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Integrated electrochromism and energy storage applications based on tungsten trioxide monohydrate nanosheets by novel one-step low temperature synthesis

Zhijie Bi[a,b], Xiaomin Li[a,*], Xiaoli He[a,b], Yongbo Chen[a,b], Xiaoke Xu[a,c], Xiangdong Gao[a]

[a] State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, No. 1295 Dingxi Road, Shanghai 200050, PR China
[b] University of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing 100049, PR China
[c] School of Materials Science and Engineering, Shanghai Institute of Technology, No. 100 Haiquan Road, Shanghai 201418, PR China

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ABSTRACT

The tungsten trioxide monohydrate ($WO_3{\cdot}H_2O$) nanosheets were directly formed on fluorine-doped tin oxide (FTO) substrates without any guidance of seed layer by a novel and quite facile one-step citric acid-assisted hydrothermal method at low temperature (90 °C). The $WO_3{\cdot}H_2O$ nanosheets possess porous morphologies and good adhesion to the substrates, which would markedly increase the surface area of $WO_3{\cdot}H_2O$ and facilitate the ion diffusion during the electrochemical processes. The $WO_3{\cdot}H_2O$ nanosheets display superior electrochemical properties of large optical modulation (79.0%), fast switching time (t_c = 10.1, t_b = 6.1 s), high areal capacitance (43.30 mF cm^{-2}) and excellent cycling stability. Furthermore, bridging electrochromic behavior with energy storage was successfully achieved. Based on the proposed $WO_3{\cdot}H_2O$ nanosheets, a smart energy storage electrode was demonstrated, which could monitor the level of stored energy by color changes. The results show great potential of the one-step synthesized $WO_3{\cdot}H_2O$ nanosheets for integrated electrochromism and energy storage applications.

1. Introduction

Recently, multifunctional energy storage and conservation devices that combine novel characteristics and functions in smart and interactive modes are gradually springing up [1–4]. Supercapacitors are deemed as promising means of energy storage because of their high power density, long cycle life and fast charge/discharge capability [5–7]. Pseudocapacitor, an important type of supercapacitor, is based on the redox reactions occurred at or near the surface of active materials to store energy [8,9]. Smart windows based on electrochromic (EC) materials could adjust the interior sunlight by color variation so as to reduce the energy consumption and improve the indoor comfort. The color change for EC materials could be realized via reversible redox reactions under applied potentials, which share similar features with pseudocapacitors [10–12]. Thus, it would be greatly attractive to integrate electrochromism and energy storage functions into one electrode for combined applications of smart windows and supercapacitors whose energy storage level can be indicated in a noticeable and predictable manner.

Various transition metal oxides, such as W, Ti, V and Ni oxides, have been extensively investigated as either electrochromic or pseudocapacitive electrodes [8,9,13,14]. Among these materials, tungsten trioxide (WO_3) is of great interest due to its low cost, large optical modulation and high capacitance [15]. WO_3 possesses suitable structures for the insertion/extraction of Li^+ ions, which induces interesting energy-storage performance. Besides, when redox reactions occur with charge transfer, WO_3 would concurrently suffer electrochromic processes. WO_3 is a typical cathodic electrochromic material, exhibiting blue color (Li_xWO_3) in reduction state and transparent (WO_3) in oxidation state. Hence, the obvious transmittance variations corresponding to the insertion/extraction of Li^+ ions make WO_3 become an ideal material to realize the integrated electrochromism and energy storage applications. Up to now, various methods have been reported for the preparation of WO_3 films, such as electrodeposition, vacuum deposition, sol-gel and hydrothermal method [16–21]. Hydrothermal technique is one of the most promising approaches to synthesize WO_3, since the nanostructures of WO_3 can be accurately and simply controlled by altering the precursor concentration, growth temperature, time and capping agents. However, the traditional hydrothermal methods always need high reaction temperature and pressure, and the assistance of crystal seed-

* Corresponding author.
E-mail address: lixm@mail.sic.ac.cn (X. Li).

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layer [13,17,18], which would not only increase the complexity of the preparation stage, but also degrade the performance of the materials due to its dense morphologies.

Herein, we demonstrate a novel and quite facile one-step citric acid-assisted hydrothermal method to synthesize $WO_3{\cdot}H_2O$ nanosheets on FTO glasses without seed-layer and post-treatment at low temperature (90 °C). The ammonium chloride (NH_4Cl) was used to further control the morphology of the products. Moreover, the bifunctional combination of electrochromism and energy storage was also realized for the $WO_3{\cdot}H_2O$ nanosheets. To the best of our knowledge, this is the first report on the use of one-step synthesized $WO_3{\cdot}H_2O$ nanosheets for integrated electrochromism and energy storage functions.

2. Material and methods

2.1. Materials

Sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$, 99.5%), lithium perchlorate ($LiClO_4$, 99.99%) and propylene carbonate (PC, 99%) were purchased from Aladdin. Citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$, ≥99.5%) and hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagant Co., Ltd. All the chemicals and reagents were used without further purification. Fluorine-doped tin oxide (FTO) glasses (1.5 × 2.5 cm^2 in size, ~15 Ω/□) were purchased from OPV Tech Co., Ltd.

