Materials Letters xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Materials Letters

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

Improved formaldehyde-sensing performance of SnO_2/Zn_2SnO_4 nanocomposites by structural evolution

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ARTICLE INFO

Article history:
Received 26 October 2016
Received in revised form 21 December 2016
Accepted 26 December 2016
Available online xxxx

Keywords:
SnO_2/Zn_2SnO_4
Nanocomposites
Porous materials
Structural evolution
Gas sensor

ABSTRACT

SnO_2/Zn_2SnO_4 hollow microspheres with porous shell (HPMSs) were successfully prepared by using ZnSn$(OH)_6$ (ZHS) hollow microspheres (HMSs) as sacrificial templates, which were pre-synthesized via a fast solid-state grinding method combined with subsequent chemical etching process. The obtained samples were characterized by XRD, SEM, TEM, and N_2 adsorption-desorption, respectively. Results indicated that the diameter of the prepared SnO_2/Zn_2SnO_4 HPMSs were around 300–700 nm and their shell-thickness was about 50 nm. On the shell of the composite HPMSs, a large number of 5–20 nm pores were in situ created. In comparison with the SnO_2/Zn_2SnO_4 porous microspheres (PMSs) that prepared directly from solid ZHS microspheres, the SnO_2/Zn_2SnO_4 HPMSs exhibited much higher sensitivity to formaldehyde, demonstrating the improved gas-sensing performance through structural evolution from PMS to HPMS.

1. Introduction

Due to the unique and prominent structure-dependent properties of nanomaterials, fabricating novel micro/nanostructures of metal oxide semiconductor (MOS) has long been a hot topic in the field of nanoscience and nanotechnology. Among various micro/nanostructures, hollow structures, especially of hollow micro/nanospheres, have attracted more and more attentions in recent years due to their features of low density, large specific surface area, and good surface permeability. These structural features can always endow the materials with superior physical and chemical properties that making them more promising for practical applications [1–3].

As two kinds of important tin-based functional semiconductors, SnO_2 and Zn_2SnO_4 have been widely studied because of their diverse functions and promising applications in photocatalysts, gas sensors, lithium ion batteries, and solar cells [4–9]. Considering that the performance can be improved by combining the individual functional materials together, SnO_2/Zn_2SnO_4 nanocomposite has attracted much research interest. In order to obtain SnO_2/Zn_2SnO_4, $ZnSn(OH)_6$ (ZHS) was usually used as a sacrificial template because it can decompose to SnO_2 and Zn_2SnO_4 (with a molar ratio of 1:1) at high temperature [10]. More importantly, during the thermal decomposition of ZHS, a great number of pores can be in situ created, resulting in the formation of SnO_2/Zn_2SnO_4 composite with porous structure. Up till now, different morphological ZHS has been fabricated via some solution-based synthesis methods [11–13]. However, these methods always suffer from long reaction time and using organic solvents or additives, as compared with the solid-grinding synthesis method [14,15]. Here, we report the synthesis of ZHS hollow microspheres (HMSs) by a fast solid-grinding method combined with subsequent chemical etching process and their successful application as sacrificial templates to synthesize SnO_2/Zn_2SnO_4 hollow microspheres with porous shell (HPMSs). The formaldehyde-sensing properties of the prepared SnO_2/Zn_2SnO_4 HPMSs were investigated to explore their possible application.

2. Experimental

Fig. 1a shows the synthesis process for the SnO_2/Zn_2SnO_4 composites. In a typical process for synthesizing SnO_2/Zn_2SnO_4 HPMSs, $SnCl_4{\cdot}5H_2O$ (0.35 g), $Zn(CH_3COO)_2{\cdot}6H_2O$ (0.22 g), and NaOH (0.32 g) were mixed in an agate mortar and grounded at room temperature for 10 min. After washing with distilled water for several times, the product was dried at 70 °C in air to obtain the white ZHS solid spheres. Subsequently, the prepared solid ZHS microspheres (1.0 g) were added into 20 mL aqueous solution of NaOH (2 M) and etched at room temperature for 10 min to obtain the hollow ZHS microspheres. The as-prepared hollow ZHS microspheres were

