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Electrochromic strategy for tungsten oxide/polypyrrole hybrid nanofiber materials

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ABSTRACT

High-quality hybrid nanofibers were fabricated with the aim of studying their feasibility as electrochromic systems. Tungsten oxide/polypyrrole films were electrochemically synthesized into four different ionic liquids: 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$), 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (BMIMTFSI), and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide (BMPTFSI), followed by electrospinning deposition. The influence of ionic liquid on the morphology of formed hybrid nanofiber samples was observed by scanning electron microscopy (SEM) measurements. Energy dispersive X-ray spectroscopy (EDX) was also employed to confirm the compositions of nanofibers. Electrochromic devices fashioned from these hybrid nanofiber arrays were found to display remarkable electrochromic performance with reversible color change, fast optical modulation and superior cycling stability. These improvements can be attributed to the high porosity of the nanofibers, their larger accessible surface area and rational combination of two electrochemically active materials. $PPy/WO_3/BMIMPF_6$ based device showed marked enhancement of electrochromic contrast and coloration efficiency over other nanofiber based devices: the transmittance change of 47.41% along coloration efficiency of 329.45 cm^2/C. These synergistic organic-inorganic nanostructures pave the way for forming new materials to be used in advanced applications.

1. Introduction

Nowadays, owing to increase in world population, growing energy demand is inevitable so researchers are trying to find innovations for decreasing energy consumption and manufacturing eco-friendly energy [1–3]. Electrochromic (EC) technology in production of "smart windows" for green buildings stands for the new frontier of advanced glazing research and it deserves the primary position among the emerging technologies since sunlight flux into the building is actively controlled for energy saving [4,5].

Tungsten trioxide (WO_3) is a widely investigated electrochromic, based on its fast switching speed between coloring and bleaching states, as well as on the long and stable reliability of its electrochromic response [6]. With the progress of nanotechnology, substantial effort has been recently dedicated to one-dimensional (1D) tungsten oxide nanomaterials (WONMs), which demonstrate enhanced EC properties due to their large surface-to-volume ratio, open structures and short diffusion length of ions. So far, a series of 1D tungsten oxide nanostructures as electrochromic materials have been prepared, such as WO_3 nanowires/nanorods [7,8], WO_3 nanowire arrays [9], WO_3 nanoplates [10], WO_3 nanofibers [11], $W_{18}O_{49}$ nanobundles [12], $W_{18}O_{49}$ nanoflowers [13].

Combination of inorganic nanomaterials with polymers has attracted enormous interest for the improvement of new-generation electrochromic materials. These unique nanostructures show outstanding electrochemical activity and long-term stability, which can be useful as promising electrode material for a wide range of application areas such as building, automobile and communication industries [14,15]. Researchers studying with EC materials have been put forth more effort on electrochromic systems based on WO_3 and organic conducting polymers. PPy/WO_3 hybrid film was prepared electrodepositing WO_3 on ITO, followed by coating of a polypyrrole (PPy) layer by using chemical bath deposition (CBD) technique. Excellent cycling stability and improved electrochromic performance were

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observed for WO_3/PPy composite [16]. Hybrid film composed of WO_3 and poly (3,4-ethylenedioxythiophene):polystyrene sulphonate (WO_3–PEDOT:PSS) was prepared by one-step inkjet printing technique. The WO_3 nanoparticles were synthesized from crystalline WO_3 powder by a wet ball milling process. The inkjet-printed WO_3–PEDOT:PSS thin films showed improvements in electrochromic properties over WO_3 films: the transmittance change of 20% at 550 nm along with the coloration/bleaching response time of 5.67/0.30 s and the coloration efficiency of 27.86 cm^2/C [17]. Ultra-thin WO_3 nanorods (NRs) embedded polyaniline (PANI) hybrid thin films were generated by surface-initiated-polymerization method, followed by spin-coating deposition. The switching response (0.9 s) and stability of the hybrid film were improved by enforcing of nanofillers when compared with the neat WO_3 NRs (5 s) film [18]. Polypyrrole (PPy) is very attracting owing to its high electrical conductivity, easy synthetic procedure, superior stability and environmental friendliness therefore it has been used in chemical sensor, photovoltaic cell and electrochromic device industries [19].

Electrospinning is a versatile and efficient fabrication method for 1D nanostructured fibers of polymers, metal oxides, composites and so forth [20]. The resulting nanofibers (NFs) with controllable diameters ranging from nanometer to micrometer scale possess unique properties [21]. Particularly, compared to 1D materials synthesized with other methods, the NFs prepared by electrospinning have larger specific surface areas, higher aspect ratio, and better pore interconnectivity making them an attractive choice for a host of advanced applications [22].

In electrochromic devices (ECDs), intercalation and deintercalation of electrons and transportation of counterions take place simultaneously under an applied electric field. The transport of electrons and ions is directly related to EC properties [23]. Nanofibers, as one dimensional nanomaterials, have been examined in order to improve the EC modulation and switching speed [24]. Oxidation state changes by ion intercalation in very thin surfaces of EC materials as well as switching speed is under the control of transport of ions. So, high surface area is important for materials to improve the EC modulation and switching speed [25].

