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Investigation of gas sensing properties of SnO_2/In_2O_3 composite hetero-nanofibers treated by oxygen plasma

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ABSTRACT

SnO_2/In_2O_3 composite hetero-nanofibers were synthesized based on a modified bipolar electrospinning with double jets. SnO_2/In_2O_3 composite hetero-nanofibers were further modified by oxygen plasma in a radio frequency (RF) plasma treatment chamber at low temperature. The morphology and structure of treated SnO_2/In_2O_3 composite hetero-nanofibers were characterized by using XRD, SEM and TEM. The composition and specific surface of treated SnO_2/In_2O_3 composite hetero-nanofibers were characterized by EDX, XPS and BET. Both SnO_2 and In_2O_3 nanofibers in the treated SnO_2/In_2O_3 composite hetero-nanofibers are hierarchical and hollow structure as same as the ones before treated. The morphology of treated SnO_2 and In_2O_3 nanofibers changed significantly. The porosity and specific surface area of the treated composite nanofibers were bigger than the ones of untreated sample. The gas sensing properties of the treated SnO_2/In_2O_3 composite hetero-nanofibers to formaldehyde were tested. The treated composite nanofibers exhibit high response values and low operating temperature. Cross-responses and humidity effect of the treated composite nanofibers sensor were tested. The gas sensing mechanism of the SnO_2/In_2O_3 composite hetero-nanofibers treated by oxygen plasma was analyzed.

1. Introduction

Electrospinning technique is a simple and easy way for fabricating nanofibers, and the nanofibers produced by this method have shown some excellent characteristics [1–3]. Electrospinning technique and electrospun nanofibers have been used in numerous applications including wound dressings [4], solar clothing [5], tissue scaffolds [6], chemical and biological protective materials [7], gas sensing materials [8,9], humidity sensitivity [10], photosensing materials [11], photovoltaic devices [12] and so on.

The gas sensors based on electrospun nanofibers showed excellent gas sensitivities [11]. In order to further improve their sensitivity to various gases, two popular strategies can be employed. One is enlarging the active surface area of gas sensing materials by reducing their grain size, constructing porous structure including hollow and hierarchical structure, meso-macroporous materials, which aims to increase interactive surface and provide more active sites [13]. Another method is modifying gas sensing materials with various ways including two kinds of metal oxide composite [14,15], noble metals doping to form hetero-junctions [13,15–18] and catalysts [19], RF plasma treating [20,21] and so on. Plasma treatment technique was proved to be an effective method to modify the properties of nanomaterials [22–24]. By this technique, it is possible to modify the surface properties of nanofibers without affecting the bulk properties. For example, the SnO_2 gas sensors treated in gaseous plasma become sensitive to propanol at room temperature and the sensitivity increases with the duration of exposure in oxygen and hydrogen gaseous plasma [25]. Recently, a carbon dioxide gas sensor was developed from the room-temperature reduction of graphene oxide via hydrogen plasma [26]. Some actions of plasma to the treated material were found during the plasma treatment process, such as plasma grafting [27], selective etching [28,29], surface modification and aging [30]. In this manuscript, SnO_2/In_2O_3 composite hetero-nanofibers were synthesized by an electrospinning system of double jets with opposite electric field, and then, were treated by using oxygen plasma. The gas sensing properties of the treated SnO_2/In_2O_3 composite hetero-nanofibers were measured in formaldehyde vapor concentration range of 0.5–50 ppm. The treated composite nanofibers showed good sensitivity to formaldehyde vapor.

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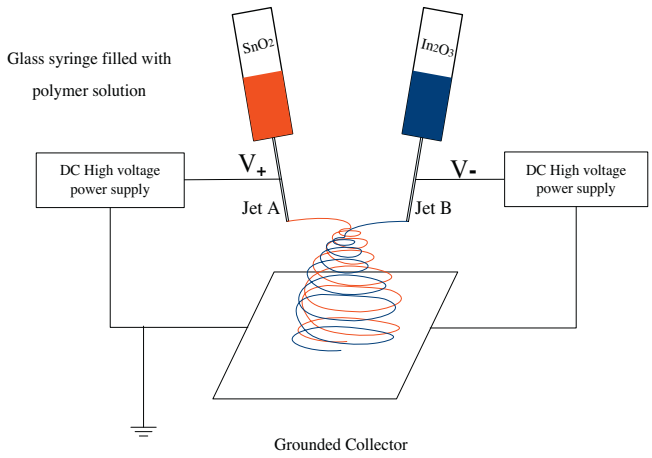

Fig. 1. Sketch of double jets electrospinning with opposite polarities.

2. Experimental

2.1. Preparation and characterization of SnO_2/In_2O_3 hetero-nanofibers

SnO_2/In_2O_3 hetero-nanofibers were prepared by using an electrospinning system with bipolar electrospinning with double jets [9]. SnO_2 nanofibers with positive and In_2O_3 with negative ejected from their nozzles at the same time and moved to opposite direction, forming netted structure SnO_2/In_2O_3 composite hetero-nanofibers. Fig. 1 shows a sketch of the modified double jets electrospinning system.

Two kinds of precursor solutions for synthesis of hetero-nanofibers were prepared. SnO_2 spinning solution was prepared as follows: 0.6 g $SnCl_2{\cdot}2H_2O$ were added into 4 ml ethanol under vigorous stirring for 30 min, and then 0.6 g PVP and 3 ml DMF were added into the as-prepared $SnCl_2$ solution in order to fully dissolve in the DMF/ethanol solution. The mixture of $SnCl_2$ solution was stirred for 8 h at room temperature to attain sufficient viscosity required for electrospinning. While the spinning solution of In_2O_3 nanofibers was prepared with 0.4 g $In(NO_3)_3{\cdot}41/2H_2O$ by the same way.

