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# Highly efficient rapid ethanol sensing based on Co-doped $In_2O_3$ nanowires

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ABSTRACT

Pristine and Co-doped $In_2O_3$ nanowires were synthesized via electrospinning with subsequent calcination. Scanning electron microscopy, X-ray diffraction, and energy-dispersive X-ray spectroscopy were used to characterize nanowire morphology and structure. Ethanol sensing performance analyzed in the range of temperatures and concentrations showed that Co-doped $In_2O_3$ nanowires exhibited significantly enhanced sensitivity and rate of performance with the response and recovery times of 2 s and 3 s, respectively. Combined with excellent selectivity and linearity, these properties make the fabricated nanowires a good candidate for practical ethanol sensing. Further performance improvements are possible with utilization of nanofiber continuity intrinsic of the used top-down nanowire nanomanufacturing process.

## 1. Introduction

The past few decades have seen rapid progress in development of chemical sensors driven by the needs of industrial process monitoring, medical and environmental diagnostics, public safety, and national security [1–4]. Sensors based on metal-oxide semiconductors attracted special attention due to their good reproducibility, low cost, high sensitivity, and ease of use [5–7]. Among these sensors, one-dimensional (1D) metal-oxide nanostructures often possessed improved sensitivity and faster response-recovery time, based on their large surface area and ease of absorption of gas molecules on the surface [8–19].

Indium oxide ($In_2O_3$), as an n-type wide-bandgap semiconductor, attracted considerable attention for its high electric conductance, transparency to visible light, and strong interaction between the poisonous gas molecules and $In_2O_3$ surface [20–22]. Recently, doping of $In_2O_3$ nanostructures with metals or metal oxides was used as an effective route for improving its gas-sensing performance. Several efficient gas sensors based on metal (Ag [23], Pt [24], Pd [25]) and metal oxide (CdO [26], rare earth oxide [27])-doped $In_2O_3$ nanostructures were demonstrated. Transition metal cobalt-doped indium oxide was also produced by spark plasma sintering in the porous nanosized-grain film form and shown to have improved thermoelectric properties [28]. However, no investigation of the sensing performance of Co-doped $In_2O_3$ nanowires is known to the authors.

In this article, we demonstrate a simple and effective method of fabricating Co-doped $In_2O_3$ nanowires via electrospinning and subsequent calcination. Highly efficient sensing performance against ethanol was observed, that makes the fabricated nanomaterial a good candidate sensing material for practical ethanol sensors.

## 2. Materials and methods

### 2.1. Chemical reagents

Ethanol (>95%), N,N-dimethyl formamide (>95%), $In(NO_3)_3{\cdot}4.5H_2O$, $Co(NO_3)2{\cdot}6H_2O$, and poly (vinyl pyrrolidone) (PVP, $M_w = 1{,}300{,}000$) were purchased from Aldrich. All chemical reagents were used as received without any further purification.

### 2.2. Preparation of Co-doped $In_2O_3$ nanowires

In a typical procedure, 0.40 g of $In(NO_3)_3{\cdot}4.5H_2O$ and suitable amount of $Co(NO_3)_2{\cdot}6H_2O$ were dissolved in 2.2 g of DMF and 6.6 g of ethanol under vigorous stirring for 1 h. Subsequently, 0.8 g of PVP was added into the above solution under vigorous stirring for 6 h. The atom molar ratio of Co:In in the final product was 0.5:100 (0.5 mol%). The mixture was loaded into a glass syringe and high voltage of 15 kV was provided between the cathode (flat aluminum foil) and anode (syringe tip) with the distance of 20 cm. The conversion of precursor into polycrystalline nanowire and removal

