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Fabrication of porous SnO_2 nanowires gas sensors with enhanced sensitivity

Rui Li[a,b,c], Shuai Chen[a,b,c], Zheng Lou[c,*], La Li[c], Tingting Huang[a,b,c], Yuanjun Song[a,b], Di Chen[a,b,*], Guozhen Shen[c,d,*]

[a] School of Mathematics and Physics, University of Science Technology Beijing, Beijing 100083, China
[b] Beijing Key Laboratory for Magneto-Photoelectrical Composite and Interface Science, School of Mathematics and Physics, University of Science and Technology Beijing, Beijing 100083, PR China
[c] State Key Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China
[d] College of Materials Science and Opto-Electronic Technology, University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

With large surface area, metal oxide porous nanostructures usually exhibited enhanced sensitivities when used as chemical sensors. In this work, porous SnO_2 nanowires (PNWs) with the diameter of about 130 nm and length up to 10 μm are synthesized by a controlled two-step method including electrospinning followed with hydrothermal etching treatment by Na_2S solution, which were used to fabricate high-performance gas sensors. Studies found that, compared with the electrospun pristine SnO_2 NWs without hydrothermal treatment, the SnO_2 PNWs exhibited remarkably enhanced gas sensing performances, including two times higher responsivity to ethanol. The method used here may be easily extended to synthesize other metal oxide nanostructures for high performance chemical sensors.

1. Introduction

With the severe environmental problems, monitoring and controlling air pollutant are more and more important and are attracting the attention of many researchers all over the world, recently. Ethanol vapour, which is one of the most popular flammable gases in our daily life, is considered seriously harmful to human life. [1] Developing high performance gas sensors to monitor ethanol in air is of great importance because it can reduce ethanol emissions, protect people from over-exposure to ethanol gas, and improve environmental quality. [2–5]

Tin oxide (SnO_2), as one of the most important *n*-type metal-oxide semiconductors, has been widely investigated for the detection of gas pollutants, due to its unique properties including low cost, low detection limit, fast response and recovery time. [6–10] However, most of the SnO_2 based sensors till now still exhibit low response and poor selectivity, which limits their applications in many fields. It is still a challenge for researchers to develop peculiar techniques for improving the sensing performance of SnO_2 based gas sensors. For example, by doping SnO_2 nanorod layered arrays with Nb, Zhao's group prepared gas sensors with improved performance toward alcohol. [11]

Cao's group used Au nanoparticles to functionalize 3D SnO_2 microstructures from the simple hydrothermal combining with subsequent annealing process to improve the gas sensing performance. [12] By controlling the microstructures of SnO_2 nanostructures, our group fabricated several high-performance SnO_2 based gas sensors. [13–16] All these results suggested that the microstructures, particle size and morphologies played significantly important roles in the sensing improvements of SnO_2 based materials. Especially, the formation of porous SnO_2 nanostructures have been proved to be an efficient way to get high-performance gas sensors, as porous nanostructures usually exhibited low density and large surface area.

Herein, we reported the fabrication of high performance gas sensors with highly porous SnO_2 nanowires (SnO_2 PNWs) as the sensing elements. SnO_2 PNWs used here is synthesized by a simple electrospinning process, followed with hydrothermal etching treatment in Na_2S solution. When fabricated into sensing device,

* Corresponding authors at: State Key Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China
E-mail addresses: zlou@semi.ac.cn (Z. Lou), chendi@ustb.edu.cn (D. Chen), gzshen@semi.ac.cn (G. Shen).

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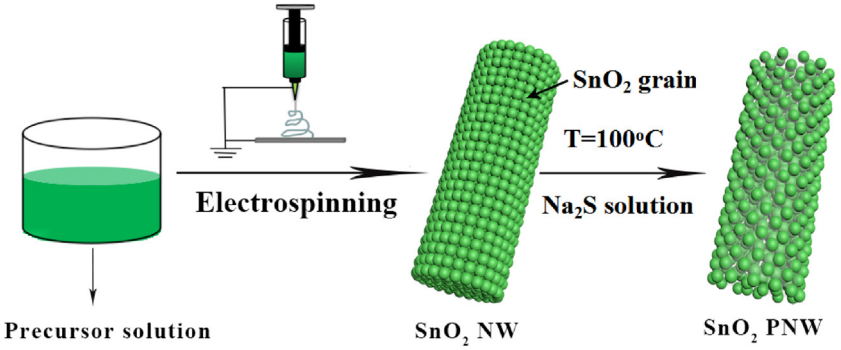

Scheme 1. Schematic illustration of the synthesis of SnO_2 PNWs.

the as-synthesized SnO_2 PNWs consisting of nanoparticles with diameters of about 130 nm showed superior gas sensing properties compared with the pristine SnO_2 nanowires (NWs) without hydrothermal etching treatment.

