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# Nickel-doped tin oxide hollow nanofibers prepared by electrospinning for acetone sensing

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ABSTRACT

In this work, pure and Ni-doped $SnO_2$ hollow nanofibers with porous structures were fabricated through combination of electrospinning technique and calcination procedure. The hollow $SnO_2$ nanofibers were characterized by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analyzer (TGA), X-ray photoelectron spectroscopy (XPS) and their gas sensing properties for acetone were also investigated. A high heating rate in calcination process would lead to the formation of hollow $SnO_2$ nanofibers with a tube-like structure. Hollow Ni-doped $SnO_2$ nanofibers could be prepared by adjusting $Ni^{2+}$ concentration in the precursor solution using a facile process with appropriate thermal treatment. Comparative gas sensing properties revealed that Ni-doped $SnO_2$ hollow nanofibers exhibited a much higher response in detecting acetone vapor than both pure $SnO_2$ hollow nanofibers and Ni-doped $SnO_2$ solid nanofibers at the same temperature. The excellent sensing performances of Ni-doped $SnO_2$ hollow nanofibers were ascribed to its hollow-core structure and Ni doping.



## 1. Introduction

Recently, the detection of volatile organic compounds (VOCs) has become a very imperative task in many countries for environmental monitor, food inspection and medical diagnostics. Many semiconducting metal oxides have been used as sensor materials for VOCs detection [1,2]. To improve their sensitivity to various gases, two popular strategies can be employed. One is increasing the active surface area of sensor materials by reducing their grain size, constructing porous structure including hollow, meso-macroporous materials, which aims to increase interactive surface and provide more active sites. Another method is modifying sensor materials with various additives including guest metal oxide and noble metals to form junctions [3–6] and catalysts [7–9].

Tin dioxide ($SnO_2$) is an environmentally friendly n-type semiconductor and has been widely used in various fields including solar cells, lithium-ion batteries, etc. In particular, it has been considered as one of most promising metal oxides for the fabrication of gas sensor with high sensitivity, excellent stability and low price [2,10]. It is generally believed that the gas sensing properties of $SnO_2$ nanomaterials can be further improved by doping with specific ions or modulating their morphology. Recently, it has been reported that $SnO_2$ nanomaterials could be doped with Nb [11], Zr [12], Pd [13], Zn [14–16], Cd [17] Ce [18,19], Co [20], Ni [21–27], etc. At the same time, various $SnO_2$ nanostructures have been fabricated for gas sensors because of their strong dependence of properties on the morphology and shape. A lot of reports claimed that these morphologies, such as hollow, porous and hierarchical structures of $SnO_2$ were beneficial for sensor properties because of a high surface to volume ratio provided from the unique loose structures [28,29].

Electrospinning technique can provide a simple and versatile route to prepare metal oxide films and nanocrystals with a highly porous fibrous morphology [6,21,30–33]. These metal oxide films fabricated by electrospinning are very suitable for gas sensing application due to the small crystalline size, high surface area and high porosity [34,35]. Inorganic metal oxides fabricated by electrospinning polymer solutions containing inorganic precursors with subsequent calcination at high temperature possess fibrous morphologies, promising to give rise to a much high sensitivity as sensor materials [9]. The fibrous morphology can form a network of interconnected nanowires in which target gas can easily diffuse through large pores between nanowires. Simultaneously, small pores between the adjacent grains of metal oxides enable gas to diffuse to the surface of nanocrystals in the fibers.

Some papers with respect to electrospun $SnO_2$ nanofibers and their sensing properties have been reported [36,37]. Pure $SnO_2$ nanofibers were fabricated by electrospinning of poly(vinyl alcohol)/$SnCl_4$ solution, and micro gas sensors based on the $SnO_2$ nanofibers exhibited large response and good reproducibility [33]. Zhang applied oxygen plasma to etch electrospun $SnO_2$ fibers and

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the resulting porous fibers exhibited high response to ethanol [1]. Zr [12], Co [20], Cu [38] and Ni [21,23]-doped $SnO_2$ nanofibers prepared by electrospinning together with their gas sensing properties were also reported. Shi reported that $SnO_2$ material with tube-like structure could be fabricated by electrospinning with appropriate thermal treatment in air [32]. All above reports encourage us to fabricate guest metal-doped $SnO_2$ nanofibers with highly porous structure, especially hollow-core $SnO_2$ nanofibers, which should be of great potential in the application of gas sensing materials. However, to the best of our knowledge, no attention has yet been focused on the fabrication of Ni-doped $SnO_2$ hollow nanofibers by electrospinning technique.

In this paper, Ni-doped $SnO_2$ hollow nanofibers were fabricated by combination of electrospinning technique and appropriate calcination. Two comparative types of sensor materials were studied. (I) Pure and Ni-doped $SnO_2$ hollow nanofibers were fabricated to examine the effect of Ni doping on the sensing properties. (II) $SnO_2$ nanofibers with hollows and those with solid cores were prepared to investigate the influence of the hollow structure. We found that the doping of Ni and hollow core feature of electrospun $SnO_2$ nanofibers both showed improved response for detecting acetone.

## 2. Experimental

### 2.1. Preparation of $SnO_2$ nanofibers

All chemicals used in this work were analytical purity and used as received without further purification. Here $SnO_2$ nanofibers were fabricated by electrospinning followed by calcination.