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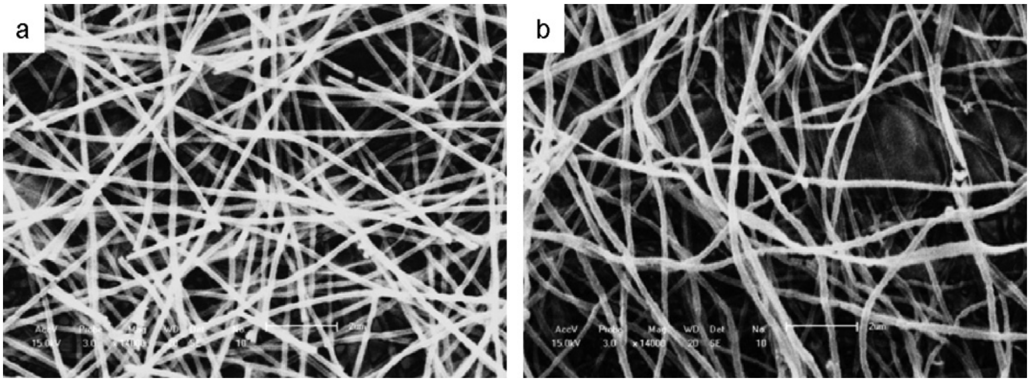

**Fig. 1.** SEM images of pristine (a) and Co-doped (b) $In_2O_3$ nanowires. The molar ratio of b is 0.5 mol.

of PVP were achieved by calcining at 700 °C for 5 h in air. All the measurements were carried out on the as-calcined nanowires.

### 2.3. Fabrication and evaluation of gas sensor based on ceramic nanowires

The as-prepared nanofibers were mixed with deionized water in a weight ratio of 100:25 to form a paste. The paste was coated onto a ceramic tube on which a pair of gold electrodes was previously printed, and then a Ni-Cr heating wire was inserted in the tube to form a side-heated gas sensor. Gas sensing properties were measured by a CGS-1 intelligent gas sensing analysis system (Beijing Elite Tech Co. Ltd., China). This multichannel system consisting of heating system, gas distribution system, measurement and data acquisition system, and measurement control software is ideally suited for comparative analysis of sensor performance in the same environmental conditions. The sensors were pre-heated to different operating temperatures for about 15 min. When the resistances of all sensors were stable, saturated target gas was injected into the test chamber (20 L in volume) by a microinjector through a rubber plug. The saturated target gas was mixed with air (relative humidity was about 25%) by two fans in the analysis system. After the sensor resistances reached a new constant value, the test chamber was opened to recover the sensors in air. All the measurements were performed in a laboratory fume hood. The sensor resistance and response values were acquired by the analysis system automatically.

### 2.4. Characterization

Nanowires were characterized by X-ray diffraction (XRD, scintag XDS 2000 diffractometer with a Cu Kα), scanning electron microscopy (SEM, SHIMADZU SSX-550, Japan), and energy dispersive X-ray spectrometer (EDX) attached to the SEM.

## 3. Results and discussion

### 3.1. Nanowire characterization

Fig. 1a shows the typical morphology of the as-synthesized pristine $In_2O_3$ nanowires after annealing at 700° C for 5 h in air, indicating that a large quantity of $In_2O_3$ nanowires with the relatively uniform average diameter of 150 nm can be produced by the proposed method. Fig. 1b presents SEM image of 0.5 mol% Co-doped $In_2O_3$ nanowires. Doped $In_2O_3$ nanowires exhibited similar morphology and diameters, indicating that the addition of Co did not have significant effect on nanofiber electrospinning.

