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## Preparation of one-dimensional $\text{SnO}_2\text{--In}_2\text{O}_3$ nano-heterostructures and their gas-sensing property

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Herein, we employ a combination of electrospinning and hydrothermal approaches to synthesize 1D  $\text{SnO}_2\text{--In}_2\text{O}_3$  nano-heterostructures with a series of morphological evolutions. Through variations in the mole ratio of  $\text{Sn}^{4+}$  and  $\text{In}^{3+}$  ions in hydrothermal condition, several 1D  $\text{SnO}_2\text{--In}_2\text{O}_3$  heterogeneous morphologies have been realized. The proposed growth mechanism for 1D nano-heterostructures is expected to be a nucleation-growth process.  $\text{In}_2\text{O}_3$  nanofibers, as templates, provide numerous nucleation sites for the growth of  $\text{SnO}_2$  nanostructures. As the  $\text{Sn}^{4+}$  concentration increases, the  $\text{SnO}_2$  nucleus can start to grow from the surface of  $\text{In}_2\text{O}_3$  template and extend out along the lateral direction until adjacent grains begin to be connected, forming morphological evolutions. The sensor of  $\text{SnO}_2$  nanocylinders, grown on  $\text{In}_2\text{O}_3$  nanofibers (SI-3 sample), exhibits highest response value at optimal operating temperature. The sensor based on SI-3 sample displays quicker recovery capability towards ethanol gas. A rapid recovery rate can be ascribed to the spillover effect and high surface area. The gas-sensing mechanism of 1D  $\text{SnO}_2\text{--In}_2\text{O}_3$  nano-heterostructures has been discussed.

## Introduction

One-dimensional (1D) semiconducting metal-oxide nanostructures have gained considerable attention as flammable and toxic gas detectors for application in environment, oil, chemicals and mining *etc.*<sup>1</sup> High sensing performance depends not only on the intrinsic property of the material itself, but also on the special structural parameters, such as high specific surface and large porosity.<sup>2</sup> 1D metal-oxide gas sensors, with small particle size and large surface area, make it easy to promote interaction between the testing gas molecules and the adsorbed oxygen molecules. Electrospinning technique is a simple and versatile route to prepare inorganic nanofibers. Nanofibers because of their interesting features, such as surface-to-volume ratio, high surface area, microporosity, and nonwoven structure, provide numerous opportunities to design novel carrier systems for gas-sensing reactions.<sup>3</sup> However, single-component one-dimensional (1D) nanomaterials have been unsatisfactory, increasing gas monitoring demands in complex conditions. To efficiently enhance gas detection capability, some studies utilize electrospun nanofibers as hard template to fabricate complex 1D nanostructures *via* suitable and compatible growth methods, in which second component is grown directly on a framework of nanowires or nanofibers. These 1D nanosized heterostructures as gas sensors have the following advantage: the

assembly of secondary nanostructures on nanofibers' surface not only provides numerous active sites and surface atoms for gas diffusion, but also improves response and recovery activities for testing gas. On the other hand, the formation of heterostructures with favorable band alignment can lead to novel interface effects and a functional integration of the properties of both the materials. In contrast with single-component nanofibers, multicomponent 1D nano-heterostructures have been shown to possess superior property or new functionality.

As a new type of gas-sensing material, indium oxides ( $\text{In}_2\text{O}_3$ ,  $E_g = 3.55\text{--}3.75$  eV) have been intensively investigated due to good conductivity and high gas response and low toxicity.<sup>4,5</sup>  $\text{In}_2\text{O}_3$  nanomaterials with various morphologies exhibit higher sensitivity and selectivity for oxidizing or reducing gas compared to conventional gas-sensing material like  $\text{SnO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{ZnO}$  *etc.*<sup>6-8</sup> Particularly,  $\text{In}_2\text{O}_3$ -based composite nanostructures produced by surface modification or doping have shown excellent enhancement in gas-sensing activity over their components. Recently, some researches made several attempts to extend response and recovery properties of  $\text{In}_2\text{O}_3$ -based nanostructures, such as doping with metal ions,<sup>9-11</sup> surface coating<sup>12</sup> and seeding secondary growth.<sup>13</sup> Among these attempts, coupled  $\text{In}_2\text{O}_3$  nanostructure with traditional semiconducting oxides to form 1D heterostructures had been a novel approach for improving gas-sensing performance. For instance,  $\text{In}_2\text{O}_3\text{/a-Fe}_2\text{O}_3$  heterostructure nanotubes,<sup>14</sup>  $\text{CuO}\text{--In}_2\text{O}_3$  core-shell nanowires,<sup>15</sup>  $\text{In}_2\text{O}_3\text{/TiO}_2$  composite nanofibers,<sup>16,17</sup> and  $\text{In}_2\text{O}_3\text{/ZnO}$  core-shell nanorods<sup>18</sup> were investigated. Although a few syntheses

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of 1D nano-heterostructure with  $\text{In}_2\text{O}_3$  component have been reported in recent years,  $\text{In}_2\text{O}_3$  has only acted as a secondary component on nano-heterostructure surface. To date,  $\text{In}_2\text{O}_3$  has never been used as a major component to fabricate multi-component 1D nano-heterostructure. Tin dioxide ( $\text{SnO}_2$ ) is the most important material for use in gas sensing applications.<sup>19</sup> It is the dominant choice for solid state gas detectors in domestic, commercial and industrial settings due to the low operating temperatures, high sensitivities, mechanical simplicity of sensor design and low manufacturing costs.<sup>20,21</sup> If the  $\text{SnO}_2$  grains are deposited onto the surface of 1D  $\text{In}_2\text{O}_3$  nanostructures, this new sensing system will effectively reveal the connection between the microstructure and the gas-sensing performance. In this study, the  $\text{SnO}_2$  nanoparticles decorated  $\text{In}_2\text{O}_3$  nanofibers were prepared by a two-step method: electrospinning combined with hydrothermal methods. We have carefully evaluated the formation mechanism of  $\text{SnO}_2\text{--In}_2\text{O}_3$  1D nano-heterostructures, and then depicted the gas sensing difference between the  $\text{In}_2\text{O}_3$  nanofibers and  $\text{SnO}_2\text{--In}_2\text{O}_3$  1D nano-heterostructures to identify the parameters that influence the gas sensing performance.

