Doping effect of In_2O_3 on structural and ethanol-sensing characteristics of ZnO nanotubes fabricated by electrospinning

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Abstract

Indium-doped ZnO (IZO) nanotubes with various indium contents (0.01–0.20) were synthesized via a facile electrospinning method. Results of X-ray diffraction and transmission electron microscopy demonstrate that all samples are consisted of hexagonal wurtzite-typed ZnO, showing a well-crystallized indium-zinc-oxide solid solution when only a small amount of zinc ions substituted by indium ions (0.01). Once the amount of indium dopants ≥ 0.05 , there will form some amorphous In_2O_3 , leading to a pronounced decrease in grain sizes. Gas-sensing performances revealed that the IZO nanotube-based sensors have enhanced ethanol-sensing characteristics, especially, sensor based on IZO-0.01 nanotubes shows the highest response ($R_a/R_g = 81.7$), which is twice that of the undoped ZnO nanotubes (40.0) toward 100 ppm ethanol at an operating temperature of 275 °C. And IZO-0.20 nanotube-based sensor presents a relatively high response at high ethanol concentrations. Our research suggested that these remarkable enhanced ethanol-sensing properties can be closely related to the formation of indium-zinc-oxide solid solutions and/or heterostructures between ZnO and amorphous In_2O_3 .

Keywords: ZnO nanotubes; In_2O_3 ; Electrospinning; Ethanol; Gas sensors

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1. Introduction

As potential building blocks for gas sensors, one-dimensional (1D) nanostructures are widely explored because of their unique geometry with high aspect ratio and specific surface area. In particular, the 1D metal oxides with tubular and/or porous structures have been suggested one of the best candidates for high-performance gas sensors, exhibiting high sensitivity, good selectivity, fast response and recovery times, and long-term stability [1-4]. However, it is often difficult to make a single metal oxide meet all of those requirements under a complex testing environment.

Recent reports show that this difficulty can be largely alleviated by using composites, hetero-metal oxide doping, or oxide heterostructures [5, 6]. Among those metal oxides, ZnO and In₂O₃, as two important n-type semiconductors ($E_g = 3.37$ eV and 3.5~3.75 eV at 300 K, respectively), play important roles in the field of gas sensors [7-11]. It has been demonstrated that the ZnO/In₂O₃ composite nanostructures (such as binary complex, core-shell heterostructures, and mixtures) can greatly enhance their application performances [12-18]. Lee *et al.* reported the preparation of ZnO-In₂O₃ composite nanofibers using electrospinning, obtaining a higher response and a better selectivity to trimethylamine compared to those of pure ZnO or In₂O₃ nanofibers, which is due to the synergetic combination of two sensing materials [16]. In addition, a double-layer structure with heterocontactacts between ZnO and In₂O₃ nanofibers exhibited excellent ethanol sensing properties [14]. On the other hand, many previous reports show that a small amount of multivalent ion (In³⁺, Al³⁺, Sn⁴⁺, etc.) doping could obviously change the crystal defect density and carrier concentration of ZnO matrix [19-24], while few work discussed how those two aspects can affect the gas-sensing performances of ZnO matrix. Therefore it is also significance to expand our understanding of indium-doped ZnO (IZO) based gas sensors.

To fabricate these desirable 1D sensing materials, hydrothermal, solvothermal, electrospinning, and template method or conjunctions between various methods have been frequently employed [25-28]. Among them, electrospinning, as a simple, versatile, and cost-effective method, has been often used to produce 1D material, such as nanofibers, nanobelts, and nanotubes. And various nanofibers or nanotubes with specific components and structures can be easily

controlled by adjusting the concentrations of the additives in the precursor solution [3, 29, 30]. In this work, ZnO nanotubes with various amounts of indium dopants were prepared by an electrospinning method. The influences of the doping amounts of indium oxide on the crystal structures and optical properties of ZnO nanotubes were investigated. And it was found that the IZO nanotube-based gas sensors show an enhanced ethanol-sensing characteristics compared with the undoped ZnO. Furthermore, a possible enhancement mechanism was proposed for the enhanced sensor performances.

