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Synthesis of SnO_2–CuO heterojunction using electrospinning and application in detecting of CO

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ABSTRACT

SnO_2–CuO heterostructures have been synthesized via electrospinning method, which overcomes the defect of SnO_2 generally prepared at high temperature. The structure, morphology, size, specific surface, thermal stability and surface composition of nanocomposite were characterized by XRD, SEM, TEM, BET, TG and XPS. The results testify that the change in property and structure of composite depends on the CuO content in composite. The SnO_2 composite with 30 wt% CuO not only exhibits excellent selectivity and high response that is 16 and 2.5 times higher than that of pure CuO and SnO_2, respectively, but also reduces the operating temperature from 295 °C to 235 °C. The mechanism enhanced sensing properties was discussed in detail, except for enhancing adsorption of gas on the material surface; the enhancement can be attributed to the formation of p–n heterojunction at the interface between the SnO_2 and the CuO.

1. Introduction

Carbon monoxide (CO) is a colorless, tasteless and odorless toxic gas, which results from the incomplete combustion of fossil fuels in motor vehicles, power plants and industrial plants. CO molecules have stronger associatively with human blood hemoglobin than oxygen molecules, which hinders the transportation of oxygen in the blood and can result in a lack of oxygen [1]. The threshold limit value of CO is about 50 ppm for human beings. When inhaling large quantities of CO over a short time period can result in fainting and even death. Thus, there is a need to sensitively and selectively monitor CO in real-time. Many attentions have been paid to develop novel sensing materials for detection of CO gas. In recent years, the sensing materials of metal oxide semiconductor (MOS) have attracted a great attention due to their structure stability, high sensitivity and inexpensive cost [2–4]. Among all the candidates of MOS, SnO_2 as a n-type semiconductor with wide band gap (Eg = 3.6 eV) is heavily favored sensing material to measure oxidizing and reducing gases [5], and is widely applied in UV-detectors [6], field-emitters [7], field effect-transistors (FETs) [8], solar cells [9] and lithium-ion batteries [10]. However, the pure SnO_2 sensing material cannot meet the requirement of highly sensitive detection for toxic gases, and generally prepared at higher temperature conditions. Therefore, many modifications have been tried to improve the sensing performance of SnO_2, such as element doping [11], noble metal loading [12] and coupling with another metal oxide to form n–n [13] or p–n [14] heterostructures. Kim et al. [15] prepared SnO_2 thin film based sensor via incorporating graphene and improved the sensitivity to 100 ppm of CO from 3.65 of pure SnO_2 to 6.84 of composite. Wang et al. [16] have synthesized the PdO-doped SnO_2 hollow nanospheres by a hydrothermal method using the silicon as templates and were applied as sensing material for detection of CO. The 1 mol% PdO/SnO_2 composite to 200 ppm of CO exhibited the highest response value of 11 at operating temperature of 150 °C. In this work, CuO, as an important p-type semiconductor with a narrow band gap (1.4 eV), was selected as the second metal oxide to couple with SnO_2 for formation of p–n heterojunction by electrospinning method, and the sensing performances of composites with different CuO contents were measured. Compared with other methods, such as chemical vapor deposition [17], pulsed laser deposition [18], the traditional sol–gel [19] and hydrothermal method [20], the electrospinning method is a relatively facile and versatile technique to prepare the pure and composites nanofibers with high surface to volume ratio. By searching literatures, we found that some of CuO–SnO_2

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Table 1
Response to CO of some SnO_2 nanomaterials and its sensing composites reported in literatures and this work.

Material	[CO] (ppm)	Response (R_{air}/R_{gas})	Operating temperature (°C)	Synthetic method
CuO/SnO_2 [26]	20	1.2	250	Electrochemical deposition
SnO_2 [25]	200	2.8	300	Hydrothermal method
PdO/SnO_2 [16]	200	11	150	Hydrothermal method
Au/SnO_2 [24]	20	32.5	200	Sputtering
Ag/SnO_2 [15]	100	17.5	400	Photochemical deposition
Pt/SnO_2 [22]	10,000	33	200	Sol–gel method
CuO/SnO_2 [23]	200	25	260	Hydrothermal method
CuO/SnO_2 (this work)	10	95	235	Electrospinning

composites have been fabricated by different methods to detect toxic gases. However, most of them were used to detect H_2S gas, while the CuO–SnO_2 composites used to detect CO has not been widely researched [21]. To comparison, Table 1 [15,16,22–26] summarizes the sensing responses to CO for various materials obtained using different synthesis methods. For example, Chen et al. [23] synthesized CuO–SnO_2 nanocomposites using hydrothermal method and the obtained sensitivity to 200 ppm CO was 25 at the operating temperature of 260 °C. In the work, we synthesized the CuO–SnO_2 nanocomposites by electrospinning method and obtained excellent sensing properties to CO. The mechanism enhanced sensing properties to CO was also discussed in detail.