## Experimental

### The synthesis of $\text{In}_2\text{O}_3$ nanofibers

The raw materials were  $\text{In}(\text{NO}_3)_3$ , polyvinylpyrrolidone (PVP), dimethylformamide (DMF) and ethanol. In a typical procedure, 1 g of polyvinylpyrrolidone (PVP,  $M_w = 1\,300\,000$ ) powder was dissolved in the mixture of 4.5 g of ethanol and 4.5 g of dimethylformamide (DMF). Subsequently, 3 mmol of  $\text{In}(\text{NO}_3)_3$  was added to the above solution and stirred for 2 h to form transparent and homogeneous precursor solution.

The precursor solution was placed in a 5 ml glass syringe equipped with a stainless steel needle. A positive electrode was connected to the steel needle tip while a piece of aluminum foil covered collector worked as the negative plate. Distance between the needle tip and the collector was fixed at 10 cm, and electrospun voltage was controlled at 13 kV.  $\text{In}_2\text{O}_3$  nanofibers were obtained by calcination of the precursor nanofibers at 600 °C for 2 h in air.

### The synthesis of 1D $\text{SnO}_2\text{--In}_2\text{O}_3$ nano-heterostructures

$\text{SnO}_2$  nanostructures were deposited on the surface of  $\text{In}_2\text{O}_3$  nanofibers by hydrothermal methods. In a typical procedure, 20 mg of  $\text{In}_2\text{O}_3$  nanofibers were put into 30 ml of deionized water to form the suspension liquid. Different amounts of  $\text{SnCl}_4$  (the mole ratio of elements,  $\text{Sn}^{4+} : \text{In}^{3+} = 1 : 10, 1 : 5$  and  $1 : 2.5$ ) were added into the above solution. Then, aqueous ammonia solution was added dropwise until pH of the solution was 10. After being ultrasonically treated, the mixture solution was transferred into Teflon-lined stainless steel autoclave of 50 ml capacity and sealed tightly. The autoclave was maintained at 140 °C for 2 h in an oven, and then cooled naturally to room temperature, as summarized in Table 1. The obtained products were washed with deionized water, filtered and dried in an oven at 80 °C for 12 h.

### The gas sensing measurement

In the gas-sensing measurement, ethanol was employed as the target gas. The as-obtained 1D  $\text{SnO}_2\text{--In}_2\text{O}_3$  nano-heterostructures were mixed with the appropriate amount of deionized water in an agate mortar to produce paste, which were subsequently brushed onto the alumina ceramic tubes. These tubes were dried under IR light for several minutes in air and calcinated at 200 °C for 1 h. Fig. 1 shows a schematic of the as-prepared sensor. Each ceramic tube is attached with a pair of gold electrodes, which were used for linking the tube with the gas detecting device (each electrode was connected to two Pt wires). A Ni-Cr heating wire was inserted in the tube as a resistor to adjust the operating temperature. The gas sensors were aged at 300 °C for 240 h in air to enhance stability and repeatability.

In general, the gas-sensing performances were tested using an intelligent gas-sensing test system (CGS-8, China). The as-prepared sensors were placed into a closed glass chamber, and the suitable concentration of ethanol gas was injected inside the chamber for measurement of the sensing performance. The gas sensors were used as a load resistor in measuring the electric circuit of the gas sensor. When a suitable amount of ethanol gas was injected into the chamber, the resistance of the sensor changed. By regulating the operating temperature, the resistance of samples was measured in air and in ethanol gas. The sensor response was defined as  $S = R_a/R_g$ , where  $R_a$  was the resistance of the sensor in air and  $R_g$  was the resistance in ethanol gas. The response time and recovery time were described as the time taken by the sensor to achieve 90% of the total resistance change after sensor was exposed to ethanol gas and air, respectively.

### Characterization

Structural analyses of the samples were carried out by X-ray diffraction (XRD) using an X-ray diffractometer (Rigaku D/max-2500) with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406\text{ \AA}$ ) and a step size of 0.02°. The morphology and surface of the nanofibers was inspected using field emission-scanning electron microscopy (FE-SEM JSM-6700F Japan) and high resolution transmission electron microscopy (HRTEM Tecnai G2 F20 America). The composition analysis of samples was performed using energy dispersive X-ray (EDX) spectroscopy combined with scanning electron microscopy (SEM). The specific surface area of the samples were analyzed by Brunauer Emmett Teller measurements (BET JW-BK100A China).

## Results and discussions

### The structure and morphology

The morphologies of three nano-heterostructures were observed by SEM, as illuminated in Fig. 2. Fig. 2a shows that the obtained nanofibers are rough and flexible with an average diameter of approximately 200 nm. Enlarged images (Fig. 2b) show that nanofibers surface is covered by a number of bulge-like spherical particles. On increasing the mole ratio of Sn/In, these bulges evolved into regular nanograins on the surface.



