Preparation and H₂S Gas-Sensing Performances of Coral-Like SnO₂–CuO Nanocomposite

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Abstract Nanocomposites composed of SnO₂ and CuO were prepared by hydrothermal method. The microstructures of obtained SnO₂–CuO powders were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and nitrogen adsorption–desorption test. The results show that the nanocomposites exhibited coral-like nanostructure, and the average crystalline size of SnO₂ was 12 nm. The specific surface area of the four samples, SnO₂–0.2CuO, SnO₂–0.5CuO, SnO₂–1.0CuO and SnO₂–2.0CuO are 72.97, 58.77, 49.72 and 54.95 m²/g, respectively. The gas-sensing performance of the four samples to ethanol, formaldehyde and H₂S was studied. The sensor of SnO₂–0.5CuO exhibited high response to hydrogen sulfide (4173 to 10 ppm H₂S, where ppm represent 10^{−6}), and low response to ethanol and formaldehyde. The good selectivity exhibited that the SnO₂–0.5CuO nanocomposite can be a promising candidate for highly sensitive and selective gas-sensing material to H₂S.

KEY WORDS: Nanocomposite; SnO₂–CuO; Gas sensor; H₂S

1 Introduction

Developing low-cost and portable gas sensors is crucial for the safety of humans in underground coal mines, petroleum industries and gas storage plants and environmental control. Metal oxide gas sensors are also called “chemiresistors” because their resistivity can be modulated upon interaction with target gases [1–3]. Metal oxide composites can provide electric junction properties at the interface of heterostructures. Among the many surface doping materials, CuO, a p-type semiconducting material with an energy band gap of 1.2 eV, can be used in a range of applications including solar energy devices, electronics, sensors,

magnetic storage media, batteries and catalysis [4–7]. Meanwhile, SnO₂ is still the most investigated gas-sensing material because the gas sensors based on SnO₂ have the advantages of low operating temperature and long-term stability [8–10]. The gas-sensing properties of sensors based on SnO₂ depend on the factors like shape, size, microstructures and specific surface area of particulates [11]. CuO-doped SnO₂ thick films were reported to have an outstanding sensitivity and selectivity to hydrogen sulfide [12]. Subsequently, various materials based on SnO₂ with CuO as catalyst for hydrogen sulfide gas sensing have been synthesized and extensively studied, such as Cu–SnO₂ bilayers and CuO–SnO₂ heterostructures, CuO-doped SnO₂ nanoribbons and CuO-doped SnO₂ nanorods [13, 14]. Their high hydrogen sulfide gas-sensing mechanism is ascribed to the formation of p–n junction between n-type SnO₂ and p-type CuO, and the strong affinity of CuO to hydrogen sulfide that leads to the disruption of the p–n junction [15]. In the previous work [16], a green and facile approach for the controlled synthesis of coral-like SnO₂ was reported, which exhibits excellent gas-sensing performances. In the

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present work, $\text{SnO}_2\text{--CuO}$ composites were prepared with different CuO content via a hydrothermal method, and the gas-sensing properties of the composites were investigated.

2 Experimental

2.1 Materials Synthesis

All the Chemical reagents were analytical grade purchased from Shanghai chemical purchasing reagent Co. Ltd and used without further purification. The coral-like $\text{SnO}_2\text{--CuO}$ composite was obtained by controlled hydrolysis of SnCl_4 and CuCl_2 , and subsequent removal of the templates by calcination in air. The typical synthesis process was as follows: 10 mmol $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 20 mmol of glucose and 35 mg CuCl_2 (CuO content 1.0 wt%) were dissolved in 70 mL distilled water to form a homogeneous solution. The solution was transferred into a Teflon-lined stainless steel autoclave with a capacity of 100 mL. The autoclave was sealed and kept in an oven at 200 °C for 12 h. The precipitate was collected by centrifugation and washed for several times with ethanol and deionized water alternately, and dried. Then, the obtained powders were annealed in a furnace at 500 °C for 1 h in air. The sample was finally obtained after grinding the dry precipitate to a uniform powder. To study the effect of CuO content, four samples with different CuO content of 0.2, 0.5, 1.0 and 2.0 wt% were obtained. The corresponding samples were named as $\text{SnO}_2\text{--}0.2\text{CuO}$, $\text{SnO}_2\text{--}0.5\text{CuO}$, $\text{SnO}_2\text{--}1.0\text{CuO}$ and $\text{SnO}_2\text{--}2.0\text{CuO}$, respectively.

