

Regulation of N-type In_2O_3 Content on the Conductivity Type of Co_3O_4 Based Acetone Sensor

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A double-jet electrospinning method was adopted to fabricate $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanofibers (NFs). The sensitivity of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ NFs and In_2O_3 NFs were compared and analyzed, and the morphology, structure, chemical composition, and gas-sensing properties of the samples were comprehensively characterized. The results show that the introduction of Co_3O_4 can improve the response of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ to acetone, to 29.52 ($\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$) and 12.34 (In_2O_3) to 200 ppm acetone at 2000°C, respectively. In addition, the doping of Co_3O_4 was found to reduce the optimum working temperature of pure In_2O_3 from 275°C to 200°C. The composite of Co_3O_4 and In_2O_3 not only enhances the sensing performance, but also leads to a conversion of p-n conductivity type. The phenomenon of the p-n transition is relevant to operating temperature and proportion of In_2O_3 and Co_3O_4 . While the enhanced acetone sensing properties of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ NFs may be attributed to the p-n heterojunction between n-type In_2O_3 and p-type Co_3O_4 crystalline grains, which promotes the electron migration. The synergistic effects between In_2O_3 and Co_3O_4 and the large specific surface area of NFs additionally contribute to the improvements of acetone sensing performance.

Keywords: *electrospinning; $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$; gas sensor; nanofibers; p-n transition*

1. Introduction

Acetone is a typical volatile organic compound (VOC) in that it is strongly volatile, highly hazardous, and extremely flammable [1]. Studies have shown that prolonged exposure to acetone can symptoms ranging from headaches and nausea to damage to the the respiratory and nervous systems [2]. With the continuous development of industrial production, the use of acetone is gradually increasing, which may lead to an increase in acetone pollution in the air [3]. Therefore, there is a need to develop a simple and highly sensitive gas sensor to detect acetone inside and outside industrial settings. Wang et al. [4] synthesized an acetone gas-sensitive element based on $\text{Ti}_3\text{C}_2/\text{a-Fe}_2\text{O}_3$ (TF) composites via microwave and etching methods. The response of the TF gas-sensitive element to 100 ppm acetone was up to 23.38. Cheng et al. [5] prepared a highly sensitive and fast-response acetone gas sensor based on p-n Co_3O_4 -ZnO heterojunction assembled by porous nanoparticles using

an environmentally friendly hydrothermal method. The response of the 1% Co_3O_4 -ZnO heterojunction sensor was up to 615.5 for 100 ppm acetone. Guo et al. [6] synthesized Co_3O_4 -x multilayer porous structures using MOF as a sacrificial template using a solvothermal method. The results showed that a typical Co_3O_4 -2 sensor responded to 50 ppm acetone at 140°C (27.6). This work was specifically applied to the development of respiratory monitoring materials for diabetic patients.

Gas sensors based on surface-controlled metal oxide semiconductors (MOSs) have been widely used for the detection of toxic and explosive gases because of their simple operation, low cost, and high sensitivity. So far, a variety of MOSs have been widely studied and used in various applications. These include SnO_2 [7], ZnO [8], In_2O_3 [9], and CuO [10]. Various methods, including chemical vapor deposition [11], solvothermal method [12], hydrothermal method [13], and electrospinning technology [14], were adopted to prepared MOSs. The types of gases detected have also been diverse, from common organic volatile gases such as ammonia [15], acetone [16] and ethanol [17], to

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human-exhaled gas markers [18]. Among diverse MOSs, In_2O_3 has attracted special attention due to its high sensitivity and good selectivity [19, 20].

As a representative n-type metal oxide (MO) with an indirect band gap of 2.8 eV, In_2O_3 has been widely used in gas-sensor applications [21]. Gas sensors based on In_2O_3 possesses superior sensitivity and selectivity to oxidizing gases. For example, Zhang et al. [22] reported a hierarchical branch-like In_2O_3 (B- In_2O_3) nanomaterials using a co-precipitation method. Gas sensing results showed that the sensors based on B- In_2O_3 showed good O_3 sensing performance at a relative low working temperature of 70°C with a low detection limit at the ppb-level. Zhang et al. [23] fabricated a high-performance room temperature NO_2 gas sensor based on In_2O_3 nanowires via electrospinning and sintering procedures. The response of the sensor toward 5 ppm NO_2 at 25°C in the dark could reach as high as 740, and its detection limit was as low as 10 ppb.