Table 1 Experimental conditions for the preparation of three  $\text{SnO}_2$ – $\text{In}_2\text{O}_3$  samples

Sample no.	Starting Sn/In mole ratio	Hydrothermal temperature and time	Secondary $\text{SnO}_2$ size (nm)	Morphology
SI-1	1 : 10	140 °C, 2 h	40	$\text{SnO}_2$ particles grown on $\text{In}_2\text{O}_3$ nanofibers
SI-2	1 : 5	140 °C, 2 h	60	$\text{SnO}_2$ nanograins grown on $\text{In}_2\text{O}_3$ nanofibers
SI-3	1 : 2.5	140 °C, 2 h	80	$\text{SnO}_2$ nanocylinders grown on $\text{In}_2\text{O}_3$ nanofibers

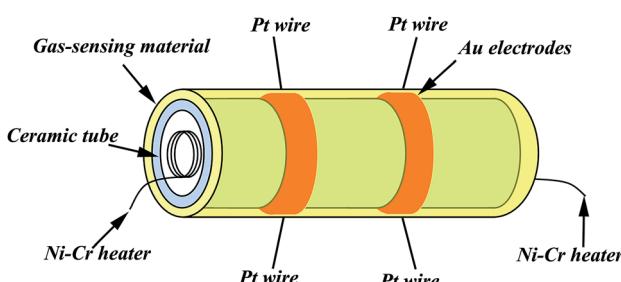
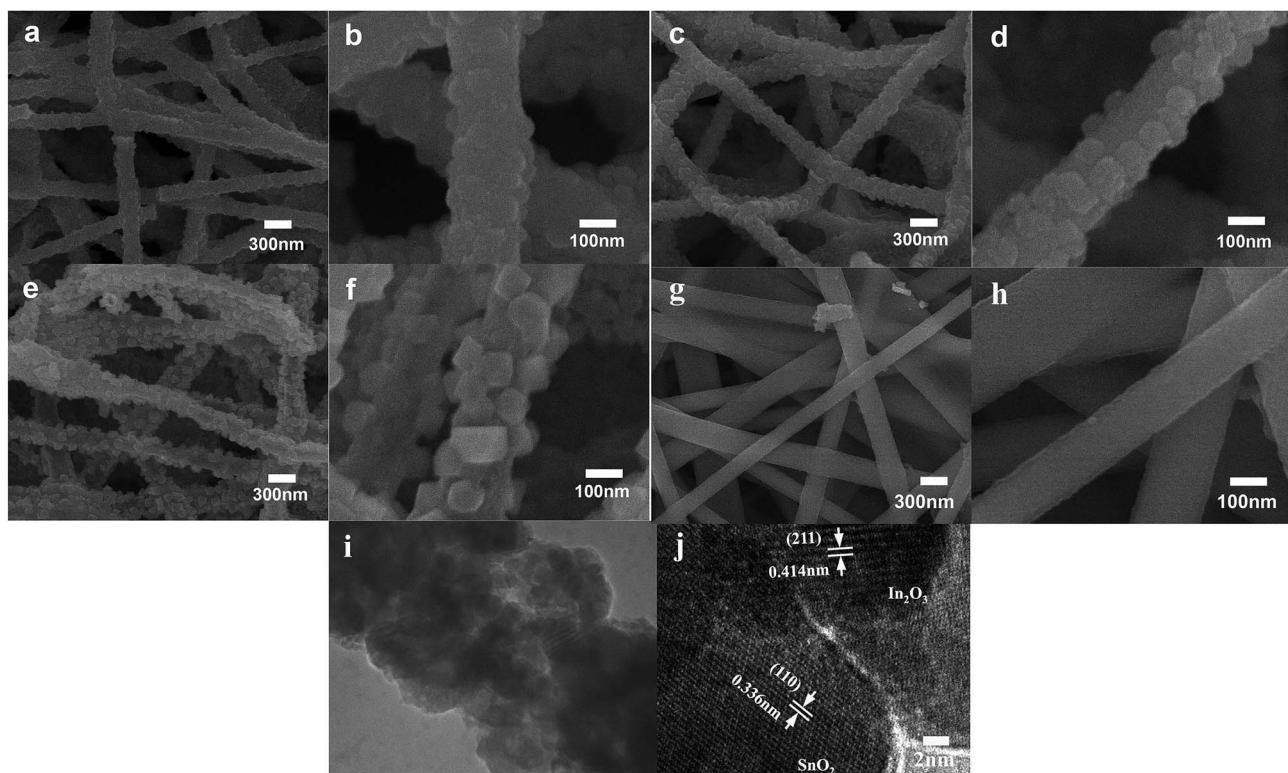


Fig. 1 Schematic diagram of the gas sensor.

These nanograins have diameters of about 50–70 nm, and their distributions are relatively uniform (Fig. 2c and d). If the starting Sn/In ratio is further increased to 4 times, numerous nanocylinders instead of regular nanograins grow on the surface of the  $\text{In}_2\text{O}_3$  nanofibers (Fig. 2e and f). It is demonstrated that additions of  $\text{SnCl}_4$  make it possible to synthesize 1D

nano-heterostructure with cylinders as large as 80 nm on the heterostructure surface. Fig. 2g shows that the pristine  $\text{In}_2\text{O}_3$  nanofibers have diameters of about 200 nm, and the surface is relatively smooth without any secondary nanostructures. Fig. 2i is a typical HRTEM image recorded from the corresponding surface area in SI-3 samples. Well-resolved lattice fringes can be clearly observed on the surface and in the internal regions. The spacing of lattice plane of surface nanostructures is approximately 0.336 nm, which agrees well with the (110) lattice index of  $\text{SnO}_2$ . Lattice spacing of internal regions is about 0.414 nm, ascribed to (211) crystal planes of cubic  $\text{In}_2\text{O}_3$ . To find the exact chemical composition of the surface nanostructures, multiple spot analysis of the surface area were carried out using Energy-Dispersive Spectrometer (EDS). Fig. 3 shows the one on SI-3 sample with two unique points identified. The resulting spectra reveal that all the spots represent the three elements of In, O, and Sn detected in the inspection field, with In being the most abundant. Note that the content of Sn element has great difference in results of the two inspection spots. Compared to

Fig. 2 SEM and TEM images of 1D  $\text{SnO}_2$ – $\text{In}_2\text{O}_3$  nano-heterostructures: (a) low and (b) high magnification Si-1 samples; (c) low and (d) high magnification Si-2 samples; (e) low and (f) high magnification Si-3 samples; (g) low and (h) high magnification  $\text{In}_2\text{O}_3$  nanofibers (i) different magnification tem images of Si-3 samples; (j) HRTEM images of Si-3 samples.

