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Regular Article

Gas sensor based on samarium oxide loaded mulberry-shaped tin oxide for highly selective and sub ppm-level acetone detection

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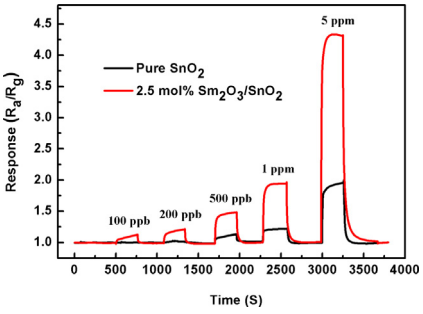
GRAPHICAL ABSTRACT

The dynamical response-recovery curves of the sensors based on the pure SnO_2 and 2.5 mol% Sm_2O_3/SnO_2 to different concentrations of acetone.



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ABSTRACT

Mulberry-shaped tin oxide (SnO_2) hierarchical architectures and samarium oxide (Sm_2O_3) loaded tin oxide with different amounts (0.5, 1, 2.5, and 4 mol% Sm_2O_3) were successfully synthesized by facile hydrothermal synthesis method and simple isometric impregnation method. The gas sensing performance of the sensors based on pure SnO_2 and Sm_2O_3 loaded SnO_2 materials were systematically investigated. The results indicated that Sm_2O_3 loading considerably affected the improvement of the sensing performance of the SnO_2 sensor. The 2.5 mol% Sm_2O_3/SnO_2 exhibited the highest response (41.14) to 100 ppm acetone, the response was 2.29 times higher than that of pure SnO_2 (18). In addition, with 2.5 mol% Sm_2O_3 loading, the low detection threshold of the sensor dropped from 500 ppb to 100 ppb. The enhanced gas sensing performance was mainly bacause of the increased oxygen vacancies created by the substitution of samarium in the SnO_2 lattice, which enhanced the adsorption of oxygen and the exceptional catalytic effect of Sm_2O_3.

1. Introduction

In recent years, the monitoring demand of toxic pollutant gases has been growing bacause of their wide-ranging applications in air quality control, environmental protection, healthcare, and security [1–5]. As a common type of volatile organic chemical (VOC),

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acetone is widely used in laboratories and industries [6,7]. However, long-term exposure to acetone can harm the nervous system and organs [8,9]. Furthermore, the concentration of acetone in respiration can be used as a key biomarker for diabetes diagnosis. As reported by clinical data, a considerable difference occurs in the exhaled acetone concentration between a healthy person and a diabetic patient, the concentration of exhaled acetone is 0.3–0.9 ppm for a healthy individual, and more than 1.8 ppm for a diabetic patient [10,11]. Therefore, it is of significance to develop a acetone sensor with high sensitivity and low detection limit for environmental protection and biomedical applications.

In the past few decades, gas sensors based on semiconductor oxide have attracted researchers worldwide because of their simple device structure, miniaturization, good reproducibility, fast response, real-time detection and low cost [12–14]. Semiconductor oxides, such as ZnO, SnO_2 WO_3 and In_2O_3, are important materials widely applied as gas sensing materials and exhibited excellent sensing properties [15–18]. Among these materials, SnO_2, as a wide band gap (3.6 eV) *n*-type semiconductor, is a proper candidate for potential applications in the gas sensing field because of its high sensitivity, low operating temperatures (200–400 °C), and good long term stability [19,20]. To date, various synthesized methods have been successfully exploited for the preparation of SnO_2, such as hydrothermal/solvothermal synthesis method [21,22], high current heating [23], sol-gel [24,25], template-assisted method [26], electrospinning [27,28], and chemical precipitation [29].

However, the gas sensing properties of single SnO_2 hardly meet all the requirements of gas sensors, and therefore restrict their practical application and development. Thus, scientific and technological efforts have been exerted to improve the gas sensing performance of SnO_2, doping/loading with suitable noble metals or metal oxides have been proved to be a simple and efficient route to enhance the sensing properties of semiconductor gas sensors [30–33]. Samarium, as a rare earth element, has special optical, electronic and magnetic properties [34]. Samarium ion with 4f electronic configuration usually exists in the form of Sm^{3+} [35,36], which has been proven to have fast oxygen ion mobility and predominant catalytic properties in previous studies [37,38].

