Electrochromics of Nanocrystalline Tungsten Trioxide*

XIE Fang-yan[1,2], CHEN Cui-lian[3], MENG Hui[1], SHEN Pei-kang[1]
(1. State Key Laboratory of Optoeletronic Materials and Technologies, School of Physics and Engineering, Sun Yat-sen University, Guangzhou 510275, China;
2. Instrumental Analysis and Research Centre, Sun Yat-sen University, Guangzhou 510275, China;
3. Department of Food and Bioengineering, Institute of Technology of Zhangzhou, Zhangzhou 363000, China)

Abstract: A new method combining the foam formation and heat treatment for preparing the nanocrystalline WO_3 powders is presented. The structure and the morphology of the powder have been characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The nanocrystalline WO_3 powder is orthorhombic structured with well-defined crystalline clusters bounded by 30～40 nm nanoparticles. The WO_3 film on ITO is prepared by dip-coating method in WO_3 suspension in which nanocrystalline WO_3 powders are dispersed in distilled-deionised water. The electrochemical measurements show that the WO_3 films have a good electrochromic reversibility and fast electrochromic response.

Key words: tungsten trioxide; nanocrystallite; electrochromics; foam; film
CLC number: O64; TP212.6 Document code: A Article ID: 0529-6579 (2006) 03-0027-04

Tungsten trioxide (WO_3) has been intensively interested owing to its potential applications in gas sensors, smart windows and catalysis[1-5]. As an electrochromic material, WO_3 can be prepared by physical and chemical methods, such as chemical vapor deposition[6,7], pulsed laser deposition (PLD)[8], vacuum evaporation[9], sputtering[10], R.F. magnetron sputtering[11], sol-gel[12,13], spray pyrolysis[14], hydrothermal[12], electrochemical deposition[15-17], electroless deposition[18] and ultrasound irradiation[19].

The electrochromic (EC) performance of WO_3 depends strongly on its morphology and structure. Recently, many researchers have focused on the preparation of nanocrystalline WO_3 using different methods[20-23]. The WO_3 nanocrystallites are bound together with differing crystal orientation and a high density of interfaces or grain boundaries[20]. A comparative study of the EC behavior of the nanocrystalline WO_3 films exhibited a higher over selective optical modulation, more efficient in the near infrared region and less in the visible, compared to the polycrystalline or amorphous films[21]. Such a formation possesses many advantages including a high porosity and large internal volume.

This paper reports the preparation of nanocrstalline WO_3 by a novel method combining the foam formation and heat treatment. The electrochromic properties of the nanocrystalline WO_3 were characterized.

1 Experimental

1.1 Preparation of WO_3 nanocrystallites

Tungsten-containing solution was prepared by dissolving 3 g W in 30 mL 30% (φ) hydrogen peroxide (H_2O_2) aqueous solution[15]. The solution was brought up to 100 mL with distilled-deionised water and ethanol (φ=30%). After decomposing the excess H_2O_2 by a platinized Pt gauze, 0.844 g of cetyltrimethyl ammonium bromide (CTAB) were mixed with 2.74 mL tungsten-containing solution and a small quantity of Pt powder, a viscous paste was formed. 2 mL of H_2O_2 (φ=30%) was then added immediately. H_2O_2 decomposes by the induction of Pt and oxygen gas evolves at the same time. A voluminous foam with bright yellow in colour formed spontaneously as reported for TiO_2 foam[24] and V_2O_5 foam[25]. The difference is that the tungsten-containing homogeneous solution was used as precursor instead of the powder. Only macrostructured foam formed using powder as precursor[24-25]. The yellow foam was further subjected to a heat treatment at 500℃ for 6h in order to remove the surfactants.

* 收稿日期: 2005-11-14
基金项目: 国家自然科学基金资助项目 (20476108); 广东省自然科学重点基金资助项目 (04105500)
作者简介: 谢方艳 (1978年生), 女, 博士; 通讯联系人: 沈培康; E-mail: stdp32@zsu.edu.cn

1.2 Preparation of the WO_3 film on ITO (indium-tin oxide) glass

The nanocrystalline WO_3 was pre-dispersed in distilled-deionised water, a yellow green suspension was obtained. The WO_3 film on ITO glass was formed by the dip-coating method at a rate of 10 cm min^{-1} and dried at 80℃. The glass was previously degreased and cleaned as described elsewhere[26]. Dip-coating and heating treatment procedures were repeated twice to obtain homogeneous WO_3 film. The as-deposited film was coated with a thin layer of Nafion film on the top to prevent the dissolution of WO_3 in the electrolyte[16] and was left in air overnight before the characterization.