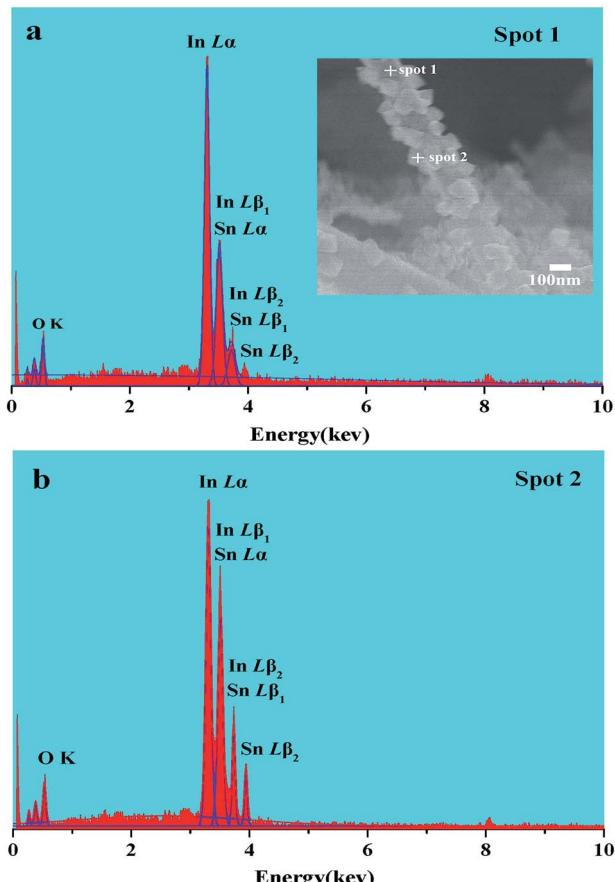


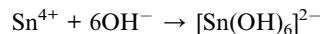
Fig. 3 (a, b) EDX spectra taken from spot 1 and 2 in the inset.

the measuring spots, it is found that the percentage of Sn element on surface nanocylinders (spot 3) is slightly higher than that on other field (spot 1 and spot 2). This indicates that secondary component grown on the nanofibers consists of  $\text{SnO}_2$  crystal grains.

In order to study the crystal structure of samples, overall phase purity and crystal structure of all the samples ( $\text{SnO}_2$ ,

$\text{In}_2\text{O}_3$ , SI-1, SI-2, and SI-3) have been analyzed by XRD, as shown in Fig. 4. All the diffraction peaks in the pattern of pure  $\text{In}_2\text{O}_3$  nanofibers can be indexed to cubic structure (JCPDS no. 71-2194). For 1D nano-heterostructure, XRD pattern shows that there are some additional diffraction peaks other than the  $\text{In}_2\text{O}_3$  peaks. These peaks at  $2\theta = 26.7^\circ, 33.9^\circ, 37.6^\circ, 51.7^\circ$  match with  $\text{SnO}_2$  phase with rutile structure, which is in agreement with the standard card (JCPDS no. 084576). With an increase in the  $\text{SnO}_2$  grain size, the intensity of two characteristic peaks assigned at  $\text{SnO}_2$  increase continuously. Combining SEM and HRTEM results, it is demonstrated that nanostructures grown on the surface of  $\text{In}_2\text{O}_3$  nanofibers possess the rutile structure of  $\text{SnO}_2$  phase. Several heterogeneous morphologies have been acquired by changing the conditions of synthesis. This indicates that the 1D  $\text{SnO}_2$ – $\text{In}_2\text{O}_3$  nano-heterostructures with a series of morphological evolutions have been successfully prepared *via* electrospinning, followed by the hydrothermal treatment.

The proposed growth mechanism for the formation of 1D  $\text{SnO}_2$ – $\text{In}_2\text{O}_3$  nano-heterostructures can be explained in terms of the chemical reaction and crystal growth, as shown in Fig. 5. In our experiment, it is observed that the shape of the as-prepared samples changes by increasing the mole ratio of  $\text{Sn}^{4+}$  and  $\text{In}^{3+}$  ions. According to previous reports,<sup>22,23</sup> the chemical reaction for the growth of secondary  $\text{SnO}_2$  nanostructures is proposed as follows:<sup>24</sup>



Tetravalent tin  $\text{Sn}^{4+}$  ions easily produce  $\text{Sn}(\text{OH})_6^{2-}$  anions in excess of alkaline solution. As the reaction temperature rises, the  $\text{Sn}(\text{OH})_6^{2-}$  ions decompose into  $\text{SnO}_2$ . From the crystallization point of view, the growth of an alkaline solution of  $\text{SnO}_2$  nanostructures is expected to be a nucleation-growth process. Electrospun  $\text{In}_2\text{O}_3$  nanofibers with a rough surface provide numerous nucleation sites for the growth of  $\text{SnO}_2$  nanostructures. Moreover, the interface regions of nanofibers are also related to a large number of unsaturated dangling bonds, which are beneficial to promote the heterogeneous nucleation of  $\text{SnO}_2$  nanostructure. These  $\text{SnO}_2$  nuclei with high surface energy are still in an unstable thermodynamic state. In this case, the nucleus continues to grow as the  $\text{Sn}(\text{OH})_6^{2-}$  ions resolve it in solution and then generate a different morphology of 1D nano-heterostructures.

