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Comparison of toluene sensing performances of zinc stannate with different morphology-based gas sensors

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ABSTRACT

Nanosheet-assembled Zn_2SnO_4 hierarchical structure had been prepared by a hydrothermal method at 180 °C. Different structures such as hierarchical sphere and solid cube are obtained by using different surfactants. The sensor based on nanosheet-assembled Zn_2SnO_4 hierarchical structure materials outperforms many other hierarchical sphere and solid cube-like Zn_2SnO_4 materials in response to toluene detection. Close investigation revealed that the Zn_2SnO_4 nanosheet-based sensors exhibited fast response speed at 280 °C after 4 cycles as the sensing materials of gas sensor, indicating that the hierarchical compounds might have a promising future in the gas sensor application field.

1. Introduction

Correct understanding and accurately measure of atmospheric pollution and flammable gases release is one of the most important issues to ensure air quality and reduce disaster [1]. Toluene (C_7H_8) is a pollutants in the volatile organic compounds (VOCs), widely used as a chemical reagent, which is known as the main nosogenesis of nasopharyngeal cancer asthma [2,3]. Therefore the demand for continuous and real-time monitoring of toluene is increasing not only in the living environment, but also in the chemical engineering industry. These demands are always associated with the research of high performance gas sensor closely [4]. In particular, sensing materials are the key factors to accomplish high performance gas sensors. Many researchers have claimed that structures of sensing materials, such as hierarchical, porous or hollow structures, can largely contribute to sensing characteristics [5–7]. This is mainly due to that, compared with solid and aggregate nanoparticles-based sensing materials, these unique well-aligned porous nanostructures can offer a large surface-to-volume ratio and well-defined/well-aligned micro/nanoporosity, which is of enormous advantage to electrons transportation and gas diffusion, thus leading to enhanced sensing performances [8]. For example, Wang et al. reported excellent *n*-butanol sensing response of hierarchical flower-like SnO_2 nanostructures synthesized by a facile one-step hydrothermal method [9]. Kim et al. reported the preparation of hierarchical ZnO nanostructures by the alkaline hydrolysis of zinc salt which revealed improved ethanol sensing characteristics [10]. TiO_2 nanotubes show high sensing performance to ethanol and ammonia at the room temperature [11]. Moreover, hierarchical flower-like α-Fe_2O_3 nanostructures have been prepared via a simple solvothermal method and revealed a excellent sensing performance [12]. These results show that achieved enhancements of gas sensing characteristics by using hierarchical structures were mainly focused on binary compounds. To date, the simple synthesis strategy for the ternary compound hierarchical structures to achieve enhanced sensing performance is still rarely reported.

Ternary oxide Zn_2SnO_4 is known as a multifunctional material [13,14]. Because of its appropriate energy gap, high electrical conductivity and electron mobility, it has promising applications in photonic devices, photovoltaic devices, energy conversion/storage, photoelectrochemistry, functional coatings, and catalysis [15–18]. Moreover, Zn_2SnO_4 nanomaterials also have important applications in gas sensors [19,20]. However, reports on Zn_2SnO_4 materials as sensing materials for gas sensors are still technological challenge. Chen et al. reported excellent ethanol sensing response of hierarchical Zn_2SnO_4 nanostructures synthesized by a facile one-step hydrothermal method [21]. Very recently, Choi et al. reported porous Zn_2SnO_4 nanofibers architectures, which were

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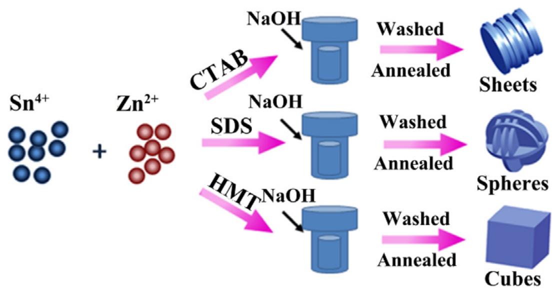

Scheme 1. Schematic illustration of the formation process of three different structures Zn_2SnO_4 materials.

prepared through an electrospinning process followed by thermal treatment, showed good ethanol sensing performances [22]. Considering the merits of structure and materials, herein, we report an environmentally friendly hydrothermal route applying different surfactant-assisted and combined with subsequent calcination to establish different Zn_2SnO_4 nanostructures in the shape of sheet/sphere/cube-like. We investigate the toluene sensing performances of three different Zn_2SnO_4 architectures (calcined at 500 °C). The sensing response of the hierarchical Zn_2SnO_4 architectures-based sensor with sheets self-assembly was significantly higher than that of the others (sphere and cube-like Zn_2SnO_4). The improved sensing properties can be attributed to the unique nanoarchitectures with large surface-to-volume ratio and well-gap between the nanosheets.

