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Hierarchical spheres In_2S_3-based cataluminescence sensor for ammonium sulfide

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ABSTRACT

In the present work, three different kinds of In_2S_3: hierarchical microspheres A, B and C (HMa, HMb and HMc), which were synthesized by a hydrothermal method in the sodium dodecyl sulfate-thiourea (SDS-thiourea) system. XRD, SEM and BET were used to characterize the prepared In_2S_3 materials. Compared with the other two kinds of In_2S_3, the as-prepared In_2S_3 hierarchical microspheres B (In_2S_3 HMb) exhibit the best cataluminescence response to ammonium sulfide. The response and recovery times of the home-made ammonium sulfide gas sensor with In_2S_3 hierarchical microspheres B as sensing materials were about 8 s and 24 s, respectively. The linear dependence of the sensitivity on the ammonium sulfide concentration was observed in the range of 4–200 ppm with an excellent selectivity. These results indicated that In_2S_3 hierarchical microspheres B would be a good candidate for fabricating practical cataluminescence ammonium sulfide sensor.

1. Introduction

As a reducing regent, ammonium sulfide has been applied in many fields such as photographic color developing agent, textile manufacture and synthetic flavor. It is, however, inescapable that ammonium sulfide is also a flammable, explosive and malodorous gas [1]. Due to its volatile features, ammonium sulfide could cause short- or long-term adverse health effects by skin contact and inhalation [2]. Therefore, there is still a strong demand for stable, simple and portable sensors for the detection of ammonium sulfide.

In recent years, as one of the promising transduction principles for gas sensors, cataluminescence (CTL) phenomenon has attracted considerable attention of researchers due to their specific advantages such as low energy consumption, fast response and rapid recovery time [3–5]. Above all, CTL approach can expand the range of detectable species by utilizing a series of responsive sensing nano/micro-materials with improved analytical performance, and is adaptable for miniaturization [6–8]. Diverse CTL sensors have been developed based on various micro/nano-materials, such as TiO_2 [9, 10], $BaCO_3$ [11], Fe_2O_3 [12], Y_2O_3 [13, 14], SnO_2 [15], In_2O_3 [16], palladium/carbon [17] and $MgSiO_3$ [18]. However, for CTL gas sensors, the development of specific and new sensing nano/micro-materials with high sensitivity and good selectivity remains a great challenge [19–22].

As an important semiconductor, In_2S_3 has been widely used in the fields of optical, electric, catalytic and gas-sensing etc. [23, 24]. In particularly, diverse micro/nano-scale In_2S_3 materials has been synthesized [25–29] due to their morphology-dependent properties, which attracted considerable attention and research interest. Fabrication of the structurally complex configurations can further enhance their functionality in many interesting ways.

Herein, three kinds of hierarchical microspheres (HMa, HMb and HMc) In_2S_3 were controllably synthesized via a simple, low-cost hydrothermal method, and the further investigation on their cataluminescence performances indicated that the prepared hierarchical microsphere B In_2S_3 (In_2S_3 HMb) was a highly efficient and selective sensing material candidate for ammonium sulfide gas sensor, along with a potential application in environmental analysis.

2. Experimental

2.1. Chemical reagents and materials

All reagents were analytical reagent grade. $InCl_3$ was purchased from Shanghai Aladdin Co. Ltd. (Shanghai, China), and the others were obtained from Chengdu Kelong Co. Ltd. (Chengdu, China).

2.2. Preparation of materials

The indium sulfide microstructures were synthesized by a typical hydrothermal method. The three kinds of hierarchical microsphere In_2S_3 synthesis can be proximately described as follows: two identical solutions were prepared by dissolving $InCl_3$ in 40 mL water in a 50 mL beaker, and 1 g sodium dodecyl sulfate (SDS) was added under a

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continuous stirring for 20 min. Subsequently, 0.5 g thiourea was respectively added in the solutions with a consistent stirring (10 min). Then, the solutions were transferred into a 60 mL polytetrafluoroethylene (PTFE) autoclave equipped with a stainless steel shell, and autoclaves were heated at 160 °C for 5 h (In_2S_3 HMa), 8 h (In_2S_3 HMb) and 12 h (In_2S_3 HMc), respectively. After the hydrothermal treatment, orange precipitates appeared at the bottom of the autoclave and then were washed by ethanol and deionized water. At last, the orange precipitates were put into oven to dry at 60 °C.

2.3. Characterization and apparatus

The as-prepared In_2S_3 materials were characterized by XRD (Philips Analytical Netherlands) with Cu Kα radiation, SEM (S-4800field-emission scanning electron microscope (FE-SEM, Hitachi, operated at 10 kV) equipped with an energy-dispersive spectrometer (EDS)) and Brunauer–Emmett–Teller nitrogen adsorption–desorption (Quantachrome, Quadrasorb SI). CTL signals were recorded by Ultraweak Chemluminescence Analyzer (type: BPCL-II, made by the Biophysics Institute of the Chinese Academy of Science, Beijing, China).