Recently, some groups used nanofibers as templates available to control the nucleation.<sup>25,26</sup> The  $\text{Sn}^{4+}$  concentration in hydrothermal solution affects the growth of the  $\text{SnO}_2$  size directly, and it is clear that the morphology of secondary  $\text{SnO}_2$  undergoes a dramatic evolution from nanoparticles to nanocylinders. A consequence of  $\text{SnO}_2$  nanograins' growth can be attributed to a synergistic effect of the Ostwald-ripening process.<sup>27</sup> In the process, numerous small  $\text{SnO}_2$  crystals formed initially slowly disappear, except for a few that grow larger, at the expense of the small crystals. The smaller crystals act as fuel for the growth of bigger crystals. In the early stage of condensation, the  $\text{SnO}_2$  nucleates at a different position along

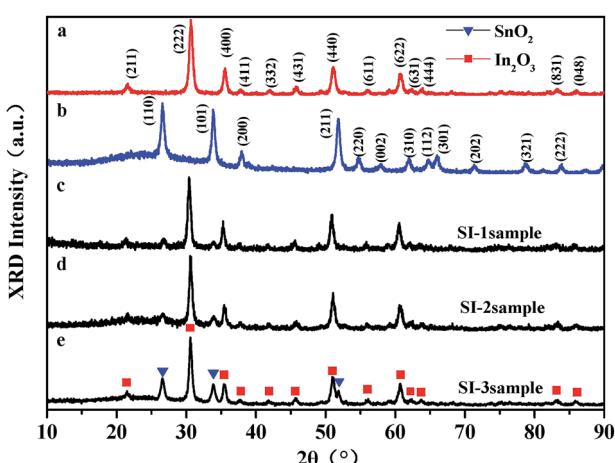


Fig. 4 XRD patterns of (a)  $\text{In}_2\text{O}_3$  nanofibers, (b)  $\text{SnO}_2$  nanoparticles, (c) SI-1 samples, (d) SI-2 samples and (e) SI-3 samples.

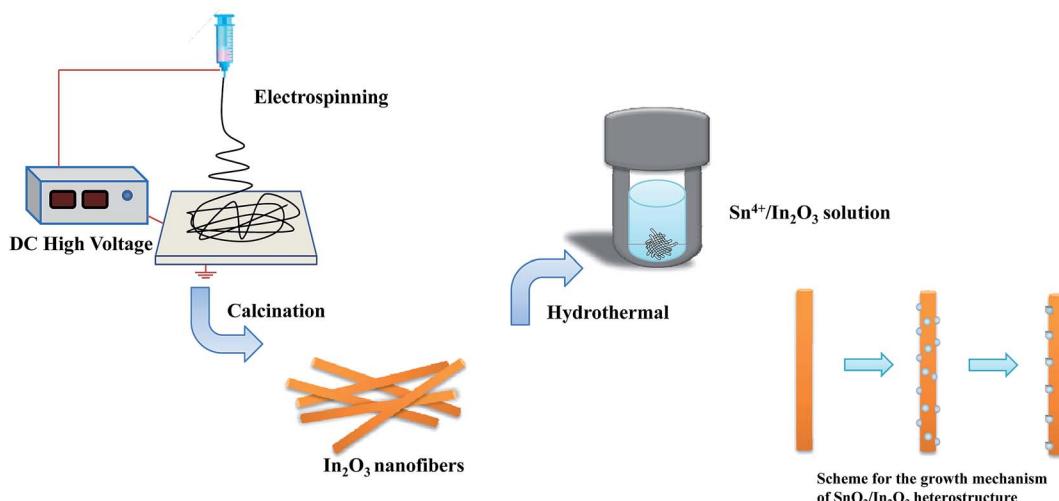


Fig. 5 The proposed formation mechanism of 1D  $\text{SnO}_2$ – $\text{In}_2\text{O}_3$  nano-heterostructures.

the indium oxide template or backbone. After a long-time in  $\text{SnO}_2$  condensation,  $\text{SnO}_2$  shows a tendency to condense on the surface of larger particles.  $\text{In}_2\text{O}_3$  nanofibers act as a reservoir for the accommodation of  $\text{SnO}_2$  nanoparticles and offer a template during the hydrothermal synthesis.

#### Gas-sensing property for alcohol

It is well-known that there are several important factors that can determine the gas-sensing performance of 1D  $\text{SnO}_2$ – $\text{In}_2\text{O}_3$  nano-heterostructures for detecting a given gas, which are as follows: optimal operating temperature, sensitivity, response and recovery time *etc.* Fig. 6a shows the responses of the as-prepared samples,  $\text{In}_2\text{O}_3$  nanofibers and  $\text{SnO}_2$  powders to 100 ppm ethanol at operating temperatures from 175 to 300 °C. It is found that the responses of the as-prepared samples have a similar trend that first increases and then gradually decreases with increase of operating temperature. The optimal operating temperature for most samples was 250 °C, and  $\text{SnO}_2$  attained its maximum value at 300 °C. As a comparison, the sensor of  $\text{SnO}_2$  nanocylinders grown on  $\text{In}_2\text{O}_3$  nanofibers (SI-3 sample) exhibited the highest response value at optimal operating temperature. The result indicates that the response reaches its maximum value of 15.4 at 250 °C, which is 1.5 times higher than response value of  $\text{In}_2\text{O}_3$  nanofibers. Fig. 6b displays the responses of the as-prepared samples to different ethanol concentrations at optimal operating temperature (250 °C). The gas sensitivity of obtained samples increases sharply in the range from 10 to 5000 ppm and then gradually reaches a saturated value at the ethanol concentration of 10 000 ppm. Pure  $\text{SnO}_2$  shows the best gas sensing activity, up to 10 000 ppm ethanol at 250 °C. This indicates that deposited  $\text{SnO}_2$  is very useful for the improvement of gas response rate on 1D heterostructure surface.