2. Experimental section

2.1. Synthesis

IZO nanotubes were prepared by electrospinning of the precursor polyvinylpyrrolidone (PVP, $M_w = 1,300,000$)/ $Zn(NO_3)_2 \cdot 6H_2O$ solution. 0.20 g of $Zn(NO_3)_2 \cdot 6H_2O$, 0.34 g PVP, and $In(NO_3)_3$ were added into 5 mL of binary mixtures of N, N-dimethylformamide (DMF) and ethanol absolute (a volume ratio of 1:1) with vigorously stirring for 10 h. In a typical electrospinning procedure, a DC high voltage of 15 kV was applied between a stainless-steel collector and needle-tip at a distance of 15 cm. The feed rate was kept constant (0.4 mL h^{-1}) via a peristaltic pump. Then the precursor fibers were collected and calcined at 500°C in air for 2 h to remove the organics. For comparison, the fibers with different contents of In^{3+} (1, 5, 10, and 20 at. %) were prepared by replacing Zn^{2+} in the precursor solutions, and marked as IZO-0.01, IZO-0.05, IZO-0.10, and IZO-0.20, respectively. All chemicals (analytical grade reagents) were used as received without further purification.

2.2. Characterization

The crystalline structures and morphologies of the samples were characterized using X-ray diffraction (XRD, Philips, X'Pert Pro), field emission scanning electron microscopy (FESEM, Hitachi, S4800), and high-resolution transmission electron microscopy (HRTEM, FEI, Tecnai G2 F30) equipped with energy dispersive X-ray analysis (EDX). The UV-vis absorption spectra were measured on a TU-1901 spectrophotometer in the wavelength range of 300–800 nm. The photoluminescence (PL) measurement was performed at room temperature using 325 nm line of a continuous-wave

He-Cd laser as excitation source.

2.3. Gas-sensing measurement

Sensor measurement was performed on a WS-30A system (Weisheng Instruments Co., Zhengzhou, China). The fabrication of the sensor element was described in detail in our previous paper [31]. A given amount of test gas was injected into an 18-L chamber by a micro-injector and mixed with air (used as a reference gas) by two fans. After the sensor resistance reached a new constant value, the test chamber was opened to recover the sensor in the air. All sensors were carried out over the operating temperature range from 200 to 375 °C at a relative humidity of 40%. The sensor response was defined as the ratio of the sensor resistance in air (R_a) to that in target gases (R_g). The response/recovery time was defined as the time taken by the sensor to achieve 90% of resistance change in the adsorption/desorption process, respectively.

3. Results and discussion

3.1. Structure and morphology

Fig. 1a shows the typical XRD patterns of the as-prepared ZnO and IZO samples, respectively. It is found that all diffraction peaks match very well with a wurtzite structure (JCPDS No. 36-1451), and no diffraction peaks of In_2O_3 or other phases are observed in the samples, even with high indium doping levels (IZO-0.10 and IZO-0.20). When the doping level increases, the diffraction peaks of IZO become progressively lower. Moreover, calculated from the (101) peak using Scherrer's formula [32], the average grain size of IZO-0.01 is ~27.4 nm, which is slightly larger than that of undoped ZnO (~25.5 nm). And it decreases remarkably with increasing the doping levels (15.9, 11.0, and 5.6 nm corresponding to IZO-0.05, IZO-0.10 and IZO-0.20, respectively), indicating that the samples with high indium doping level have a poor crystallinity. Furthermore, the major diffraction peaks ((100), (101), and (110), marked with star in Fig. 1a) of IZO-0.20 shift slightly towards lower diffraction angles compared to those of the pure ZnO sample, which can also be observed in IZO-0.10 sample (the shift of peak (101) is $\Delta 2\theta = 0.01^\circ$), suggesting the structural defects of ZnO caused

by indium dopants [33]. It should also be noted that the lattice constant will be increased when the indium atoms incorporated into the ZnO lattice as a substitutional impurity (due to the fact that indium is larger than both zinc and oxygen) [21]. In addition, the EDX spectrum of the IZO samples (Fig. 1b) clearly shows that the ZnO is doped with indium atoms, and no other impurity elements are detected. Cu and C elements come from the carbon-coated copper grid used as a support during TEM observation.