2.2 Gas Sensor Characterization

Gas sensor is fabricated as a side heated structure, as schematically shown in Fig. 1. The paste prepared from a mixture of $\text{SnO}_2\text{--CuO}$ composite with polyethylene glycol (PEG) and ethanol solution was coated onto an Al_2O_3 tube (4 mm in length, 1.2 mm in external diameter and 0.8 mm

in internal diameter) on which Au electrodes and Pt wires have been fixed at both ends. The sensor was sintered at 400 °C for 1 h after drying in air to remove ethanol and PEG. Finally, a heater of Ni–Cr wire with resistance of about 35 Ω was inserted into Al_2O_3 tube to control the operating temperature with the range of 80–500 °C. The gas sensors were aged at 400 °C for 2 days to improve their stability. Gas-sensing properties were measured under room condition (relative humidity range is 30–60%) using a static test system made by Henan Hanwei Electronics Co. Ltd, which included a test chamber (about 18 L in volume) and a data acquisition/processing system. The operating temperature of a gas sensor was adjusted through varying the heating voltage, because each heating voltage has its corresponding operating temperature. Sensor response (S) in this paper is defined as $S = R_a/R_t$, where R_a and R_t are the resistance of the sensor in air and in tested gas, respectively. The response and recovery time were expressed as the time taken for the sensor output to reach 90% of its saturation after applying or switching off the gas in a step function.

XRD data were collected in the 2θ region of 20°–80° with a scan rate of 4 deg./min at room temperature on the Bruker D8 Advance diffractometer with a theta–theta geometry and a $\text{CuK}\alpha_1$ radiation ($\lambda = 0.154056$ nm). The average grain size and strain were estimated by Williamson–Hall method and determined from a convolution-based full pattern fitting using the Topas software package [17]. The peaks were fitted using a simplified integral breadth method to account for both strain and grain size effects [18].

N_2 sorption isotherms were measured with a NOVA 2000e at 77 K (–196 °C, which is the temperature of liquid nitrogen under atmosphere pressure). Before the measurements, all samples were degassed at 120 °C under vacuum for 12 h. The pore volume and size distributions were derived from the adsorption branches of isotherms using the Barrett–Joyner–Halenda (BJH) model. The specific surface area A_s (m^2/g) was estimated via the BET method.

Scanning electron micrographs were obtained using an emission SEM JEOL JSM-6460LV fitted with an energy dispersive spectrometer (EDS) for elemental analysis. Transmission electron microscopy (TEM) experiments were performed on a JEOL JEM-200CX operated at 160 kV.

3 Results and Discussion

3.1 Structure and Morphology

Figure 2 shows the XRD pattern of $\text{SnO}_2\text{--}2.0\text{CuO}$ powders, which were calcined at 500 °C for 1 h. All the

Fig. 1 Schematic diagram of the sensor

Fig. 2 XRD pattern of $\text{SnO}_2\text{-}2.0\text{CuO}$

diffraction peaks are perfectly indexed to the rutile SnO_2 structure (JCPDS card, No. 41-1445). And the peaks of the doping element were not observed, which may attribute to the low doping amount. The average grain size of $\text{SnO}_2\text{-CuO}$ is about 12 nm, which is calculated by Topas software package. The small grain diameter suggests that the sensor would exhibit better gas-sensing performances to tested gases [19–21].

Figure 3 shows the SEM and TEM images of $\text{SnO}_2\text{-}1.0\text{CuO}$ composite. The SEM image exhibits a coral-like structure of $\text{SnO}_2\text{-}1.0\text{CuO}$ composite. From the TEM image, it is obvious that the $\text{SnO}_2\text{-CuO}$ coral-like nanostructure is assembled by nanocrystal. The formation of the coral-like structure should be ascribed to $\text{Sn}(\text{OH})_4$ colloid obtained by hydrolyzed Sn^{4+} on the surface of carbonaceous sphere which is conglomerated from small carbonaceous spheres by OH^- groups [22–24]. After removing carbonaceous materials by annealing treatment, the final products with coral-like porous structure are fabricated. Moreover, the coral-like $\text{SnO}_2\text{-CuO}$ have many

pores piled up by $\text{SnO}_2\text{-CuO}$ particles. The nanostructure of $\text{SnO}_2\text{-CuO}$ not only possesses large surface area and relatively mass reactive sites, but also forms relatively loose film structure which is an advantage for gas diffusion [25]. Mesopores provide plenty of active sites for surface chemical reactions, on the one hand. On the other hand, the gas diffusion in the sensing film can be improved by macropores greatly [26]. As a result of the coral-like porous structure, the sensitivity of the sensors will be remarkably high.

