



Synergistic tungsten oxide/organic framework hybrid nanofibers for electrochromic device application



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ABSTRACT

We report the first successful applications of tungsten oxide/conducting polymer hybrid nanofiber assemblies in electrochromic devices. Poly(3,4-ethylenedioxythiophene)/tungsten oxide (PEDOT/WO₃) and polypyrrole/tungsten oxide (PPy/WO₃) composites were prepared by an *in situ* chemical oxidative polymerization of monomers in 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). Electrospinning process was used to form hybrid nanofibers from chemically synthesized nanostructures. The electrospun hybrid samples were compared from both morphological and electrochemical perspectives. Importantly, deposition of nanofibers from chemically synthesized hybrids can be achieved homogeneously, on nanoscale dimensions. The morphologies of these assemblies were evaluated by SEM, whereas their electroactivity was characterized by cyclic voltammetry. Electrochromic devices made from hybrid nanofiber electrodes exhibited highest chromatic contrast of 37.66% for PEDOT/WO₃/BMIMPF₆, 40.42% for PPy/WO₃/BMIMBF₄ and show a strong electrochromic color change from transparent to light brown. Furthermore, the nanofiber devices exhibit outstanding stability when color switching proceeds, which may ensure a versatile platform for color displays, rear-view mirrors and smart windows.

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1. Introduction

Electrochromism is described as the reversible color change of a material between the redox states induced by application of an electrical potential [1]. Electrochromic devices (ECDs) are able to control the throughput of visible light and solar radiation entering the buildings and provide energy efficiency by modulating optical transmittance. ECDs have many application areas such as smart windows of green buildings, full-angle information displays, controlled reflectance mirrors and thermal control of satellites [2]. Various chemical compounds have been investigated and developed for the ECDs, such as inorganic complexes [3], organic molecules [4], metallo-supramolecules [5], electroactive polymers [6] and metal oxides [7].

To date, Tungsten oxide (WO₃) has been regarded as one of the most promising “cathodic” oxide due to its prompt color change and large optical contrast as well as facile synthesis [8]. WO₃ is a thermally stable and water insoluble tungsten compound. WO₃ nanoparticles appear in the form of a yellow powder having a nearly spherical morphology. Its density is 7.16 g/cm³ and molar mass is 231.84 g/mol. WO₃ exhibits a cubic perovskite like structure based on the corner sharing of regular octahedra with the oxygen atoms at the corner and the tungsten atoms at the center of each octahedron. The crystal structure of WO₃ is temperature dependent. It is tetragonal at temperatures above 740 °C, orthorhombic from 330 to 740 °C, monoclinic from 17 to 330 °C and triclinic from –50 to 17 °C. Nanostructures, including nanowires, nanorods and nanosheets, have been proven to be effective for fabricating high-performance electrochromic (EC) films since this architecture can ensure fast ion/electron diffusion and large active surface area, giving rise to improved optical contrast and fast switching time. Electrophoretic deposition was applied in coating hydrothermally synthesized crystalline WO₃ nanorods for EC

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application by Lee et al. [9]. The WO₃ nanorods exhibited a fast switching time of 28.8/4.5 s for coloring/bleaching due to the porous nature of the oxide layer and high surface area. Hexagonal structured WO₃ films having tree-like morphology were obtained on tungsten foils by Zhang et al. [10]. Because of the large tunnels of hexagonal structure and rather porous surface morphology, a switching time of 12.8/8 s for coloring/bleaching and a coloration efficiency (CE) value of 43.6 cm²/C were achieved for thermal treated (400 °C/2 h) WO₃ nanotree. A hexagonal WO₃ nanowire array was attained utilizing a template-free hydrothermal method by adding ammonium sulfate as a capping agent [11]. A switching speed of 7.6/4.2 s for coloring/bleaching and a CE value of 102.8 cm²/C were acquired for the WO₃ nanowire array, which showed better EC performance than nanorods [9] and nanotrees [10]. The results above suggest that the enhanced EC performance of WO₃ nanostructure film stems from the large active surface area, wide tunnels in the hexagonal WO₃ and good contact between the film and the substrate [12].

Hybrid films based on tungsten oxide and conducting polymers have gained considerable attention, since desirable electrochromic characteristics such as high optical modulation, rapid response time and excellent stability can be readily achieved [13]. Nanostructured hybrid thin films of the system tungsten oxide-poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (WO₃-PEDOT:PSS) were synthesized by first forming a tungsten-oxide layer by surfactant-assisted electrochemical method, followed by deposition of a PEDOT:PSS layer. The hybrid film, being a dual electrochrome, exhibits a much larger CE (227 cm²/C at 600 nm), a higher redox activity (larger currents for ion ingress and egress are obtained within the same potential range), and most importantly, a superior electrochemical cycling stability when compared to the neat polymer film [14]. Molecular assembling route was used to synthesize nanostructured polyaniline (PANI)/WO₃ hybrid thin films in a solution of aniline utilizing peroxotungstic acid (PTA) as the dopant and ammonium persulfate as the oxidant. PANI/WO₃ hybrid films exhibited higher coloration efficiency and better durability compared to sulfate doped PANI film. The improved electrochromic characteristics such as faster switching rate and outperforming durability are ascribed to the assembling of advantages of both materials and the occurrence of the donor-acceptor system [15].

