Improved Methane Sensing Properties of Co-Doped SnO₂ Electrospun Nanofibers

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Co-doped SnO₂ nanofibers were successfully synthesized via electrospinning method, and Co-doped SnO₂ nanospheres were also prepared with traditional hydrothermal synthesis route for comparison. The synthesized SnO₂ nanostructures were characterized by X-ray powder diffraction, scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray spectroscopy, and X-ray photoelectron spectra. Planar-type chemical gas sensors were fabricated and their sensing properties to methane were investigated in detail. Gas sensors based on these two samples demonstrate the highest CH₄ sensing response at an operating temperature of 300°C. Compared with traditional SnO₂ nanospheres, the nanofiber sensor shows obviously enhanced gas response, higher saturated detection concentration, and quicker response-recovery time to methane. Moreover, good stability, prominent reproducibility, and excellent selectivity are also observed based on the nanofibers. These results demonstrate the potential application of Co-doped SnO₂ nanofibers for fabricating high performance methane sensors.

1. Introduction

As an interesting chemically and thermally stable n-type semiconductor with wide band gap energy and large exciton binding energy, tin oxide (SnO₂) has attracted increasing attention and been extensively studied for catalysis [1], solar cells [2], optoelectronics [3], lithium-ion batteries [4], chemical sensors [5, 6], and so on [7–9]. Moreover, it has been proved to be a highly sensitive material for the detection of both reducing and oxidizing gases [10, 11]. Since the gas sensing properties of SnO₂-based sensors are closely related to the reactions between gas molecules and SnO₂ surfaces, interest in tailoring the microstructure and morphology of SnO₂ nanostructures has been greatly stimulated [12–14]. Over the past years, many scientific and technological efforts have been made to improve the sensitivity, response-recovery characteristic, selectivity, and stability of SnO₂-based sensors [15–17].

Recently, one-dimensional (1D) [18, 19] and quasi-one-dimensional [20] SnO₂ nanostructures with different morphologies including nanorods [21], nanotubes [22], nanowires [23], nanobelts [24], nanosheets [25], and nanofibers [26, 27] have been successfully fabricated and reported. Taking advantage of the small grain size, large surface-to-volume ratio, high density of surface sites, special hole, and pore structure, these novel low-dimensional SnO₂ nanostructures demonstrate excellent gas sensing performances than those of traditional SnO₂ nanoparticles or thin films. Currently, electrospinning [10, 11, 28, 29], sol-gel method [5], thermal evaporation technology [30], hydrothermal method [31], and chemical vapor deposition [32] are the main methods used to synthesize low-dimensional oxide nanostructures. Among all the fabrication techniques, electrospinning [17, 28] has been demonstrated as a relatively facile and versatile method for the large-scale synthesis of 1D
Figure 1: Structure chart of the planar sensor. (a) A top view of the substrate, (b) fabricated gas sensor, (c) sensing materials, (d) Ag-Pd interdigital electrodes, and (e) ceramic substrate.

Figure 2: (a) The CGS-ITP gas sensing analysis system and (b) a photography of the operating platform.

Figure 3: XRD diffraction patterns of the prepared ZnO nanostructures.
nanostructures that are exceptionally long in length, uniform in diameter, and large in surface area.

On the other hand, doping oxide sensors with various elements, for example, noble metals [33], rare-earth metals [34, 35], transition metals [36–38], and metal oxides [39–41], has been proved to be another effective method to improve sensing properties. Transition metal Co is a widely used dopant which acts as an activating catalyst to accelerate the chemical reaction process and consequently improve the performances [42–44]. Up to now, there are many reports on synthesis of 1D SnO$_2$ nanofibers and their gas sensing properties. However, most of these gas sensors focus on HCHO [45], C$_2$H$_6$OH [46, 47], C$_6$H$_5$OH [13], CO [48], NO [49], H$_2$ [44], H$_2$S [50], and NH$_3$ [11], and rare studies concern CH$_4$, a very important fault characteristic gas for transformer fault diagnosis and condition assessment. Meanwhile, a systematic
comparison of gas sensing performances between 1D SnO₂ nanofibers and traditional nanospheres may be one missing possibility along this direction.

In this paper, we reported a simple and facile approach to fabricate high-quality Co-doped SnO₂ nanofibers by electrospinning. Gas sensors were fabricated with the synthesized SnO₂ nanofibers and their sensing properties toward CH₄ are systematically investigated. The as-prepared Co-doped SnO₂ nanofibers exhibit excellent sensing characteristics, such as high sensitivity, rapid response-recovery time, and good stability than that of traditional nanospheres.

