Sensors and Actuators B 205 (2014) 329–337

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Micropored Sn-SnO_2/carbon heterostructure nanofibers and their highly sensitive and selective C_2H_5OH gas sensing performance

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ARTICLE INFO

Article history:
Received 26 May 2014
Received in revised form 30 July 2014
Accepted 21 August 2014
Available online 16 September 2014

Keywords:
C_2H_5OH sensor
Sn-SnO_2/carbon
Nanofibers
Electrospinning

ABSTRACT

Sn-SnO_2/carbon heterostructure nanofibers were synthesized by electrospinning and following heat treatment, and their C_2H_5OH sensing properties were studied. The hetero-nanofibers composed of amorphous carbon and homogeneously distributed Sn-SnO_2 particles were characterized by SEM, TEM, EDS, XRD, XPS, FT-IR, Raman and nitrogen adsorption–desorption experiment. A gas sensor was fabricated from the as-synthesized heterostructures of Sn-SnO_2/carbon nanofibers and used to test the sensing performance to C_2H_5OH. The Sn-SnO_2/carbon nanofibers showed improved sensing properties compared to pure SnO_2 nanofibers. It exhibits a 2-time enhancement in ethanol response compared to the SnO_2 nanofibers counterparts at its optimum operating temperature, good linear dependence of response on C_2H_5OH concentration in the range of 10–100 ppm, excellent recovery property and selectivity to C_2H_5OH. The excellent performance in C_2H_5OH sensing of Sn-SnO_2/carbon nanofibers arises from (i) high specific surface and pore structure provided by one-dimensional carbon nanofibers, (ii) the unique sensing mechanism based on the hybrid Sn-SnO_2/carbon nanostructures.

1. Introduction

Metal oxide semiconductor such as ZnO, SnO_2, In_2O_3 and Fe_2O_3 are increasingly demanded for combustible gas detection, environmental monitoring, food security and chemical process control [1–4]. In particular, alcohol sensors have drawn much attention for they play a key role in preventing drunk driving. Among many metal oxide sensing materials, SnO_2, a n-type semiconductor with a wide band-gap of 3.62 eV is a promising candidate for it shows high sensitivity to both reducing and oxidizing gas [5]. It has been accepted as one of alcohol sensing materials in practical use. However, its applications are hindered by some drawbacks such as relatively high operation temperature, long response/recovery time and poor selectivity [6]. To solve these drawbacks, better design and control of microstructure are needed.

One dimensional (1D) nanostructures exhibit unique fibrous morphology, which facilitates easy penetration of target gas to the inner layer of sensing materials [7]. Many 1D nanostructure materials have been successfully synthesized by different methods, such as hydrothermal method [8], sol-gel [9], chemical vapor deposition [10], ultrasonic irradiation [11], UV lithography and dry plasma etching [12], electrospinning [13] and so on. Among these methods, electrospinning is considered to be a simple and versatile method to prepare 1D nanostructures of organic, inorganic and composite materials with the capability of large-scale production [14]. Furthermore, electrospinning has been proven to be an effective technique for controllable synthesis of 1D nanostructures including nanoribbons [15], nanotubes [16], nanowires [17], porous nanofibers [18], nanobelts [19], and other novel structures [20]. For instance, SnO_2 porous nanofibers, synthesized by electrospinning with the addition of block copolymer P123 as pore creating material, exhibited enhanced response value, higher saturated detection concentration and lower minimum-detection-limit to C_2H_5OH compared to their none additives counterparts [18]. Highly sensitive SnO_2 hollow nanofiber-based gas sensor, fabricated via electrospinning that used phase-separated polymer solutions, showed four times higher response value to NO_2 gas compared to planar SnO_2 thin films [21]. SnO_2–Fe_2O_3 interconnected nanotubes which were prepared through single nozzle electrospinning and thermal treatment methods were proven to have excellent sensitivity and remarkable selectivity to toluene, and long-term stability [22]. However, a major drawback of pristine or composite metal oxide materials was their large resistance

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http://dx.doi.org/10.1016/j.snb.2014.08.062
0925-4005/

(100 MΩ or above for SnO_2 sensors) [23], leading to difficulties of signal acquisition and relatively high working temperature. Therefore, higher sensitivity at lower operation temperature can be achieved by reducing the base resistance of sensing materials.

1D carbon materials, due to their high electrical conductivity and good chemical stability, have been widely accepted as excellent support materials [24–26]. As support material for gas sensors, the high electrical conductivity ensures high sensitivity, and the chemical stability guarantees the superior sensing performance within a relatively wide range of operation temperature. Moreover, carbon nanofibers (CNFs) with unique fibrous morphology and porous structure could provide high surface permeability, allowing easy penetration of the surrounding gas into the sensing layer [27]. Therefore, introducing CNFs to metal oxide materials could effectively reduce the device resistance and get 1D morphology at the same time. Consequently, high-performance sensing device is achieved. However, CNFs have turned out to be difficult to decorate with metal or metal oxide for the lack of functional groups on their surface [28]. Therefore, additional processes are needed to obtain such heterostructures. For example, Mu and co-workers fabricated SnO_2/carbon nanofibers heterostructures by combining electrospinning and solvent-thermal process [29]. In their work, the CNFs were pretreated with HNO_3 to induce a certain amount of functional groups to facilitate the coating of SnO_2 nanoparticles on the surface of CNFs. Yang et al. fabricated SnO_2/CNF heterostructures by combining electrospinning with subsequent thermal treatment in an Ar/H_2O atmosphere [30]. However, such activation processes would break the graphite structure of CNFs that will sacrifice their conductivity.