2.2. Preparation of $WO_3{\cdot}H_2O$ nanosheets

The $WO_3{\cdot}H_2O$ nanosheets were prepared by a quite facile citric acid-assisted hydrothermal method. Briefly, 4.1231 g $Na_2WO_4{\cdot}2H_2O$ and 2.6268 g citric acid monohydrate were uniformly dissolved into 100 ml deionized water by magnetic stirring. The citric acid acted as chelating agent, forming tungsten acid-citrate complexes with Na_2WO_4, which would assist the nucleation and enhance the adhesion to the FTO substrates of the products. After stirring for 10 min, 0.5 g NH_4Cl as capping agent was added into the solution to further control the morphology of the products. Afterwards, 5 M HCl solution was dropwise added into the solution to adjust the pH value to 1, assisting the formation of tungsten acid and the growth of the products. A transparent FTO glass was then transferred into the solution, which was maintained at 90 °C for 30 min at oven. Then, the FTO glass with $WO_3{\cdot}H_2O$ was taken out and rinsed with deionized water several times to remove any residual reagent. Finally, the FTO glass was baked at 60 °C for 1 h to remove any residual water.

2.3. Characterizations

The X-ray diffraction (XRD, Bruker D8 discover diffractometer) and field emission scanning electron microscope (SEM, Hitachi S-4800) were used to characterize the phase structures and morphologies. The Fourier transform infrared (FTIR) spectra were measured by a Lambda Scientific FTIR-7600 spectrometer. The electrochemical properties were investigated by a CHI660B electrochemical workstation in a three-electrode configuration, where the sample was served as the working electrode; Ag/AgCl, Pt plate and 1 M $LiClO_4$ in propylene carbonate (PC) were used as reference electrode, counter electrode and electrolyte, respectively. The optical properties were recorded using a Persee TU-1901 UV–vis–NIR spectrophotometer.

3. Results and discussion

3.1. Microstructural characterizations

Fig. 1 shows the X-ray diffraction (XRD) patterns and morphologies of the as-prepared thin film grown on FTO glass without the assist of citric acid. The obtained film exhibits orthorhombic phase of $WO_3{\cdot}H_2O$ (JCPDS No. 43–0679) as indicated in Fig. 1a. A quite irregular and non-uniform morphology with piled column-like and cluster-like

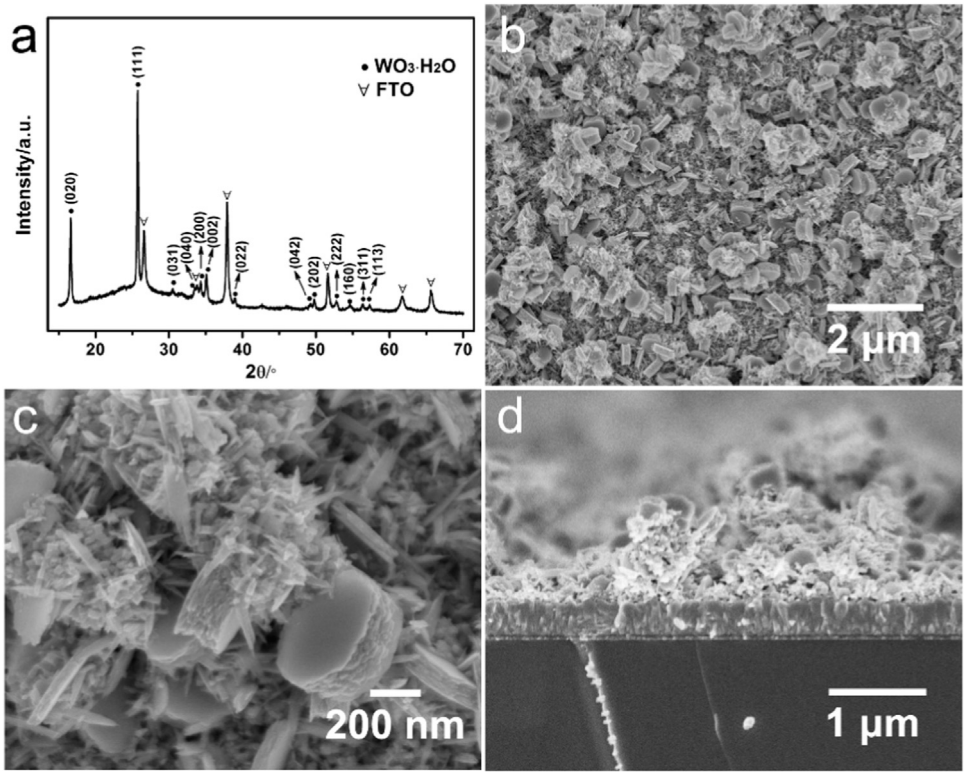

Fig. 1. (a) XRD pattern of the as-prepared $WO_3{\cdot}H_2O$ grown on FTO glass without the assist of citric acid. Top-view SEM images of $WO_3{\cdot}H_2O$ without the assist of citric acid in (b) low and (c) high magnifications. (d) Cross-sectional SEM image.