Chethana et al. [24] prepared heterostructure Fe_2O_3 - In_2O_3 nanoparticles as H_2 gas sensor by the thermal decomposition technique, and the sensitivity varied from 2% to 21% as the H_2 increased from 2 to 100 ppm. Zhao et al. [21] prepared a highly sensitive and selective ethanol sensor based on Ca-doped In_2O_3 nanotubes (Ca- In_2O_3 NTs). The 3% Ca- In_2O_3 sensor showed an especially high response (183.3, at 100 ppm) and excellent selectivity for ethanol at 240°C . For the above listed gas sensors based on In_2O_3 and its composites, we were impressed by the high responses of pure In_2O_3 at relatively high temperatures. Through modification, their composites could exhibit good gas-sensing performance at low or room temperature, though in these conditions, the response was relatively low and response/recovery time was long.

With the aim of enhancing the gas sensing properties of pure In_2O_3 , in this work, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ NFs using double-jet electrospinning as low operating temperature gas sensors were prepared. The gas sensing test showed that compared with In_2O_3 , the optimal operating temperature of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ NFs was reduced from 275°C to 200°C , and the response of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ to 200

ppm acetone at 200°C was 29.52, 2.4 times higher than that of intrinsic In_2O_3 . The synergistic effect allowed the sensing performance of the heterojunction to exceed that of pure In_2O_3 and Co_3O_4 . We found that the modulation of the conductivity type of Co_3O_4 -based acetone sensors can be achieved by controlling the N-type In_2O_3 content. The dual-jet electrostatic spinning method is more controllable, reproducible, and stable than other processes for preparing heterogeneous structures.

2. Experimental details

2.1. Materials

Indium nitrate hydrate ($\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$), Cobalt nitrate hydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), anhydrous ethanol, 2N-dimethylformamide (DMF) and polyvinylpyrrolidone (PVP, Mw = 1,300,000) were all used as purchased, without further purification.

2.2. Synthesis of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ NFs

Typically, the $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ NFs were synthesized via electrospinning and subsequent sintering. Firstly, 900 mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved into 6 ml ethanol and 7 ml DMF, then 900 mg PVP was added into the above solution, with magnetic stirring for 10 h to fully dissolve the PVP. Electrospinning precursor solutions of In_2O_3 NFs were obtained by the same method. Then, the electrospinning precursor solution of In_2O_3 NFs and Co_3O_4 NFs was put into two identical 10 ml syringes. The molar ratio of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to $\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ was 1:1. The ratio of In to Co could be controlled by setting different propulsion speed. The spinning voltage was set to 20 kV and thus the platform moved back and forth at a speed of 20 cm/min. The prepared PVP/ $\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}/\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was torn off from the aluminum plate collector and placed in a crucible, sintering in a muffle furnace with a heating rate of $2^\circ\text{C}/\text{min}$. The calcination process was divided into two stages: the first stage was maintained at 300°C for 2 h to ensure the volatilization of PVP, and the second stage was maintained at 500°C for 2 h to crystallize and form oxide composites. In order to explore the ef-

fects of different content ratios of cobalt oxide on the structure, morphology, and gas sensing properties of the composites, four kinds of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ NFs with different molar ratios – (1) In: Co=1:3, (2) In: Co=1:1, (3) In: Co=3:1, (4) In: Co=6:1 – were prepared. The obtained samples were named as $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -1, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -2, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3 and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -4. Intrinsic In_2O_3 and intrinsic Co_3O_4 NFs were prepared by the same process with only one syringe.

2.3. Characterization

The X-ray powder diffraction (XRD) analysis was performed on Bruker D8 Advance over the 2θ range from 10° – 80° in steps of 0.03° . The field emission scanning microscopy (FE-SEM) images were obtained on a Sigma500. The elemental distribution of the sample was characterized by X-ray Energy Dispersive Spectrometer (EDS) Analysis. High-resolution transmission electron microscopy (HRTEM) images were acquired on a Fei Tecnai G2 F20.

