Rare Metal Materials and Engineering
Volume 46, Issue 5, May 2017
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2017, 46(5): 1241-1244.

ARTICLE

Synthesis, Characterization, and Gas Sensing Properties of WO_3 Nanoplates

Xiao Jingkun, Song Chengwen, Dong Wei, Li Chen, Yin Yanyan

College of Environment Science and Engineering, Dalian Maritime University, Dalian 116026, China

Abstract: WO_3 nanoplates were synthesized by a hydrothermal method. Morphology and structure of the WO_3 nanoplates were analyzed by SEM and XRD, respectively. Gas sensing properties of the as-prepared WO_3 sensor were investigated by a static gas-sensing system. The results show that the WO_3 nanoplates reveal good crystallinity with mean edge length of 200~300 nm and wall thickness of about 50 nm. The optimal operating temperature of the WO_3 sensors is 300 ℃. At this operating temperature, the WO_3 sensor exhibits ultra-fast response (2~4 s) and fast recovery time (4~16 s) for ethanol detection, and high selectivity to other gases such as methanol, benzene, dichloromethane and hexane, which indicates its excellent potential application as the gas sensor for ethanol detection.

Key words: preparation; gas sensor; ethanol; WO_3

Electronic nose is a complex electronic system, which tries to emulate the mammalian nose by employing an array of chemical gas sensors that can simulate mammalian olfactory responses to odours[1-3]. In recent years, electronic nose has become a powerful tool in the identification and quantification of hazardous chemicals[4]. Currently, many semiconductor metal oxides, such as SnO_2, TiO_2, ZnO, and WO_3, have been most widely used in electronic nose systems for the detection of hazardous chemicals because they possess a broad range of chemical and physical properties that are often highly sensitive to the changes of their chemical environment[5,6]. Among them, tungsten oxide, as an n-type semiconductor with a band gap of 2.7 eV, has attracted considerable attention because of its great potential applications as gas sensors, field emission devices and photocatalysts[7]. Generally, high gas response for detecting trace gases is accomplished by employing well-defined nanostructures[8]. Therefore, various morphologies of tungsten oxide like nanorods[7,9], nanowires[10,11], nanofibers[12,13], nanotubes[14,15] and microspheres[16,17] have been synthesized and they are used to prepare high sensitive gas sensors. However there are few reports on two-dimensional (2D) WO_3 nanostructures. Moreover, in many cases, 2D nanostructures have specific properties superior to those of 1D and 3D ones [18]. 2D nanoplates with flat surfaces and regular shapes have attracted tremendous attention in various disciplines because of their promising electrical and optical properties, which makes them better choices for gas sensors[19]. In the present work, we synthesized WO_3 nanoplates using a simple hydrothermal method, investigated the morphology and structure characteristics of the WO_3 nanoplates, and further evaluated their gas sensing properties and potential applications in ethanol detection.

1 Experiment

1.0 g $Na_2WO_4 \cdot 2H_2O$ and 0.5 g citric acid were added to 50 ml of distilled water under stirring, and 10 mL HCl solution (4 mol/L) was added dropwise to the above mixture. The mixture was sealed in a Teflon-lined stainless steel autoclave of 100 mL capacity and heated at 160 ℃ for 12 h, and then cooled to room temperature. The resulting precipitates were collected by centrifugation and washed three times by deionized water and ethanol to remove possible impurities, and subsequently dried at 60 °C for 4 h.

Received date: May 05, 2016
Foundation item: The Scientific Research Project of Education Department of Liaoning Province (L2013203); The Natural Science Foundation of Liaoning Province (2014025014); The Fundamental Research Funds for the Central Universities (3132015219)
Corresponding author: Song Chengwen, Ph. D., Professor, College of Environment Science and Engineering, Dalian Maritime University, Dalian 116026, P. R. China, Tel: 0086-411-84724342, E-mail: chengwensong@dlmu.edu.cn

X-ray diffraction (XRD) patterns of WO_3 were recorded using a D/Max-2400 diffractometer (Cu Kα radiation, λ =0.154055 nm) in a range of diffraction angle 2θ from 20° to 80° to analyze the diffraction peaks of WO_3. The morphology of WO_3 was observed by SEM (Philips XL30 FEG).

WO_3 nanoplates were mixed with several drops of ethanol to form a slurry, and then the slurry was brush-coated onto the surfaces of an alumina tube with two Au electrodes and four Pt wires. A Ni-Cr heating wire was inserted into the alumina tube and used as a heater. The alumina tube was then welded onto a pedestal with six probes to obtain the final sensor unit. Gas sensing tests were performed on a WS-30A static gas-sensing system (HanWei Electronics Co., Ltd, Henan, China) using ambient air as the dilute and reference gas. The test gas with a calculated volume was introduced into the test chamber by a microsyringe.

2 Results and Discussion

2.1 Morphology and Structure of WO_3 nanoplates

Fig.1 shows the XRD pattern of the WO_3 sample. All the diffraction peaks are indexed to a monoclinic WO_3 phase according to the JCPDS card No. 83-0950, and no other peaks arising from tungstic acid or other phases are observed[20]. The morphology of the WO_3 sample is shown in Fig.2. The WO_3 sample exhibits the morphology of nanoplates with mean edge length of 200~300 nm and wall thickness of about 50 nm.