2.4. Cataluminescence sensing measurements

The schematic diagram of the main features for ammonium sulfide sensing measurement is shown in Fig. 1. About 0.1 g of In_2S_3 material was coated as a layer on a ceramic heating rod, which was put into a quartz cell (laboratory-constructed, 110 mm long × 7 mm i.d.). The procedure of dipping a layer of In_2S_3 present as follows: firstly, 0.1 g In_2S_3 powder was dispersed in a certain amount of ethanol; secondly, turbid ethanol was uniformly dipped on to the surface of cylindrical ceramic heater, and then slightly blew the ethanol to dry; thirdly, repeated the second step until the In_2S_3 powder was completely coated on the surface of cylindrical ceramic heater. The temperature of the ceramic heater was controlled by a digital temperature controller. The air flow was supplied by a compressed gas cylinders and a precision flow meter was employed to control the gas flow rate. Ammonium sulfide was injected into the vaporizing chamber where ammonium sulfide was vaporized and was taken into the CTL quartz cell by the carrier gas at a certain flow rate with an about 60 s sampling pulse. In the CTL quartz cell, ammonium sulfide vapor was catalytically oxidized on the surface of In_2S_3 by the O_2 from the air and emitted lights for detection.

3. Results and discussion

3.1. Structure and morphology

The phase purity and the crystallinity of as-prepared In_2S_3 with different morphologies were examined by XRD. As shown in Fig. 2, the XRD patterns of hierarchical microsphere A (HMa) In_2S_3 (Fig. 2(a)), hierarchical microsphere B (HMb) In_2S_3 (Fig. 2(b)) and hierarchical microsphere C (HMc) In_2S_3 (Fig. 2(c)) all can be closely indexed to pure cubic In_2S_3 (space group Fd3m (no. 227)) with lattice parameter a = 10.77 Å. All strong peak positions and profiles were in good agreement with cubic In_2S_3 (JCPDS: 84-1385). The size and morphology of the products were characterized by scanning electron microscopy (SEM). Fig. 3(a, b) shows In_2S_3 HMa was composed by microspheres with plenty of particles covering. Fig. 3(c, d) shows the size and morphology of In_2S_3 HMb. One can see that the diverse pores were formed by plate-like nanostructures covering the surface of microspheres. The size and morphology of In_2S_3 HMc was shown in Fig. 3(e, f). In_2S_3 HMc was composed by microspheres with hollow structures and a large quantity of irregular polyhedrons, the diameters of the microspheres and irregular polyhedrons were around 5 μm and 500 nm, respectively. As shown in the EDS spectrums of three kinds of materials (Fig.4), the ratio of In atom to S atom is closer to 2:3, revealing that all the three kinds of materials are pure In_2S_3. The controllable synthesis and formation mechanism of as-prepared In_2S_3 was shown in Supporting Information.

3.2. Cataluminescence responses of ammonium sulfide vapor on the surface of In_2S_3

The CTL emissions of ammonium sulfide on the surfaces of micro-In_2S_3 materials with different morphologies were investigated. When gaseous ammonium sulfide passed through the surfaces of the three

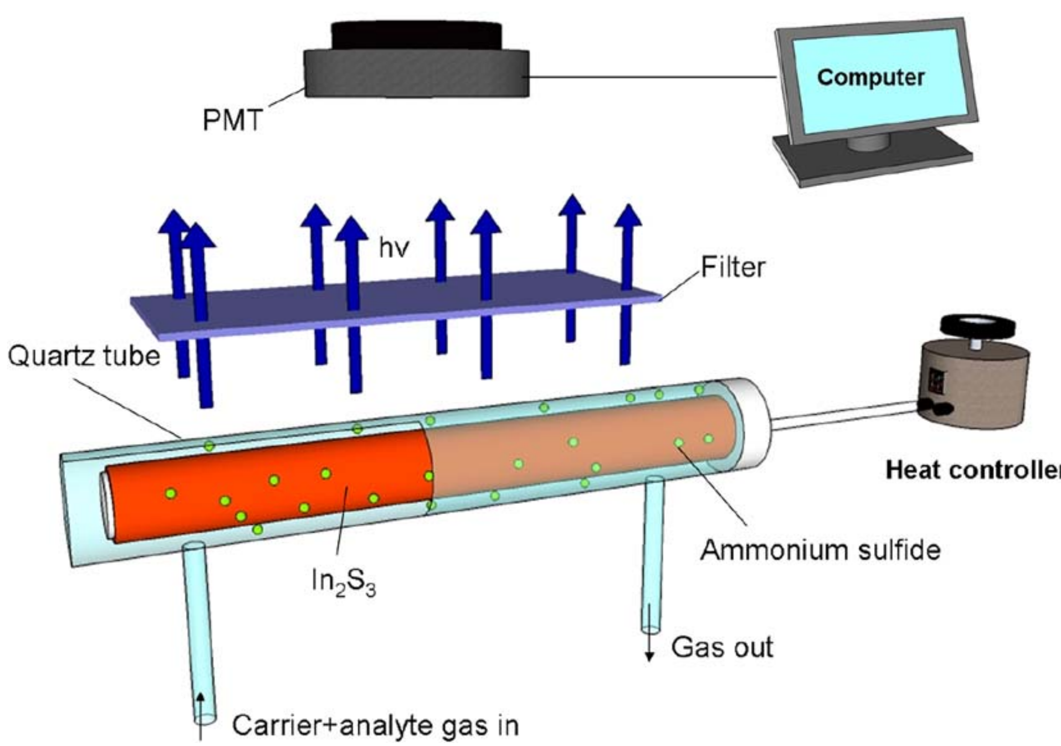

Fig. 1. Schematic diagram of CTL sensing system.