2.4. Fabrication and measurement of gas sensors

The calcined sample was mixed with a small amount of deionized water in an agate mortar. The mixture was then ground to a paste in the agate mortar. It should be noted that the grinding needed to be carried out in the same direction to make it uniform. The ground paste sample was evenly coated on the silver palladium electrode, which was placed at room temperature for 10 h to dry and volatilize deionized water, and then the silver palladium electrode coated with the sample was aged in a muffle furnace at 300°C for 10 h three times. Gas-sensing measurements were carried out by the CGS-MT integrated test platform, consisting mainly of static gas distribution and a data acquisition system (SA3101 Configuration), which recorded the change in the resistance value. The target gas volume was calculated using software (EtLiquidVolume) and then injected into the test chamber using a microinjection needle. The conversion formula between the injection volume of the liquid (V) and the concentration of the gas (C)

was $Q = (V \times C \times M)/(22.4 \times d \times \rho) \times 10^{-9} \times (273 + \text{TR})/(273 + \text{TB})$, where Q is the volume of liquid to be taken (ml), V is the volume of test bottle (ml), M is the molecular weight (g), d is the purity of liquid, C is the concentration of the gas to be prepared (ppm), ρ is the density of the liquid ($\text{g}\cdot\text{cm}^{-3}$), TR is the test ambient temperature ($^\circ\text{C}$), and TB is the temperature in the test bottle ($^\circ\text{C}$) [25]. The schematic diagram of the whole experimental process using homopolar double-jet electrospinning is shown in Figure 1.

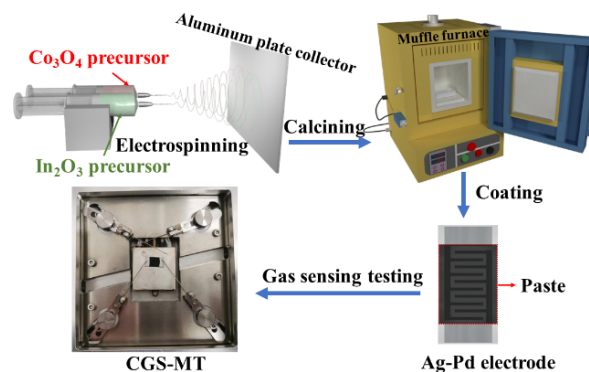


Fig. 1. A schematic diagram of the whole experimental process

3. Results and discussion

3.1. Structural and morphological characteristics

Characterization was necessary to verify the composition and crystallinity of the as-prepared $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ NFs. XRD. As shown in Figure 2, the crystal structure information of In_2O_3 NFs, Co_3O_4 NFs and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ NFs ($\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -1, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -2, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3 and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -4) was characterized. The XRD spectrum was analyzed according to the PDF#06-0416 for In_2O_3 (space group Ia-3), and PDF#43-1003 for Co_3O_4 (space group Fd-3m). The diffraction peaks of intrinsic In_2O_3 were observed at 2θ of 21.498° , 30.580° , 35.466° , 51.037° , and 60.676° , and assigned to (211), (222), (400), (440) and (622) crystal planes of tetragonal rutile In_2O_3 , respectively. While the diffraction peaks of Co_3O_4 at 2θ values of 19.000° , 31.271° , 36.845° , 38.546° ,

44.808°, 59.353°, and 65.231° corresponded to the (111), (220), (311), (222), (400), (511) and (440) crystal faces, respectively, indicating the absorption peaks matched well with the standard figure of Co_3O_4 phase. Meanwhile, there were still characteristic diffraction peaks of Co_3O_4 in the curves of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -1, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -2, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3 and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -4. With the increase of Co_3O_4 loading, the characteristic diffraction-peak intensity of Co_3O_4 increased, indicating that Co_3O_4 has been successfully loaded on In_2O_3 . No diffraction peaks of other phases were detected, indicating high purity in the sample.

