Sensors and Actuators B 241 (2017) 298–307

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

# Synthesis of the porous $NiO/SnO_2$ microspheres and microcubes and their enhanced formaldehyde gas sensing performance

Cuiping Gu [a], Yanwei Cui [a], Liyou Wang [a], Enhong Sheng [a], Jae-Jin Shim [b,*], Jiarui Huang [a,*]

[a] Key Laboratory of Functional Molecular Solids, Ministry of Education, Center for Nano Science and Technology, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, PR China
[b] School of Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk 712749, Republic of Korea

ARTICLE INFO

*Article history:*
Received 15 August 2016
Received in revised form 9 October 2016
Accepted 14 October 2016
Available online 18 October 2016

*Keywords:*
Tin dioxide
Nickel oxide
Porous
*p-n* Heterojunction
Formaldehyde
Gas sensor

ABSTRACT

Porous $NiO/SnO_2$ microspheres and microcubes were obtained using a facile chemical solution route combined with a subsequent calcination process. The morphologies and crystal structures of the products were comprehensively characterized via X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy, thermogravimetric-differential thermal analysis, and Brunauer–Emmett–Teller $N_2$ adsorption-desorption analyses. The process of inducing porosity began with the $NiSn(OH)_6$ precursors formed by the co-precipitation of the metal ions from the aqueous solution. Thermal decomposition of the precursors led to an intimate mixture of cubic phase NiO and tetragonal phase $SnO_2$ and formed the porous $NiO/SnO_2$ microspheres and microcubes. The gas-sensing properties of the as-prepared porous $NiO/SnO_2$ microspheres and microcubes for toxic volatile organic compounds (VOCs), such as formaldehyde, ethanol, benzene, methanol, acetone, and toluene, were investigated. Compared with other VOCs gases, the porous $NiO/SnO_2$ microsphere and microcube sensors exhibited a high response to formaldehyde. As for the porous $NiO/SnO_2$ microsphere sensor, the detection limit of formaldehyde was approximately 0.13 ppm (signal-to-noise ratio, S/N = 3). The relationship between the gas-sensing performance and the microstructure of the porous $NiO/SnO_2$ micro/nanomaterials was also discussed.



## 1. Introduction

In the recent years, poor indoor air quality (IAQ) has aroused public concern all over the world [1–3]. It is well known that formaldehyde is a colorless, strong-smelling gas used in making building materials and many household products, which is used in pressed-wood products, such as particleboard, plywood, and fiberboard, glues and adhesives, permanent-press fabrics, paper product coatings and certain insulation materials. Several experts believe that formaldehyde is the most important indoor air pollutant found in virtually all homes and buildings and at elevated levels is highly irritating to the eyes, nose, lungs, central nervous system, immune system, blindness and respiratory, which has been recognized as a known human carcinogen by the International Agency for Research on Cancer (IARC). Furthermore, many governing agencies have established limits of long-term exposure to HCHO: 0.07 ppm (30 min average) by World Health Organization (WHO) [4], 1 ppm by National Institute for Occupational Safety and Health (NIOSH), USA [5], 0.06 ppm (1 h average) by Chinese environmental protection agency (EPA) [6], 80 ppb for newly constructed building by Ministry of Environment, Korea [7]. Thus, it is very necessary to detect formaldehyde accurately.

Many methods were investigated to detect the concentration of indoor formaldehyde including spectrophotometry, potentiometric [8,9], mid-IR difference-frequency generation [10,11], amperometric [12–14], electrochemical biosensors [15–18], optical methods [19–22], piezoelectric sensors [23,24], and filter color testing methods [4]. Fortunately, nanostructure metal oxide semiconductors which are cheap to prepare and easy to use have shown the advantages of low cost, high sensitivity, fast response, quick recovery, and excellent stability in detecting gas pollutants. Gas sensor based on semiconductor functional materials, such as $SnO_2$ [25] or doped $SnO_2$ [26–31], NiO [32–34], ZnO [35–38] or doped ZnO [39–41], $ZnO/ZnSnO_3$ [42] and $\alpha$-$Fe_2O_3$@NiO nanofibers [43] and so on, have been investigated for formaldehyde detection. Unfortunately, this sensing material usually cannot meet the demand for detecting formaldehyde in the practical application.