The electrochemical measurements were performed in a three-electrode cell with WO_3/ITO electrode as a working electrode. A Pt wire and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. All the tests were carried out in 0.5 mol dm^{-3} H_2SO_4 solution at room temperature. Cyclic voltammetric and potentiastatic investigations were carried out on a Voltlab 80 Universal Electrochemical Laboratory (Radiometer Analytical, France).

The crystallinity of the nanocrystalline WO_3 was confirmed by the X-ray diffraction pattern. A X-ray diffratometer D/Max-IIIA (Rigaku Co., Japan) using CuKα1 ($\lambda = 1.54056 \times 10^{-8}$ cm) as radiation source was used. The morphology of the WO_3 nanocrystallite was observed by the scanning electron microscopy (SEM) (LEO 1530 VP, Germany).

2 Results and Discussion

2.1 Structural characterization

The structure of the WO_3 nanocrystallite was identified by X-ray diffraction. Fig.1 shows the X-ray diffractogram of the WO_3 nanocrystallite. The d values were compared with the standard JCPDS values and are consistent with those of the orthorhombic structure (JCPDS 20—1324).

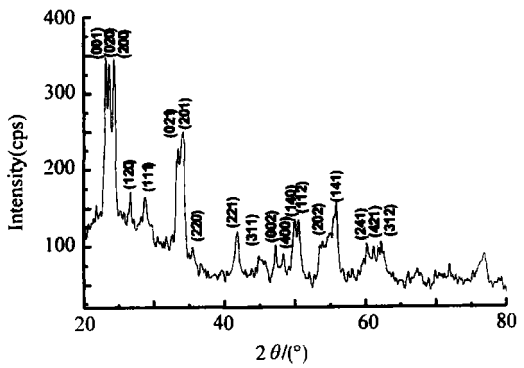

Fig.1 The X-ray diffraction pattern of nanocrystalline WO_3

The morphology of the WO_3 nanocrystallite was observed by SEM. Fig.2 shows the SEM mocrographs of the WO_3 nanocrystallites at different microscopic magnitudes. It is clear that the WO_3 powder is composed of the well-defined crystal clusters with the nanocrystalline size of less than 50 nm. Such structure can provide high surface area that is favorable for electrochromic application. The high surface area would significantly accelerate the colouration/bleaching rate. The results revealed that the modified "foam" method in this study could rapidly prepare the nanocrystalline WO_3.

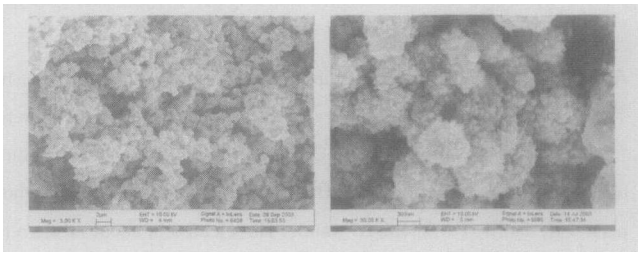

Fig.2 SEM mocrographs of the nanacrystalline WO_3 at different microscopic magnitudes (left ×3000; right ×30000)

2.2 Cyclic voltammetry of WO_3/ITO electrode

The cyclic voltammogram of the WO_3/ITO electrode is shown in Fig.3 and the characteristic redox peaks of WO_3 were as reported previously[15, 26]. The cathodic current is associated with the colouring process (the formation of hydrogen tungsten bronze, H_xWO_3) and the blue colour appeared obviously. Tungsten at highest valence was reduced to lower valence states at the first reductive peak and the blue colour was intensified with the further increase in the cathodic potential.

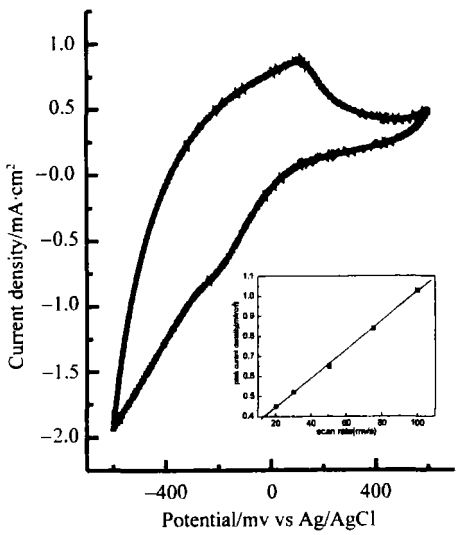

Fig.3 Cyclic voltammogram of a WO_3 electrode in 0.5mol dm^{-3} H_2SO_4 solution, scan rate: 50 mV s^{-1}. Inset: a plot of the anodic peak current density vs. scan rate.