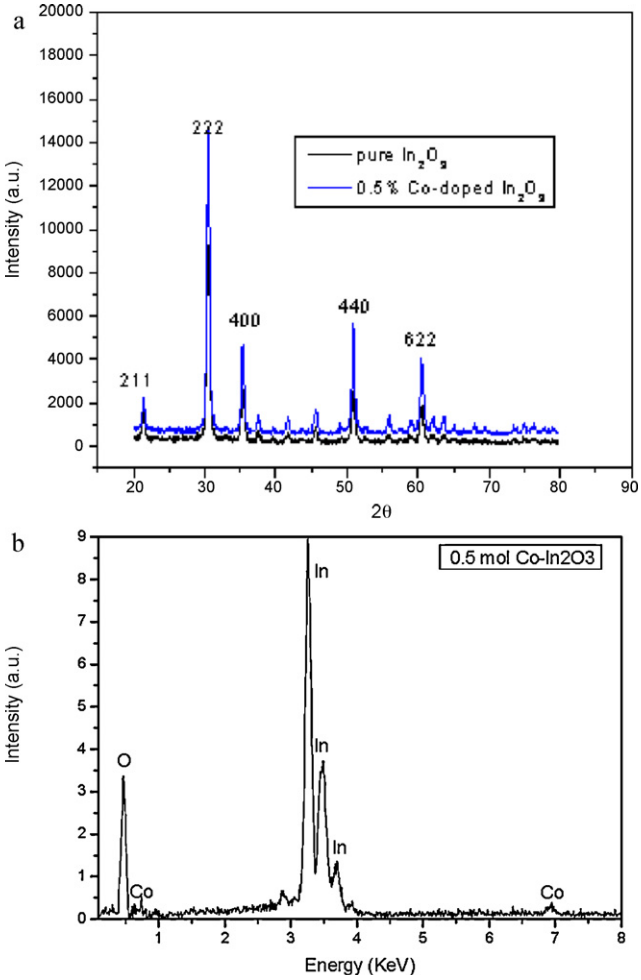

**Fig. 2.** (a) XRD patterns of pristine $In_2O_3$ and 0.5 mol% Co-doped $In_2O_3$ nanowires and (b) EDX spectra of 0.5 mol% Co-doped $In_2O_3$ nanofibers.

Fig. 2a displays X-ray diffraction (XRD) patterns of the pristine and Co-doped $In_2O_3$ nanowires. All of the peaks can be readily indexed to the cubic phase $In_2O_3$ (JCPDS card 06-0416). No peaks of cobalt oxide or cobalt can be observed, indicating that Co element were effectively inserted into the $In_2O_3$ crystal lattice and formed stable solid solution. To further confirm the presence of Co in the nanowires, EDX spectra were recorded and analyzed (Fig. 2b). From the EDX spectra, Co peak can be detected, confirming the presence of Co in the nanowires sample.

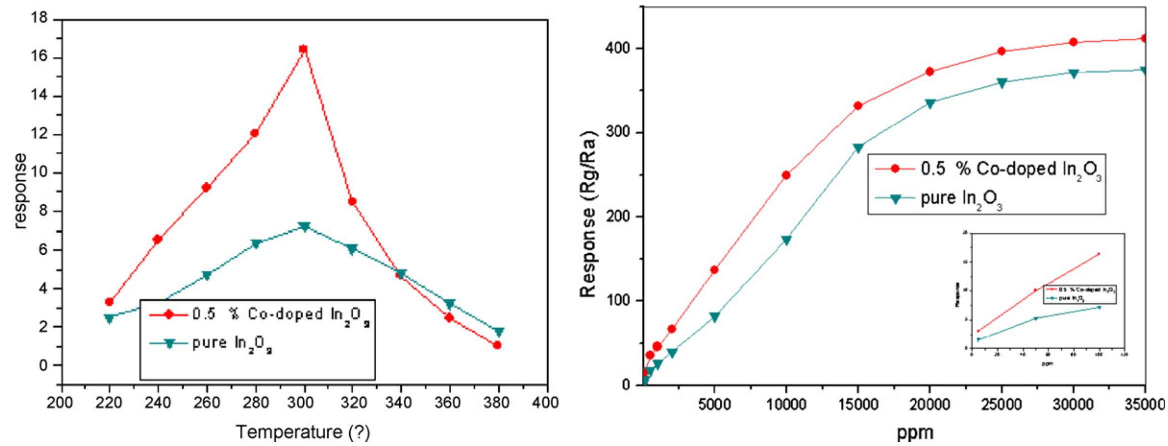

**Fig. 3.** Sensitivity of the pristine and Co-doped $In_2O_3$ nanowires to 100 ppm ethanol vapor measured at different operating temperatures (a) and response of the pristine and Co-doped $In_2O_3$ nanowires to different concentrations of ethanol. The inset in (b) shows the expanded sensitivity curves at small ethanol concentrations: 5–100 ppm.