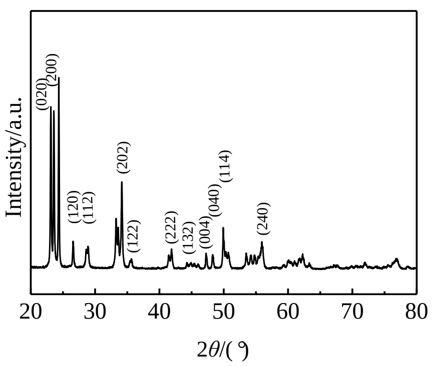

Fig.1 XRD pattern of the WO_3 sample

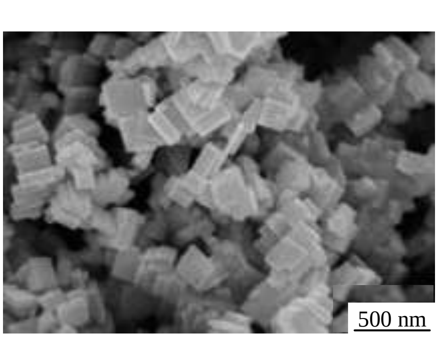

Fig.2 SEM image of the WO_3 sample

2.2 Gas sensing properties of WO_3 sensor

Gas sensing properties of the WO_3 sensor towards 100 µL/L ethanol were studied at different temperatures in order to find out the optimum operating temperature. As shown in Fig.3, the response increases with operating temperature rising and reaches a maximum of 5.6 at 300 °C, which indicates that the high response can be obtained by improving the operating temperature. However, when the operating temperature is too high, the response decreases sharply. Therefore, the optimal operating temperature of 300 °C is chosen for gas sensing tests.

Fig.4 displays the response of the WO_3 sensor to 20~300 mg/L ethanol at the optimal operating temperature of 300 °C. As observed, the response increases sharply at the initial stage with the increasing of ethanol concentration, and gradually reaches a saturation state as the ethanol concentration exceeds 200 mg/L. It may be ascribed to the fact that less active sites are available to react with ethanol molecules at high ethanol concentration[21]. Fig.5 shows the response- recovery curves the WO_3 sensor to ethanol with concentrations ranging from 20 to 300 mg/L at 300 ℃. The WO_3 sensor exhibits fast response and recovery for ethanol detection, and the response and recovery times are 2~4 s and 4~16 s, respectively. Such a rapid

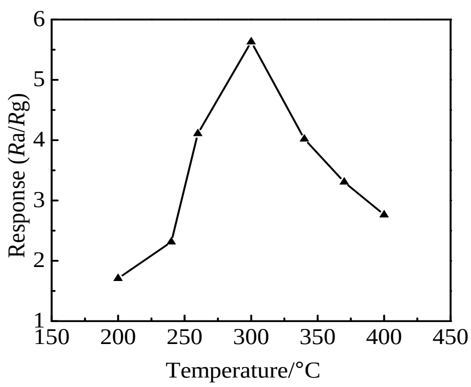

Fig.3 Response of the WO_3 sensor at different operating temperatures

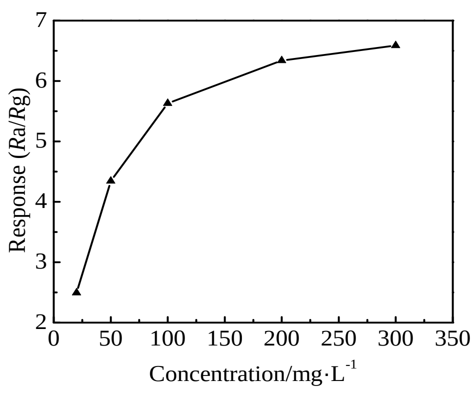

Fig.4 Response of the WO_3 sensor to different ethanol concentrations

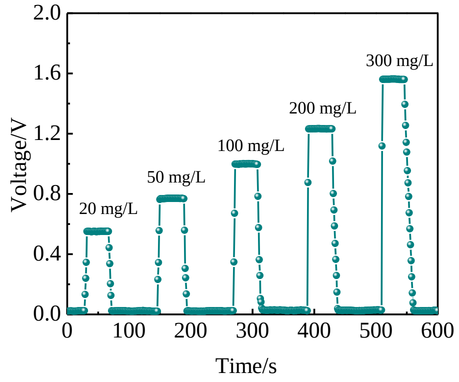

Fig.5 Response-recovery curves of the WO_3 sensor to different ethanol concentrations

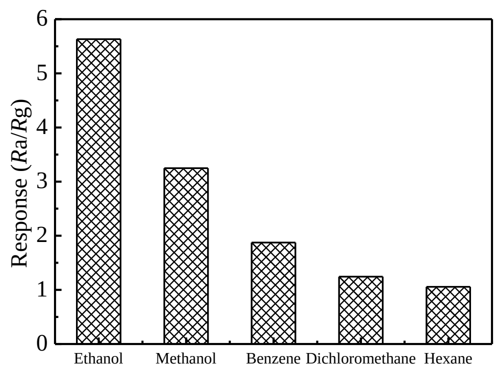

Fig.6 Response of the WO_3 sensor towards various gases

sensing performance can be attributed to the fact that the diffusion of ethanol and its oxidation with O^- or O^{2-} are very rapidly in nanoplates structures.

