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Preparation and hydrogen sulfide gas-sensing performances of $RuO_2/NaBi(MoO_4)_2$ nanoplates

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ABSTRACT

The $NaBi(MoO_4)_2$ nanoplates and $RuO_2/NaBi(MoO_4)_2$ composites were synthesized by hydrothermal processes. XRD, SEM, TEM were employed to determine their phase composition and morphology, and the specific surface areas were obtained by BET. The results showed the $NaBi(MoO_4)_2$ nanoplates were tetragonal scheelite phase with average crystalline size of 25 nm. The $NaBi(MoO_4)_2$ nanoplates and $RuO_2/NaBi(MoO_4)_2$ composites were fabricated into gas sensors, and the gas-sensing results showed that the sensors were highly sensitive and selective to H_2S, especially the sensor of 1 wt% $RuO_2/NaBi(MoO_4)_2$. The sensing response of 1 wt% $RuO_2/NaBi(MoO_4)_2$ sensor was 19 to 5 ppm H_2S, 6.4-fold higher than that of pure $NaBi(MoO_4)_2$ sensor, the sensor also showed a fast response time of 11 s and a short recovery time of 4 s at 370 °C. Therefore, the $RuO_2/NaBi(MoO_4)_2$ could be a promising candidate material for fast detection of H_2S.

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1. Introduction

Hydrogen sulphide (H_2S) is a colourless, water-soluble gas, which usually is produced in sewage plants, kraft mills, asphalt plants and natural gas industries. H_2S is primarily viewed as a toxic gas and as an environmental hazard for many decades [1–4]. According to American Conference of Government Industrial Hygienists, the threshold limit value stipulated for H_2S is 10 ppm [5,6]. However, recent work has revealed that H_2S is a gaseous biological mediator that is produced in mammalian species, including humans. In addition, H_2S, as a vascular relaxant agent, may be a participant in the regulation of cardiovascular function [7,8]. Hydrogen sulfide is also recognized as low MW signaling molecule and mediator of a variety of human physiological functions. Thus the detection of H_2S at a low concentration is very important for safe protection and physical heath monitor.

Gas chromatography/mass spectrometry [9], ion chromatography [10], and selected ion flow tube mass spectrometer can detect low concentration H_2S with high precision [3]. However, these methods are not suitable and effective for real-time monitoring due to the limitations of the long time and high cost. In recent years, many efforts to develop sensitive H_2S detection sensors based on metal oxides (i.e. SnO_2, In_2O_3, ZnO, WO_3 etc.) were made owing to their high sensitivity, small sensor sizes, low cost, facile preparation, and low power consumption [11–16]. However, the present binary metal oxides based sensors still suffer from some drawbacks such as poor gas-sensing stability and long response and recovery times, which limit their application [17]. Qi et al. presented that ZnO nanorods decorated with a 2 nm-thick ZnS layer possess superior response to ppm-level H_2S at room temperature but with a slow recovery and the response curve could not recover to the original baseline after the release of H_2S [18]. Yong et al. reported the CuO/ZnO nanorod sensor exhibited high response (895 to 50 ppm H_2S), reversibility in the working temperature range of 300–500 °C, unfortunately, the response time of their sensor was more than 10 min [19].

Thus, it is necessary to develop highly sensitive H_2S-sensors with shorter response and recovery times and long-term stability. Much effort needs to be made to explore new H_2S-sensitive materials and further to improve the gas sensitivity of those materials. Koskela et al. reported the CuAC nanoparticle based H_2S sensors

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could detect H_2S gas with the sensitivity of less than 1 ppm at room temperature and can be processed as printable inks [20,21]. Many multi-metallic compounds such as Bi_2WO_6, α-Ag_2WO_4, $Fe_2(MoO_4)_3$ exhibited gas-sensing properties [22,23]. Zhu et al. presented the porous $Fe_2(MoO_4)_3$ nanorods which exhibited very good H_2S sensing properties at a low working temperature (80 °C) [24], and showed relatively fast response and recovery times, good selectivity, and long-term stability.

$NaBi(MoO_4)_2$, a scheelite type multi-metallic oxide with a band gap of 3.1 eV, has attracted considerable attention due to their excellent luminescent properties and photocatalytic activities [25–27]. It is promising materials for applications as luminophores, and laser devices and photocatalyst. Recently, the good gas sensing properties of $NaBi(MoO_4)_2$ nanocrystals have been found by our group [28]. Furthermore, doping semiconductor gas sensors has attracted a lot of interest because of the ability to tailor the electrical and microstructure properties, which has been proved to be pivotal [29–31]. Many studies have showed that the M (M = Ag [32], C_{60} [33], Ru [34], Au [35], Pb [36], Pd [37]) which is added in sensors can act as catalysts and improve the gas sensing properties.

In this work, the $NaBi(MoO_4)_2$ nanoplates were prepared by a simple hydrothermal method. A comparative investigation of H_2S sensing properties of pure and $RuO_2/NaBi(MoO_4)_2$ composites were carried out to depict the superior H_2S-sensing performances of $RuO_2/NaBi(MoO_4)_2$. In addition, the effect of the RuO_2 concentrations on gas sensitivity to H_2S was investigated. The results showed that 1 wt% RuO_2 caused significant variation in the specific surface area, electrical resistance, sensitivity and response-recovery time of $RuO_2/NaBi(MoO_4)_2$ nanoplates on exposure to H_2S gas.