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http://dx.doi.org/10.1016/j.matlet.2016.12.080
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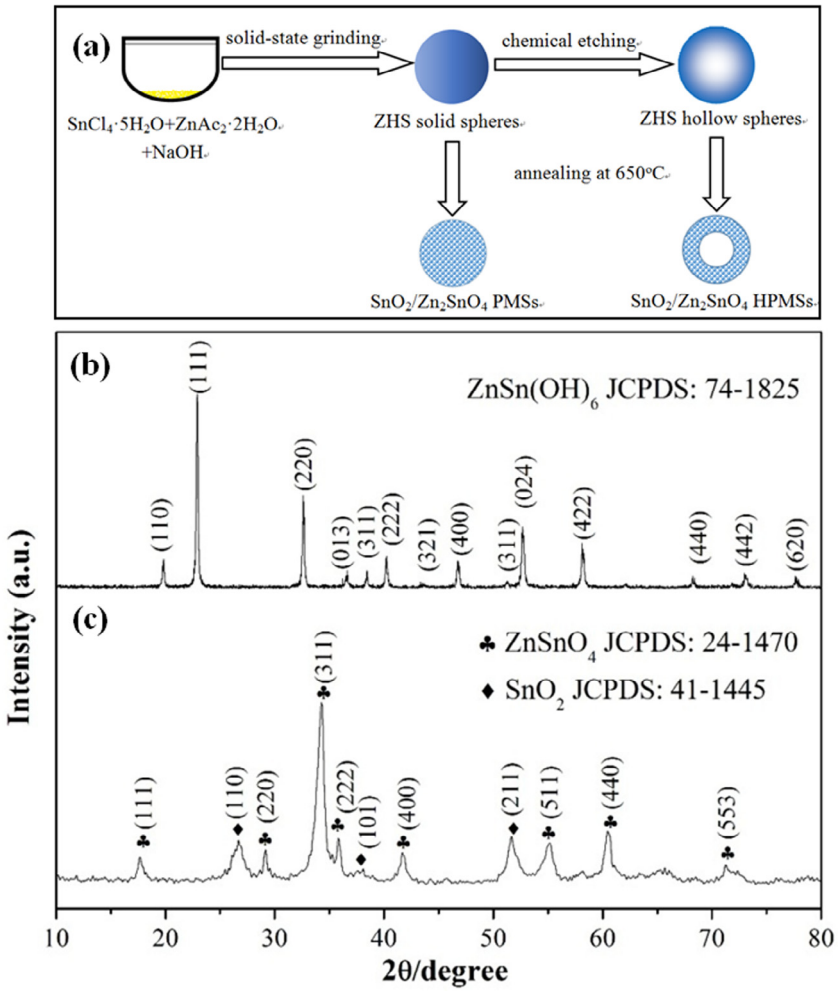

Fig. 1. (a) Schematic illustration for the synthesis of SnO2/Zn2SnO4 HPMSs and PMSs, and XRD patterns of the prepared (b) ZHS solid spheres and (c) SnO2/Zn2SnO4 HPMSs.

then annealed at 650 °C in air for 2 h to obtain the final SnO_2/Zn_2SnO_4 HPMSs. For comparison, SnO_2/Zn_2SnO_4 porous microspheres (PMSs) were also prepared by directly annealing the above ZHS solid microspheres at the same condition.

The phase and purity of the prepared samples were analyzed by X-ray diffraction (XRD, Bruker D8 diffractometer). The morphology and microstructure were investigated by scanning electron microscopy (SEM, JEOL, JSM-6390LV) and transmission electron microscopy (TEM, JEOL, JEM-2100). Nitrogen adsorption-desorption isotherms were collected on a Quantachrome AsiQM0000-3 sorption analyzer. The gas sensing property was measured on an intelligent analysis system of CGS-4TPS (Beijing Elite Tech Co., Ltd., China). The sensor was fabricated by coating the mixed slurry of deionized water with as-prepared sample onto a ceramic substrate (13.4 mm × 7 mm) screen-printed with interdigitated Ag-Pd electrodes. Before testing, the sensor was allowed to be aged at 200 °C for 24 h in air to improve the stability. The sensor response (S) was defined as the ratio of R_a/R_g, where R_a and R_g were the resistance of sensor in air and in target gas, respectively.

3. Results and discussions

Fig. 1b and c display the XRD patterns of the prepared samples. In Fig. 1b, all of the diffraction peaks were good agreement with the standard cubic $ZnSn(OH)_6$ (JCPDS No. 74-1825), and no diffraction peaks from other impurities were detected, indicating the synthesis of crystalline ZHS phase with high purity in the first solid-state grinding step. Fig. 1c shows the XRD pattern of the sample obtained by annealing the chemically etched ZHS. After the annealing process, the prepared ZHS was completely transformed to a mixture of SnO_2 (JCPDS No. 46-1088) and Zn_2SnO_4 (JCPDS No. 24-1470), resulting in the formation of SnO_2/Zn_2SnO_4 composite.

The SEM and TEM images of the prepared ZHS and SnO_2/Zn_2SnO_4 samples are presented in Fig. 2. From the SEM images showed in Fig. 2a and b, one can see that in the first solid-state grinding step ZHS microspheres with the diameter around 300–700 nm were obtained. The TEM images displayed in Fig. 2c and d further reveals the solid structure of these formed ZHS microspheres. After the chemical etching process, theses solid ZHS microspheres were successfully evolved into the hollow microspheres (Fig. 2e). The shell-thickness of these formed ZHS hollow microspheres is measured to be about 50 nm. Considering that ZHS can decompose to a mixture of SnO_2 and Zn_2SnO_4 at high temperature, the obtained ZHS hollow microspheres were then used as sacrificial templates to prepare SnO_2/Zn_2SnO_4. Fig. 2g shows the typical low-magnification TEM image of the prepared SnO_2/Zn_2SnO_4 sample. It can be seen that the hollow structure of the prepared ZHS precursor was basically passed on to its thermal decomposition product. Moreover, from the enlarged TEM image in Fig. 2h, we can clearly observe that a great number of nanosized pores were in situ created on the shell of the hollow microspheres, resulting in the formation of the unique hollow SnO_2/Zn_2SnO_4 microspheres with porous shell. The corresponding selected area

Please cite this article in press as: G. Sun et al., Improved formaldehyde-sensing performance of SnO_2/Zn_2SnO_4 nanocomposites by structural evolution, Materials Letters (2016), http://dx.doi.org/10.1016/j.matlet.2016.12.080