2. Experimental

Ethanol (>95%), N, N-dimethyl formamide (>95%, DMF), CoCl₂·2H₂O, and SnCl₂·2H₂O were used and purchased from Chongqing Chuanlong Chemical Reagent Co., Ltd (China). Poly(vinyl pyrrolidone) (PVP, Mw = 1,300,000) was obtained from Aldrich. All chemicals were analytical grade and used as received without any further purification.

In a typical procedure of Co-doped SnO₂ nanofibers [11, 13, 15, 26, 29], 0.4 g of SnCl₂·2H₂O was dissolved in 4.42 g of DMF and 4.42 g of ethanol under vigorous stirring at 90°C for 30 min. Subsequently, 1.0 g PVP and appropriate quantity of CoCl₂·2H₂O (3 at%) were added into the above solution under vigorous stirring for 2 h until the salt was completely dissolved. Then the well-mixed precursor solution was loaded into a glass syringe with a needle of 1 mm in diameter at the tip and connected to a high-voltage DC power supply (ES 30-0.1P, Gamma High Voltage Research Inc.), which was capable of generating DC voltages of up to 30 kV. In our experiment, an optimal voltage of 10 kV was provided between the tip of the spinning nozzle and the collector at a distance of 20 cm. Finally, the fibers were peeled off from the collector with tweezers and placed in a crucible. The conversion of tin dichloride to SnO₂ and the removal of organic constituents PVP in the as-spun nanofibers were achieved by calcining at 600°C for 5 h in air.

Traditional Co-doped SnO₂ nanospheres (3 at%) were synthesized via hydrothermal method and the synthesis process is similar to our previous works [6, 12, 40]. Typically, 20 mL of absolute ethanol and distilled water (V/V, 1/1), 3.0 mmol SnCl₂·2H₂O, 0.09 mmol CoCl₂·2H₂O, and 20 mmol ammonia hydroxide were mixed together in a round-bottom flask (100 mL) and heated at 180°C for 60 min. Then the fully mixed precursor was transferred into a 50 mL Teflon-lined stainless steel autoclave, sealed, and heated at 180°C for 16 h in an electric furnace for hydrothermal reaction. Finally, the product was harvested by centrifugation, washed with distilled water and absolute ethanol several times, and dried at 100°C in air for 24 h.

The crystalline structures of the prepared SnO₂ nanofibers and nanospheres were investigated by X-ray powder diffraction (XRD, Rigaku D/Max-1200X) with Cu Kα radiation (40 kV, 200 mA and λ = 1.5418 Å). The microstructures and morphologies were characterized by means of field emission scanning electron microscope (FESEM, Hillsboro equipped with energy dispersive X-ray (EDS) spectroscopy) and transmission electron micrographs (TEM, Hitachi S-570). Analysis of the X-ray photoelectron spectra (XPS) was performed on an ESCALAB MKII using Al as the exciting source.

Gas sensors were fabricated by screen-printing technique with planar ceramic substrates, purchased from Beijing Elite Tech Co., Ltd. China. Figure 1 shows the schematic diagram of the planar sensor. It can be clearly seen in Figure 1 that the sensor consists of three kinds of significant components: ceramic substrate, Ag-Pd interdigital electrodes, and sensing materials. The length, width, and height of the planar ceramic substrate are suggested to be about 13.4, 7, and 1 mm, respectively. The as-prepared nanostructures were mixed with deionized water and absolute ethanol in a weight ratio of 100:20:10 to form a paste. Then the paste was subsequently screen-printed onto the planar ceramic substrate to form a sensing film with a thickness of about 50 μm. Finally, the fabricated sensor was dried in air at 80°C to volatilize the organic solvent and further aged in an aging test chamber for 36 h.

Gas sensing properties were investigated by a Chemical Gas Sensor-1 Temperature Pressure (CGS-1TP) intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd.) [41]. It could offer an external temperature control ranging from room temperature to 500°C with adjustment precision of ±1°C. As seen in Figure 2(b) two adjustable probes were pressed on the sensor electrodes to collect electrical signals. When the sensor resistance was stable, certain amount of target gas was injected into the test chamber (18 L in volume) by a microinjector through a rubber plug. After its resistance value reached a new constant value, the test chamber was opened to recover. The sensor resistance and sensitivity were collected and analyzed by the system. And the environmental temperature, relative humidity, and working temperature were automatically recorded by the analysis system.

