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Improved electrochromic performance of WO_3 films with size controlled nanorods

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ABSTRACT

Electrochromic WO_3 films with size controlled nanorods were successfully fabricated by a wet chemistry method. The structure and electrochromic properties of tungsten oxide nanorods and films were studied by High resolution transmission electron microscope, Scanning electron microscope, X-ray photoelectron spectroscopy, X-ray diffraction, and electrochemical methods. The average length and diameter of the monodispersed tungsten oxide nanorods increase from 38 × 3.2 nm to 89 × 4.5 nm with help from surfactants. The results show that the electrochromic response time of WO_3 nanorod films are strongly dependent on the size of the nanorods. By simply changing the size of the nanorods, the response time of the nanorod films can be regulated nearly by about five times. The electrochemical impedance spectroscopy study showed that such trend can be attributed to the size effect of WO_3 nanorods upon the dynamics of H ions diffusion. At the same time, all the nanorod films showed good electrochemical stability as there were no significant performance declines after 1000 cycles. The electrochromic modulations of transmittance at 633 nm were around 22%–49%. The above stated results demonstrate that, by controlling the size of WO_3 nanorods, the electrochromic properties can be easily adjusted, especially the response time, indicating potential values for different response time required at different occasions.

1. Introduction

The optical properties of Electrochromic (EC) materials (darken/lighten) can be reversibly changed by applying small electric voltage, which are highly suitable for applications such as smart windows, antiglare automobile rear-view mirrors and displays [1–3]. In recent years, it is also recognized as an effective energy saving technology because electrochromic glazing can dynamically control the in or out radiation heat transfer, even better than low-emissivity glazing [4–6]. Despite lots of efforts have been carried out to study electrochromic materials including organic and inorganic ones, tungsten trioxide (WO_3) is still recognized as one of the most promising candidates due to its high color contrast and low-cost [7–10].

To evaluate an EC material, there are four important parameters that are contrast modulation, coloration efficiency, durability and response time. Response time or switching time, which is the time that the coloration/bleaching process takes to react to the electric field applied on electrochromic materials, is a very important parameter and application dependent, with display devices require low response times, while smart windows can tolerate response time of up to several minutes [11–14]. Many efforts have been made to shorten the response time in the previous few years. Forming a distinctive structure is turned out to be an effective strategy to achieve a fast response, for example, double-layer structure or porous structure. Because these structures may increase the reaction surface area and ion-insertion kinetics [13,14]. Zhang and coworkers reported a periodical bowl-like macro porous WO_3 array film electrodeposited on ITO glass using self-assembled monolayer polystyrene spheres as the template, with the response time of 3.6 s (coloration) and 1.0s (bleaching) [15]. Giannuzzi and coworkers reported a tree-like WO_3 films with exceptionally short coloration time (<1 s at an applied voltage of 1.3 V) [16]. In some other reports, doping or compositing was also used to shorten response time by improving the conductivity of electrochromic films [17,18]. However, the above mentioned works are either involving a complex experimental process or deteriorating the durability and coloration

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efficiency [17,19]. Moreover, the researchers only focused on reducing the response time instead of regulating it.

With the progress of material synthesis technology, the nanostructure is found to be an excellent approach to improve the electrochromic performance such as coloration efficiency and stability against electrochemical cycling [20]. Nanoparticle materials are usually desired, aiming at modulation of electrolyte accessibility and ion diffusion length, which makes it possible to regulate the electrochemical process in a certain extent [21]. As nanostructure will create a multifold and high surface or interface area, the optical contrast may also be affected [22]. The feature of nanocrystal is greatly affected by its size. Various kinds of nanostructured WO_3 electrochromic films such as nanoclusters, nanotrees, nanowires, nanoplates or hydrothermal nanorods have been investigated [8,22–24]. They were prepared by hydrothermal or template-free solvothermal method. However all these nanoshaping WO_3 are not monodispersed size controllable and the studies on the size effects of the nanoparticles upon the response time are still insufficient. As a typical one-dimensional nanostructure, nanorods have attracted great interest for dimensionality and size which may bring novel and excellent properties [24]. Synthesis of monodispersed WO_3 nanorods has been proven to be feasible with colloidal approaches [36,37]. Though tungsten oxide nanorods have been studied or applied in electrochromic application [11], the size effects of the nanorods have not been studied yet.

In the present work, monodispersed WO_3 films with size controlled nanorods were fabricated by colloidal approach and their electrochromic properties have been investigated. By introducing 1-octodecene (ODE) as surfactant, the controllable size of the monodispersed nanorods ranges from 38 × 3.2 nm to 89 × 4.5 nm with the decreasing molar ratio between oleyamine and ODE. The results demonstrate that the electrochromic response time of WO_3 nanorod films strongly depends on the size of the nanorods, that is minimizing the size of the WO_3 nanorods results in faster response time and vice versa. The response time of the nanorods can be regulated about five times by controlling accurately the size of the nanorods. And the electrochromic films also exhibit good reversible and cyclic stability.