In a typical synthesis, $(5–0.05x)$ mmol $SnCl_2{\cdot}2H_2O$ and $0.05x$ mmol $NiCl_2{\cdot}2H_2O$ (where $x = 0$, 3, 5 and 10) were dissolved into a mixture solution of 11 mL *N*,*N*-dimethylformamide (DMF), 11 mL absolute ethanol and 1 mL glacial acetic acid. Then 2 g PVP was added into above solution by magnetic stirring at 50 °C for 2 h. The precursor solution was subsequently stirred at room temperature for about 5 h to obtain a homogeneous mixture. The mixture was loaded into a 10 mL syringe needle for electrospinning and a piece of copper plate was selected as a collector. An electrostatic voltage of 8 kV was applied between the needle and the collector and their distance was about 10 cm. The feed speed of the mixture was controlled to be 0.7 mL/h by a syringe pump. Then, white fibrous mats were collected for every 6 h electrospinning. The collected fibers were dried at 80 °C overnight to ensure a full vaporization of the solvents.

To obtain crystalline $SnO_2$ nanofibers, the electrospun samples were subsequently calcined at 600 °C in air for 2 h, assuming that all the hydrocarbons in the fibers were fully burned out. During calcination procedure, the samples were heated from room temperature to 600 °C with different heating rates from 2 to 10 °C/min, and then kept at 600 °C for 2 h in air in an electric resistance furnace. After it cooled down to room temperature naturally, $SnO_2$ nanofibers were obtained. Moreover, different amounts of Ni were added to the precursor solution to obtain Ni-doped $SnO_2$ and the products were summarized in Table 1.

**Table 1**
Name and composition of pure and Ni-doped $SnO_2$ nanofibers fabricated under different experimental conditions.

| Sample name | Atomic content of Ni (%) | Heating rate (°C/min) | Morphology |
|---|---|---|---|
| SN0-10 | 0 | 10 | Hollow fiber |
| SN3-10 | 3 | 10 | Hollow fiber |
| SN5-10 | 5 | 10 | Hollow fiber |
| SN10-10 | 10 | 10 | Hollow fiber |
| SN5-2 | 5 | 2 | Solid core fiber |
| SN5-5 | 5 | 5 | Partial hollow fiber |

### 2.2. Characterization of $SnO_2$ nanofibers

The morphology and phase structure of the prepared samples were characterized by a field emission scanning electron microscope (FESEM, Hitachi S-4800), a transmission electron microscope (TEM, Philip CM200), and a powder X-ray diffractometer (Shimadzu XRD-6000) using Cu $K\alpha$ irradiation. Energy dispersive X-ray spectroscopy (EDS) analysis was carried out to identify the composition. Thermogravimetric analysis (TGA) was carried out using a TA Q600 instrument in a temperature range from 25 to 1000 °C with a heating rate of 10 °C/min in air. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250 Xi instrument using the X-ray source of Al $K\alpha$.

### 2.3. Fabrication and measurement of sensors

The gas sensors were fabricated by coating paste-like films with thickness about 100 μm prepared by mixing $SnO_2$ products and deionized water (in a weight ratio of 100:25) onto $Al_2O_3$ ceramic tubes (length: 4 mm, external diameter: 1.2 mm, inner diameter: 0.8 mm). A ceramic tube with two gold electrodes at the ends was used as a substrate for $SnO_2$ film. The distance between two electrodes was 2 mm. A Ni–Cr alloy coil crossed the tube was employed as a heater to control the operating temperature. The fabricated gas sensors were then dried at 80 °C overnight to ensure the evaporation of water. Before the gas-sensing measurement, every sensor was aged at 200 °C for 2 h. The gas-sensing measurement was performed by a static test system (WS-30A, Winsen Electronics Co. Ltd., China). A detailed work mechanism for the measurement system was described in Ref. [39]. A specific amount of VOCs was injected onto a flat heater inside the chamber of the gas sensing system in which sensors were installed and then immediately evaporated into gas so as to fill the chamber evenly. The gas-sensing properties were assessed by gas response, $S$, as the resistance ratio $R_a/R_g$, where $R_a$ and $R_g$ were the sensor resistance in air and in the analyte gas, respectively.

## 3. Results and discussion

### 3.1. General composition and morphology

The general morphology of the as-spun polymeric fibers containing 5 at.% Ni–Sn salts before calcination was observed by SEM and shown in Fig. 1a. It indicates that a large number of nanofibers with the diameter range from 120 to 200 nm and lengths up to several tens of micrometers can be obtained. These fibers are uniform in diameter with smooth surface. They are connected and overlapped randomly to form a porous network. TGA/DSC curves of the as-spun nanofibers were measured in air between 25 and 1000 °C to investigate the decomposition temperature of PVP and Sn precursor. From the TGA curve in Fig. 1b, we can observe the weight loss as a function of temperature: about 11% loss between room temperature and 230 °C, followed by 35% between 230 and 320 °C, and finally 33% within the 330–500 °C range. Above 500 °C, there is no evident weight loss. The first weight loss below 230 °C is likely due to the loss of water vapor and trapped solvent. The latter two weight losses are assigned to the burn of PVP and the crystallization of $SnO_2$ crystal. Thus two obvious exothermic peaks at about 300 and 450 °C are aroused by the decomposition of PVP and metal salts, respectively. The yield of the as-spun polymeric fibers was about 240 mg for 6 h electrospinning. After its calcination, we could obtain approximately 50 mg crystalline $SnO_2$ product.

The crystal structure of the $SnO_2$ products after calcination was characterized by XRD analysis and shown in Fig. 2. All the diffraction