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Preferentially epitaxial growth of β-FeOOH nanoflakes on SnO_2 hollow spheres allows the synthesis of SnO_2/α-Fe_2O_3 hetero-nanocomposites with enhanced gas sensing performance for dimethyl disulfide

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ABSTRACT

Hetero-nanocomposites have shown extraordinary potential for improving the properties of nanomaterials originated from the interfacial interaction. Herein, we report the synthesis of the "sea urchin"-like SnO_2/α-Fe_2O_3 hetero-nanocomposites, which was constituted of SnO_2 hollow spheres and α-Fe_2O_3 needle-like nanoparticles, via integrating a two-step hydrothermal route with an annealing process. The detailed studies revealed that the preferentially epitaxial growth of two-dimensional β-FeOOH nanonanoflakes on three-dimensional SnO_2 hollow spheres in the second hydrothermal process is the main reason for the formation of such hetero-nanocomposites, which is also directly observed by the characterization on high resolution transmission electron microscopy. Significantly, such SnO_2/α-Fe_2O_3 hetero-nanocomposites were demonstrated as a promising sensing material for dimethyl disulfide and showed excellent gas sensing performances, prominently superior to the gas sensor based on pristine SnO_2 hollow spheres. More importantly, further H_2-TPR, CO-TPR and NH_3-TPD measurements for such hetero-nanocomposites shows that the enhanced sensing performances probably arise from the improvement of oxidizability induced by change of surface basic property of nanocomposites, as well as the formation of "electron accumulation layer" driven by the heterojunctions between SnO_2 and α-Fe_2O_3.

1. Introduction

Hetero-nanocomposites with well-defined architecture, which are comprised of the distinguishing building blocks, have shown extraordinary promise in many applications owing to their enhanced physical/chemical properties [1–7]. Moreover, the heterojunction generated at the nanoscale interface would be endow nanomaterials with the novel functionalities. Recently, great efforts have been dedicated to the synthesis of diverse nanostructures, including branched [8,9], core-shell [10–12], raspberry-like [13] and hollow [14,15] hetero-nanocomposites. Particularly, researchers are more focused on the hollow porous hetero-nanocomposites due to its merits of high specific area, short electron transport paths and more active sites. For example, hierarchical double-shell SnO_2/TiO_2 hollow spheres will improve solid-state dye-sensitized solar cell performance in contrast to nanotube-based materials [16]. Although a much progress has been acquired, it is still challenging to fabricate the complex hollow hetero-nanocomposites with tunable sizes, morphologies and compositions, and to explore their functional applications, such as in gas sensing.

Dimethyl disulfide (DMDS), a kind of typical volatile organic sulfur, widely existed in sewage treatment, petroleum-refining process, the wood-pulping industry and energy-related activities, is one of the toxic contaminants [17,18]. It is also found that DMDS gas are extremely toxic to human respiratory and nerve systems even in low concentrations [19]. To the best of our knowledge, various analytical techniques have been developed in the detection of the DMDS, including gas chromatography-mass spectrometry [20,21], biosensors [22], electrochemical sensors [17], and optical sensors [23]. Most of these techniques, however, have their own disadvantages of high power consumption, high cost, intricate instruments or testing procedures and time-consuming. Metal-oxide semiconductor (MOS) sensors have received significant attentions owing to their low-cost, high sensitivity, low detection limit and fast response/recovery speed. Nevertheless, there is very little report on the use of MOS sensors for the detection of DMDS, and it is very important to explore the DMDS gas sensors with high sensitivity, excellent selectivity, and outstanding stability.

SnO_2 and α-Fe_2O_3, two of the fundamental semiconductors, have been attracted tremendous research interests in various field, including

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catalysis [24–26], energy storage [27,28], gas sensors [29–32] and photo-conversion [33]. Until now, several types of the SnO_2/α-Fe_2O_3 composite with different morphology have been successfully constructed by various strategies. For example, Niu and co-workers fabricated the branched SnO_2/α-Fe_2O_3 semiconductor hetero-nanocomposites by a hydrothermal strategy, which exhibit better visible light photocatalytic capacities than α-Fe_2O_3 precursors [34]. Wang et al. have reported a two-step hydrothermal method to assemble ultra-thin α-Fe_2O_3 nanorod arrays on the surface of SnO_2 nanosheet [35]. In addition, branched hetero-nanocomposite consisted of SnO_2 nanowire stem and α-Fe_2O_3 nanorod branches has also been synthesized via integrating a vapor transport deposition with a facile hydrothermal approach, such α-Fe_2O_3/SnO_2 nanocomposites showed superior performances as a lithium-ion anode material than pure SnO_2 and α-Fe_2O_3. [9] However, despite these exciting nanocomposites were achieved, a common defect of relatively low specific surface area of the above-mentioned composites was encountered. Therefore, the SnO_2/α-Fe_2O_3 nanocomposite materials with hollow porous structure, incorporating both advantages of SnO_2 and α-Fe_2O_3, were expected. However, there are few reports on the synthesis of this structure, especially by using a simple hydrothermal method. Very recently, the assembly of α-Fe_2O_3 nanosheet on SnO_2 hollow nanospheres was realized by a microwave-assisted hydrothermal method [36]. Further efforts are needed to achieve microwave-free synthesis.