The cathodic current at a given potential can be used as a comparative indication of the amount of hydrogen inserted into the WO_3 film and hence the degree of colouration. The colouration/bleaching processes of the nanocrystalline WO_3 films prepared by the present method are reversible and repeatable. The inset of Fig. 3 shows a linear relationship between anodic peak current and scan rate below 100 mV s^{-1}. The result demonstrated that the redox reaction of the nanocrystalline WO_3 film is controlled by the electrode surface reaction in a Nernstian manner.

2.3 Potential pulse response of WO_3/ITO electrode

Fig. 4 shows the current-time response of a WO_3 electrode under a periodical potential pulse from −0.6 V to 0.6 V at the frequencies of 0.1 Hz. From Fig. 4 it can be found that the response of the coloration and bleaching of the WO_3 film are very fast due to the porous structure. The peak currents produced during the coloration and bleaching processes are hardly changed, indicating the reversibility and stability of the WO_3 film. The results are significant since the improvement in the response time is extremely important for the scale up of the WO_3 based electrochromic devices.

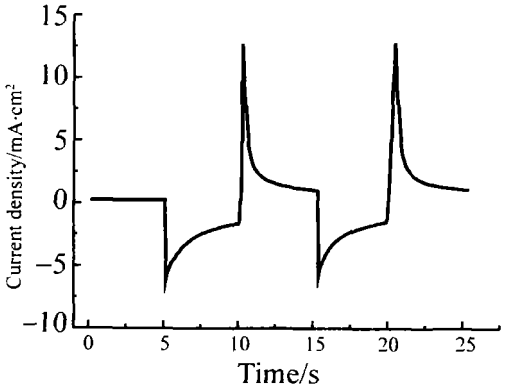

Fig. 4　Current-time response of a WO_3 electrode under potential pulse from −0.6 V to 0.6 V in 0.5 mol dm^{-3} H_2SO_4 solution.

The morphologic analysis of the WO_3 powder indicated that the WO_3 powder prepared by the present method was nanocrystallites with a large area interfaces or grain boundaries. Such nanocrystalline WO_3 can provide good inter-granular contacts and provide more channels for the ions in and out easier than that of other forms of WO_3 due to their high porosity and large internal volume.

3 Conclusion

Nanocrystalline WO_3 powder which possesses a high porosity and large internal volume has been prepared by a new method combining the foam formation in the presence of the surfactants. The as-prepared WO_3 powders were orthorhombic structured. SEM observation proved that the WO_3 powders in the form were of well-defined crystal clusters with 30—40 nm nanoparticles. The results revealed that the modified "foam" method could be used to rapidly prepare nanocrystalline WO_3.

The results of the cyclic voltammetric measurements and the chronoamperometric response of the WO_3/ITO electrode showed that the nanocrystalline WO_3 films possessed a good electrochromic reversibility and faster coloration and bleaching rates.

References:

[1] AGUIR K, LEMIR C, LOLLMAN B B. Electrical properties of reactively sputtered WO_3 thin films as ozone gas sensor [J]. Sens Actuators B, 2002, 84: 1—5.

[2] GRANQVIST C G. Electrochromic tungsten oxide films: Review of progress 1993 - 1998 [J]. Solar Cells, 2000, 60 (3): 201—262.

[3] YAO J N, CHEN D, FUJISHIMA A. Electrochromic behavior of electrodeposited tungsten oxide thin films [J]. J Electroanal Chem, 1996, 406: 223—226.

[4] VINODGOPAL K, HOTCHANDAN S, KAMAT P V. Electrochemically assisted photocatalysis: titania particulate film electrodes for photocatalytic degradation of 4—chlorophenol [J]. J Phys Chem, 1993, 97 (35): 9040—9044.

[5] BACH U, LUPO D, COMTE P. Solid—state dye—sensitized mesoporous TiO2 solar cells with high photon—to—electron conversion efficiencies [J]. Nature, 1998, 395: 583—585.

[6] KIRSS R U, MEDA L. Chemical vapor deposition of tungsten oxide [J]. Appl Organometallic Chem, 1998, 12 (3): 155—160.

[7] CROSS W B, PARKIN I P. Tungsten Oxide Coatings from the Aerosol—Assisted Chemical Vapor Deposition of W (OAr)$_6$ (Ar = C_6H_5, C_6H_4F—4, $C_6H_3F_2$—3, 4); Photocatalytically Active γ—WO_3 Films [J]. Chem Mater, 2003, 15: 2786.

[8] PONIATOWSKI E H, JOUANNE M, MORHANGE J F. Micro—Raman characterization of WO_3 and MoO3 thin films obtained by pulsed laser irradiation [J]. Appl Surf Sci, 1998, 127: 674—678.