In the present work, we report our strategy for building up electrochromic hybrid nanofibers of tungsten oxide/polypyrrole synthesized by electrochemical method in different ionic liquid media and deposited via electrospinning onto a transparent conductor substrate (ITO). Ionic liquids, on account of their good thermal stability, high conductivity and wide electrochemical window, have been proven to be potential media for electrochemical synthesis of electrochromic materials [26]. To our best knowledge, the preparation of electrochromic films by assembling electrochemically synthesized PPy/WO_3 hybrid nanofibers and realization of its electrochromic performance have not been verified to date. In this work, a straightforward process is developed to synthesize high-quality PPy/WO_3 nanofibers for electrochromic device applications. Besides, hybrid nanofibers are compared from electrochemical, electrochromic and morphological perspectives.

2. Experimental section

2.1. Materials

All chemicals used in this research were commercial products and used as received without further purification. Ionic liquids $BMIMBF_4$, $BMIMPF_6$, BMIMTFSI, BMPTFSI and the monomer Pyrrole (Py) were purchased from Sigma Aldrich. W nanopowder was supplied from SkySpring Nanomaterials. Poly(methyl methacrylate) (PMMA) (Alfa Aesar, Mw: 550.000 g/mol), propylenecarbonate (PC) (Sigma Aldrich), lithium perchlorate ($LiClO_4$) (Fluka) and acetonitrile (ACN) (Merck) were used for transparent gel electrolyte preparation. N-methylpyrrolidone (NMP) (Merck) was used to dissolve the PPy/WO_3 hybrid film. Dimethylformamide (DMF) (Merck) was used as a carrier solvent for electrospinning process.

2.2. Electrodeposition of PPy/WO_3 hybrid film

WO_3 film was synthesized starting from tungsten powder according to the literature method [27]. Hydrogen peroxide was used for oxidation of tungsten powder. This reaction provided the formation of peroxotungstic acid ($WO_3{\cdot}H_2O$) which then converted into WO_3 film through electrodeposition. Typical three-electrode system was used including a platinum sheet with dimensions 1.5 × 2 cm, an Ag/AgCl/3M KCl and a Pt wire, serving as the working electrode, reference electrode and counter electrode, respectively. The WO_3-deposited platinum was subsequently used as working electrode in a solution containing 1 M Pyrrole and 10 mL ionic liquid. Ionic liquid is used for both growth medium and supporting electrolyte in electrochemical polymerization. 1 M of pyrrole (67.09 g/mol) and 10 mL of ionic liquid was the solution for electrochemical polymerization. 1.3 V potential was used for 1 h in controlled potential coulometry for electrosynthesis of pyrrole on WO_3.

2.3. Fabrication of PPy/WO_3/PMMA hybrid nanofibers

As-prepared PPy/WO_3 hybrid which was coated on Pt sheet electrode was dissolved in N-methylpyrrolidone (NMP) for 5 days to attain homogeneity. 2 mL of PPy/WO_3/NMP solution was mixed with 2 mL of PMMA/DMF solution which has a concentration of 7.3% (w/w) under continuous stirring for 2 days. A plastic syringe equipped with a 21-gauge flat tip needle was used for loading this solution. A high-voltage supply (EMCO 4300) was in connection with the needle. Feeding rate of electrospinning solution was controlled by a syringe pump (New Era Pump System Inc., USA). 15 μl/h feeding rate, 15 kV driving voltage and 5 cm distance between spinneret and ITO were selected as optimized electrospinning parameters.

2.4. Gel electrolyte preparation and assembly of electrochromic devices

$LiClO_4$:ACN:PMMA:PC mixture in the weight ratio of 3:70:7:20 was used for preparation of transparent gel electrolyte. The ECD cell was assembled with nanofiber coated ITO electrode and bare ITO electrode separated by the gel electrolyte. The structure of device can be represented as ITO/WO_3/PPy nanofiber//gel electrolyte//ITO.

2.5. Characterization setup

The surface and cross-section morphologies of the hybrid nanofibers were registered by a SEM-EVO LS10 ZEISS model scanning electron microscope. The cyclic voltammetry experiments were conducted on a Gamry 300 Model electrochemical workstation. Standard three-electrode configuration was used, with a WO_3/PPy nanofiber layer on ITO glass as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. 1 M $LiClO_4$ dissolved in PC was used as electrolyte for electrochemical measurements. Measurements were fulfilled between + 3V and − 3V at a scanning rate of 100 mV/s. Optical properties of the hybrid electrochromic devices were determined by a spectrophotometer (Ocean optics HR 4000, Mikropack Halogen Light Source HL-2000-FHSA in the 450–900 nm wavelength range).

3. Results and discussion

3.1. Materials morphology

SEM images of electrospun nanofibers from PPy/WO_3 solutions produced with different ionic liquids and PMMA co-spinning polymer are shown in Fig. 1.

Electrochromic nanofibers having different diameters,