



Research Paper

Bi-functional flexible electrodes based on tungsten trioxide/zinc oxide nanocomposites for electrochromic and energy storage applications



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ABSTRACT

In this paper, the tungsten trioxide/zinc oxide (WO₃/ZnO) nanocomposites were formed on flexible substrates by combining facile hydrothermal process and pulsed laser deposition (PLD) method. As bi-functional electrodes, the WO₃/ZnO nanocomposites possess large specific surface area and a great number of micro channels, significantly increasing the area of WO₃ active layer and facilitating the diffusion of Li⁺ ions during the electrochemical process. Compared with dense WO₃ film, WO₃/ZnO nanocomposites exhibit enhanced electrochromic and capacitive performance of wider optical contrast (68.2%), greater coloration efficiency (80.6 cm²C⁻¹) and higher areal capacitance (15.24 mF cm⁻²). Furthermore, based on the WO₃/ZnO nanocomposites structure, a novel flexible electrochromic-supercapacitor was demonstrated, which functions as a smart energy storage device able to visually monitor the level of stored energy by rapid and reversible color variation. The results present great potential of WO₃/ZnO nanocomposites for electrochromic and energy storage applications.

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1. Introduction

With rapid depletion of fossil fuels and increasing pollution of the environment, energy-saving and emission-reduction have become an inevitable tendency around the world [1,2]. Smart windows based on electrochromic (EC) materials, which are able to reversibly change their optical properties (reflectance, transmittance and absorbance) to control the indoor sunlight and solar heat, can effectively reduce the heating or cooling loads of building interiors [1,3,4]. The optical modulation of electrochromic materials can be realized by the insertion/extraction of ions and electrons under applied electric field [5,6]. Meanwhile, supercapacitors, a form of electrochemical energy storage device with high power density, rapid charging/discharging rate and long cycle life have attracted numerous attention recently [2,7–9]. Pseudocapacitor, using reversible redox reactions to store energy, delivers higher capacitance than electrochemical double layer capacitor (EDLC) which is charged/discharged by adsorption/desorption of ions [8,10,11]. Furthermore, when a reversible redox reaction occurs with charge transfer in pseudocapacitor, some particular

electrode materials will simultaneously undergo electrochromic processes [12]. Thus, it would be interesting to integrate energy-storage and electrochromism functionality into one electrode for various applications [13–16]. Such electrode can be used not only for smart windows, but also for supercapacitors in which energy storage stage could be visually monitored by accompanied color change [14].

In order to achieve the mentioned bi-functionality, conductive layer and active material are two key factors. First, transparent conductive substrates should be utilized to replace conventional nickel foam or carbon cloth as current collector [15]. Then, various transition metal-oxides, such as WO₃, V₂O₅, TiO₂ and NiO, have been widely investigated as either supercapacitive or electrochromic electrodes [7,8,16]. Among these materials, tungsten trioxide (WO₃) exhibits superior electrochromic performance and its capacitive process is typically accompanied by obvious color variations [16–19]. Since the reversible redox reactions occur at or near the surface of active materials, nanostructured WO₃ exhibiting high specific surface area is usually desired for both electrochromism and supercapacitors [2,20].

In our previous study, we have systematically investigated the growth process and mechanisms of ZnO nanowires, and furthermore, we have successfully prepared TiO₂ nanotubes as photoanodes for dye-sensitized solar cells (DSCs) using the ZnO

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nanowires as template [21–24]. The vertically well-aligned ZnO nanowires with few grain and particle boundaries provide many direct pathways for fast electron transport along their axes [25,26], making porous ZnO nanowires a suitable template for loading WO_3 nanoparticles. WO_3 would also exhibit nanostructures under the guidance of ZnO nanowires, increasing active sites for redox reactions and reducing diffusion paths of the ions [27]. To the best of our knowledge, there have been no reports on the use of WO_3/ZnO nanocomposites on flexible substrates for electrochromic-supercapacitor applications yet.

Herein, we report a novel flexible bi-functional electrode based on the WO_3/ZnO nanocomposites. Benefit from the distinct porous structures, the WO_3/ZnO nanocomposites display enhanced electrochemical properties of wider optical contrast, greater coloration efficiency and higher areal capacitance compared with dense WO_3 film. Furthermore, bridging electrochromic behaviors with energy storage is achieved. We demonstrated a smart electrochromic-supercapacitor electrode, in which the level of stored energy can be constantly and visually monitored by color changes during capacitive process.

2. Experimental

2.1. Preparation of Al-doped ZnO (AZO) layer and synthesis of ZnO nanowires

Polyethylene terephthalate (PET) was employed as flexible substrate and cleaned by acetone, ethanol and deionized water in sequence. Then transparent conducting Al-doped ZnO (AZO, 3 at% Al) layer was deposited on PET by RF magnetron sputtering at room temperature for 2 h.

Afterwards, ZnO nanowire arrays were grown via the polyethyleneimine (PEI)-assisted hydrothermal method (PAHT), as reported previously [22]. The PET substrate with sputtered AZO layer was transferred into a growth solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.05 M), hexamethylenetetramine (0.05 M) and PEI (0.007 M, branched, Sigma Aldrich), which was maintained at 90 °C for 4 h to obtain ZnO nanowires.

