI (d) PEDOT/WO₃/BMPTFSI.

Conclusions

In summary, we have demonstrated a facile strategy for producing PEDOT/WO₃ hybrid nanofibers prepared by electrochemical method and electrospinning. Development of the nanofibers was monitored by SEM, and evidence for incorporation of its components into hybrid structures was presented by EDX analysis. The nanofibers based ECDs showed reversible electrochemical processes and stable color changes when they were switched between the oxidized (transparent) and reduced (light brown) states. These device architectures, combined with the hybrid nanofibers used, afforded high optical modulations as well as exceptional long-term stability over 1000 cycles. These superior electrochromic performances can be ascribed to the synergetic effect between PEDOT and WO₃ and the morphological features of ultrathin nanofibers. The present results should open new perspectives for the application of hybrid nanofibers in electrochromic applications.

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