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Review

Synthesis of SnO_2 nano-dodecahedrons with high-energy facets and their sensing properties to SO_2 at low temperature

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ABSTRACT

Dodecahedron-like SnO_2 nanomaterial was synthesized via a solvothermal method under mild reaction condition. The morphological and structural characterization results indicated that the as-prepare dodecahedral SnO_2 nanocrystallines with the average length of 130 nm and width of 45 nm were partially surrounded by high surface-energy {221} facets. The gas-sensing performance of the sample was investigated and the experiment results showed that the sensor had a good sensitivity to sulfur dioxide (SO_2) at 183 °C. To 800 ppb SO_2, the response could reach 1.32 and the response time was about 10 s. The good SO_2-sensing performance of SnO_2 nanocrystallines was closely related to the high surface-energy {221} facets whose surface possessed more dangling bonds and the corresponding SO_2-sensing mechanism was discussed.

Contents

1. Introduction

With the development of the industry, a large number of gas pollutants are releasing into air leading to serious damagement on environment and human health. For instance, sulfur dioxide (SO_2), coming from the burning of coal, gasoline and other sulfur-

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containing substances, will form acid rain to corrode buildings and plants. In a closed space, a low concentration of SO_2 can cause respiratory diseases and even pose a threat to one's life. In order to detect SO_2, a great deal of work has been undertaken since an early time [1,2]. From a practical aspect, it is perfect that a SO_2 sensor has high sensitivity, low cost, simple structure and good portability. And it is of great importance to fabricate a reliable gas sensor which can detect SO_2 at ppb level under a mild working condition. The sensors based on metal oxide semiconductor have attracted increasingly attention in gas sensor field [3,4],due to their advantages of high response, short response/recovery time and simple structure. For example, Das et al. reported the nano-sized bismuth ferrite ($BiFeO_3$) material showed excellent low-ppm SO_2-sensing behavior and its response to 5 ppm SO_2 could reach 2.03 at an operating temperature of 300 °C [5].

Tin dioxide (SnO_2) is a versatile n-type metal oxide semiconductor with a wide band gap of 3.6 eV [6]. Owing to the excellent physical properties, SnO_2 nanomaterials have been attracting much attention of research and application in the fields of lithium batteries, dye-sensitized solar cell, photocatalysis, ultraviolet photodetector, etc [7–11]. In gas sensor field, SnO_2 nanomaterials also show a superior ability to detect variety of combustible and poisonous gases including methane, carbon monoxide, ethanol, formaldehyde and so on [12–14]. Since gas sensing process involves chemical reactions occurred on the surface of a semiconductor nanomaterial, the gas sensitivity remarkably depends on the spatial structure and surface state of semiconductor nanomaterial [12–14]. Therefore, the gas-sensitive properties of SnO_2 nanomaterials with various morphologies (like nanowire, nanofiber, nanosheet, porous structure, hierarchical structure, etc.) have been extensively researched [11–18].

Due to rich dangling bonds, it is considered that high surface-energy facet of a crystal material has a higher surface-activity than that with low surface-energy, which is of great benefit to the surface-activity-depended applications like gas sensor, photocatalysis and lithium storage [19,20]. However, a crystalline grain usually prefers to expose crystal planes with low surface-energy. For example, both natural and synthetic SnO_2 crystals are usually enclosed by (1 1 0), (1 0 1) or (1 0 0) facets with low surface-energy. In order to obtain nanomaterials with exposed high surface-energy facets, researchers have been making great efforts to develop the synthetic methods and the hydro-/solvo-thermal method is more popular due to the abundant controllable conditions (PH, temperature, concentration, etc.) and simple equipment requests [19–25].