Fig. 2 shows the TEM images of IZO samples with various indium contents. The obtained IZO samples consist of tubular-like nanofibers, and each nanotube has a uniform size of 60-80 nm in diameter, as shown in Figs. 2a, 2c, 2e, and 2g. Moreover, from Fig. 2b, it can be seen that the rough wall of IZO-0.01 nanotubes are built up of numerous nanograins. When increasing indium concentration up to 20 at. % (as shown in Figs. 2d, 2f, and 2h), the tubular structure becomes more and more compact with the diameter narrowing. On the other hand, IZO-0.01 and IZO-0.05 nanotubes possess a rather clear grain boundaries (in Figs. 2b and 2d), while the grain boundaries of IZO-0.10 and IZO-0.20 nanotubes become blurred, implying that the surfaces become partially amorphous.

In order to better understand the effect of indium oxide on the microstructures of the IZO nanotubes, HRTEM images were observed and shown in Fig. 3. Fig. 3a (IZO-0.01 nanotubes) displays the lattice fringes (lattice spacing of about 0.281 nm) at the (100) plane of wurtzite ZnO, which further indicates a good crystallinity. In Figs. 3b–d, the average grain size obviously decreases with the increasing indium contents, which is consistent with the above XRD results. From the previous literature [21], it is reported that excessive indium (≥ 2 at. %) cannot be accommodated into ZnO lattice due to its limited solid solubility. In this case, as for the excessively doped samples, especially IZO-0.20, large numbers of fine grains disorderly stack, leading to the unclear lattice fringes. The excrescent In_2O_3 components will form into amorphous In_2O_3 on the tube surface.

Therefore the effect of indium oxide on the structures of IZO nanotubes can be explained as follows: (1) only a small amount of indium atoms can be completely dissolved into the ZnO crystalline structure, and form an

indium-zinc-oxide solid-solution. (2) The undissolved indium atoms can work as new nucleation centers and restraint the grains' growth. More indium dopants will lead to more undissolved indium atoms, and accordingly introduces more nucleation centers, which cause the decrease in grain size. (3) Besides a small part of indium atoms are dissolved into the ZnO crystalline, the undissolved indium atoms will segregates at the ZnO grain boundaries in the form of amorphous to form heterostructures, all of which can be considered together to inhibit grain growth.

3.2. UV-vis absorption and PL spectra

The UV-vis absorption spectra were measured and shown in Fig. 4a. The absorption edge of each sample is determined by the first derivative method. The spectrum of ZnO exhibits a clear absorption edge at around 386 nm wavelength, which corresponds to a band gap $E_g = 3.21$ eV of the pure ZnO (insets, Fig. 4a). Meanwhile the absorption edge of the IZO nanotubes shows an obvious red-shift, and the light adsorption intensities between 400 and 450 nm are raised up. It should be noted that the optical band gap energy of the IZO nanotubes decreases with increasing doping levels. Similar results can also be observed in some previous studies [21, 34, 35].

Fig. 4b shows the room-temperature PL spectra of IZO nanotubes, which are consisted of a UV emission peak (around 390 nm) and a broad emission band in the visible light region (450–600 nm). This strong UV emission peak can be well-understood as the near-band-edge emission, which usually arises from the recombination of photogenerated charge carriers across the band gap. For ZnO, superior optical properties with a large ratio of UV to visible PL emission intensities are in high demand of high crystallinity [36, 37]. Moreover, both of zinc and oxygen interstitials are suggested to be responsible for the visible light emission. In this study, the UV emission of IZO-0.01 nanotubes becomes sharper than that of the undoped ones, indicating their higher crystallinity (corresponding to the bigger grain size). With further increasing indium doping levels, the UV emission intensity of the samples decreases with their crystallinities.

