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Hydrothermal deposition and photochromic performances of three kinds of hierarchical structure arrays of WO_3 thin films

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ABSTRACT

Three kinds of tungsten oxide (WO_3) thin films have been fabricated by a simple hydrothermal deposition method. Scanning electron microscopy images of the products revealed that the capping agents did impact the microstructure of WO_3 films. Films prepared without capping agents were ordered nanorod arrays, while the ones obtained with ethanol and oxalic acid revealed peeled-orange-like and cauliflower-like hierarchical structure arrays, respectively. Both of the two hierarchical structures were composed of much thinner nanorods compared with the one obtained without capping agents. All the WO_3 films exhibited good photochromic properties and the two with inducers performed even better, which could be due to the changes in the microstructure that increased the amount of photogenerated electron–hole pairs and the proton diffusion rates.

1. Introduction

Photochromic materials are attractive and promising for a variety of applications, due to a wide range of optical properties [1]. Although most photochromic materials are organic so far, the inorganic materials have better thermal stability, strength, chemical resistance, and macroscopic shape molding (can be easily shaped as thin films, coatings, monoliths, or other suitable forms) than the organic counterparts. After Deb's pioneering work [2,3], a widespread interest has focused on transition-metal oxides, specifically on MoO_3 and WO_3. In the past decades, tungsten oxide (WO_3), as an exceptionally important semiconductor material, has drawn much attention in various applications [4–8]. Since the photochromic performance of WO_3 film has been observed, the WO_3 film materials have displayed considerable potential applications in reusable information storage media, data displays, optical signal processing, smart windows, and the like [1,9]. Although Avellaneda et al. prepared doped and un-doped WO_3 film by the dip-coating technique; they stated that the films of WO_3:Zr with three layers showed the best photochromic response [10]. Xu et al. prepared WO_3 films by colloid chemistry method and argued that the pH of the solution would affect the structure and photochromic behavior of the films [11]. At present the photochromic properties of WO_3 films are seldom reported yet, due to the challenging preparation of WO_3 film with good photochromism.

As we all know, performances of materials usually require a large contact area with the reaction medium [12–14]. In this regard, numerous efforts have been devoted to the formation of morphologies and structures of film, which generally goes with a relative large exposed area. Li et al. prepared tungsten oxide films in a vacuum thermal vapor deposition system, the as-prepared films contained hybrid of nanowire and 3D nanowire network [15]. Deki et al. prepared tungsten oxide thin films by the liquid phase deposition method. As the reaction progressed to different period, the films revealed rod-like crystals and irregular plate-like particles respectively [16]. However, the structure of these as-prepared WO_3 films was disordered and the amounts of deposited films were rather small, resulting in low absorptivity and low conversion efficiency of light energy. In consequence, the photochromic performance of these films was weak. To overcome these problems related to the simplex and disordered structures, some WO_3 films with hierarchical structures were prepared. For example, Shankar et al. synthesized tungsten oxide (WO_3) films using CNTs as templates under typical diamond growing conditions in a hot-filament chemical vapor deposition system, these films were hierarchical structures composed of nanorods [17]. Nonetheless, the difficile fabrication conditions with special instruments usually limited their practical application.

In this work, we prepared a kind of ordered nanorod arrays of WO_3 film via a facile hydrothermal deposition process. Additionally, we found that some small molecular organics, which with certain functional groups, can bring an advantageous influence to the morphologies of WO_3 nanocrystals during hydrothermal conditions [18,19]. Therefore, two kinds of hierarchical structure arrays of WO_3 films were also

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fabricated by adding ethanol and oxalic acid as capping agents via the same hydrothermal deposition process. These morphologies and structures of WO_3 films can solve the preceding problems efficiently and improve the photochromic properties. Mechanisms of the enhanced photochromic performances of the WO_3 films have been analyzed.

2. Experimental details

2.1. Preparation of the WO_3 films

All of the chemicals were of analytical grade and used without further purification, and the autoclaves are 100-mL (Yi Zhi Instrument Limited Company, Wuhan China). In a typical procedure, the sodium tungstate powder was dissolved by distilled water to a concentration of 0.08 M, and the Na_2WO_4 solution was acidified to a pH of 1 using H_2SO_4 (95%–98%) solution. The mixed solution was transferred into a stainless steel autoclave. Then a soda-lime glass substrate with rough surface was degreased using detergent powder under sonication for 15 min and then cleaned with 1.0 M HCl, boiling water and absolute ethanol. After it dried at 100 °C, the substrate was immersed into the reaction solution. The autoclave was sealed and maintained at 120 °C for 48 h, and then was let to cool down to room temperature, the white film was formed on the surface of the substrate and then washed by ethanol and distilled water for several times and dried in an oven of 60 °C. The product obtained with this procedure was called sample S1. To prepare the WO_3 film in the presence of ethanol which is called sample S2, the Na_2WO_4 solution was prepared by adding ethanol to the solution, the volume ratio of ethanol to distilled water is 1:50. The procedure continues in the same way as the preparation procedure for sample S1. The same preparation method was done using oxalic acid instead of ethanol to the sample labeled S3, and the volume ratio of oxalic acid to distilled water is 1:50. The chemical reactions that take place during the film deposition can be described as follows: $H_2WO_4 \rightarrow WO_3 + H_2O$.