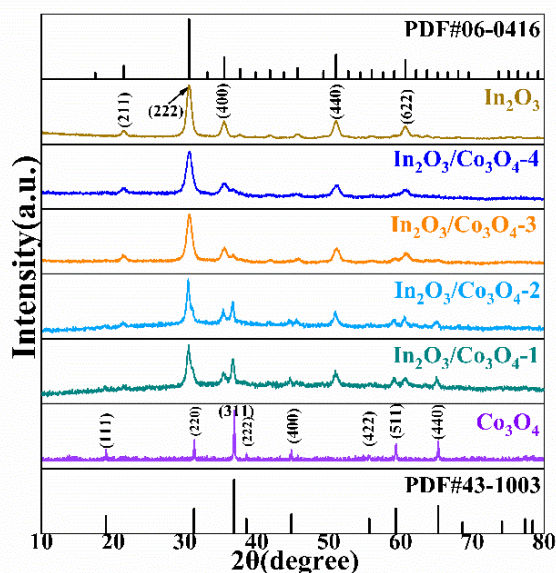


Fig. 2. XRD patterns of In_2O_3 , $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -4, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -2, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -1 and Co_3O_4 NFs

Figure 3A–L show the SEM images of In_2O_3 NFs, Co_3O_4 NFs, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -1, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -2, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -4 before and after sintering. For the as-spun fibers, all the samples have a uniform diameter of about 150–250 nm. For pure In_2O_3 and Co_3O_4 NFs, as shown in Figures 2G and H, the surface of the Co_3O_4 NFs was rougher than that of In_2O_3 NFs. The diameter of both the Co_3O_4 and In_2O_3 NFs was about 60–70 nm. Figure 3I–L shows the cross-sectional views of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -1, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -2, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3 and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -4. It was found in Figure 3I–K

that the majority of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -1, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -2 and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3 were hollow structures. As In_2O_3 increased, nanofibers with hollow structures became fewer. As shown in Figure 3L, most of the $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -4 were solid structures. In order to further prove the existence of In_2O_3 and Co_3O_4 in the sample, the $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3 was characterized by EDS, as described in the next section.

According to the TEM images of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3 NFs in Figure 4A–B, the size and morphology were similar to the SEM characterization results in Figure 3K. For the purpose of verifying whether In_2O_3 and Co_3O_4 were composited on a single nanofiber, the samples were further characterized by HRTEM, as shown in Figure 4C. Analyzing the lattice fingerprint information in HRTEM showed that the lattice spacings of 0.2928 nm and 0.4122 nm corresponded to the (222) and (211) planes of In_2O_3 , respectively, and the lattice spacings of 0.2868 nm and 0.2445 nm corresponded to the (220) and (311) planes of Co_3O_4 , respectively. The lattice fingerprints of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -NFs were consistent with the XRD patterns.

The elements of Au, In, Co and O appeared on a single nanofiber, as seen from Figure 5A–E. The existence of Au element came from the gold sprayed on the sample surface to enhance the conductivity of material. From above analysis, it could be concluded that $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ NFs had been compounded in the process of double-jet electrospinning. Under the influence of positive high voltage electrodes, homopolar double-jet electrospinning made the two materials contact alternately during collection. The EDS of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3 was shown in Figure 5F. The weight ratio and atom ratio of Co:In were 17.5% and 34.0%, respectively.

It was worth noting that during the calcination process, the electrospinning precursors gradually formed a hollow nanofiber structure due to the Kirkendall effect [26]. The Kirkendall effect is the process of surface ion oxidation crystallization and internal ion as surface exudation oxidation crystallization. When the temperature in the muffle furnace was high, the PVP on the NFs surface was calcined and volatilized, while the PVP inside was not volatilized in time and thus was in a molten state. At the same time, the surface ions were oxi-