* Corresponding authors.
*E-mail addresses:* jjshim@yu.ac.kr (J.-J. Shim), jrhuang@mail.ahnu.edu.cn (J. Huang).

http://dx.doi.org/10.1016/j.snb.2016.10.060
0925-4005/

Therefore, it is still a great challenge for metal oxides gas sensors to detect formaldehyde accurately and quickly for practical application.

As a type of wide-band gap semiconductor, $SnO_2$ sensors have been proven to be a kind of excellent gas-sensing material with predominant sensitivity and excellent chemical stability for formaldehyde gas [27]. How to obtain high sensitivity and selectivity to formaldehyde for $SnO_2$ sensors is still a challenge. It has been widely accepted that doping is one of the best ways to enhance selectivity and reduce sensing temperature of a gas sensor. Doping is mainly divided into two aspects, one is metal oxides doping and the other is noble metal doping. Recently, there were some reports on doped $SnO_2$ gas sensors for formaldehyde gas. For example, Tian et al. prepared the Pd-functionalized mesoporous $SnO_2$ fibers and its responses to 500 ppb formaldehyde is 4.63 where the sensitivity is a little low at working temperature of 190 °C [31]. Zheng et al. electrospun NiO-$SnO_2$ nanofibers which is very selective toward formaldehyde and the responses to 100 ppm formaldehyde is approximately 20.0 at working temperature of 200 °C [28]. Zhang et al. synthesized NiO-$SnO_2$ hybrid nanospheres for a formaldehyde gas sensor and the responses to 100 ppm formaldehyde is approximately 25.0 at working temperature of 100 °C [44]. These demonstrate that doping and hetero-structures can significantly improve the performance of formaldehyde gas sensors.

To improve the sensing properties of the $SnO_2$ gas sensor, three dimensional (3D) porous $SnO_2$ hetero-structures with high surface area are demanded. Here, porous NiO/$SnO_2$ microspheres and microcubes via a facile wet-chemical approach combined with a decomposition process. The gas-sensing properties of the porous NiO/$SnO_2$ microspheres and microcubes to VOCs, such as formaldehyde, ethanol, benzene, and toluene, were also investigated. A comparative gas sensing study between the as-prepared porous NiO/$SnO_2$ microspheres and microcubes was performed to confirm the superior sensing properties of the porous NiO/$SnO_2$ microspheres.

## 2. Experimental details

### 2.1. Synthesis of porous NiO/$SnO_2$ microspheres and microcubes

All chemicals were of analytical grade and used without further purification. A typical synthesis of the porous NiO/$SnO_2$ microspheres was as follows: 0.79 g of $SnCl_4{\cdot}5H_2O$ was first dissolved in 100 mL distilled water at 50 °C, followed by the addition of 0.76 g NaOH and 14.0 mL of 15.0 M ammonia with vigorous stirring. Subsequently, 50 mL of a 0.044 M $NiCl_2{\cdot}6H_2O$ solution was added to the above mixed solution with vigorous stirring at 40 °C for 10 min, resulting in a mixture with a blue precipitate. The mixture was then placed in an oven at 40 °C for 5 h. The resulting precipitate was centrifuged, washed and dried at 40 °C. The product was then annealed at 650 °C for 2 h in air, resulting in a gray product. The synthesis procedure of porous NiO/$SnO_2$ microcubes was similar as that of porous NiO/$SnO_2$ microspheres except that the reaction temperature is 95 °C.