3.3. Gas-sensing properties

As reported in the previous work, the doped indium atoms could exist in the ion state of In^{3+} atoms can act as donor

impurities at the substitutional sites of Zn^{2+} , or the existence of amorphous In_2O_3 [21, 33]. Both of them may make a great difference in carrier (free electron) concentrations and their gas-sensing properties. Gas-sensing characteristics of the as-prepared IZO nanotubes were studied using ethanol as a target gas. Fig. 5a shows the responses toward 100 ppm ethanol as a function of operating temperatures (200–375 °C). The responses of all five IZO nanotube-based sensors increase with the operating temperature and reach their maximum values at 275 °C, then decrease with further increasing the temperature. It is noted that the optimal operating temperature of 275 °C was thus chosen for further sensing measurements. Moreover, at the same operating temperature (275 °C), the IZO nanotube-based sensors with different indium contents show the response values of 81.7, 52.1, 55.4, and 47.2, respectively, indicating that the gas response can decrease with higher indium doping levels. In particular, the IZO-0.01 nanotube-based sensor shows the maximum response, which is twice that of the undoped ZnO nanotubes (~ 40.0).

Further investigation is to examine ethanol sensitivity of the IZO nanotubes. The sensors are exposed to various ethanol concentrations (5–5000 ppm) at 275 °C. The response sharply increases with the increasing ethanol concentration below 100 ppm. Above 1000 ppm, the increase rate in the response of ZnO-based sensor slows down with further increasing ethanol concentration, which indicates that the sensor response would become saturated at a certain concentration. As for the ZnO-based sensor, its response can reach saturation at about 2000 ppm. However, for IZO nanotube-based sensors, their responses are far from their saturation, even increasing ethanol concentration up to 5000 ppm, indicating the ethanol-sensing improvement of ZnO-based sensors with indium dopants. Additionally, at high ethanol concentrations (above 1000 ppm), IZO-0.10 and IZO-0.20 nanotube-based sensors present relatively higher response values. While at low ethanol concentrations (5–100 ppm, inset of Fig. 5b), the IZO-0.01 nanotube-based sensor shows the best performance, and the lowest resistance ($\sim 10^3$ k Ω) in air, as shown in Fig. 5c). Moreover, IZO-0.01 nanotube-based sensor presents the corresponding response and recovery times of 2–6s and 56–63s, respectively, which are shorter than those of the ZnO (a response time of 3–8s and a recovery time of 59–66s). The responses of IZO-0.01

nanotube-based sensor are about 8.0 (5 ppm), 14.6 (10 ppm), 25.2 (20 ppm), 49.2 (50 ppm), and 81.7 (100 ppm), respectively. By contrast, the responses of the undoped ZnO ($R_a \approx 8.1 \times 10^3 \text{ k}\Omega$) are about 4.6 (5 ppm), 8.5 (10 ppm), 14.6 (20 ppm), 26.6 (50 ppm), and 40.0 (100 ppm), respectively.

Fig. 6 exhibits the response of the ZnO and IZO sensors at 275 °C toward 100 ppm of various target gases, including ammonia (NH₃), hydrogen (H₂), methane (CH₄), methanol (CH₃OH), acetone (C₃H₆O), ethanol (C₂H₅OH), and trimethylamine (TMA). All sensors show insensitivity to ammonia, hydrogen, and methane, and similar responses to methanol and acetone, indicating their good gas selectivity toward those five gases. When exposed to ethanol, IZO-0.01 shows the highest response in all sensors. In order to further explore their selectivity, the TMA gas response indicates that a significant enhancement of the sensor response with high indium doping levels in IZO nanotubes, which agrees with the Lee's report [16]. Overall, IZO-0.01 sensor shows a relatively better selectivity to ethanol at 275 °C, which could be mainly due to the difference in the optimized operating temperature of the sensor to various gases.

For n-type semiconductor oxide gas sensors (ZnO and In₂O₃), the change in their resistances is primarily caused by the adsorption and desorption of gas molecules on the surface of the sensing films [38]. When the IZO nanotubes are surrounded by air, oxygen molecules will adsorb on the tube surface, and generate chemisorbed oxygen species (O₂⁻, O²⁻, and O⁻) by capturing electrons from the conductance band, which consequently leads to a decrease in the electron density in the tube surface. Then, a depletion region will form on the surface, which accordingly leads to an increase in sensor resistance (R_a). When the nanotubes are exposed to ethanol at a moderate temperature, the ethanol molecules will react with the adsorbed oxygen species, forming CO₂ and H₂O, and re-injecting the trapped electron back to the depletion layer, which can decrease the width of depletion region and accordingly decrease sensor resistance (R_g).