In this paper, we designed a novel material of Sn-SnO_2/CNFs heterostructure which was synthesized by electrospinning and following heat treatment. We systematically investigated their C_2H_5OH sensing properties including optimum working temperature, concentration-dependent response and sensitivity, recovery property and selectivity. Moreover, contrast experiments of the corresponding properties of Sn/CNFs, SnO_2/CNFs and SnO_2 nanofibers were conducted. We believe that we provide a novel composite material prepared by facile and low-cost method with improved C_2H_5OH sensing performance which could be valuable in alcohol detecting application.

2. Experimental

2.1. Preparation of Sn-SnO_2/CNFs heterostructure

Polyacrylonitrile (PAN, M_w = 150,000) and Tin(IV) chloride pentahydrate ($SnCl_4$•$5H_2O$) were used as received without further purification. Dimethylformamide (DMF) was used as solvent. Typically, PAN solution (8 wt%) was prepared at 70 °C with vigorous stirring overnight. Subsequently, this solution was added to $SnCl_4$•$5H_2O$ under vigorous stirring of another 6 h to obtain the homogeneously distributed solution. The weight ratio of PAN and $SnCl_4$•$5H_2O$ is 1:1.14. The result mixture was loaded into a 20 ml plastic syringe with a stainless-steel needle of 0.5 mm internal diameter. The flow rate of solution was 0.4 ml/h controlled by a syringe pump. At a distance of 20 cm, a voltage of 10 kV was applied between the needle and a piece of aluminum foil which works as a collector for fiber mats.

The as-collected nanofibers were stabilized at 270 °C for 2 h in air, and carbonized at 800 °C for 30 min in Ar with a heating rate of 2 °C/min to get carbonized fibers. For a further heating process, the carbonized fibers were oxidized at 350 °C for another 30 min in air. The obtained samples were carbonized Sn/C nanofibers and oxidized Sn/C nanofibers, respectively. We also prepared SnO_2 nanofibers (SnO_2•NFs) for comparison using the same raw nanofibers described previously only to change the heat treatment atmosphere to air. Additionally, we prepared SnO_2/CNFs served as comparison in gas sensing measurement, the synthesis method is described in Supplementary Materials.

2.2. Characterization

The morphology and microstructure of the as-spun, carbonized and oxidized fiber were observed by field emission scanning electron microscope (FE-SEM, JEOL, S-4800) and transmission electron microscope (TEM, JEOL JEM-1230). Energy dispersive X-ray spectroscopy (EDS) analysis was performed on an EDS system attached to the same FE-SEM apparatus. The composition and crystallinity of the nanofibers were analyzed by X-ray diffraction (XRD) on Bruker D8 with Cu $K\alpha$ radiation source at λ = 0.154 nm. X-ray photoelectron spectroscopy (XPS) was conducted by AXIS Ultra DLD. FT-IR spectra were collected by using EZ OMNIK. Nitrogen adsorption–desorption isotherms were measured at 77 K on a Macromeritices Tristar-3000 surface area analyzer, and the surface area was evaluated using Brunauer–Emmett–Teller (BET) method. The Raman spectra were carried out with an Invia confocal Raman system.

2.3. Fabrication and measurement of sensors

The as-synthesized sample was made in a paste form using ethanol as solvent and applied to a ceramic tube with a pair of Au electrodes. Then, a piece of Ni–Cr heating wire which was used to control the operating temperature was placed in the interior of the tube to form a side-heated gas sensor. The prepared gas sensing device was then stabilized using age equipment at a constant sensing temperature for 48 h to fully evaporate ethanol and achieve closer contact between ceramic tube and sample. The target gas was prepared by injecting ethanol liquid on a heating plate which was placed in the test chamber (18 L in volume) to get C_2H_5OH gas, and the concentration of which can be controlled by changing the ratio of target gas and air. The gas sensing properties were measured by monitoring the response value of $R = R_a/R_g$, where R_a was sensor resistance in air and R_g was resistance during exposure to the mixture of target gas and air. Another parameter of gas sensing property is recovery time which was defined by the time to reach 90% variation of the total resistance.

3. Results and discussion

3.1. Characteristic of the as-prepared nanofibers

Fig. 1(a) shows the as-collected raw fibers of $SnCl_4$/PAN, which shows continuous and uniform morphology and relatively rough surface with a fiber diameter ranged from 800 to 900 nm. In the precursor solution, a very slow hydrolytic process of $SnCl_4$ had taken place. After electrospinning process, the as-received white color film was peeled off and aged for more than two days to complete the hydrolysis. Fig. 1(b) shows the image of carbonized Sn/C nanofibers, of which the diameter is in the range of 400–450 nm. Much thinner fibers were achieved due to large volume shrinkage of PAN and weight loss caused by the decomposition of heteroatoms (nitrogen and hydrogen). Compared with carbonized Sn/C nanofibers, slight shrinkage was observed from oxidized Sn/C nanofibers, shown in Fig. 1(c), with a fiber diameter range of 350–400 nm, due to the densification of carbon atoms during the oxidization process. Moreover, coarse surface and relatively loose morphology were obtained from both samples, shown from the cross section images in Fig. 1(b) and (c). TEM images of the carbonized and oxidized Sn/C nanofibers are shown in Fig. 1(e) and (f) to further investigate their microstructures. As shown in Fig. 1(e), very limited amount of particles