### *3.2. Evaluation of gas-sensing performance*

To determine the optimum operating temperature, sensitivities of pristine and Co-doped $In_2O_3$ nanowires to 100 ppm ethanol vapor were measured at different operating temperatures as shown in Fig. 3a. From the curves, the ethanol vapor response of both sensors showed the maximum at 300° C. This temperature was identified as the optimum operating temperatures for the detection of ethanol vapor. Further analysis of Fig. 3a shows that Co-doped $In_2O_3$ nanowires exhibited significantly higher sensitivity than pristine nanowires with the maximum sensitivity of 16.5–100 ppm ethanol vapor. Fig. 3b shows the relationship between the sensor response and ethanol concentration at 300° C. It can be seen that the response increases nearly linearly with concentration until about 25,000 ppm. The sensor reaches a saturation state above this concentration. Additionally, the Co-doped sensor shows improved linearity with the ethanol concentration ranging from 5 ppm to 100 ppm (the inset in Fig. 3b).

The selectivity of the gas sensor based on Co-doped $In_2O_3$ nanowires was also tested by measuring the response of the sensor to some typical combustible gases such as dimethylbenzene, benzene, CO, $CH_4$, butane, and $H_2$ (the concentration of all these gases was 100 ppm). The results are presented in Fig. 4. As can be seen from this figure, the Co-doped indium oxide sensor exhibits the largest response to ethanol. The observed high sensitivity and selectivity of the Co-doped nanowires make the developed material suitable candidate for monitoring low concentrations of ethanol.

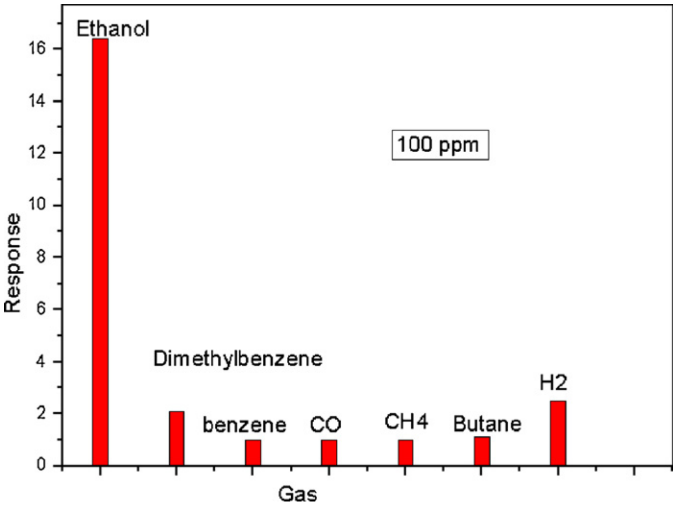

**Fig. 4.** The cross sensitivities of the sensor to ethanol, dimethylbenzene, benzene, carbon monoxide, methane, butane, and hydrogen.