In this contribution, we report on the synthesis of tungsten oxide/conducting polymer hybrids and characterization of electrochromic devices made with nanofibers of these structures. Our fabrication method involves chemical oxidative polymerization of EDOT(Pyrrole) with WO₃ nanoparticles in different ionic liquids media for subsequent electrospinning of these hybrid materials. Moreover, our study goes one step beyond electrospinning as well, since nanofiber production from chemically synthesized tungsten oxide hybrids and their application in electrochromic devices have not been indicated heretofore to the best of our knowledge.

2. Experimental section

2.1. Synthesis of PEDOT/WO₃ and PPY/WO₃ hybrids

2.1 g of WO₃ powder was dispersed in 5 mL ionic liquid, then 300 μL EDOT (or 420 μL Py) was added and the solution was stirred for 20 min. 1 M iron (III) chloride was dissolved in 5 mL ionic liquid, this solution was added dropwise to the monomer containing solution so polymerization process was performed. After stirring for 4 h, a black dispersion formed owing to the polymerization of

monomer. Eventually, the product was filtered, washed with methanol several times until clear solution was obtained and dried at 80 °C for 24 h.

2.2. Fabrication of PEDOT/WO₃/PMMA and PPY/WO₃/PMMA nanofibers

Chemically synthesized PEDOT(PPy)/WO₃ hybrid (0.25 g) was dissolved in N-methylpyrrolidone (NMP) (5 mL) for 7 days for obtaining a homogenous solution. Electrospinning solution was prepared by mixing 2 mL of the above solution and 2 mL polymer carrier solution, in which the latter was prepared by dissolving PMMA in DMF at a concentration of 7.3% (w/w) under continuous stirring for 2 days. The aforementioned mixture solution was immediately loaded into a plastic syringe equipped with a 21-gauge flat tip needle made of stainless steel. The needle was connected to a high-voltage supply (EMCO 4300) that is capable of generating DC potentials up to 30 kV. A syringe pump was utilized to control the feeding rate of electrospinning solution (New Era Pump System Inc., USA). Electrospinning was performed at 15 μl/h feeding rate and driving voltage of 15 kV. The distance between the spinneret and ITO coated glasses was 5 cm which was optimized for collecting nanofibers.

2.3. Assembly of electrochromic devices

The gel electrolyte to be used for attaching the layers of electrochromic devices was prepared by utilizing LiClO₄:ACN:PMMA:PC in the weight ratio of 3:70:7:20. The electrochromic device had the following structure: ITO || WO₃/PEDOT (PPy) nanofiber || ACN:PC:PMMA:LiClO₄ || ITO. A detailed schematic fabrication of the ECDs is shown in Scheme 1.

2.4. Materials characterization

Surface morphology of all films were probed by Scanning Electron Microscopy. The electrochemical characteristics of all films were studied using a standard three electrode system, which consists of counter (Pt), reference (Ag/AgCl) and working thin film of PEDOT(PPy)/WO₃ nanofiber grown on ITO coated glass substrate electrodes. A solution of lithium perchlorate (LiClO₄)/propylene carbonate (PC) (1 M) acted as the electrolyte during all measurements. Cyclic voltammetry tests (CV) were carried out in the potential region -3.0 to +3.0 V versus Ag/AgCl, using 100 mV/s scanning rate. Besides, chronoamperometry at +3.0 V and -3.0 V for a step of 1 s and a total time period of 2000 s was performed to determine the long term stability of devices. All electrochemical measurements were performed using a Gamry 300 Model potentiostat. Finally, a spectrophotometer (Ocean optics HR 4000, Mikropack Halogen Light Source HL-2000-FHSA in the wavelength range of 450–900 nm) was used to obtain the optical transmittance spectra of solid-state devices.

3. Results and discussion

Prepared electrochromic devices indicate different transmittance behavior according to the DC voltage applied. The visible transmittance spectra of the various PEDOT/WO₃ and PPY/WO₃ nanofibers under 0, +3.0 and -3.0 V were recorded in Fig. 1 and Fig. 2, respectively. The highest contrast value (optical contrast) at a specific wavelength λ can be expressed as ΔT% (λ) = T_{max} (%) - T_{min} (%) and it is exhibited by the 37.66% at PEDOT/WO₃/BMIMPF₆

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