In this paper, dodecahedron-like SnO_2 nanomaterial was synthesized via a solvothermal method and its gas sensing properties were investigated. The morphological and structural characterizations revealed the as-prepared SnO_2 nanocrystallines were partially enclosed by high surface-energy {221} facets. And the test results about gas sensing properties showed the as-prepared SnO_2 had a good sensitivity to ppb-level sulfur dioxide (SO_2) at a low operating temperature. The good SO_2-sensing performance of SnO_2 nanocrystallines was closely related to their exposed facets and the possible SO_2-sensing mechanism was discussed.

2. Experimental

2.1. Chemical reagent

All chemical reagents were purchased and used without further purification including: Tin (IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, analytical grade, Mw = 350.6, Sinopharm Chemical Reagent Co., Ltd.), polyvinylpyrrolidone (PVP K88-96, analytical grade, Aladdin Industrial Co., Ltd.), hydrochloric acid (HCl, analytical grade, Mw = 36.46, Beijing Chemicals Works) and ethanol (CH_3CH_2OH, Mw = 46.07, Beijing Chemicals Works).

2.2. Synthesis process

In a typical procedure, SnO_2 dodecahedron nanomaterial was synthesized by a solvothermal method [19]. Firstly, certain volume of ethanol (6 mL) was mixed with deionized water (6 mL) to form a clear solution. Secondly, 0.7 g $SnCl_4 \cdot 5H_2O$ was dissolved into the mixture solution and 0.2 g PVP was dispersed into the solution by continuous stirring. Then, 0.8 mL HCl was added into the solution under constant stirring for 20 min. After 30 min of ultrasound treatment, the solution was transferred into a 20 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 10 h (heating rate was about 6 °C/min). After cooling down to room temperature naturally, the product was separated by centrifugation and washed with distilled water and ethanol for several times. Finally, the product was annealed at 600 °C for 2 h (the heating rate was 1 °C/min).

2.3. Characterization

X-Ray diffraction (XRD) analysis was conducted on a Scintag XDS-2000 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) to analyze the structure of the as-prepared product. Scanning electron microscopy (SEM, XL30 ESEM FEG) was used to observe the micromorphology of the as-prepared product. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and selected area electronic diffraction (SAED) images were obtained on a HITACHI S-570 microscope with an accelerating voltage of 200 kV. N_2 adsorption–desorption isotherms were measured at 77 K on a Micromeritics ASAP2000 system. Surface areas were evaluated by Brunauer-Emmett-Teller (BET).

2.4. Fabrication and measurement of gas sensor

The details of the sensor fabrication have been discussed in the previous work [26]. The as-prepared material was mixed with deionized water at a weight ratio of 4:1 and ground in a mortar for 10 min to form a paste. Then the paste was coated on an Al_2O_3 ceramic tube with a couple of Au electrodes. And the Au electrodes were previously fabricated by jetting Au paste on the ceramic tube through a metal-jetting system (MJ-10, Beijing Elite Tech Co., Ltd., China). The Pt wires attached to Au electrodes were used as conductors and were used to fix the ceramic tube on a six-leg holder by welding. A Ni–Cr heating wire was inserted into the ceramic tube and welded on the holder as a heater to control the operating temperature. The structure of the sensor was shown in Fig. 1.

Gas sensing properties were tested by a chemical gas sensor-8 (CGS-8) intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd., China) under laboratory condition (25 °C, 40 RH%). The system can control the operating temperature of sensor by adjusting the current of heating coil and collect the real-time resistance of the sensor. A testing circle (last for 1000 s) of sensor's sensitivity to SO_2 was as follows: first, the sensor was put into a chamber (1 L in volume) until the resistance was stable; then test gases were transferred into another chamber in which a certain concentration (0.2, 0.4, 0.8, 5 or 10 ppm) of SO_2 was pre-filled; at last, when the resistance was stable again, the sensor was transferred back to the air chamber and gradually recovered to the initial state. The gas concentrations were controlled by DGD-3 dynamic gas distribution system (Beijing Elite Tech Co., Ltd.) which could exactly control the concentration of tested SO_2 gas. The response of the sensor was expressed as the value of R_a/R_g, where R_a represented the resistance of the sensor in air and R_g represented the