In addition, rapid response/recovery times are also important parameters to measure the gas-sensing performance of the material. Fig. 7 shows the response transient of the sensor based on the as-prepared samples,  $\text{SnO}_2$  powders and  $\text{In}_2\text{O}_3$

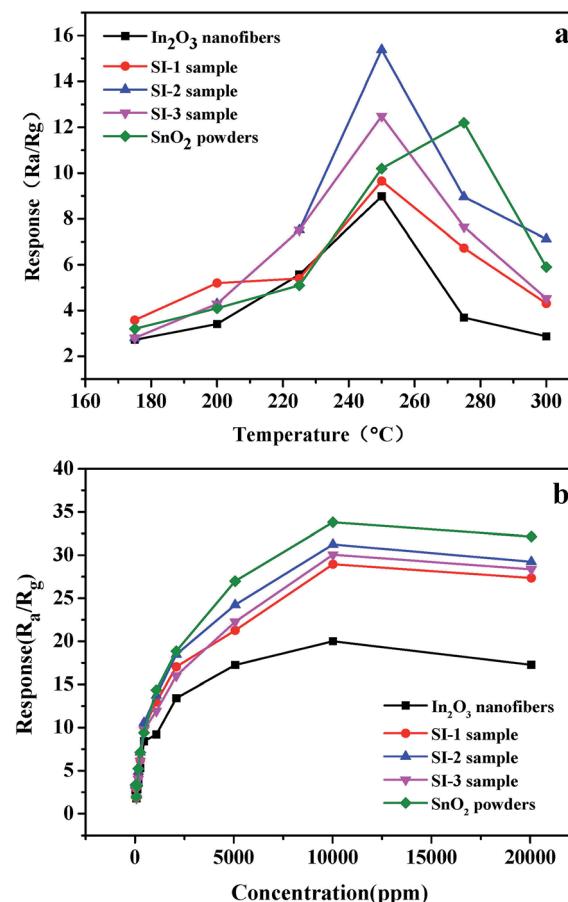


Fig. 6 (a) Gas response of the  $\text{In}_2\text{O}_3$  nanofibers,  $\text{SnO}_2$  powders, Si-1 sample, Si-2 sample and Si-3 sample based sensor toward 100 ppm ethanol at series of operating temperatures ranging from 175 to 300 °C, respectively; (b) gas response of the  $\text{In}_2\text{O}_3$  nanofibers,  $\text{SnO}_2$  powders, Si-1 sample, Si-2 sample and Si-3 sample based sensor toward 250 °C at different ethanol concentration.



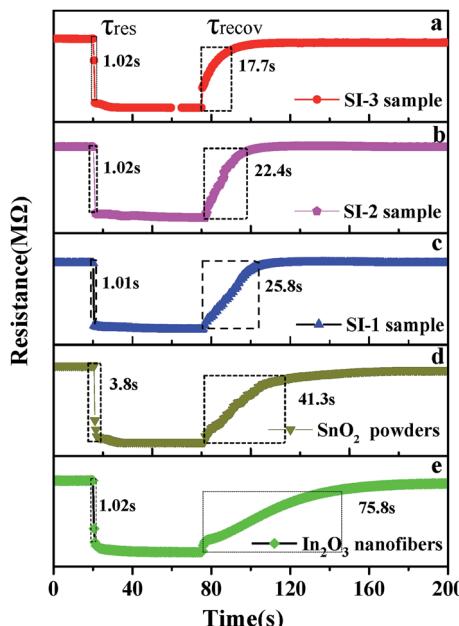


Fig. 7 (a–e) Response and recovery time of the Si-3 sample, Si-2 sample, Si-1 sample,  $\text{SnO}_2$  powders and  $\text{In}_2\text{O}_3$  nanofibers to 100 ppm ethanol at 250 °C.

nanofibers to 100 ppm ethanol at 250 °C. It can be observed that response curve starts a precipitous decline and reaches a stable state when the five sensors are exposed to ethanol. The response times of three sensors are 1.02 s (SI-3), 1.01 s (SI-2), 1.02 s (SI-1), 3.8 s ( $\text{SnO}_2$ ) and 1.02 s ( $\text{In}_2\text{O}_3$ ), respectively. After exposure to air, the recovery times are 17.7 s, 22.4 s, 25.8 s, 41.3 s and 75.8 s for SI-3, SI-2, SI-1,  $\text{SnO}_2$  and  $\text{In}_2\text{O}_3$ , respectively. As can be observed, response time does not vary greatly when several sensors are exposed to 100 ppm ethanol. In contrast, the recovery times are significantly different for three sensors. Some researchers<sup>28</sup> reported that the response and recovery times of as-prepared  $\text{In}_2\text{O}_3$ – $\text{SnO}_2$  composites to 100 ppm ethanol at 250 °C are about 15 s and 60 s, respectively. As compared with previous reports,  $\text{SnO}_2$  deposited  $\text{In}_2\text{O}_3$  nanofibers exhibit better gas sensitivity. The rapid response rates, particularly recovery time, are remarkable. It is noteworthy that the sensor based on SI-3 sample displays quicker recovery capability toward ethanol gas.