### 2.2. Characterizations

The products were characterized through X-ray diffraction (XRD, Shimadzu XRD-6000, with high-intensity Cu Kα radiation with a wavelength of 1.54178 Å), scanning electron microscopy (SEM, Hitachi S-4800, operated at 5 kV), thermogravimetric analysis (TGA, SDT Q600, heating rate 10 deg/min in flow air), transmission electron microscopy (TEM, Hitachi H-800 with an accelerating voltage of 200 kV), and Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption (Nova 2000E). Pore-size distribution was determined from the adsorption branch of the isotherms using the Barett–Joyner–Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) measurements were carried out under a Thermo ESCALAB 250 system using an Al-Kα 150 W non-monochromatized X-ray source and a hemispherical energy analyzer at a pass energy of 30 eV.

### 2.3. Gas-sensor fabrication and response test

The structures of the sensor device and the measurement system are identical to a previous report [45]. The as-prepared porous NiO/$SnO_2$ microspheres and microcubes dispersed in an ethanol solution were coated directly on the outer surface of an alumina tube-like substrate using a pipette onto which a pair of Au electrodes had been printed previously, followed by drying at 60 °C for approximately 2 h and then annealing at 300 °C for approximately 2 h. Finally, a small Ni-Cr alloy coil was inserted into the tube as a heater, which provided the working temperature of the gas sensor. To improve the long-term stability, the sensors were kept at the working temperature (240 °C) for 2 days. A stationary state gas distribution method was used to test gas response. The test was operated in a measuring system from ART-2000A (Art Beijing Science and Technology Development Co. Ltd., PR China). Detecting gasses, such as formaldehyde vapor, were injected into a test chamber by a syringe and mixed with air (temperature between 27 and 29 °C, relative humidity 40–50%). The high-concentration formaldehyde vapor mixed with air (temperature 28 °C, relative humidity ca. 69%) is obtained from the saturated vapor of formaldehyde solution (40 wt%) without drying. In this study, only 1–100 mL high-concentration formaldehyde vapor mixed with air (temperature 28 °C, relative humidity ca. 69%) was injected into a 1000 mL test chamber by a syringe. Therefore, the relative humidity change of the final mixed gasses in the test chamber is in the range of 0.02–2.4% when the high-concentration formaldehyde vapor mixed with air is injected. The gas response of the sensor in this paper is defined as $S = R_a/R_g$ (reductive gases), where $R_a$ is the resistance in air and $R_g$ is the resistance in the air mixed with detected gases. In this measurement system, the gas response of the sensor also can be calculated using the following equation: $S = V_{gas}(5000\,\text{mV}\text{-}V_{air})/V_{air}(5000\,\text{mV}\text{-}V_{gas})$, where $V_{air}$ and $V_{gas}$ are the output voltages in air and the test gas, respectively. The response or recovery times are expressed as the time needed for the sensor output to reach 90% of its saturation after applying or switching off the gas in a step function.

## 3. Results and discussion

### 3.1. Structure and morphology

The porous NiO/$SnO_2$ microstructures were produced using two steps. First, sphere-like and cube-like nickel tin hydroxide [$NiSn(OH)_6$] precursors were derived from an aqueous solution process. Then, a thermal decomposition process of nickel tin hydroxide precursors in air at high temperature generated NiO/$SnO_2$ hybrids with similar morphologies. During the calcination process, NiO and $SnO_2$ crystals nucleate, grow, and aggregate. The reaction of the annealing process could be formulated as follows:

$$NiSn(OH)_6 = NiO + SnO_2 + 3H_2O(\text{massloss}19.3\%) \quad (1)$$

Fig. 1 presents the typical SEM images of the microsphere and microcube samples prepared at different stages. The as-prepared nickel tin hydroxide sample has micrometer-sized sphere-like shape as shown in Fig. 1a. All of them show the same morphology. The diameter of the nickel tin hydroxide spheres is approximately 700 nm. From the inset in Fig. 1a, the microsphere looks like solid