The two kinds of spinning solutions were loaded into the syringe *A* and syringe *B* (Fig. 1), respectively. Two D.C. high voltages applied at jet *A* and jet *B* were positive electrode and negative electrode, respectively. The collector was connected zero potential. Both of the distances between one jet and the collector, between two jets were all 5 cm. The SnO_2 and In_2O_3 nanofibers were ejected from jets *A* and *B* simultaneously to form a wet netted polymer of SnO_2/In_2O_3 composite nanofibers. The as-synthesized composite nanofibers net was heated at 600 °C for 2 h in air. The PVP and water in the polymer composite volatilized during heating process, and finally, the netted SnO_2/In_2O_3 composite hetero-nanofibers were obtained.

After that, the SnO_2/In_2O_3 composite hetero-nanofibers were put in the RF plasma treatment chamber. Fig. 2 gives a schematic illustration of the RF plasma treatment system, which works at a frequency of 14 MHz, oxygen was used as the reactant. The SnO_2/In_2O_3 composite hetero-nanofibers were exposed to RF-generated oxygen plasma with a plasma RF discharge power of 450 W. The chamber pressure was 30 Pa. After 30 min, the treated SnO_2/In_2O_3 composite hetero-nanofibers were obtained. The gas sensor was fabricated by using the treated SnO_2/In_2O_3 composite hetero-nanofibers.

The structures of the treated SnO_2/In_2O_3 composite hetero-nanofibers were characterized by an X-ray diffraction instrument (XRD: D/Max 2400, Rigaku, Japan) in 2θ region of 20–80° with

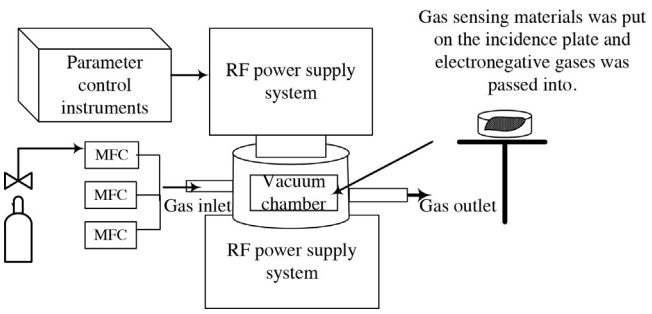

Fig. 2. A schematic illustration of the RF plasma treatment system.

Cu $K\alpha 1$ radiation. The morphology images of nanofibers were obtained by using field emission scanning electron microscope (FE-SEM: Hitachi S-4800, Japan) and transmission electron microscope (TEM: Tecnai 20, USA). The composition and contents of nanofibers were analyzed by energy dispersive X-ray spectroscopy (EDX: Tecnai 20, USA) and X-ray photoelectron spectroscopy (XPS: Thermo ESCALAB 250Xi, USA). The specific surface of the nanofibers was measured from nitrogen adsorption analysis by Brunauer–Emmett–Teller (BET: Quanta AUTOSORB-1-MP, USA) method. Nitrogen adsorption–desorption isotherm analysis was measured to calculate the pore size distribution using the Barret–Joyner–Halenda (BJH) model.

2.2. Sensors fabrication and measurements

The treated SnO_2/In_2O_3 composite hetero-nanofibers were mixed with deionized water to form a paste. The paste was coated onto a ceramic tube with a pair of gold electrodes to form a sensing film (250–300 μm in thickness) and dried at 100 °C for 2 h, and subsequently annealed at 500 °C for 2 h in air. Finally, a Ni–Cr heating wire was inserted into the ceramic tube to form an inside-heated gas sensor.

The gas sensing properties of the treated SnO_2/In_2O_3 composite hetero-nanofibers sensor were measured using a static state gas sensing characterization system. In the gas response measurement, a given amount of target gas was injected into a test chamber (50 L in volume) by a syringe through a rubber plug. For a required

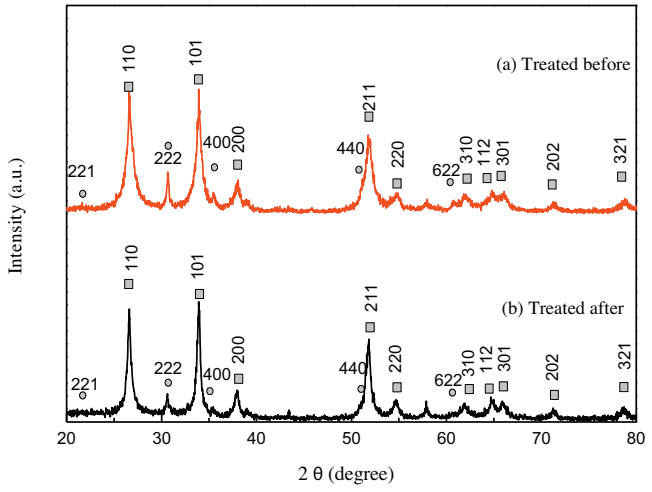

Fig. 3. XRD patterns of the SnO_2/In_2O_3 composite hetero-nanofibers treated before (a) and after (b) by oxygen plasma.