In general, the gas-sensing performances of ZnO are governed by a certain amount of structural defects. In this case, the structural distortion defects can also be a significant factor for the enhancement of sensing response to target gases. Herein, the enhancement mechanisms of the IZO nanotubes can be explained as the following two aspects: on the one

hand, when a small amount of indium atoms doped in the samples, most of them can be directly incorporated into the lattice of ZnO to form indium-zinc-oxide solid-solutions. And these dopants can improve the growth of ZnO grain, leading to a larger grain size, which is reported to impose an unfavorable effect on the improvement of the gas-sensing performances. However, from the UV-vis results above, we can see that the bandgap energies of ZnO matrix are effectively decreased by the indium dopants (in Fig. 4a), which can work as a donor state. Consequently, the decrease in the height of the grain boundary potential barrier appears to improve the process of electron feedback, leading to the sharp decrease in R_a , and accordingly enhance the ethanol-sensing performance. On the other hand, when excessive indium dopants are added, some of them exist in the form of amorphous In_2O_3 . To some extent, amorphous In_2O_3 would inhibit the response of the whole material toward low concentration ethanol [39]. But it shows high responses to high concentration ethanol, which can be due to the heterostructures between ZnO and amorphous In_2O_3 . Because of the difference band structure between two oxides, the special interface modulation process, to influence the response resistance of the entire devices (in Fig. 5c). However, a high indium doping level also shows a high response to TMA gas, which reveals a decreased selectivity for IZO-0.20. Based on the above results and analysis, the enhancement in the ethanol-sensing performance of the IZO nanotubes may be attributed to the formation of indium-zinc-oxide solid-solutions and/or heterostructures between ZnO and amorphous In_2O_3 . Overall, the IZO nanotube-based sensors with some solid-solutions present a high performance for ethanol detection at a low indium doping level. Additionally, this work discusses the ethanol-sensing characteristics of IZO nanotubes, and more discussions on their sensing mechanism still need further experimental verification.

4. Conclusions

In summary, IZO nanotubes were prepared by a simple electrospinning method combined with a post-calcination in air at 500 °C. The indium atoms incorporated into the ZnO grains are characteristic of a donor state at low doping levels. And amorphous In_2O_3 segregates at the ZnO grain boundaries when exceeding its solid solubility. It was found that the

indium dopants play an important role in the sensor performances. Importantly, the as-obtained IZO-0.01 nanotube-based sensor exhibited an excellent ethanol-sensing performance at 275 °C, and the response and recovery times are 2–6s and 56–63s, respectively. Both the formation of indium-zinc-oxide solid-solutions and heterostructures between ZnO and amorphous In₂O₃ should be considered to explain the ethanol-sensing characteristics of IZO nanotubes. On the basis of these 1D tubular IZO composites, it is useful to exploit the features of other composites with certain chemical components for gas sensor applications.

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Fig. 1. (a) XRD patterns of the ZnO and IZO samples, and (b) energy-dispersive X-ray spectrum (EDX) recorded from the IZO.

Fig. 2. TEM images of samples: (a, b) IZO-0.01, (c, d) IZO-0.05, (e, f) IZO-0.10, and (g, h) IZO-0.20.

Fig. 3. HRTEM images of: (a) IZO-0.01, (b) IZO-0.05, (c) IZO-0.10 and (d) IZO-0.20.

Fig. 4. (a) UV-vis absorption spectra of the ZnO and IZO nanotubes; insets are curves of $(ah\nu)^2$ versus photon energy ($h\nu$), and the band gap energy can be calculated by linear fitting the absorption edge. (b) Room-temperature PL spectra of the primary ZnO and IZO nanotubes.

Fig. 5. (a) Gas-sensing characteristics of ZnO and IZO nanotube based sensors: (a) response of sensors to 100 ppm ethanol as a function of operating temperature; (b) response versus ethanol concentrations (5–5000 ppm) at an operating temperature of 275 °C, insert shows the corresponding responses with increasing ethanol concentrations (5–100 ppm); (c) response-recovery characteristic curves of sensor resistance to ethanol.

Fig. 6. Selectivity of the sensors to various test gases (100 ppm) at 275 °C.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6