### Gas-sensing mechanism of 1D $\text{SnO}_2$ – $\text{In}_2\text{O}_3$ nano-heterostructures

According to the above results, the sensor based on 1D  $\text{SnO}_2$ – $\text{In}_2\text{O}_3$  nano-heterostructures show outstanding ethanol gas sensitivity and response transient compared with pure 1D  $\text{In}_2\text{O}_3$  nanostructures. Fig. 8 shows nitrogen adsorption–desorption isothermal curves of pure  $\text{In}_2\text{O}_3$  and SI-3 samples. BET analysis reveals that the surface area of SI-3 samples is  $47.3 \text{ m}^2 \text{ g}^{-1}$ , which is much larger than that of pure  $\text{In}_2\text{O}_3$  ( $21.4 \text{ m}^2 \text{ g}^{-1}$ ) nanofibers. This illustrates that the surface area of nanofibers increases significantly after deposition of  $\text{SnO}_2$ . The characteristics of gas sensors depend on the change in the surface

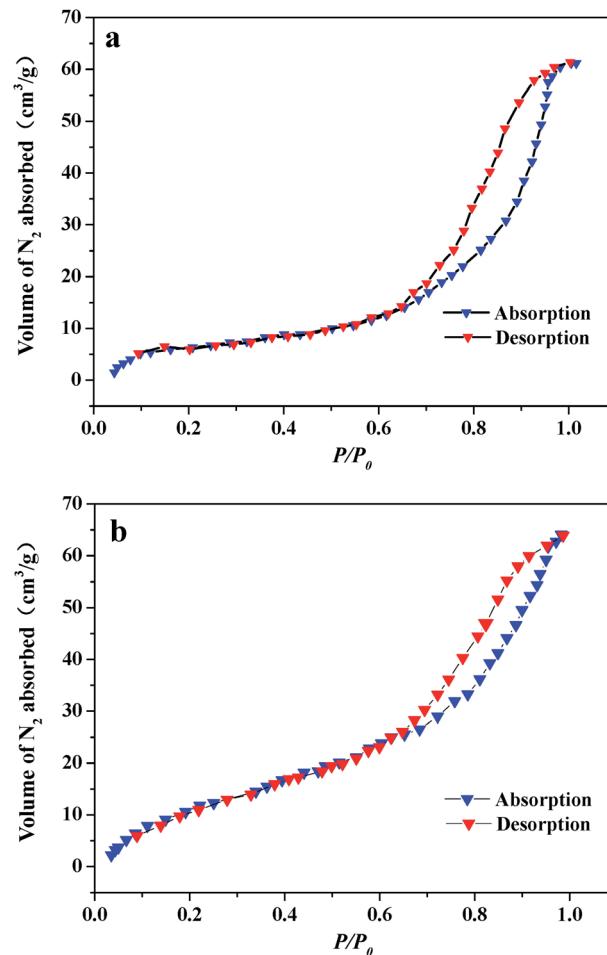


Fig. 8 Nitrogen adsorption–desorption isothermal curves of (a) pure  $\text{In}_2\text{O}_3$  nanofibers, nitrogen adsorption–desorption isothermal curves of (b) SI-3 sample.

resistance in the presence of gas, and adsorption/desorption behavior between gas molecules and surfaces have a direct impact on surface resistance of heterostructures.  $\text{SnO}_2$ -deposited  $\text{In}_2\text{O}_3$  nanofibers have a high specific surface area, which not only provides a large adsorption region for the oxygen species and target gas but also promotes the interaction between the oxide surface and the gas molecules.<sup>29</sup> Secondary nanostructures on the surface of nanofibers,  $\text{SnO}_2$  nanocylinders, are used to modulate electric transport of  $\text{In}_2\text{O}_3$  nanofibers in order to improve the gas-sensing property of individual semiconductor sensors.<sup>30</sup> Gas-sensing mechanism of 1D  $\text{SnO}_2$ – $\text{In}_2\text{O}_3$  nano-heterostructures is shown in Fig. 9. After being exposed to air, oxygen will be adsorbed on the surface of the  $\text{SnO}_2$  nanostructures and then trap electrons from the conduction band to form ionized oxygen species ( $\text{O}_{\text{ads}}^-$ ,  $\text{O}_2^-$ , and  $\text{O}_2^-$ ), resulting in increase of barrier height at the interface between  $\text{SnO}_2$  nanostructure and  $\text{In}_2\text{O}_3$  nanofibers. As a consequence, this tends to increase the resistance of 1D heterostructures. When the obtained 1D heterostructures are exposed to target gas, ethanol molecules react with the adsorbed oxygen species, and the trapped electrons are released to the conduction band of  $\text{SnO}_2$  and  $\text{In}_2\text{O}_3$ , leading to remarkable changes in

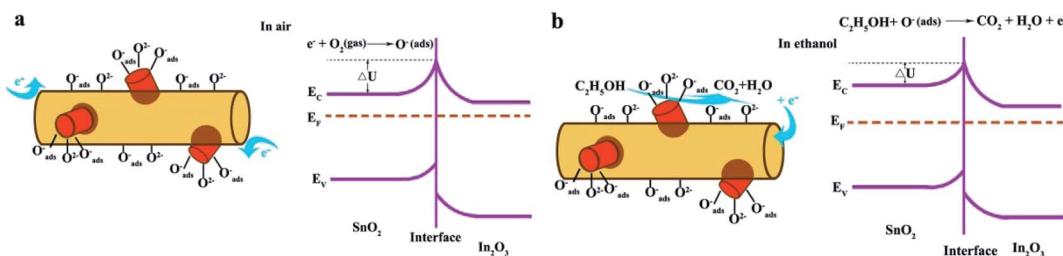


Fig. 9 (a, b) Schematic diagrams of gas-sensing mechanism of 1D  $\text{SnO}_2$ – $\text{In}_2\text{O}_3$  nano-heterostructures in air and ethanol.

electric conductivity because of lower barrier height at the interfaces.

