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Gas sensing characteristics of novel twin-layered SnO_2 nanoarray fabricated by substrate-free hydrothermal route

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ABSTRACT

Novel twin-layered SnO_2 well-oriented nanorods arrays have been synthesized by a substrate-free hydrothermal route of using sodium stannate and sodium hydroxide at 190 °C for 48 h. The characteristic results of the morphology and structure show that the synthesized nanoarray can be well indexed to tetragonal phase SnO_2 nanorods with a diameter of 20 nm and length of several hundred nanometers. The twin-layered SnO_2 nanorods array was tightly combined together by two layers of nanrods array with an apparent interface in the center. The results of the gas-sensing characteristics for various volatile organic compounds show that the sensor based on layered SnO_2 nanoarray exhibits the highest gas sensitivity, very fast response and recovery to isopropanol at the operating temperature of 250 °C, and good gas-sensing performances to ethanol and acetone have also been found at the operating temperature of 278 and 300 °C, respectively. The enhanced response is attributed to the numbers of the gas transport channels increasement leading to more effective surface areas and the additional modulation of the sensor resistance due to the potential barrier at nanorod/nanorod junctions of twin-layered SnO_2 well-oriented nanorods array.

1. Introduction

In recent years, the investigations of gas sensor have received considerable attention for the profound influence on personal safety and detection of pollutants and toxins, and the transportation industries [1]. Semiconducting metal oxide-based gas sensors that are based on resistance changes provide a promising alternative for monitoring toxic and volatile organic compound vapors (VOCs) since they can offer good sensing properties and can be easily mass-produced [2]. Among the n-type metal oxide semiconductors, tin dioxide (SnO_2), wide a band gap (E_g = 3.6 eV, at 300 K), is one of the earliest – discovered and the most widely applied gas sensing material owing to its attractive features such as good chemical and thermal stability [3], which has been extensively studied for detection of a wide variety of inflammable and toxic VOCs gases [4,5]. In order to improve the gas sensing performance, many novel nanostructures SnO_2 such as nanospheres [6], nanotubules [7,8], follower-like nanomaterials [9], porous films [10,11] and so on, have been reported to enhance the response of gas sensors. Among them, One dimensional (1-D) nanomaterials of SnO_2 have attracted more attention for the detection of a range of harmful gases due to the high mobility of their conducting electrons and ultra-high response, and to their good chemical and thermal stability under the operating conditions of sensors [12–14]. However, these products are usually randomly oriented and cannot be made into nanostructured devices.

By comparison, nanoarray is advantageous as building blocks for the fabrication of functional devices because the oriented geometry provides direct conduction paths for carriers to transport from the junction to the external electrode [15]. Attributing to their inherent high surface-to-volume ratio and ordered arrangement, 1-D array structures are preferable for the detection of pollutant gases. On the one hand, highly ordered n-type semiconductor nanorods provide larger effective surface areas, which is of great benefit for gas diffusion and mass transport in sensor materials [16]. On the other hand, many nanorod/nanorod junctions built at the contact

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of each two nanorods. These junctions may augment the active sites that can enhance the response of the gas sensors [17]. In recent years, a few 1-D SnO_2 nanoarrays with different morphologies have already been synthesized by different methods, including chemical vapor deposition (CVD), thermal evaporation (TE), template, hydrothermal approach and so on. However, these methods always involve growth substrates, such as indium tin oxide glass (ITO) [18], Si [19], SiO_2 [20], metal or alloy substrates [21,22], which are always harsh, costly and employed sophisticated equipments. What is more, these substrates not only affect the sensing performance of the materials due to the chemical stability, conductivity, toughness and so on, but also obstruct the measurement of the gas sensing properties. Thus, it is very important to develop ways of synthesizing aligned 1-D SnO_2 arrays without substrates.

Isopropanol (IPA) is a colorless transparent liquid, with slightly bitter taste and similar smell of ethanol. It is widely used in many applications including solvents, disinfectants, pharmaceuticals, cosmetics, lubricants and so on. After evaporation, IPA vapor has moderate toxic, disgusting smell and can cause harmful effects on human health. It causes a mild irritation of human upper respiratory tract and can cause discomfort of the eyes when its concentration is below 400 ppm, while a high concentration inhibits the central nervous system, resulting in dizziness, severe vomiting, excessive sweating, decreased respiration, internal bleeding and so on. Many countries specified a threshold limit value of the highest 8-h time-weighted average (8-h TWA) exposure to isopropanol at the workplace is only 200–400 mL/m^3. The U.S. Occupational Safety and Health Administration permissible exposure limit is 400 ppm (8-h TWA). The American Conference of Governmental Industrial Hygienists Threshold Limit Values are 200 ppm (8-h TWA) and 400 ppm for short-term exposure limit. Therefore, development of various IPA vapor detection techniques and devices to monitor IPA have been demanded for atmospheric environmental measurements and control.