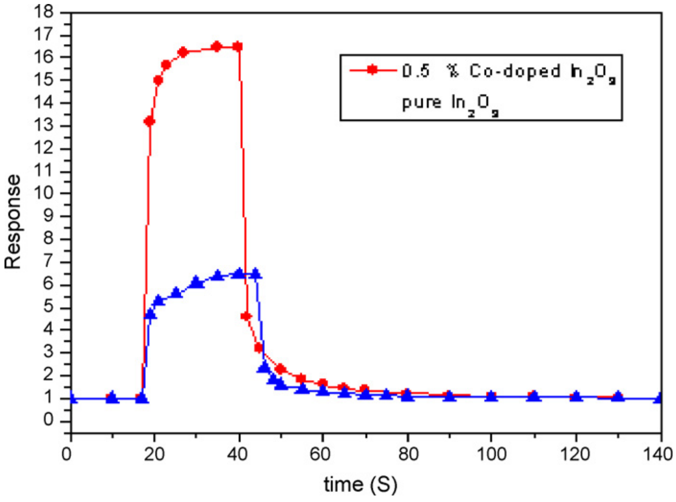

**Fig. 5.** Response and recovery behavior of the pristine and Co-doped $In_2O_3$ nanofibers against ethanol at 300 °C.

For many gas sensing applications, rapid response and recovery is of great importance. Fig. 5 shows the response and recovery behavior of the pristine and Co-doped sensors to 100 ppm ethanol at 300° C. The sensor resistivity increased rapidly when the target gas was injected it the testing chamber (2 s response time defined as the time required to reach 90% of the final resistance [29]). The sensor recovery to the initial state when subjected to air was also rapid (3 s measured recovery time).

The results above show that Co-doped indium oxide nanofibers possess not only fast response and recovery characteristics but also have higher sensitivity and linearity. The rapid response and recovery behavior can be explained by the 1D nanostructure of our sample that facilitates fast mass transfer of the target molecules to and from the interaction region and improves the transport rate of the charge carriers induced by molecular recognition along the 1D nanostructure [19]. The latter is improved via reduction of the number of interfaces and barriers that need to be traversed by the carriers in the 1D nanomaterials. The observed higher sensitivity may be attributed to the Co doping. Analysis of data in Fig. 2 indicates that the developed nanofabrication method results in Co ions being incorporated within the $In_2O_3$ crystal. Mismatch between smaller diameters of Co ions ($Co^{2+}$:0.72 Å; $Co^{3+}$:0.62 Å) and larger

In ion diameters ($In^{3+}$:81 Å) can lead to larger concentration of crystal defects formed during the growth of doped $In_2O_3$ crystals. These can in turn generate more oxygen vacancies on the surface of the doped $In_2O_3$ nanofibers, resulting in higher sensitivity [30]. Note that although the measurements in this paper were performed on the discontinuous nanowires scrapped off the substrate used to collect and calcine nanofibers, the electrospinning nanomanufacturing method normally produces continuous ceramic nanofibers [31]. These continuous nanofibers can be incorporated into sensors in their intact form, e.g., by depositing electrodes directly onto calcined nanofiber deposits. This, along with the possibility to align and span long nanofibers between the electrodes by using known electromechanical alignment techniques [31] is likely to result in further improvement in sensor response rate and sensitivity by eliminating the need for the charge carriers to traverse interfaces between the wires.

## 4. Conclusions

Pristine and Co-doped $In_2O_3$ nanofibers were synthesized via electrospinning and calcination and their ethanol-sensing performance was analyzed. The results showed that the gas sensor based on the Co-doped $In_2O_3$ nanowires not only exhibited rapid response and recovery rates but also demonstrated higher sensitivity, good linearity and selectivity against ethanol. These properties make the developed nanomaterial a promising candidate for practical ethanol sensing applications. Unique versatility of the top-down electrospinning nanomanufacturing process and feasibility of nanomanufacturing a broad range of continuous ceramic nanofibers make this technique an excellent platform for the development of fast and sensitive chemiresistive gas sensors.