The sensitivity (S) was defined as $S = \frac{R_g}{R_a}$ [11,13], where $R_g$ was the sensor resistance in air and $R_a$ in a mixture of target gas and air. The time taken by the sensor to achieve 90% of the total resistance change was designated as the response time in the case of gas desorption or the recovery time in the case of gas adsorption.
3. Results and Discussion

Figure 3 shows the XRD patterns of the as-prepared Co-doped SnO₂ nanofibers and nanospheres after calcinations. It can be clearly seen in Figure 3 that the synthesized samples are polycrystalline in nature. The prominent peaks of (110), (101), and (211) and other smaller peaks coincide with the corresponding peaks of rutile SnO₂ given in the standard data file (JCPDS File no. 41-1445). Due to the high dispersion and the low amount of Co ions (3 at%) doped in the synthesized samples, there is no indication of the presence of Co or other metal oxide diffraction peaks, implying a high purity of our products.

The overall surface morphologies of the products were performed firstly by SEM as shown in Figures 4(a) and 4(b). As shown in Figure 4(a) the disordered and bended nanofibers are randomly distributed to form a fibrous nonwoven. The average diameter of the as-spun nanofibers ranges from 200 to 120 nm, and the length of the fibers ranges from hundreds of nanometers to several ten micrometers. Figure 4(b) displays the typical SEM image of Co-doped SnO₂ nanospheres, where one can clearly note that the beautiful nanospheres are uniformly distributed across the whole sample and no other morphologies are detected. These nanospheres are rather dispersed and highly uniform in size and shape with an average diameter of 500 nm. Further
morphology characterization was examined by TEM and shown in Figures 4(c) and 4(d). The insets present the corresponding TEM images of individual fiber and sphere.

To check whether dopants have been successfully doped into the synthesized nanostructures, energy dispersive X-ray spectroscopy (EDS) measurement was conducted. Figures 5(a) and 5(b) show the EDS spectra of the as-prepared 3 at% Co-doped SnO$_2$ nanofibers and nanospheres, which confirm the availability of Co dopant on the SnO$_2$ matrix.

To further verify the existence of Co element and its valences in the synthesized samples, XPS data of the as-spun SnO$_2$ nanofibers is collected and presented in Figures 6 and 7. Figure 6 shows the wide spectrum, confirming the existence of Sn, O, and Co. The binding energies in Figure 7(a) at 486.5 and 493.8 eV correspond to Sn$^{4+}$ of SnO$_2$. From the narrow spectrum of Co element as shown in Figure 7(b), the peak at 780.7 and 796.8 eV is identified as Co 2p$_{3/2}$ and 2p$_{1/2}$, respectively, which possibly can be attributed to Co$^{2+}$ ions [8]. Meanwhile the positions of the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ peaks ruled out the presence of metallic Co and Co$_2$O$_3$ in the Co-doped SnO$_2$ nanofibers [9]. Moreover, the composition of the Co dopant in our products is calculated to be about 2.88 at%, which matches well its nominal concentration. Thus, based on the EDS and XPS results, the Co$^{2+}$ ions are believed to be successfully incorporated into the SnO$_2$ nanocrystals.

The responses of the nanofiber and nanosphere sensors to 50 ppm of CH$_4$ gas as a function of operating temperature are measured and shown in Figure 8. For each sensor, the response is measured to increase rapidly with increasing operating temperature and arrive to the maximum and then decreases with a further rise of the operating temperature. The optimum operating temperatures of the nanofibers and nanospheres are both suggested to be about 300°C with response values of 30.28 and 11.59, respectively.

The concentration dependence of Co-doped SnO$_2$ nanofibers and nanospheres was investigated in the range of 1–2000 ppm of CH$_4$ and the plots of the gas response against gas concentration are shown in Figure 9. As displayed in Figure 9, the gas response increases linearly with increasing the CH$_4$ concentration below 100 ppm but increases more slowly from 100 to 500 ppm, which indicates that the sensor becomes more or less saturated. Finally, the sensor reaches saturation after exposure to more than 2000 ppm. Although a similar trend was also observed for pure Co-doped SnO$_2$ nanospheres, the responses are much weaker. The inset in Figure 9 shows the response characteristics of the sensors to 1–20 ppm of CH$_4$, which indicates that the nanofibers sensor is much more favorable to detect CH$_4$ with a low concentration.

It is well known that response and recovery characteristics are important for evaluating the performances of semiconductor oxide sensors. Figure 10 shows the response transients of the two sensors exposed to 20 ppm of CH$_4$ at 300°C. According to the response-recovery time definition in Section 2, the response time and recovery time of nanofibers sensor were calculated to be 15 s and 12 s, and they were 22 s and 18 s for nanospheres.