2. Experiments

2.1. Preparation of colloidal tungsten oxide nanorods

0.7 g tungsten hexacarbonyl and 1.33 g trimethylamine N-oxide were dissolved in 10 mL oleyamine (OLa) in a flask. The temperature of the reaction mixture was gradually increased to 270 °C and kept for 24 h under nitrogen atmosphere. When cooled to room temperature, toluene and ethyl alcohol were added in order to wash the product out. The resultant colloidal nanorods were well dispersed in 10 mL hexane. By changing the content of OLa from 10 mL to 9 mL, 8 mL and 7 mL with some 1-octadecene (ODE) added while the total volume was kept as 10 mL, tungsten oxide nanorods with various sizes were synthesized.

2.2. Preparation of electrochromic WO_3 films

Commercial untreated ITO substrates (3 cm × 3 cm) were ultrasonically cleaned by detergent and ethanol each for 30 min in sequence and dried in an oven at 80 °C. The WO_3 nanorods dispersed in hexane were deposited onto ITO substrates with spin coating method and the films were annealed at 400 °C for 1 h in air. The film samples fabricated from the nanorods with the OLa content of 10 mL, 9 mL, 8 mL and 7 mL were labeled as S1, S2, S3 and S4 respectively.

2.3. Characterization

The as-prepared tungsten oxide nanorods were characterized by X-Ray diffraction (XRD, Empyrean 200895, PANalytical B·V with Cu Kα radiation). For structural and morphology features of the films transmission electron microscope (TEM) Tecnai F20 from FEI at an accelerating voltage of 200 keV and scanning electron microscopy (SEM, S-4800 Hitachi) were used. The X-ray photoelectron spectroscopy measurement (XPS, KRATOS, AXIS, ULTRADLD) was used to characterize the valence state of W atoms. The electrochromic performance was *in-situ* characterized by UV–Vis–NIR spectrophotometer (Cary 5000, Agilent) and CHI 660 E (Shanghai Chenhua) electrochemical workstation. A three-compartment system containing 0.5 M H_2SO_4 as electrolyte, Pt foil as the counter electrode and Ag/AgCl as a reference electrode was employed for the electrochromic characterization. Electrochemical impedance spectroscopy, Chronoamperometry, Chronocoulometry and cyclic voltammetry were conducted to analysis the electrochromic and electrochemical properties of the films. The electrochemical impedance spectroscopy (EIS) experiments were conducted at open-circuited potential in the frequency range of 1 Hz–100 kHz with a bias of 5 mV. The chronoamperometry (CA) and chronocoulometry (CC) measurements were conducted in which applied voltages were swept between −0.5 V and +1 V. The cyclic voltammetry (CV) measurements were scanned at the rate of 100 mV/s with the applied voltage between −0.5 V and +1 V. All electrochemical measurements of the WO_3 films were performed after the samples were tested for 5 cycles.

3. Results and discussion

The typical TEM image of the as-prepared tungsten oxide nanorods (NRs) with 8 mL OLa is shown in Fig. 1a. The statistical graphs demonstrate that the nanorods are well monodispersed (Supplementary information-SFig.1). The fine crystalline tungsten oxide NRs show an atomic lattice fringe of 0.38 nm (See Fig. 1b), which corresponds to the (001) plane of W_5O_{14} (PDF#41-0745). Fig. 1e shows the XRD patterns of the as-prepared tungsten oxide NRs powders in the range of 10° to 80°, indicating that the tungsten oxide NRs are composed of tetragonal W_5O_{14} (PDF#41-0745). Moreover, the intensity ratio of (001) to (871) diffraction peaks is far more than the standard ratio (≈ 1) given by standard PDF card, suggesting that the orientation of tungsten oxide rods along ⟨001⟩ direction [36].

Fig. 1d shows the dependence of length and diameter of the nanorods with the concentration of OLa after measuring about 100 nanorods. It shows that the average length and diameter of the nanorods increase from 38 nm × 3.2 nm–89 nm × 4.5 nm as the concentration of OLa decrease from 10 mL to 7 mL (See Fig. 1d), resulting the aspect ratio range from 11.9 to 19.8. Subsequently, tailoring the concentration of surfactant, OLa, is a productive approach to control over nanocrystal size. High surfactant-to-reagent concentrations favor the formation of more small nuclei initially and results in a smaller nanorod size. During nanorod growth, the surfactants in solution adsorb reversibly to the surfaces of the nanocrystals, providing a dynamic organic shell (capping layer) that stabilizes the nanocrystals in solution and mediates their growth. That is, the dynamically adsorption/desorption process gives a chance for the addition of tungsten oxide precursor (seed) to