2.2. Deposition of WO_3

WO_3 was deposited on PET/AZO/ZnO nanowires by pulsed laser deposition (PLD) in 10 Pa O_2 pressure at room temperature for 2 h. Here, the WO_3 thin film directly deposited on the PET/AZO was used as reference. The schematic diagram of the formation process of WO_3/ZnO nanocomposites is shown in Fig. 1.

2.3. Characterizations

The crystal structures of the samples were characterized by a high resolution Bruker D8 Discover X-ray diffractometer equipped with $\text{Cu } K_{\alpha 1}$ radiation ($\lambda = 1.5406 \text{ \AA}$). The morphologies and chemical compositions were investigated using a field emission scanning electron microscope (FESEM, Hitachi S-4800) attached with an Energy-Dispersive Spectrometer (EDS). The sheet resistance of AZO was measured by a ST-2258A multifunction digital four-probe tester. Electrochemical properties of the

products were measured by a CHI660B electrochemical workstation in a conventional three-electrode cell. The WO_3/ZnO nanocomposites and WO_3 film fabricated on PET/AZO were served as the working electrodes, respectively. Pt plate was acted as counter electrode, Ag/AgCl was the reference electrode and the electrolyte solution was 1.0 M LiClO_4/PC . The optical properties of the flexible electrochromic-supercapacitor electrode were recorded using a Persee TU-1901 UV-Vis-NIR spectrophotometer.

3. Results and discussion

3.1. Microstructural Characteristics

Fig. 2(a) displays the X-ray diffraction (XRD) patterns of as-sputtered AZO film and ZnO nanowires on PET/AZO. The unique sharp (0002) peak of AZO indicates its high crystalline quality and well preferred growth direction, providing good guidance for the growth of ZnO nanowires. The sheet resistance of the sputtered AZO is $\sim 30 \Omega/\square$. The (0002) peak of ZnO nanowires at 34.42° can be indexed to the hexagonal phase of ZnO (JCPDS No. 36-1451) with corresponding lattice constants of $a = 3.25 \text{ \AA}$ and $c = 5.21 \text{ \AA}$. The absence of any other peaks of ZnO confirms that the nanowires are well orientated along c axis perpendicular to substrates. The EDS spectra of AZO film and ZnO nanowires are shown in Fig. 2(b) and (c), respectively. The quantified contents of Zn, Al and O are approximately 44.65 at. %, 1.43 at. % and 53.92 at. % for AZO thin film which are similar to those of the stoichiometric AZO target. Besides, the XRD patterns of final WO_3 film and WO_3/ZnO nanocomposites (depicted in Fig. S1(a)) show no phase structure of WO_3 , declaring that WO_3 deposited at room temperature exhibits amorphous structure. The EDS spectrum of the WO_3 layer is illustrated in Fig. S1(b), where atomic ratio of O to W is approximately 3.

Fig. 3(a)–(c) present the morphologies of WO_3 film, as-grown ZnO nanowires and final WO_3/ZnO nanocomposites, respectively. The pure WO_3 film exhibits a smooth and compact morphology with several irregular cracks on the surface (from Fig. 3(a)). It can be seen from Fig. 3(b) that the uniform ZnO nanowires with average diameter of $\sim 135 \text{ nm}$ are grown vertically from the substrate, which is consistent with the XRD results. Different from the featureless plane morphology of WO_3 film, a rough surface morphology is observed in the WO_3/ZnO nanocomposites from Fig. 3(c). The diameter of the nanocomposites increases to $\sim 190 \text{ nm}$ (estimated from Fig. 3(d)) due to the adhesion of WO_3 on the surface of ZnO nanowires. Therefore, WO_3/ZnO exhibits a nanorod-like composite structure (Fig. 3(d)) with the inner part of ZnO nanowires and the outer part of WO_3 layer instead of forming an integrated film. A plausible formation mechanism of the nanocomposites can be described as follows: the as-grown ZnO nanowires act as a porous template during the deposition, leading to the preferential growth of WO_3 along the nanowires. Due to the constant deposition, WO_3 gradually covers the nanowires to form final porous composite structures [28,29]. Fig. S2 shows the cross-sectional SEM images for AZO film, WO_3 film and WO_3/ZnO nanocomposites. The thicknesses of AZO, WO_3 and WO_3/ZnO nanocomposites are approximately 500 nm, 330 nm and 800 nm. The nanocomposites with a quite rough morphology markedly

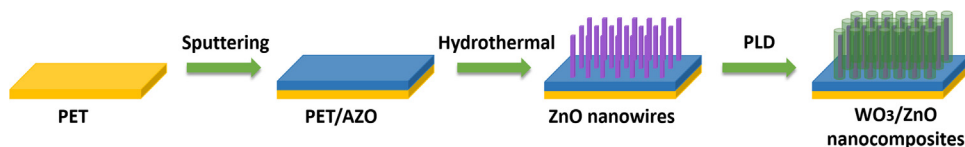


Fig. 1. Schematic diagram of the formation process of WO_3/ZnO nanocomposites.

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