To investigate the stability and repeatability of the Co-doped SnO$_2$ nanofibers sensor, it was sequentially exposed to different levels of CH$_4$ gas as shown in Figure 11 (3, 5, 8, 10, 20, and 50 ppm) and equal concentration as shown in Figure 12 (20, 20, 20, 20, and 20 ppm). As shown in Figures 11 and 12, the sensor response increases rapidly when exposed to certain concentration of CH$_4$ and decreases dramatically...
when exposed to air for recovering. Meanwhile, the gas response of the sensor always returns to its initial value during the continuous test period, implying a very satisfying reproducibility of the prepared sensor.

Figure 13 depicts the histogram of the gas response of the Co-doped SnO$_2$ nanofiber sensor to 50 ppm of various gases, including CH$_4$, CH$_3$OH, C$_2$H$_5$OH, NH$_3$, NO, and CO at 300°C. One can clearly see in Figure 13 that this sensor shows obvious CH$_4$ sensing response than other potential interface gases, which can be mainly attributed to the effect of sensor operating temperature on the activity of gas molecules.

A possible sensing mechanism is depicted as follows to understand the gas sensing reaction process of SnO$_2$-based sensor against CH$_4$ gas and explain the enhanced CH$_4$ sensing properties of the as-spun nanofibers. It is well known to all that SnO$_2$ belongs to typical n-type semiconductor sensing materials and its sensing properties are dominantly controlled by the change of SnO$_2$ surface resistance, especially the adsorption and desorption of oxygen on the surface of sensing materials [5]. Owing to the nonstoichiometry of the as-synthesized SnO$_2$ nanostructures, many oxygen vacancies are formed in SnO$_2$ crystal [6]. When the sensor is aged in ambient air, free oxygen could be absorbed on its surface and act as a trap capturing electrons from the conduction band of SnO$_2$ to generate chemisorbed oxygen species, namely, O$_2^-$, O$^{2-}$, and O$. These chemisorbed oxygen species would cause an energy band bending of SnO$_2$ and depletion layers are formed around the surface area, increasing the energy barrier of SnO$_2$ and decreasing its carrier concentration and electron mobility [11]. Thus, a less conductive SnO$_2$-based sensor is measured. When the sensor is exposed to ambient CH$_4$, chemical reactions take place between the CH$_4$ molecules and the chemisorbed O$_2^-$, O$^{2-}$, and O$, which releases the trapped electrons back to the conduction band, increasing the carrier concentration and electron mobility; thus a decreased resistance is found in our measurements [12].

Many former papers have reported and demonstrated that Co is an effective dopant to improve the gas sensing properties of metal oxide semiconductor materials, which is mainly due to the excellent electronic and chemical sensitization [42–44]. The improved CH$_4$ sensing properties of Co-doped SnO$_2$ nanofibers measured above are mainly based on the unique fiber structure [13]. Compared with traditional nanospheres, the as-spun 1D SnO$_2$ nanofibers possess larger surface to volume ratio, providing much more reaction sites for the target gas adsorption. Moreover, there are many nanofiber-nanofiber junctions in the netlike SnO$_2$ nanofibers [43]. Such junctions could form a depleted layer around the intersection, which promotes the oxygen species adsorption onto the interfacial region significantly. Then electron capture and release could undergo in a relatively easier way, accelerating the electron flow; as a result, more efficient charge transfer takes places and enhanced CH$_4$ sensing properties are observed.

4. Conclusions

In that summary, 3 at% Co-doped SnO$_2$ nanofibers have been synthesized via a simple electrospinning method and characterized by XRD, SEM, TEM, EDS, and XPS. The as-spun 3 at% Co-doped SnO$_2$ nanofibers exhibit high sensitivity,
supersaturated detection concentration, and rapid response and recovery against CH\textsubscript{4} than that of 3 at% Co-doped SnO\textsubscript{2} nanofibers, prepared by traditional hydrothermal synthesis route. In addition, the nanofiber sensor demonstrates excellent selectivity, prominent stability, and good reproducibility to CH\textsubscript{4}. All results suggest that the as-spun 3 at% Co-doped SnO\textsubscript{2} nanofibers sensors are potential candidates for CH\textsubscript{4} detection. Furthermore, this method may be extendable to develop high performance semiconductor sensors monitoring other fault characteristic gases dissolved in transformer oil.

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