[9] CANTALIN C, SUN H T, FACCIO M. NO_2 sensitivity of WO_3 thin film obtained by high vacuum thermal evaporation [J]. Sens Actuators B, 1996, 31: 81—87.

[10] XU Z, VETELINO J F, LEC R. Electrical properties of tungsten trioxide films [J]. J Vac Sci Technol A, 1990, 8: 3634—3640.

[11] TOKURO N, TADASHI T J. Characterization of amorphous tungsten trioxide thin films prepared by rf magne-

tron sputtering method [J]. Non-crystalline Solids, 1994, 178: 233-237.

[12] CHENG W, BAUDRIN E, DUNNA B. Synthesis and electrochromic properties of mesoporous tungsten oxide [J]. J Mater Chem, 2001, 11 (1): 92-97.

[13] BADILESCU S, ASHRIT P V. Study of sol-gel prepared nanostructured WO_3 [J]. Solid State Ionics, 2003, 158 (2): 187-197.

[14] REGRAGUIA M, ADDOUA M. Preparation and characterization of pyrolytic spray deposited electrochromic tungsten trioxide films [J]. Thin Solid Films, 2000, 358: 40-45.

[15] SHEN P K, TSEUNG A C C. Study of electrodeposited tungsten trioxide thin films [J]. J Mater Chem, 1992, 2 (11): 1141-1148.

[16] SHEN P K, HUANG H T, TSEUNG A C C. Improvements in the life of WO_3 electrochromic films [J]. J Mater Chem, 1992, 2 (5): 497-500.

[17] SOLDO O Y, FAURE R. XAS Study of Amorphous WO_3 Formation from a Peroxo-Tungstate Solution [J]. J Phys Chem B, 2003, 107 (34): 8861-8867.

[18] BAECK S H, JARAMILLO T F, STUCKY G D. Synthesis of Tungsten Oxide on Copper Surfaces by Electroless Deposition [J]. Chem Mater, 2003, 15: 3411-3413.

[19] KOLTYPIN Y, NIKITENKOB S I, GEDANKEN A. The sonochemical preparation of tungsten oxide nanoparticles [J]. J Mater Chem, 2002, 12 (4): 1107-1110.

[20] GLEITER H. Nanostructured materials: state of the art and perspectives [J]. Nanostruct Mater, 1995, 6: 3-14.

[21] ASHIRT P V. Dry lithiation study of nanocrystalline, polycrystalline and amorphous tungsten trioxide thin-films [J]. Thin Solid Films, 2001, 385: 81-88.

[22] SANTATO C, ODZIEMKOWSKI M, ULMANN M. Crystallographically Oriented Mesoporous WO_3 Films: Synthesis, Characterization, and Applications [J]. J Am Chem Soc, 2001, 123: 10639-10649.

[23] BAECK S H, JARAMILLO T, STUCKY G D, MCFARLAND E W. Controlled Electrodeposition of Nanoparticulate Tungsten Oxide [J]. Nano Lett, 2002, 2: 831-834.

[24] ARABATZIS I M, FALARAS P. Synthesis of Porous Nanocrystalline TiO_2 Foam [J]. Nano Lett, 2003, 3: 249-251.

[25] CHANDRAPPA G T, STEUNOU N, LIVAGE J. Macroporous crystalline vanadium oxide foam [J]. Nature, 2002, 416: 702.

[26] SHEN P K, SYED-BKHARI J, TSEUNG A C C. The Performance of Electrochromic Tungsten Trioxide Films Doped with Cobalt or Nickel [J]. J Electrochem Soc, 1991, 138 (9): 2778-2782.

纳米晶体三氧化钨的电变色研究

谢方艳[1,2], 陈翠莲[3], 孟 辉[1], 沈培康[1]

(1. 中山大学光电材料与技术国家重点实验室//物理科学与工程技术学院, 广东 广州 510275;
2. 中山大学测试中心, 广东 广州 510275;
3. 漳州职业技术学院食品与食品生物工程系, 福建 漳州 363000)

摘 要: 报道了一种结合泡沫形成和热处理技术制备纳米晶体三氧化钨的新方法。经 X射线衍射 (XRD) 和扫描电子显微镜 (SEM) 对 WO_3的结构和表面形貌的表征证实, WO_3呈正交结构, 并形成由 30～40 nm的纳米颗粒组成的晶体簇。以浸涂的方法将 WO_3修饰在 ITO导电玻璃上制备成电极, 电化学测量表明由该方法制备的 WO_3具有很好的电变色可逆性和很快的响应特性。

关键词: 三氧化钨; 纳米晶体; 电变色; 泡沫; 薄膜

中图分类号: O64; TP212.6