Herein, we present the synthesis of the uniform “sea urchin”-like hollow SnO_2/β-FeOOH structures by a two-step hydrothermal process, followed by calcination to yield SnO_2/α-Fe_2O_3 hetero-nanocomposites. The ultrathin β-FeOOH nanoflakes were preferentially epitaxial grown on the hollow SnO_2 hollow spheres, which was regarded as the main reason for the formation of SnO_2/α-Fe_2O_3 hetero-nanocomposites and proved by high resolution transmission electron microscopy (HRTEM). Moreover, we use these nanocomposites as the sensing materials for DMDS, the detection limit could reach as low as 200 ppb at 177 °C. More importantly, the SnO_2/α-Fe_2O_3 based sensors exhibited enhanced performances in contrast with the pristine SnO_2 based sensors in terms of the sensitivity and selectivity. Through analysis of H_2-TPR, CO-TPR and NH_3-TPD for these products, the performance improvement may be derived from the enhancement of oxidizability induced by variation of surface basic property of nanocomposites, as well as the formation of “electron accumulation layer” driven by the heterojunctions between SnO_2 and α-Fe_2O_3.

2. Experimental section

2.1. Materials

stannic chloride, concentrated hydrochloric acid (36–38 wt%), iron chloride, iron dichloride, iron nitrate, potassium ferricyanide, and ethanol were purchased from Sinopharm Chemical Reagent Co.,Ltd. All chemicals were used without purification.

2.2. Synthesis of SnO_2 hollow spheres

The monodispersed SnO_2 hollow spheres were fabricated via a modified method according to the literature [37]. Briefly, 0.8 g of $SnCl_4$ was dispersed in 55 mL of the mixture of ethanol and deionized water (v/v = 4:1). Then, 2 mL of concentrated hydrochloric acid (36–38 wt%) was added in above solution and stirred 30 min. The solution was subsequently transferred to Teflon-lined autoclave and reacted for 12 h at 200 °C. The products were collected by centrifugation and washed three times by ethanol and deionized water. The products were dispersed in 20 mL of deionized water again for following use.

2.3. Synthesis of SnO_2/α-Fe_2O_3 hollow nanocomposites

The 5 mL of the SnO_2 dispersion was added into 25 mL of deionized water with ultrasonication for 5 min. Then, 50 mg of $FeCl_3$ was dissolved into the SnO_2 dispersion with stirring 10 min. The obtained dispersion was put into Teflon-lined autoclave and heated at 120 °C for 60 min. The products were collected via centrifugation and washed by ethanol and deionized water. At last, the products was dried at 60 °C for 2 h and annealed in air for 2 h at 400 °C.

2.4. Characterization

The field-emission transmission scanning electron microscopy (TEM), high-resolution TEM (HRTEM) and the energy dispersive X-ray spectrometry (EDS) mapping were taken with a Tecnai G2 F20 operating at 200 kV. The field-emission scanning electron microscopy (FE-STM) was performed with SU8020. The power XRD was performed with a Philips X’Pert powder X-ray diffractometer using Cu Kα radiation (λ = 0.15419 nm). X-ray photoelectron spectroscopy (XPS) was carried out on a PREVAC system.

The catalyst activity of the as-prepared products was measured by H_2 and CO temperature programmed adsorption (H_2/CO-TPR; TP-5076, China) and the acid/basic property of the as-fabricated products was evaluated by NH_3 temperature programmed desorption (NH_3-TPD; TP-5076, China). For H_2-TPR and CO-TPR, the products were pretreated in a N_2 flow at 150 °C for 60 min, then 1% H_2/N_2 and 5% CO/N_2, respectively, were flowed at a temperature range of 150 ~ 600 °C with a heating rate of 10 °C/min. NH_3-TPD was conducted in N_2 flow after pretreated with NH_3/N_2 (2%) at 120 °C for 60 min.The heating rate was 10 °C/min.

2.5. Gas sensing measurement

The gas sensors were prepared by brushing the ethanol dispersion of the samples on the plate electrode. Then, the as-prepared sensors were sintered at 500 °C in air for 2 h at heating rate of 2 °C/min and aged at 300 °C for a week. Gas sensing measurement was conducted in a static measurement system with a multimeter/DC power supply and a test chamber (~2 L). During the testing process, the target gas was injected into chamber by an injection syringe, and the concentration of the target gas in chamber can be calculated based on the ratio between the injected amount and total volume of the chamber. The gas response of the sensors is defined as R_a/R_g, where R_a and R_g present the resistances of the sensors measured in air and target gas, respectively [38]. The definition of the response and recovery time were the time taken by the sensor to reach 90% of the total resistance change [39]. The relative humidity and temperature in the chamber were 35% and 26 °C, respectively. Here, we must point out, the relative humidity and temperature in ambient air were measured and recorded by moisture apparatus and thermodetector, respectively. According to the detection result, the provided values of both humidity and temperature were average values. The absolute humidity was in a range of 1.109 ~ 1.219 kpa with a temperature range of 25 ~ 27 °C in ambient air.

3. Result and discussion

The monodispersed SnO_2 nanospheres were fabricated by a hydrothermal approach, the morphology and configuration of the as-synthesized samples were exhibited in Fig. 1 (a and d). It was demonstrated that a mass of uniform spheres with a diameter of approximately 180 nm were achieved. Moreover, the TEM image (Fig. S1, Supporting Information) further shown that the obtained products possessed well-defined hollow structure and were constructed by plenty of free-standing zero-dimensional nanoparticles. In addition, the power XRD pattern of the as-fabricated products indicated that all diffraction peaks could be assigned to the SnO_2 phase with a tetragonal structure (JCPDS No. 41–1445) (Fig. S2, Supporting Information). It is well known that the hydrolysis reaction of the Fe^{3+} ions easily occurred under hydrothermal conditions. In order to acquire the SnO_2/β-FeOOH structures