2. Experimental

2.1. Synthesis of materials

2.1.1. Synthesis of the hierarchical sheet-like Zn2SnO4 nanostructures

Briefly, 0.875 g of $SnCl_4·5H_2O$ and 0.545 g $Zn(Ac)_2·2H_2O$ were dispersed in a certain amount of deionized water by constantly stirring at room temperature to form a clear solution. Then, 0.227 g cetyltrimethyl ammonium bromide (CTAB) was put in the solution. After magnetic stirring of 30 min, a certain amount of (10 mL) NaOH was put in the mixed solution and form a suspension solution. The suspension was injected into a Teflon-lined. The Teflon-lined was heated to 180 °C and maintained for 12 h. The products were obtained by centrifugation, drying and annealing process. The precursor with a white color was annealed at 500 °C for 2 h in a muffle furnace. Two other types of the Zn_2SnO_4 materials are synthesized for comparison with similar method but using different surfactants, which were 0.2 g of sodium dodecyl sulfate (SDS) and 0.31 g of hexamethylenetetramine (HMT), respectively and designated as hierarchical Zn_2SnO_4 spheres and solid Zn_2SnO_4 cubes. The Teflon-lined was also heated to 180 °C for 12 h. Different structures of the Zn_2SnO_4 samples were obtained. The mainly reason that the capping molecules can tailor the surface energy according to the capping of the nuclei's surface and control the shapes of microcrystals [23,24]. The fabrication process for three different structures Zn_2SnO_4 samples is showed in Scheme 1.

2.2. Characterizations

Field emission scanning electron microscopic (FESEM) characterization was performed on SHIMADZU Japan, SSX-550. Transmission electron microscopy (TEM) images were achieved applying a JEOL JEM-2100 transmission electron microscope operating at 200 kV. The crystal structure and shape of the achieved materials were demonstrated with X-ray diffraction patterns (XRD) characterized via a Rigake D/Max-2550 diffractometer with Cu Kα radiation (λ = 0.15418 nm) (40 kV, 350 mA) in the range of 20–80° (2θ) at a scanning rate of 10° min^{-1}. The Brunauer–Emmett–Teller (BET) specific surface area was performed by N_2 gas adsorption using a Quantachrome NOVA 1000e analyzer.

2.3. Fabrication and measurement of gas sensing properties

A series of detailed fabrication, measurement, and parameters of the sensor are shown in Fig. 1, which are similar to the reports in the literature [25,26]. First, the obtained samples were mixed with moderate amounts of deionized water (about 1/4 weight to the samples), and this sensing paste was deposited onto a ceramic tube (diameter: 1.2 mm × length: 4.0 mm) with two Au electrodes. Then a heating wire (Ni–Cr) was put into the center of the ceramic tube to fabricate an indirect-heated gas sensor (Fig. 1(a)). The different operating temperatures of the sensor were obtained by adjusting heating current of RQ-2 gas-sensing test system. Finally, the gas sensor was achieved after aging at 100 mA relative current with a voltage of 5 V, for 24 h to the perfection of durability and stability. The photograph of the sensor is shown in Fig. 1(b).

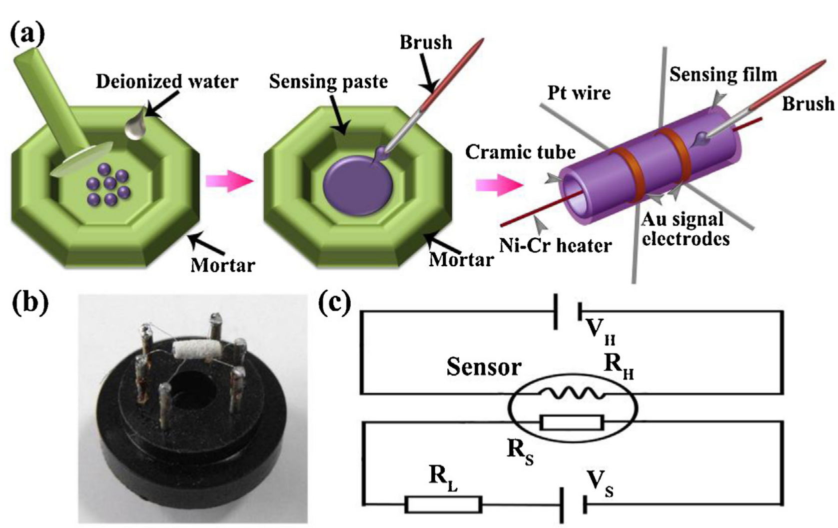

Fig. 1. (a) The preparation processes of sensors based on Zn_2SnO_4 samples (b) photograph image of the Zn_2SnO_4-based sensor, and (c) schematic diagram of the electrical circuit for measuring the gas sensor.