Sensors and Actuators B 227 (2016) 475–481

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Applications for rapid formaldehyde nanoreactor with hierarchical and spherical structure

Ying Wang [a], Dingsheng Jiang [a], Wei Wei [b], Linghui Zhu [a], Jingran Zhou [a,*], Dongming Sun [a], Shengping Ruan [b,*]

[a] State Key Laboratory on Integrated Optoelectronics, Jilin University, Changchun 130012, PR China
[b] College of Electronic Science and Engineering, Jilin University, Changchun 130012, PR China

ARTICLE INFO

Article history:
Received 14 August 2015
Received in revised form
11 December 2015
Accepted 17 December 2015
Available online 24 December 2015

Keywords:
Mesoporous structure
Rapid response
Nanoreactor
Formaldehyde

ABSTRACT

Cu@SnO_2 spherical nanoreactor with hierarchical structure was prepared through a simple solvothermal method, the structure and morphology were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) showing the materials with extraordinary 3D nanoarchitectures. The gas sensing properties of the as-prepared pure SnO_2 and Cu-doped SnO_2 were tested toward various gases. The results showed that Cu-doped SnO_2 sensor displayed an excellent selectivity toward formaldehyde at the operating temperature 230 °C, which was much lower than most formaldehyde sensor in heater type among previous reports. The τrec and the τrec values of the Cu-doped SnO_2 to 1000 ppm formaldehyde were 2 s and 2 s, respectively, demonstrating extraordinary gas sensing properties, while those of the pure SnO_2 sensor were relatively long. The enhancement might be attributed to increased oxygen vacancy due to formation of active centers around doped elements and broad surface of unique mesoporous structure.
© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Unique morphologies involving porous structure have frequently developed. Hierarchical structures composed by low dimensional blocks and porous oxide structures with well-aligned pore structures were studied by many reports [1]. Hierarchical nanostructures are the higher dimensional structures consisted of low dimensional structure, nanoscale blocks such as 0D nanoparticles, 1D nanofibers, and 2D nanosheets. In addition, hierarchical nanostructures show well-aligned porous structures with high surface area and less agglomerated configuration, while the non-agglomerated form of oxide nanoparticles is extremely difficult to accomplish. It should be known that beside higher dimensional morphology, hollow structure also attracts considerable attention because of their hollow interior architectures, which endow them not only with high specific areas and abundant inner voids, but also with controllable physical and chemical microenvironment. Compared with other techniques, solvothermal method possesses unique advantages, such as being simple but efficient, adaptable and less demanding for processing conditions. What's more, solvothermal processes may be used to control shape for fabrication of different dimensional nanomaterials [2]. Metal oxide materials made by these methods can exhibit unique application potential in microscopic physics and nano-devices [3].

As we all known that SnO_2 is one of the most important metal oxides, which has high temperature stability, with a direct bandgap of 3.6 eV, harsh environment tolerance and high surface reactivity. It has been widely used as gas sensing materials to detect gases such as C_2H_5OH, CO, NO_2, H_2S, due to its strong interaction with gas molecules and well controlled morphology [4]. Productive, low-cost and effective strategies for fabrication of nanomaterials with high specific surface area are urgently expected in potential applications of different applications.

In the past decades, amounts of analytical methods for the detection of VOCs have been reported, containing spectrophotometry [5], optical sensor detection [6] and ion chromatography [7] which are usually expensive requiring high energy-consumption and complex operation procedure, and unable to provide VOCs exposure information on a real-time basis. Thus, detection of gaseous formaldehyde (HCHO) is so difficult, leading to highly challenging to quantify and monitor. To maintain environmental safety, gas sensors are required for examining poisonous and hazardous gases, which have been widely applied in the fields of healthcare, safety, environmental monitoring and chemical process control since the introduction of chemical sensors [8–11]. Over the years, researchers have developed different sensors closely related to

* Corresponding authors. Fax: +86 431 85168242.
E-mail addresses: zhoujr@jlu.edu.cn (J. Zhou), ruansp@jlu.edu.cn (S. Ruan).

http://dx.doi.org/10.1016/j.snb.2015.12.063
0925-4005/© 2015 Elsevier B.V. All rights reserved.

both species and morphologies. With the rapid development of nanoscience and technology, considerable efforts have been made to synthesis of new-type material.

In present work, Cu@SnO_2 microspheres formed by 2D nanosheets with mesoporous and hierarchical structure were successfully fabricated by using elaborately designed experimental scheme of one-step solvothermal method. Their super formaldehyde sensing properties and response mechanism were investigated via a convenient and lossless measurement technique which was reported for the first time. Highly efficient sensing performance against formaldehyde was observed, which is much better than published reports, making the fabricated material a good candidate sensing material for high performance formaldehyde sensors.

2. Experimental

2.1. Materials synthesis

All the used chemical reagents in this work were analytical grade and used as purchased without further purification: $SnCl_2{\cdot}2H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, NaOH, $Na_3C_6H_5O_7{\cdot}2H_2O$.