2. Experimental details

2.1. Preparation of SnO_2–CuO composite nanofibers

All the chemicals were analytical grade and used without further purification. SnO_2–CuO nanofibers were synthesized by an electrospinning method and followed by annealing. In a typical procedure, 1.048 g $SnCl_2{\cdot}2H_2O$ and certain amount of $CuCl_2{\cdot}2H_2O$ (CuO (wt%) = 0, 10%, 30% and 50%) were added into 12 mL of N,N-dimethylformamide (DMF) under vigorous stirring for half an hour. Subsequently, 1.2 g of poly(vinylpyrroridone) (PVP, Mw = 1,300,000) was dissolved slowly into the solution under vigorous stirring for 2 h. The solution then was introduced into a 20 mL plastic syringe with a metallic needle of 1 mm inner diameter for electrospinning. The distance between the tip of syringe needle and Al plate collector was fixed at 15 cm, the feeding rate was adjusted at a constant rate of 0.5 mL/h and electric potential between the needle tip and the Al plate was maintained at 18 kV. The pure CuO nanofibers was prepared as the same process without adding $SnCl_2{\cdot}2H_2O$. The resulting nanofibers were annealed at 600 °C for 2 h with a heating rate of 5 °C min^{-1}. The electrospinning setup schematic illustration is shown in Fig. 1.

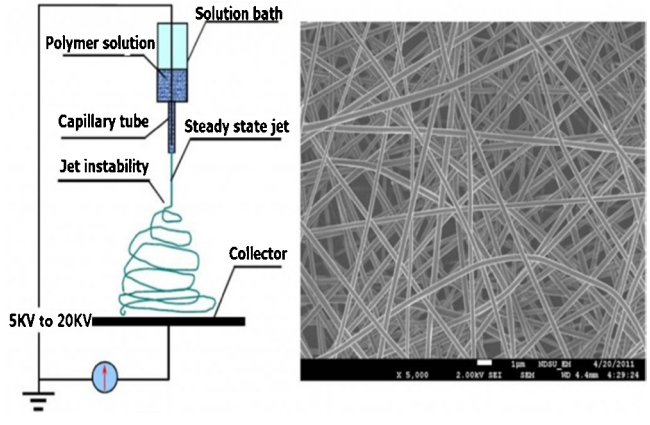

Fig. 1. Schematic illustrations of electrospinning setup and SEM image of electrospinning nanofibers.

2.2. Characterization

The crystal structure of SnO_2–CuO nanocomposites was analyzed by X-ray diffraction (XRD) with a Rigaku D/MAX-2500 X-ray diffractometer with copper Kα radiation (λ = 1.54178 Å), with a scanning speed of 10°/min for 2θ in the range from 20° to 80°. Field emission scanning electron microscopy (FE-SEM) images were obtained with a ZEISS Supra 55 instrument operated at 20.0 kV. Transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images were recorded with a JEOL JEM-2100F instrument operating at an acceleration voltage of 200 kV. Fourier transform infrared spectra (FTIR) were recorded on a FTIR absorption spectrometer (Nicolet 6700) in the range of 400–4000 cm^{-1} at room temperature. The sample was mixed with KBr at a mass ratio of 1:100. The thermogravimetric (TG) analysis was carried out in dynamic air atmosphere (75 mL min^{-1}) with a heating rate of 10 °C min^{-1} using NETZSCH STA449 F3 thermal analyser. The specific surface area of the powders was characterized with Brunauer–Emmett–Teller (BET) method (ASAP2020 M+C, Micromeritics Co., Ltd.). Surface elemental analysis was performed using an ESCALAB250 X-ray photoelectron spectrometer.

2.3. Response measurement to CO of SnO_2–CuO nanocomposites

To examine the sensing properties of CuO–SnO_2 composite to CO, the CuO–SnO_2 based sensor was fabricated by annealing the composite powder at 600 °C for 2 h and the response was measured by monitoring resistance change of the sensor in a temperature-controllable flowing system [27]. The annealed powder was pressed into a pellet with a diameter of 8.0 mm and a thickness of 0.5 mm under a pressure of 8 MPa and a pair of platinum filament was attached on both sides of the pellet to form the sensing element. Then the sensing element was placed in a response test apparatus and pretreated at 320 °C for 3 h to remove the adsorbents on the surface of the sensor. The target gas and air were introduced through two flow meters, respectively, to control the concentration of the target gas in air. Response measurement was carried out in the temperature range from 60 °C to 420 °C by adjusting the temperature controller of the heating. For the sensor of semiconductor metal oxide, the resistance was monitored as a function of the operating temperature for samples annealed at different temperatures. When air and ppm-level target gas flowed through the sensing element, the corresponding steady-state resistance of the element in air (R_{air}) and in the air–gas mixture (R_{gas}) was recorded, respectively. The response for reducing CO gas is defined as R_{air}/R_{gas}.

3. Results and discussion

3.1. Morphology, structure and thermal stability

The morphology of as-spun nanofibers was observed by FE-SEM, the microstructures of as-spun nanofibers for the other compositions were basically similar, so we took composite with