2. Experiment

2.1. Materials

All materials used in our experiments are of analytical purity and used without further treatment. Stannic chloride pentahydrate ($SnCl_4{\cdot}5H_2O$), sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$), ethanol and *N*,*N*-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagents Co., Shanghai, China. Polyvinylpyrrolidone (PVP, M = 13,00,000g mol-1) was supplied by Qi Fuqin Materials Technology Co., LTD. Shanghai, China.

2.2. Synthesis of material

Synthesis of SnO_2 nanowires: SnO_2 nanowires were synthesized from the simple electrospinning process. First, the precursor solution was prepared by dissolving 3 g of $SnCl_4{\cdot}5H_2O$ into 27 g of ethanol/DMF mixture solution with the weight rate of 1:1 under magnetic stirring. Then 3 g of PVP was added into the solution and kept stirring for 2 h at 60 °C. Using a Medical propulsion pump, the transparency and uniformity precursor solution was delivered to a needle at a constant flow rate of 0.3 mL/h. Upon applying a high voltage of 18 kV, the solution was electrospun from the stainless steel needle, formed a fibrous mat on an aluminum foil collector. The distance between the needle and the collector was 22 cm. The electrospun fibers were then calcinated at 600 °C for 4 h with a heating rate of 0.5 °C/min. [17]

Hydrothermal etching in Na_2S solution: To prepare SnO_2 PNWs, the freshly electrospinning fabricated nanowires were added into 0.1 M $Na_2S{\cdot}9H_2O$ aqueous solution. After vigorous stirring for 30 min, the mixture was transferred into a 20 mL Teflon-lined autoclave and sealed. Finally, the system was heated at 100 °C for 1 h. When cooling to room temperature, the obtained products were washed with deionized water 3 times and then dried in air for 6 h at 100 °C.

2.3. Characterizations

The morphology and microstructure of the obtained products were characterized by field emission scanning electron microscopy (FEM, SUPRA 55) and transmission electron microscope (TEM, JEM 2200FS). The elemental analyses of the products were determined by X-ray diffraction (XRD, DMAX-RB) and X-ray photoelectron spectroscopy (XPS, Thermo escalab 250XI). The Brunauer–Emmett–Teller (BET) specific surface area of the products was examined through measuring N_2 adsorption-desorption isotherm (QS-18,0.01 M).

2.4. Fabrication and measurement of gas sensor

To fabricate the gas sensors, in the experiments, we mixed the grinding SnO_2 products with a small amount of deionized water to form a paste and then coated on a ceramic substrate with patterned gold electrodes. The gas-sensing properties of the sensor were measured by a CGS-1 TP intelligent gas sensitivity analysis system. The gas-sensing sensitivity was assessed through the response value of the electric resistance, which was defined as S = Ra/Rg (where Rg and Ra were the sensor resistance in target gas and in dry air, respectively).

3. Results and discussion

The schematic diagram for the formation of the SnO_2 PNWs is shown in Scheme 1. SnO_2 nanowires composed of small nanoparticles were firstly prepared from the electrospinning process, followed with high temperature calcination. The as-prepared SnO_2 NWs were then dispersed in Na_2S solution and performed hydrothermal etching reaction at 100 °C for 1 h. Pure SnO_2 NWs with porous structure were prepared, suggesting the possible chemical reactions occurred as following in the Na_2S solution:

$$Na_2S + H_2O \rightarrow H_2S + NaOH \quad (1)$$

$$SnO_2 + H_2S + S^{2-} \rightarrow SnS_3^{2-} + 2H_2O \quad (2)$$

Typically, in the Na_2S solution, SnO_2 NWs reacted with H_2S and S^{2-} to form SnS_3^{2-} according to the above equations, which resulted in the formation of porous samples due to the partially etching reaction with short time of 1 h. Compared with SnO_2 NWs, the SnO_2 PNWs after etching showed increased BET surface area, which might exhibit superior properties in sensing field.

The morphology and microstructure of the as-synthesized SnO_2 NWs and PNWs were observed by SEM, respectively. Fig. 1a shows the SEM image of the SnO_2 NWs after electrospinning/calcination process. SnO_2 NWs with uniform diameter of about 130 nm were prepared on a large scale. Inset is a higher magnification SEM image of the SnO_2 NWs, demonstrating that the NWs are composed of numerous particles with rough surface. TEM image of a typical SnO_2 NW is shown in Fig. 1b, clearly displaying that the NWs are composed of nanoparticles with uniform size of about 30 nm. The high-resolution TEM (HRTEM) of a single SnO_2 NW in Fig. 1c further illustrates that the SnO_2 nanoparticles are of high crystallinity. The marked lattice spacing was estimated to be 1.76 nm and 3.35 nm, which are in good agreement with the (211) and (110) d-spacing of rutile SnO_2 phase, respectively. The corresponding selected area electron diffraction (SAED) pattern shown in Fig. 1c inset revealed the polycrystalline nature of the SnO_2 NW.