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## References

[1] S. Zampolli, I. Elmi, J. Stürmann, S. Nicoletti, L. Dori, G.C. Cardinali, Sens. Actuators B 105 (2005) 400–406.
[2] D.D. Lee, D.K. Lee, IEEE Sens. J. 1 (2001) 214–224.
[3] S. Ehrmann, J. Jungst, J. Goschnick, D. Everhard, Sens. Actuators B 65 (2000) 247–249.
[4] A.A. Tomchenko, G.P. Harmer, B.T. Marquis, Sens. Actuators B 108 (2005) 41–55.
[5] J. Janata, M. Josowicz, D.M. Devaney, Anal. Chem. 66 (1994) 207–228.
[6] Y. Shimizu, T. Hyodo, M. Egashira, Sens. Actuators B: Chem. 121 (2007) 219–230.
[7] D.S Dhawale, R.R. Salunkhe, U.M. Patil, K.V. Gurav, A.M. More, C.D. Lokhande, Sens. Actuators B: Chem. 134 (2008) 988–992.
[8] N.K. Reddy, Q. Ahsanulhaq, Y.B. Hahn, Appl. Phys. Lett. 93 (2008) 083124.
[9] N.K. Reddy, Q. Ahsanulhaq, J.H. Kim, Y.B. Hahn, Appl. Phys. Lett. 92 (2008) 043127.
[10] Q. Ahsanulhaq, A. Umar, Y.B. Hahn, Nanotechnology 18 (2007) 115603.
[11] Y. Li, C.H. Ye, L. Yang, C. Wang, C.R. Zheng, L.D. Zhang, Chem. Lett. 36 (2007) 442–443.
[12] Q. Ahsanulhaq, J.H. Kim, Y.B. Hahn, Nanotechnology 18 (2007) 485307.
[13] C.S.C. Navale, S.W. Gosavi, I.S. Mulla, Talanta 75 (2008) 1315–1319.
[14] A. Kolmakov, D.O. Klenov, Y. Lilach, S. Stemmer, M. Moskovits, Nano Lett. 5 (2005) 667–673.
[15] Y. Cui, Q. Wei, H. Park, C.M. Lieber, Science 293 (2001) 1289–1292.
[16] M. Law, H. Kind, B. Messer, F. Kim, P. Yang, Angew. Chem. Int. Ed. 41 (2002) 2405–2408.
[17] A. Kolmakov, Y. Zhang, G. Cheng, M. Moskovits, Adv. Mater. 15 (2003) 997–1000.
[18] Y. Wang, X. Jiang, Y. Xia, J. Am. Chem. Soc. 125 (2003) 16176–16177.
[19] Z. Li, H. Zhang, W. Zheng, W. Wang, H. Huang, C. Wang, A.G. MacDiarmid, Y. Wei, J. Am. Chem. Soc. 130 (2008) 5036–5037.
[20] J. Yang, C.K. Lin, Z.L. Wang, J. Lin, Inorg. Chem. 45 (2006) 8973–8979.
[21] A. Murali, A. Barve, V.J. Leppert, S.H. Risbud, I.M. Kennedy, H.W. Lee, Nano Lett. 1 (2001) 287–289.
[22] J. Liu, T. Luo, F. Meng, K. Qian, Y. Wan, J. Liu, J. Phys. Chem. C 114 (2010) 4887–4894.
[23] Y. Zhang, Z. Zheng, F. Yang, Ind. Eng. Chem. Res. 49 (2010) 3539–3543.
[24] G. Neri, A. Bonavita, G. Micali, G. Rizzo, S. Galvagno, M. Niederberger, N. Pinna, Chem. Commun. 48 (2005) 6032–6034.
[25] L. Liu, T. Zhang, S. Li, L. Wang, Y. Tian, Mater. Lett. 63 (2009) 1975–1977.
[26] T. Chen, Q.J. Zhou, Y.D. Wang, Sens. Actuators B 131 (2008) 301–305.
[27] X. Niu, H. Zhong, X. Wang, K. Jiang, Sens. Actuators B 115 (2006) 434–438.
[28] Y. Liu, Y.-H. Lin, J. Lan, W. Xu, B.-P. Zhang, C.-W. Nan, H. Zhu, J. Am. Ceram. Soc. 93 (2010) 2938–2941.
[29] C.-D. Kohl, in: R. Waser (Ed.), "Electronic Noses" in Nanoelectronics and Information Technology, Wiley-VCH, Berlin, 2005, pp. 835–864.
[30] E. Comini, Anal. Chim. Acta 568 (2006) 28–40.
[31] Y. Dzenis, Science 304 (2004) 1917–1919.

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