In this work, we prepared mulberry-shaped SnO_2 hierarchical architectures and Sm_2O_3 loaded SnO_2 via facile hydrothermal synthesis method and simple isometric impregnation route. The gas sensing properties of the above materials were systematically investigated to examine the best Sm_2O_3 loading amount and the enhanced effect of Sm_2O_3 on the gas sensing properties of SnO_2 based acetone sensor.

2. Experimental

2.1. Synthesis of mulberry-shaped SnO_2 and loading with Sm_2O_3

All the reagents (analytical-grade purity) were purchased and used without any further purification. The initial precursors were tin (II) chloride dihydrate ($SnCl_2{\cdot}2H_2O$, ≥98.0%, Sinopharm Chemical Reagent Co., Ltd, China), samarium nitrate hexahydrate ($Sm(NO_3)_3{\cdot}6H_2O$, 99.99%, Sahn Chemical Technology (Shanghai) Co., Ltd, China) and ammonium sulfate ($(NH_4)_2SO_4$, ≥99.0%, Sinopharm Chemical Reagent Co., Ltd, China). For the synthesis of SnO_2 materials, the hydrothermal synthesis method [6,32] was introduced. The detailed process was as follows: A total of 0.15 g $(NH_4)_2SO_4$ was dissolved into a mixture of ethanol and water (1:1, v/v) with vigorous stirring to form a homogeneous solution. Then, 0.677 g $SnCl_2{\cdot}2H_2O$ was added into the above solution. The resulting mixture was subsequently transferred into a Teflon-lined stainless steel autoclave and reacted at 120 °C for 8 h. Finally, the precipitate was centrifuged, washed, dried at 80 °C and calcined at 500 °C for 2 h.

After SnO_2 materials were obtained, Sm_2O_3 was loaded on SnO_2 by isometric impregnation [39]. The preparation details were shown as follows: the maximum volume of samarium nitrate solution absorbed by SnO_2 powder was dropped into 0.05 g SnO_2 at room temperature and steeped for 4 h. The concentrations of samarium nitrate solution were adjusted on the basis of the loading amount of Sm_2O_3. Finally, the products were dried and calcined at 500 °C for 2 h. The samples were named 0.5, 1, 2.5, and 4 mol% Sm_2O_3/SnO_2.

2.2. Characterization of samples

X-ray diffraction (XRD, Rigaku D/max-2550 diffractometer, Cu kα radiation at wavelength λ = 0.1541 nm) was carried out to analyze the crystalline phases of the as-synthesized products, The morphologies and structures of the samples were recorded by field emission scanning electron microscopy (SEM, JEOLJSM-7500F), transmission electron microscopy (TEM, JEOL JEM-2100F), high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopic (EDS) elemental mapping

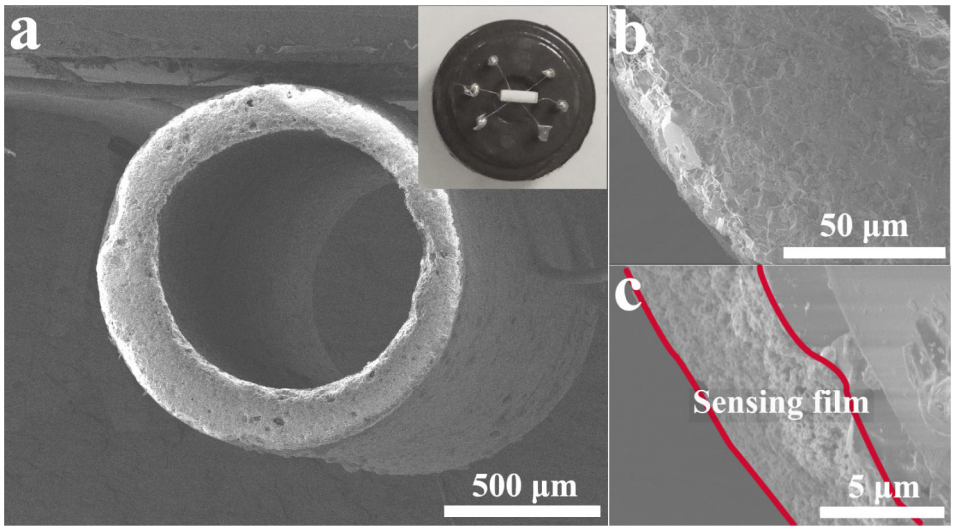

Fig. 1. The cross-section view of SEM images for the sensing film.