In the present work, novel twins-layered SnO_2 well-aligned single-crystalline nanorods array was prepared via a substrate-free hydrothermal route without any surfactants. The twins-layered SnO_2 nanoarray architecture can provide many quick passages to absorb and desorb gas, which is conducive to enhancing the gas response. The gas sensing properties of the sensor based on the layered SnO_2 nanoarrays have been investigated. As expected, we found that the sensor showed high response to isopropanol, ethanol and acetone. To our best knowledge, few works have reported SnO_2 semiconductor-based isopropanol gas sensors up to now.

2. Experimental details

2.1. Preparation and characterization of layered SnO_2 nanoarray

The starting materials used in the present study are sodium stannate four-hydrate ($Na_2SnO_3{\cdot}4H_2O$), sodium hydroxide (NaOH) and absolute ethanol (C_2H_5OH) are of analytical grade. All chemicals were obtained from the Sinopharm Chemical Reagent Co. (Shanghai, China) and were used without further purification.

The novel twin-layered SnO_2 nanoarray was synthesized via a facile hydrothermal process neither the substrates nor the surfactants presented. Briefly, the raw materials, including sodium stannate four-hydrate ($Na_2SnO_3{\cdot}4H_2O$, 3.76 mmol) and sodium hydroxide (NaOH, 7 mmol) were dissolved in 20 ml distilled water, respectively, and mixed with vigorous stirring for 30 min to form 40 ml homogeneous solutions. After that, 40 ml absolute ethanol (C_2H_5OH) was slowly added into the mixed solution to form white uniform suspension aqueous/ethanol mixed solution stirring for 60 min. The mixed solution was then transferred into a 100 ml Teflon-lined stainless steel autoclave and maintained at 190 °C for 48 h. After the autoclave naturally cooled to room temperature, the collected precipitates were washed several times with absolute ethanol and distilled water, and then dried at 80 °C in air to get the final products.

Powder X-ray diffraction (XRD) data were carried out with a Rigaku D/MAX-3B powder diffractometer with copper target and K_α radiation (λ = 1.54056 Å). We characterized the general morphology of the novel twins-layered SnO_2 well-aligned SnO_2 nanoarray product by an FEI Quanta 200 scanning electron microscope, while performing detailed structural characterizations with a transmission electron microscope (TEM, JEOL 2010, 200 kV) equipped with selected area electron diffraction (SAED) pattern capabilities. X-ray photoelectron spectroscopy (XPS) was measured at room temperature in PHI X-tool. UV/Vis measurements were made with a UV-2401PC spectrophotometer. The surface area, pore size, and pore-size distribution of the product were determined by Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption and Barett–Joyner–Halenda (BJH) methods (Quantachrome, Autosorb-1MP).

2.2. Fabrication and measurement of gas sensor

The indirect heating structure was elected to prepare sensors. The sensor fabrication and gas test were detailly depicted elsewhere [13]. Before measuring the gas sensing properties, the gas sensors were aged at 350 °C for 150 h in dry air. Gas-sensing properties test was performed on a JF02F gas sensing measurement system (Jin Feng Electronics of Sino-Platinum Metals Co. Ltd., China), which is a static system using atmospheric air as the interference gas and the diluting gas to obtain desired concentrations of target gases in a test chamber (about 15 L in volume). The export signal of the sensor was measured by using a conventional circuit in which the element was connected with an external resistor inseries at a circuit voltage. The gas-sensing properties were assessed through sensor response *S*, which was defined as the ratio Ra/Rg, where Ra and Rg stand for the electrical resistance of the sensor in atmospheric air and in the target gas, respectively. All of the tests in gas sensing properties were carried out at a relative humidity range of 40–60%.

3. Results and discussion

3.1. Morphology and structure of twin-layered SnO_2 nanoarrays

The typical XRD pattern of the as-prepared SnO_2 product shown in Fig. 1 displays a substantial texture effect in accordance with

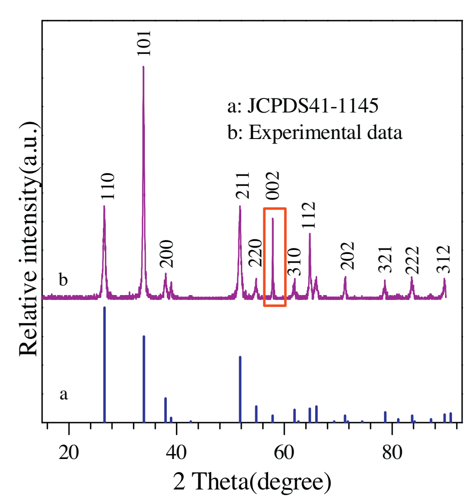

Fig. 1. XRD pattern of as-synthesized twin-layered SnO_2 nanorods array sample.