2.2. Characterization

The crystal structures of the resulting products were analyzed by X-ray diffraction (XRD, Philips Dy 2198X, Holland) with a Cu-Kα radiation source ($\lambda = 0.1541$ nm) and settings of 40 mA and 40 kV at a scanning rate of 0.02°/s in the 2θ range from 10 to 70°. The morphologies of the resulting products were investigated by scanning electron microscopy (SEM, JSM-5610LV, Japan, 20 kV). Furthermore, optical properties of the resulting products were measured by UV–vis diffuse reflectance spectroscopy (Shimadzu UV 2550) with $BaSO_4$ as the baseline correction.

2.3. Photochromic property study

The photochromic properties of the film samples were determined using a color difference meter (SC-80C, Beijing Kangguang Instruments Ltd.). The color differences (ΔC) of the obtained samples were characterized after being exposed under a UV lamp device (a sealed box, containing 3 parallel UV tubular lamp in it, each UV lamp possess a wavelength of 365 nm, 3 W) and the samples were placed 15 cm away from the lamps. The Commission Internationale de'Eclairage Lab uniform color space for color sheet system was used to figure out the color difference. L^*, a^* and b^* are the three-dimensional rectangular coordinates, which are worked out from the tristimulus values. L^* refers to the transparency index while a^* and b^* refer to the chroma indexes. The color difference is calculated according to the formula below:

$$\Delta C = \left\{ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right\}^{1/2}.$$

ΔC shows the color difference of the corresponding films before and after being irradiated.

3. Results and discussion

3.1. Phase analysis

The X-ray diffraction patterns of samples are presented in Fig. 1. Three samples show the same crystalline phase, and all the diffraction peaks of the products can be indexed to hexagonal structure of WO_3 (PDF card no. 75-2187). No additional phases are detected. The average grain sizes of samples S1, S2 and S3 calculated from XRD data are about 49.2 nm, 35.8 nm and 32.9 nm, respectively (by Scherrer's equation) [20]. It is clear that the grain size of products prepared with the ethanol or oxalic acid showed a decrease, which might be attributed to the suppression crystal growth resulting from the inducers [21,22].

3.2. Microstructure investigations

The top-view SEM images of the WO_3 films are shown in Fig. 2(a–f). It can be seen from Fig. 2(a, b) that the WO_3 film obtained without inducer is largely made of vertically oriented nanorod arrays, together with some disoriented nanorods. The nanorods are densely populated on the glass substrate and have an almost uniform diameter of about 200 nm. The cross-section image also reveals that the nanorods are packed densely and the film is about 2 μm in thickness. Significantly, it was discovered that the capping agents did impact the morphological evolution of the WO_3 films. In Fig. 2(c, d), the WO_3 film prepared with ethanol presents peeled-orange-like hierarchical structures, which are spirally assembled by each section; and the each "orange-section" was formed by ordered and much thinner nanorods compared with the nanorods prepared without capping agents, and the thickness of the film is around 4 μm. It has been noticed that the nanorods of each section are of varied orientations. Film prepared with oxalic acid reveals cauliflower-like hierarchical structures, which are softly and randomly assembled from nanorods thinner than those of sample S1, and is about 4 μm in thickness.

The SEM results suggested that ethanol and oxalic acid played an important role during the formation of the WO_3 film morphologies. Both ethanol and oxalic acid possessed functional groups; ethanol has one hydroxyl (–OH) group and oxalic acid has two carboxylic (–COOH) groups [23], these functional groups may selectively adsorb on the nanoparticle surfaces to decrease the polarity of particles and electrostatic attraction among particles [24]. This result will efficiently change the original orientation of WO_3 particle during the deposition procedure, and different functional groups may cause completely different particle orientation. Hence, in the presence of ethanol, WO_3 nanorods were induced to assemble peeled-orange-like hierarchical structures, unlike that, oxalic acid guided the WO_3 nanorods to assemble cauliflower-like hierarchical structures rather than ordered

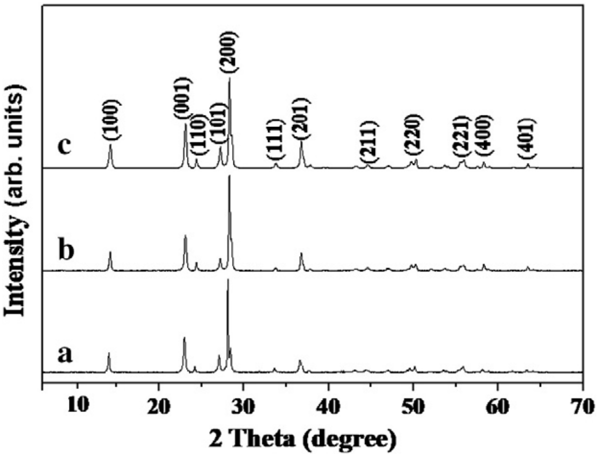

Fig. 1. The XRD patterns of all samples: (a) sample S1, (b) sample S2 and (c) sample S3.