2. Experimental

2.1. Samples preparation

All of the chemicals were analytical grade and used without further treatment. $NaBi(MoO_4)_2$ nanoplates were synthesized by two steps at different temperatures under auto generated pressure. In the first step, the precursor ($Bi_2(OCH_2CHOHCH_2O)_3$) was gained by a solvent-thermal method drew lessons from Goia [38]. In the second step, the same precursor with the weight of 0.4568 g was dissolved in 70 mL distilled water and treated in KQ3200DB–type ultrasonic cleaner for 30 min, and then 0.4530 g $Na_2MoO_4 \cdot 2H_2O$ was added to the above solution under vigorous magnetic stirring at room temperature. After being magnetically stirred at room temperature for 2 h, the precursor suspension was transferred into a 100 mL Teflon-lined autoclave. The autoclave was then sealed and maintained at 170 °C for 12 h. Subsequently, the autoclave was taken out and cooled to room temperature naturally. After filtration, the white precipitate was collected and washed with distilled water several times, then dried in vacuum at 80 °C for 12 h. The $NaBi(MoO_4)_2$ sample was finally obtained after grinding the dry precipitate to a uniform powder. $RuO_2/NaBi(MoO_4)_2$ samples were obtained by mixing (0.5, 1, 2, 3 and 5 wt% ratio) $RuCl_3$ with $NaBi(MoO_4)_2$ nanoplates in ethanol solution and then annealed at 400 °C for 30 min. The prepared samples were denoted as 0% Ru, 0.5% Ru, 1% Ru, 2% Ru, 3% Ru and 5% Ru.

2.2. Characterization

The crystalline phase was determined by powder X-ray diffraction (XRD) with a Bruker D8 Advance diffractometer using Cu Kα1 radiation (λ = 0.154056 nm) in the range 20–80° (2θ) at a scanning rate of 4° min^{-1}. The morphology and size of the samples were analyzed by a JEOL JSM-6460LV scanning electron microscopy (SEM) and a JEOL JEM-2100 transmission electron microscopy (TEM) operated at 200 kV. The specific surface area was obtained upon the multi-point Brunauer-Emmett-Teller (BET) analysis of N_2 sorption isotherms recorded at 77 K with a Nova 2000e surface area and pore size analyzer. The Ru content was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using an OPTIMA 8000DV spectrometer, USA Pekin-Elmer Corp.

2.3. Fabrication and measurement of gas sensor

Gas-sensing properties were measured under room condition (humid range 30–60%) using a WS-30A static gas-sensing system (Zhengzhou Weisheng Electronics Technology Co., Ltd., Henan, P.R. China). The gas sensors were side-heated type made as follows: a gas sensing sample was mixed with ethanol in an agate mortar to form the paste. The paste 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. A spring-like Ni–Cr wire was inserted into the Al_2O_3 tube to provide the operating temperature (Fig. 1). The thickness of the pasted films was in the range from 0.5 mm to 1 mm. All the sensors were aged at 400 °C for 24 h to improve their stability. The sensor signal voltage (V_{out}) was collected by computer at a constant test voltage of 5 V. The sensitivity, S, was determined as the ratio, $S = R_a/R_g$, where R_a was the resistance in air and the R_g was the resistance in the tested gas atmosphere. The response-recovery time was counted as the interval between the time when the response reached 90% of its maximum and that when it dropped to 10% of its maximum.

3. Results and discussion

3.1. Characterization of $RuO_2/NaBi(MoO_4)_2$

To determine chemical composition of the prepared powder, we firstly presented XRD patterns of the pure and $RuO_2/NaBi(MoO_4)_2$ samples as shown in Fig. 2. All of the peaks could be readily indexed to the same tetragonal scheelite phase $NaBi(MoO_4)_2$ (JCPD card no.51-1508). The diffraction peaks of samples at the angle of 28.4°, 30.8°, 33.9°, 46.5°, 53.3° and 57.4°, corresponded to the (112), (004), (200), (204), (116), and (312) lattice planes, respectively. And the Ru phase was not observed after doping low content $RuCl_3$ in the grinding process. That's should be owing to the low Ru content out of the measurement range of XRD or not crystallization. The average crystalline size of $NaBi(MoO_4)_2$ was estimated by (112), (004), (200) and (204) crystalline peaks to be 25 ± 2 nm.

Fig. 3a and b shows the SEM morphologies of the pure and 1 wt% $RuO_2/NaBi(MoO_4)_2$. It's clear that all of the samples were composed of nanoplates. In order to further study the structure of the samples,

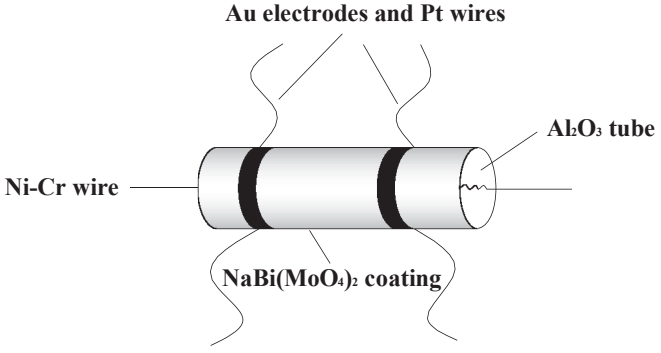

Fig. 1. Schematic diagram of the sensor.

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