Applied Surface Science 447 (2018) 569–575

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Facile synthesis of layered V_2O_5/ZnV_2O_6 heterostructures with enhanced sensing performance

Bingxin Xiao[a], Hao Huang[b], Xiantong Yu[a], Jun Song[a,*], Junle Qu[a,*]

[a] College of Optoelectronic Engineering, Key Lab of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, Shenzhen University, Shenzhen 518060, China
[b] Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, China

ARTICLE INFO

Article history:
Received 12 February 2018
Revised 24 March 2018
Accepted 4 April 2018
Available online 5 April 2018

Keywords:
V_2O_5/ZnV_2O_6
Layered nanostructure
Formation mechanism
Ethanol-sensing
Sensing mechanism

ABSTRACT

A low-cost and environment-friendly hydrothermal approach was used for the synthesis of layered V_2O_5/ZnV_2O_6 hybrid nanobelts. Characterization results indicate that the V_2O_5/ZnV_2O_6 nanobelts are composed of several thin layers. Additionally, it is illustrated that the chemical formation process of V_2O_5/ZnV_2O_6 occurred in the solution. The synthesized V_2O_5/ZnV_2O_6 heterostructures were subjected to detailed ethanol sensing tests. Results demonstrate that V_2O_5/ZnV_2O_6 based sensor shows about 4.3 of response to 100 ppm of ethanol gases, reveals relatively high sensitivity at relatively low optimal operating temperature of 240 °C, as well as relatively good selectivity and stability. The performance of the sensor is better than most of reported vanadium based sensing devices. Thus this work offers a new insight into the rational regulation of vanadium based sensing devices.

1. Introduction

Improvements in the industrial development inevitably lead to the emission of harmful pollutants causing environmental pollution [1,2]. Additionally, hazardous chemicals are prone to fire and explosions which has become the important problems that cannot be ignored [3]. Ethanol as one of the common volatile organic compounds (VOC), is capable of igniting for accidents in case of high temperature or any flame beyond a threshold vapor concentration. Hence, gas sensors have an important role to play in this process due to the fact that they can provide real time feedback to emissions management systems and timely warnings for avoiding any accidents. Over the past several decades, tremendous efforts in terms of the design and synthesis for high performance sensors to monitor the environment have led to great developments in gas sensing [4–7].

Among the various materials ever used in gas sensors, semiconductor metal oxides exhibit outstanding sensitive performances that make them good candidates for gas sensors [8]. Also layered inorganic analogues of transition metal dichalcogenides (TMDs) have attracted great attention in recent years due to their unique electronic structures, high conductivity and high surface activities as well as extraordinary physical and chemical properties [9–13]. As a result, as the layered materials, the transition metal oxides (TMOs) have also been widely explored for the fabrication of functional materials recently. With strong in-plane bonds and weak van der Waals coupling between layers, TMOs are beneficial to the adsorption of gas molecules, and the exposure of active sites facilitates the transfer of electrons to trigger the change of electronic properties [14].

Given these unique properties and diversity of polymorphs, the layered vandium nanostructure are outstanding candidates for lithium ion batteries, photocatalysts, supercapacitors, catalysts, etc [15–18]. In addition, significant progress has been achieved towards the realization of vandium gas sensors [19–21]. Nevertheless, some disadvantages always exist in the V_2O_5 gas sensors and limit their further expansion and practical application. Therefore, there is a need to develop effective strategies to promote the sensing performance of V_2O_5 gas sensors while retaining the architectural advantages of V_2O_5 nanostructures.

Until now, three routes are commonly selected by researchers to obtain modified metal oxides to fabricate high performance gas sensors, including: ionic doping and adding noble metals as catalysts as well as fabricating the heterostructures. On one hand, for the ionic doping, due to the introduction of impurity level and surface defects, the doping can increase the sensitivity of metal oxide gas sensor. However, it is challenging to control this process and the desirable nanostructure is always changed [22]; On the other hand, for the introducing of metal catalyst, catalysts based

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* Corresponding authors.
E-mail addresses: songjun@szu.edu.cn (J. Song), jlqu@szu.edu.cn (J. Qu).

https://doi.org/10.1016/j.apsusc.2018.04.027
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on noble metals (gold, silver, platinum, palladium, etc.) exhibit outstanding catalytic performances at relatively low temperature, but their high cost, and susceptibly to poisoning have greatly limited practical application of modified gas sensors [23,24]. Among these methods, to fabricate the heterostructures is a relatively simple and feasible way to enhance the gas sensing performance of metal oxide gas sensors involving increasing the electrons in the conduction band (n-n heterostructures) and emptying orbits into valence band (n-p heterostructures) of the semiconductor metal oxides heterostructures [25]. For instance, Zhang et al. designed SnO_2-TiO_2 hybrid materials with yolk double-shelled microspheres that exhibit a rapid response rate to ethanol gas with good reproducibility, which have showed great potential for designing practical ethanol devices [26]. Zhou et al. demonstrated the hetero assembly of n–type α-Fe_2O_3 nanoparticles on a p–type $LaFeO_3$ matrix into a pore-rich hollow nanostructure, which showed improvement at a relatively low working temperature (240 °C), high response (10.1 for 100 ppm ethanol) and fast response/recovery time [27]. Fu et al. prepared titanium oxide coated vanadium oxide core-shell nanostructures exhibit superior sensing performance toward ammonia than pure TiO_2 or V_2O_5 sensor materials [28].