In a typical procedure, Cu@SnO_2 microspheres were synthesized by a typical solvothermal method. Firstly, certain volumes of ethanol (15 mL) were dissolved in deionized water (15 mL) to form a clear solution, then $SnCl_2{\cdot}2H_2O$ (0.9 g), NaOH(4 mmol), sodium citrate(1 mmol) and certain amount of $Cu(NO_3)_2{\cdot}3H_2O$ (the molar ratio of Cu to Sn is 0.062) were added into above solution under constant stirring. After stirred vigorously for 5 h, the solutions were transferred into 50 mL Teon-lined stainless steel autoclaves. The autoclaves were heated at 180 °C for 10 h, and then cooled down to room temperature naturally. The precipitates were separated by centrifugation, washed with distilled water and ethanol 5 times, and dried at 80 °C for 24 h. Finally, microspheres with hierarchical structure were obtained. We referred to these samples as S0 and S1, representing pure SnO_2 and the Cu@SnO_2, respectively.

2.2. Characterization

X-Ray diffraction (XRD) analysis was conducted on a Scintag XDS-2000 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) to analyze the structure of the prepared products. Scanning electron microscopy (SEM) images were performed on a SHIMADZU SSX-550 (Japan) instrument to observe the morphology of the prepared products. Transmission electron microscope (TEM) images were obtained on a JEM-ARM200F microscope to observe detailed microstructures and detect elements of the prepared products, respectively.

2.3. Fabrication and measurement of gas sensor

The as-prepared material was mixed with deionized water in a weight ratio of 4:1 and ground in a mortar for 3 h to form a paste. The paste was then coated on an Al_2O_3 ceramic tube to form a sensing film (a thickness of about 300 μm) on which a couple of parallel Au electrodes was previously printed. Pt lead wires attached to these Au electrodes were used as electrical contacts. After the ceramic tube was calcined at 300 °C for 2 h, a Ni–Cr heating wire was inserted into the ceramic tube as a heater for controlling the operating temperature. The structure of a sensor is shown in Fig. 1. The details of the sensor fabrication were similar to our previous works [12].

Gas sensing properties were measured by CGS-8 intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd., China) under laboratory condition (25 °C, 40 RH%). The response value (S) was defined as $S = (R_a - R_g)/R_a \times 100\%$, where R_a and R_g denoted the sensor's resistance in the air and presence of the target gases. The time taken by the sensor to achieve 90% of the total resistance change was defined as response time when the target gas was introduced to the sensor (target gas adsorption) or the recovery time when the chamber was full of air replacing target gas (target gas desorption) [13].

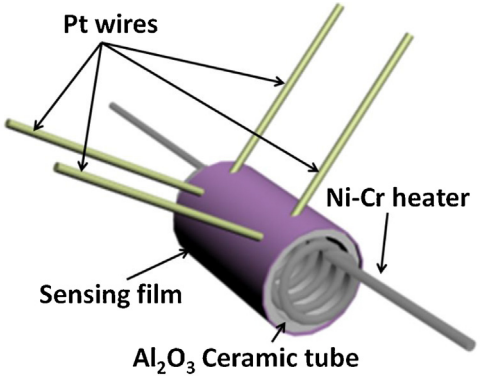

Fig. 1. Illustration of a gas sensor coated with sensing material.

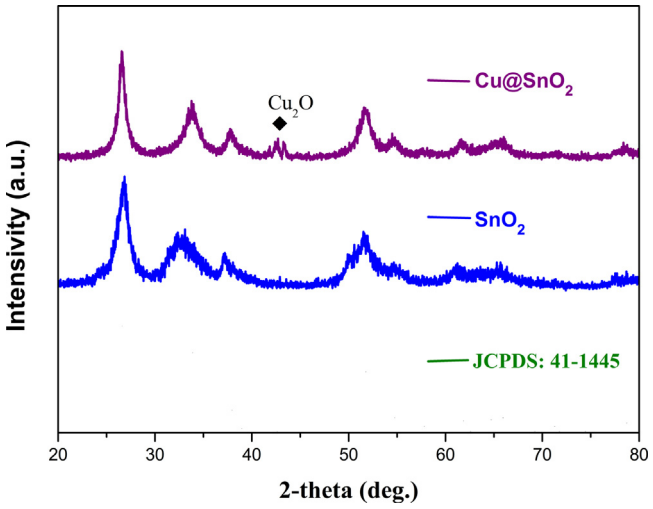

Fig. 2. XRD patterns of pure SnO_2 and Cu@SnO_2.

3. Results and discussion

3.1. Structural and morphological characteristics

The XRD patterns of S0 and S1 are shown in Fig. 2. It can be observed that all of the diffraction peaks of S0 and most peaks of S1 can be indexed to SnO_2, which were consistent with the Joint Committee on Powder Diffraction Standards card (JCPDS, 41-1445). The characteristic peak of Cu_2O (JCPDS, 35-1091) was also found, manifesting the place in lattice atom of Sn^{4+} was substituted by Cu^+. Therefore, the required products were successfully prepared.

To get further information about the unique architecture, SEM analysis was performed. The morphologies and nanostructures of the as-prepared S0 and S1 were characterized using FESEM (field emission scanning electron microscopy) as shown in Fig. 3. (a) and (b) displayed SEM images of S0; (c) and (d) displayed the SEM images of S1 in different magnifications.

Fig. 3(a) is the enlarged FESEM of a single sphere, showing that the sphere-like architectures consist of many nanosheets, estimated a diametral quotient in 1.8 μm and thickness in 25 nm.

Download English Version:

https://daneshyari.com/en/article/7144736

Download Persian Version:

https://daneshyari.com/article/7144736

Daneshyari.com