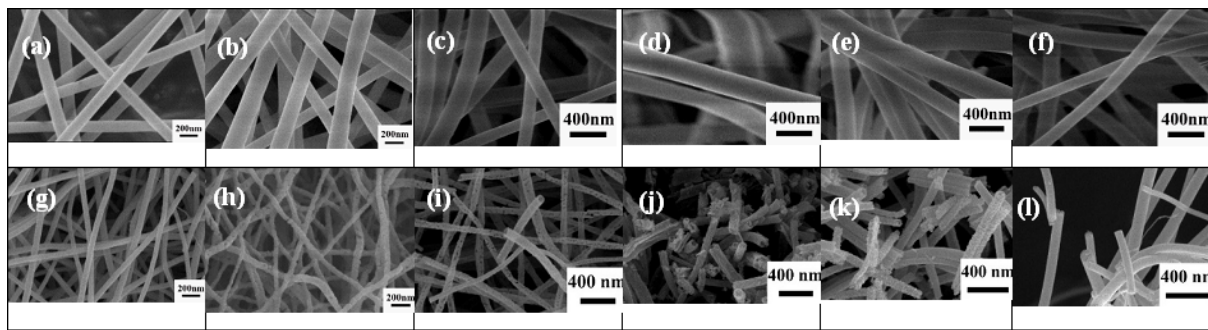


Fig. 3. SEM images of In_2O_3 NFs, Co_3O_4 NFs, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -1, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -2, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3 and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -4 :(a-f) before calcination, and (g-l) after calcination

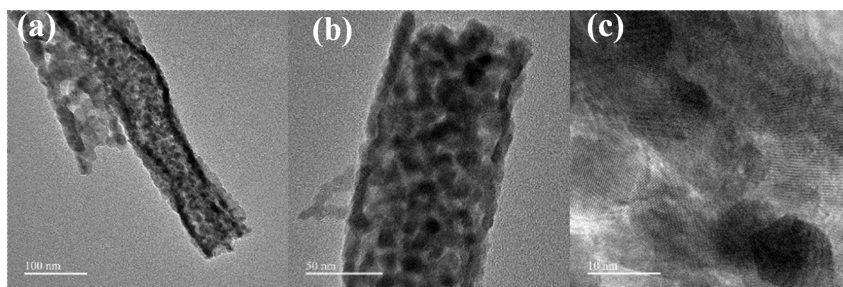


Fig. 4. TEM images of (a-b) $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3 nanofibers and (c) HRTEM of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3

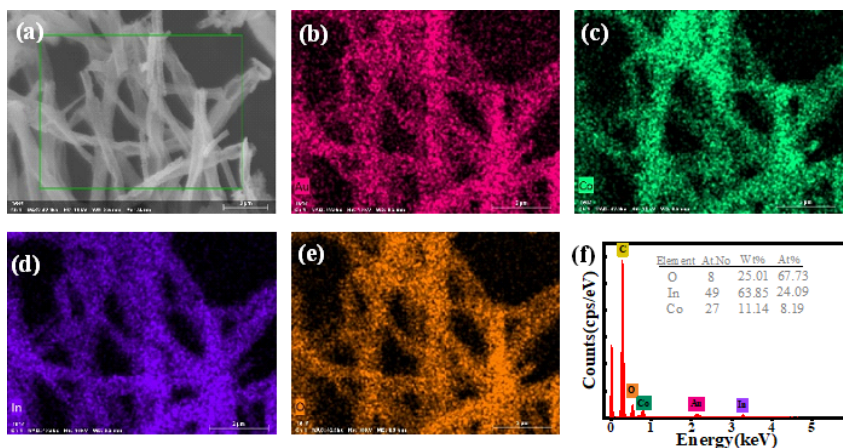


Fig. 5. The elemental composition chart of (a) $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ NFs, (b) Au element, (c) Co element, (d) In element, (e) O element, and (f) EDS of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3

dized and crystallized, while the internal ions were not oxidized and crystallized due to the warping of the surface. Thus, there was a gradient difference between the surface and the interior of the NFs, resulting in the internal ions seeping to the surface with the carrier of molten PVP. The PVP as exudate was calcined and volatilized, and the ions were oxi-

dized and crystallized. The process was repeated to form a hollow nanofiber structure. The schematic diagram of calcination process model is shown in Figure 6.