The nitrogen adsorption isotherm and pore size distribution curves of the mesoporous $\text{SnO}_2\text{-CuO}$ calcined at 500 °C are shown in Fig. 4. When the relative pressure (P/P_0) is in the range of 0.60–0.99, there is a hysteresis loops, which can be attributed to the filling and emptying of microspore by capillary condensation. Large textural porosity of the $\text{SnO}_2\text{-CuO}$ samples has been exhibited according to the results. Another factor that affects the sensing mechanism qualitatively is the specific surface area, which is measured by the BET method. The specific surface area of the four samples of $\text{SnO}_2\text{-}0.2\text{CuO}$, $\text{SnO}_2\text{-}0.5\text{CuO}$, $\text{SnO}_2\text{-}1.0\text{CuO}$ and $\text{SnO}_2\text{-}2.0\text{CuO}$ are 72.97, 58.77, 49.72 and 54.95 m^2/g , respectively. The higher specific surface area and the mesoporous structure have advantage for gas adsorption–desorption and result in the enhancement of the gas-sensing properties.

3.2 Gas-Sensing Properties

The resistances of sensors based on pure SnO_2 and $\text{SnO}_2\text{-CuO}$ composites in air as function of temperature are shown in Fig. 5. At low temperature, all the sensors show high resistance (in the grade of 10 MΩ) except that based on $\text{SnO}_2\text{-}2.0\text{CuO}$. The high resistances are partly attributed to the porous microstructure of the samples. The

Fig. 3 SEM image **a**, TEM image **b** of $\text{SnO}_2\text{-}1.0\text{CuO}$ composite

Fig. 4 Nitrogen adsorption isotherms and corresponding pore size distribution (*inset*) of samples: **a** SnO₂-0.2CuO; **b** SnO₂-0.5CuO; **c** SnO₂-1.0CuO; **d** SnO₂-2.0CuO

Fig. 5 Resistances of the sensors based on different coral-like SnO₂-CuO composites at different working temperatures

resistances of sensors based on SnO₂-0.2CuO, SnO₂-0.5CuO and SnO₂-1.0CuO increased rapidly than that of SnO₂. The high resistances are attributed to the doping

effect. It can be considered that a p-n junction formed between SnO₂-CuO grains to hinder electron transfer. The resistance of SnO₂-CuO decreased with the increasing working temperature, as more electrons are excited into the conduction band to increase its conductivity. But the resistance of SnO₂-2.0CuO is smaller than that of pure SnO₂, which do not attribute to p-n junction forming.

The responses to different gases of the sensors changed with different working temperature, as shown in Fig. 6. The responses of the sensors are the highest to hydrogen sulfide at 100 °C and decrease when the working temperature is over 100 °C. The results are not consistent with previously reported results which have an optimum working temperature about at 200–300 °C [27–31]. It is usually explained that oxygen species on the surface are not so active at low temperatures, while some of the adsorbed oxygen species desorb possibly from the surface at high temperatures; there should be an optimal temperature to balance the two effects in order to achieve the maximum

Fig. 6 Responses of sensor based on coral-like $\text{SnO}_2\text{-CuO}$ to different gases at different working temperature: **a** 100 ppm ethanol; **b** 100 ppm formaldehyde; **c** 1 ppm hydrogen sulfide

gas response. Here, the average crystallite size of the porous SnO_2 nanoparticles was about 12 nm, which is very close to the $2L$ (L is the thickness of depletion layer) of SnO_2 [32]. The high surface energy of these nanocrystalline SnO_2 increase oxygen species active energy, then the optimal working temperature shift to lower temperature.

Figure 7 shows the corresponding responses of $\text{SnO}_2\text{-CuO}$ gas sensors to ethanol (in the range of 100–1600 ppm), formaldehyde (100–1200 ppm) and hydrogen sulfide (0.1–10 ppm) under different gas concentrations at the optimal working temperature of each sensor. In general, the response of sensor has an increasing trend with increasing gas concentration. In all these cases, however, there is a saturation trend beyond a critical concentration. This is due to the change of stoichiometry of the elementary reactions and the competitions between volatile gas molecules for adsorption sites when gas concentration increases progressively [33, 34].