As we mentioned in the results, it is found that recovery rate is observed to increase with increasing of surface size of  $\text{SnO}_2$ . In order to understand gas reaction of special surface nanostructure, it is necessary to consider some surface chemistry concepts. In general, the gas sensing principle depends on the adsorption/desorption behavior between gas molecules and surfaces. Under similar measuring condition (same gas concentration and temperature), adsorption and desorption of gas molecules depends not only on the intrinsic property of the adsorbed gas, but also on the surface structure of sensors. From chemisorption kinetics, the adsorption rate of gas molecules is proportional to the gas concentration and to the number of unoccupied adsorption sites. The rate constant of the desorption process ( $R_{\text{des}}$ ) is given *via* the Arrhenius equation as follows:

$$R_{\text{des}} = A_{\text{des}} \exp\left(-\frac{E_{\text{D}}}{RT}\right)$$

where  $A_{\text{des}}$  is the pre-exponential factor,  $E_{\text{D}}$  is the activation energy for desorption (which may depend upon the surface coverage and the frequency of the gas molecule-surface bonding),  $T$  is the temperature and  $R$  is the universal gas constant.<sup>31,32</sup> In some cases, adsorbed gas molecules are chemically bonded to the surface, providing a strong adhesion and limiting desorption. If this is the case, the surface bond of adsorbed molecules can be rapidly cleaved by enhancing activation energy. In 1D nano-heterostructure-based gas sensors, the surface area is enlarged because of the growth of secondary  $\text{SnO}_2$  nanostructures, resulting in increase of the number of adsorption sites. When ethanol gas is injected, 1D  $\text{SnO}_2$ – $\text{In}_2\text{O}_3$  nano-heterostructures enable the gas-sensing layer to possess a larger internal space compared with regular nanofibers. Once ethanol gas is removed, the residual ethanol molecules require activation energy supplied either thermally or by photoexcitation to achieve desorption process, which often requires a chemical reaction to cleave the chemical bonds. One way to accomplish this is to apply a number of electrons to the surface, resulting in either reduction or oxidation of the adsorbed molecule. From the foregoing results, as the size of these particles to fiber surface increases, the desorption rate increases sharply. Combining the deposition and sensing characterization, one concept can be invoked to explain the improvement of nanofiber's desorption rate upon  $\text{SnO}_2$  deposition.  $\text{SnO}_2$

nanoparticles are regarded as a catalyst, which activates dissociation of molecular oxygen. The catalytic process increases both quantity of atomic oxygen that can repopulate vacancies on 1D nano-heterostructures surface and rate at which this repopulation occurs, resulting in a cloud of electron withdrawal from the  $\text{In}_2\text{O}_3$  to surface. This is called the spillover effect in catalysis.<sup>33,34</sup> As a result, surface-adsorbed oxygen and residual alcohol react rapidly under catalysis of active  $\text{SnO}_2$  particles, leading to observed improvement in gas recovery effect. In addition, high surface area is helpful for ethanol diffusion and its reaction on the surface. However, the situation for 1D nano-heterostructures is much more complex than the simple 1D nanostructures and further research is needed to be done to explain the desorption reaction mechanisms. In a word,  $\text{SnO}_2$ -deposited  $\text{In}_2\text{O}_3$  nanofibers show a significant improvement in gas-sensing activity compared to single component  $\text{In}_2\text{O}_3$  nanofibers. In a real application, fast response and recovery rate may be able to deduce whether ethanol leak has occurred in short succession.

## Conclusion

1D  $\text{SnO}_2$ – $\text{In}_2\text{O}_3$  nano-heterostructures with a series of morphological evolutions have been successfully synthesized *via* electrospinning, followed by the hydrothermal treatment. Through variations in the mole ratio of  $\text{Sn}^{4+}$  and  $\text{In}^{3+}$  ions in hydrothermal condition, several 1D  $\text{SnO}_2$ – $\text{In}_2\text{O}_3$  heterogeneous morphologies have been realized. With an increase in the mole ratio of Sn/In, surface  $\text{SnO}_2$  morphology changes from nanoparticles to nanograins and further to nanocylinders, and the size increases from 30 nm to about 80 nm. The underlying mechanisms of morphology control for 1D nano-heterostructures is expected to experience a nucleation-growth process.  $\text{In}_2\text{O}_3$  nanofibers as templates provide numerous nucleation sites for the growth of  $\text{SnO}_2$  nanostructures. Sensors based on 1D  $\text{SnO}_2$ – $\text{In}_2\text{O}_3$  nano-heterostructures displayed numerous advantages in terms of greater reliability, high sensitivity to ethanol gas. The sensor of  $\text{SnO}_2$  nanocylinders grown on  $\text{In}_2\text{O}_3$  nanofibers (SI-3 sample) exhibits highest response value at 250 °C. The as-prepared SI-3 sample displays quicker recovery capability towards ethanol gas, which exceeds those reported in literature. The improvement of desorption rate is ascribed to the effect of spillover of atomic oxygen formed catalytically on the  $\text{SnO}_2$  particles. Due to catalytic activity of the deposited  $\text{SnO}_2$ , surface-adsorbed oxygen and residual alcohol

undergo a rapid oxidation reaction, resulting in the observed reduction in the gas recovery time.

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