In order to evaluate the selectivity of the WO_3 gas sensor, the responses towards 100 mg/L of methanol, benzene, dichloromethane and hexane are obtained. As shown in Fig.6, the WO_3 sensor demonstrates higher response to ethanol than to other gases, indicating the WO_3 nanoplates have great advantages in ethanol detection.

3 Conclusions

1) We have synthesized WO_3 nanoplates using a simple hydrothermal method.

2) The response of the as-prepared WO_3 sensor to 100 mg/L ethanol increases with operating temperature rising and then reaches a maximum.

3) The WO_3 sensor demonstrates ultra-fast response (2~4 s) and fast recovery time (4~16 s) towards 20~300 mg/L ethanol, and high selectivity to other gases at the optimal operating temperature of 300 °C, implying the WO_3 nanoplates are promising gas sensing materials for ethanol detection.

References

1 Gutiérrez J, Horrillo M C. *Talanta*[J], 2014, 124: 95
2 Capelli L, Sironi S, Rosso R D *et al. Atmospheric Environment*[J], 2013, 79: 731
3 Arshak K, Moore E, Lyons G M *et al. Sensor Review*[J], 2004, 24: 181
4 Wilson A D. *Procedia Technology*[J], 2012(1): 453
5 Kolmakov A, Moskovits M. *Annual Review of Materials Research*[J], 2004, 34: 151
6 Yamazoe N, Shimanoe K. *Sensors and Actuators B*[J], 2009, 138: 100
7 Hieu N V, Quang V V, Hoa N D *et al. Current Applied Physics*[J], 2011, 11: 657
8 Kim S J, Hwang I S, Kang Y C *et al. Sensors*[J], 2011, 11: 10 603
9 Kim S, Park S, Park S *et al. Sensors and Actuators B*[J], 2015, 209: 180
10 Park S, Kim H, Jin C *et al. Thermochimica Acta*[J], 2012, 542: 69
11 Park S, Park S, Jung J *et al. Ceramics International*[J], 2014, 40: 11051
12 Feng C, Li X, Ma J *et al. Sensors and Actuators B*[J], 2015, 209: 622
13 Leng J, Xu X, Lv N *et al. Journal of Colloid and Interface Science*[J], 2011, 356: 54
14 Song C, Li, C, Yin Y *et al. Vacuum*[J], 2015, 114: 13
15 Chi X, Liu C, Liu Li *et al. Sensors and Actuators B*[J], 2014, 194: 33
16 Gui Y, Dong F, Zhang Y *et al. Materials Science in Semiconductor Processing*[J], 2013, 16: 1531
17 Lee C, Kim S, Hwang I *et al. Sensors and Actuators B*[J], 2009, 142: 236
18 Mao W, Bao K, Sun R *et al. Journal of Alloys and Compounds*[J], 2015, 620: 5
19 Wang W S, Zhen L, Shao W Z *et al. Materials Letters*[J], 2014, 131: 292
20 Li J, Liu X, Han Q *et al. Journal of Materials Chemistry A*[J], 2013(1): 1246
21 Xu X, Sun J, Zhang H *et al. Sensors and Actuators B*[J], 2011, 160: 858

WO_3纳米片的制备、表征及气敏性能研究

肖井坤，宋成文，董　伟，李　晨，尹妍妍

(大连海事大学环境科学与工程学院，辽宁 大连 116026)

摘　要：采用水热法合成 WO_3 纳米片，利用扫描电镜（SEM）和 X 射线衍射仪（XRD）对 WO_3 纳米片的形貌特征和结构性能进行表征，并进一步系统地考察了利用 WO_3 纳米片制备的传感器的气敏性能。结果表明，合成的 WO_3 纳米片尺寸规则，边长在 200~300 nm，厚度在 50 nm 左右，结晶性好。以 WO_3 纳米片为材料制备的气体传感器的最佳工作温度为 300 ℃，在此工作温度下，WO_3 纳米片传感器对乙醇表现出超快的响应（2~4 s）和恢复时间（4~16 s）。与其他还原性气体如甲醇，苯、二氯甲烷和正己烷对比检测发现，WO_3 纳米片传感器对乙醇表现出高的灵敏度和选择性，表明 WO_3 纳米片在乙醇检测气体传感器方面具有极大的应用潜力。

关键词：制备；气体传感器；乙醇；三氧化钨

作者简介：肖井坤，男，1964 年生，博士，副教授，大连海事大学环境科学与工程学院，辽宁 大连 116026，电话：0411-84724342，E-mail: xiaojingkun@yeah.net