The response of $\text{SnO}_2\text{-CuO}$ sensors to H_2S is much higher than that of ethanol and formaldehyde. The highest response is found for $\text{SnO}_2\text{-0.5CuO}$, 712 and 4173 to

0.1 ppm and 10 ppm H_2S , respectively. The response of pure SnO_2 is very high to ethanol [16], while the responses of $\text{SnO}_2\text{-CuO}$ composites to ethanol are lower. It was widely reported that the mechanism of gas sensor in general is as follows: Metal oxides (ZnO or SnO_2) trap molecular oxygen from air in the form of O^- or O^{2-} on its surface. The electrons of O^- or O^{2-} come from the bulk of the metal oxides, and such trapping of the electrons by O^- or O^{2-} on the surface of the semiconductor increases the resistance. When the target gas comes on the surface of the metal oxides layer, it reacts with the O^- or O^{2-} and the trapped oxygen releases the electrons on the surface of metal oxides, and thus the resistance decreases. When the gas is purged by air (which contains oxygen), metal oxides again starts to absorb the molecular oxygen. But at the beginning of the second cycle, the electron density of the metal oxide surface is already higher by the electrons released at first cycle. So, some extra electrons come from the bulk of the semiconductor to the surface to absorb oxygen species, which in turn lowers the electron concentration in the bulk of the semiconductor and increases the base resistance at the beginning of the second gas in-

Fig. 7 Correlations between gas concentration and response of the sensor based on different coral-like $\text{SnO}_2\text{-CuO}$ composites to ethanol at 260 °C **a**, formaldehyde at 260 °C **b**, hydrogen sulfide at 100 °C **c**

out cycle [35, 36]. In these cases, the responses are limited, which is no more than 100 in general. But for $\text{SnO}_2\text{-CuO}$ composites, the responses to H_2S are much higher than 100, this is because CuO acts as the promoter in sensing action of $\text{SnO}_2\text{-CuO}$ [37]. It is supposed that CuO is dispersed on the intersection of the SnO_2 particles. Since CuO and SnO_2 were p type and n type semiconductor, p-n junction formed at the interface between SnO_2 and CuO . As a result of the p-n junctions, the bands of SnO_2 are bent upward at the surface region, resulting in increasing in the work function of SnO_2 . Thus, in air, $\text{SnO}_2\text{-CuO}$ gives rise to very large electrical resistance of the sensor element. CuS is a metallic conductor, and when CuO is converted to CuS on exposure to the reducing H_2S and air mixture, p-n junctions will be destroyed, and band structure of pure SnO_2 will be restored; the electrical resistance leads to drastic decrease and hence to the extremely large H_2S sensitivity. Sulphurization in H_2S -containing atmosphere takes place as follows:

CuS is not stable at high temperature; when the reaction temperature is higher than 220 °C, CuS changes into Cu_2S as follows:

On subsequent exposure to O_2 , sulfide will be brought back to oxide as follows:

As shown in Fig. 8a, the response of coral-like $\text{SnO}_2\text{-0.5CuO}$ sensor to hydrogen sulfide is high at 100 °C and the response time is about 25 s, but the resistance can not be recovered at 100 °C. Li et al. [26] simply attributed the slow recovery characteristic to the low operating temperature. Figure 8b is the response and recovery of the sensor at 300 °C to 30 ppm hydrogen sulfide. At the temperature, since the reactions (2) and (3) could be carried out easily, the sensors recovered quickly and the recovery time is about 40 s. In this method, after a test, the sensor should be operated at high temperature (300 °C) for 1 min to refresh it.

Figure 9 shows the response of $\text{SnO}_2\text{-0.5CuO}$ sensor at optimal working temperature and recovering at high temperature. The sample exhibits high sensitivity and recovers well. The sensor recovers rapidly, when the working temperature increase to 300 °C for 1 min after response at the optimal working temperature.

Fig. 8 Response and recovery curves of coral-like SnO₂-0.5CuO sensor at 100 °C **a**, 300 °C **b**

Fig. 9 Response–recovery curves of coral-like SnO₂ sensor, response to 30 ppm hydrogen sulfide at 100 °C and recovery at 300 °C

4 Conclusions

The coral-like SnO₂-CuO nanocomposites prepared by controlled hydrolysis of SnCl₄ and CuCl₂ exhibit high sensitivity to hydrogen sulfide at 100 °C. The response of SnO₂-0.5CuO sensor is from 4173 to 10 ppm H₂S at 100 °C. Meanwhile, the sensors show poor gas-sensing performances to ethanol and formaldehyde. The good selectivity implies that the gained SnO₂-CuO nanocomposites are promising candidates for highly sensitive and selective gas-sensing material to H₂S.

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