In addition, researches primarily focused on binary oxides gas sensors in the past decades, which indicates that the research on ternary oxides gas sensors is still in a nascent stage currently. Only recently, some reports indicate that the ternary oxides nanocrystals are potential candidates in sensing area due to their inherent properties, such as high dielectric constant and active ability of electron transportation [29,30].

Upon the above consideration, a novel layered V_2O_5/ZnV_2O_6 hybrid structure is designed and synthesized using a one-step hydrothermal process without any surfactants. The layer nanostructures effectively promote electron transfer and the n-n heterostructures can increase the number of electrons in the conduction band during the sensing process. The synthesized V_2O_5/ZnV_2O_6 gas sensors also present better sensing performances than most of other V_2O_5 sensors earlier reported. A new insight is provided in the improvement of the sensing performance of V_2O_5 sensing devices in order to meet increasing sensing demands.

2. Experimental methods

2.1. Synthesis and characterization of V_2O_5/ZnV_2O_6 nanobelts

All reagents (analytical-grade) were used without further purification. 0.364 g of V_2O_5 was dispersed in 30 mL of distilled water; 5 mL of 30% H_2O_2 was introduced by dripping slowly under vigorous magnetic stirring at room temperature. The mixture was maintained for 1 h until the yellow solution turned orange in color. It was then transferred to a 40 mL autoclave and heated in an oven at 230 °C for 24 h. The final product was obtained after washing and drying at 80 °C for 2 h.

2.2. Physical characterization of the V_2O_5/ZnV_2O_6 nanobelts

The crystallographic structures were investigated by X–ray diffraction (XRD) using Cu Kα radiation with a wavelength, $\lambda = 0.15418$ nm (Rigaku D/Max–2550 diffractometer). The morphologies of the samples were analyzed using a combination of field emission scanning electron microscopy (FESEM, XL 30 ESEM FEG) and transmission electron microscopy (TEM, JEOL JEM–2100F). Surface chemical analysis was performed using an X–ray photoelectron spectrometer (XPS, ESCALAB MK II). The gas sensing characterization was carried out using a WS-30A gas sensing measurement system at a relative humidity of 30–40%.

2.3. Fabrication and measurement of gas sensor

The as-prepared V_2O_5/ZnV_2O_6 powder was uniformly dispersed in anhydrous ethanol to form a paste. And then it was coated on an alumina tube-like substrate (the outer and inner diameter of the ceramic tube substrate are about 0.8 mm and 1.2 mm) along with a pair of gold electrodes. The sample was subsequently dried in air at room temperature and aged at 120 °C for 24 h to improve stability and repeatability. A Ni-Cr heating coil was inserted and a static process was adapted to measure the electrical properties of the sensor. The sensor was first placed in a test chamber filled with air, and then transferred into another chamber also filled with air after which the test gas was injected into the chamber by an injector until the response reached a steady value. According to the chemical properties of different test gases, the response (R) of sensor is defined as, $R = R_a/R_g$ for the test gases. Here, R_a and R_g are resistances of the sensor when exposed to air and test gas atmosphere, respectively. The time taken to achieve 90% of the total resistance change in the case of adsorption and desorption, is designated as the response time and recovery time, respectively.

3. Results and discussion

3.1. Characterization of V_2O_5/ZnV_2O_6 nanobelts

The powder X-ray diffraction (XRD) pattern was used to examine the crystal structure of the V_2O_5/ZnV_2O_6 heterostructure. As seen in Fig. 1, distinct diffraction peaks of V_2O_5 and ZnV_2O_6 were obtained. The peaks are assigned to the corresponding crystal faces of V_2O_5 and ZnV_2O_6 and they can be perfectly indexed as the orthorhombic structure of V_2O_5 (JCPDS 65-131) and monoclinic structure of ZnV_2O_6 (JCPDS 23-757). No other crystals phases are detected, indicating a high purity of the samples.

Typical SEM images of the as-synthesized V_2O_5/ZnV_2O_6 samples at different magnifications are shown in Fig. 2. From the overall morphology (Fig. 2a), it is evident that the samples consist almost entirely of nanobelts, and the nanobelts are uniform in morphology and size. The high magnification image (Fig. 2b) indicates that the V_2O_5/ZnV_2O_6 structure adopt a not very homogeneous belt-like morphology.

TEM is then employed to gain further insights into the structure of V_2O_5/ZnV_2O_6 nanobelts. Fig. 3a and b shows a section of one single nanobelt with a diameter of ~1 μm at different magnifications. From the enlarged TEM image shown in Fig. 3b, it is evident that the nanobelt is composed of many thin layers packed together, which reveals the inherent layered structure. The high-resolution

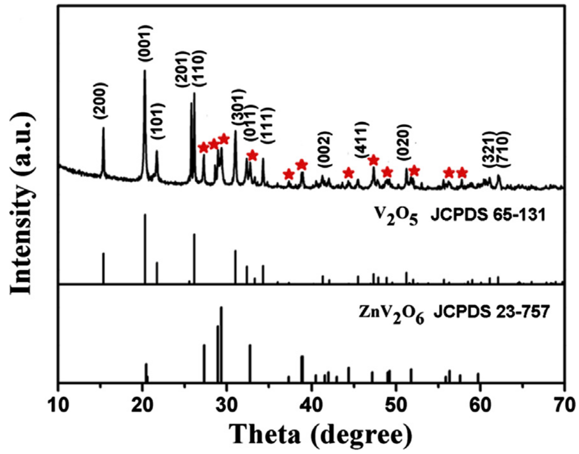

Fig. 1. XRD pattern of V_2O_5/ZnV_2O_6 products.