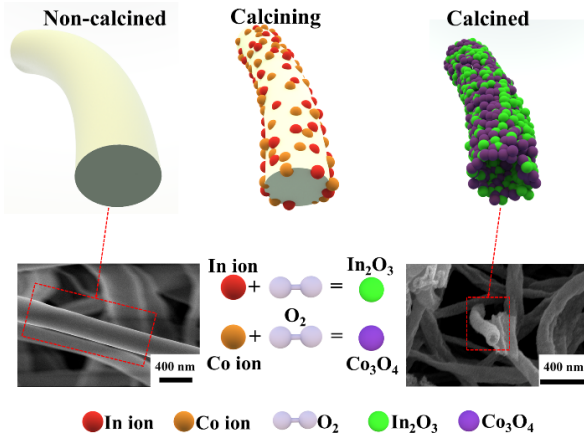


Fig. 6. The schematic diagram of the calcination process model

3.2. Gas sensing properties

The operating temperature strongly influenced the gas-sensing properties of the MOSs gas sensor. Figure 7 shows the response of Co_3O_4 , In_2O_3 , $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -1, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -2, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3 and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -4 to 40 ppm acetone at different working temperatures. The responses R_g/R_a of Co_3O_4 and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -1 were defined as R_g/R_a . The response R_g/R_a of In_2O_3 , $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -2, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3, and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -4 were defined as R_g/R_a , with R_a being the stable resistance in air and R_g being the stable resistance in probe gas. For Co_3O_4 , $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -1, and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -2, response values under their respective optimal operating temperatures are very low, lower than 2. Their optimal operating temperatures are 200°C , 175°C and 300°C , respectively. For $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -4, the sensor reaches its highest response of 6 at 200°C . The response values of In_2O_3 are higher than that of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3, but the optimal working temperature of the latter is 100°C lower. Considering both the high response value and low operating temperature, we consider $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3 to be the optimal device, with a high response value of 9.5 at 200°C to 40 ppm acetone.

Figure 8A presents the dynamic resistance curve of Co_3O_4 and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -1 to acetone with a concentration range of 1–100 ppm at 200°C . When the sensors are transferred from an air environment to an acetone environment, their response

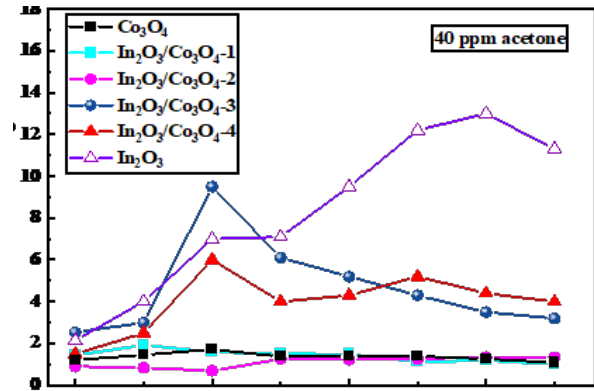


Fig. 7. Response of Co_3O_4 , In_2O_3 , $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -1, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -2, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3 and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -4 sensors to 40 ppm acetone at different operating temperatures

values increase until they reach a maximum and equalize. When the acetone gas supply stops, the response values decrease and return to baseline resistance. This confirms the sensor's perceptibility and recovery. As observed, the conductivity type of Co_3O_4 and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -1 were p-type, while that of In_2O_3 , $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3, and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -4 were n-type, as shown in Figure 8B. $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -2 had almost no response, indicating that the composite is in the critical state of p-type to n-type transition. From the above analysis, it can be seen that with the increase of indium oxide content, the complex gradually changes from p-type to n-type and is in a critical state when the content of both is equal. Therefore, we can conclude that the content of n- In_2O_3 in composite $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ can regulate the final conductivity type of the sensor. The sensing behavior of the $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -1 was p-type, which might be due to the contribution of holes being greater than that of the electrons [27]. The $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ sensor has a wide detection range for acetone, and the response increases with concentration, obeying a linear relationship. When the acetone concentration increased from 1 to 100 ppm, the gas response, based on the In_2O_3 sensor and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ sensor, increased from 1.3 and 1.86 to 4.04 and 19.2. This indicates that the presence of Co_3O_4 helps to improve the response of the In_2O_3 -based sensor to acetone.

The responses of Co_3O_4 , In_2O_3 , $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -

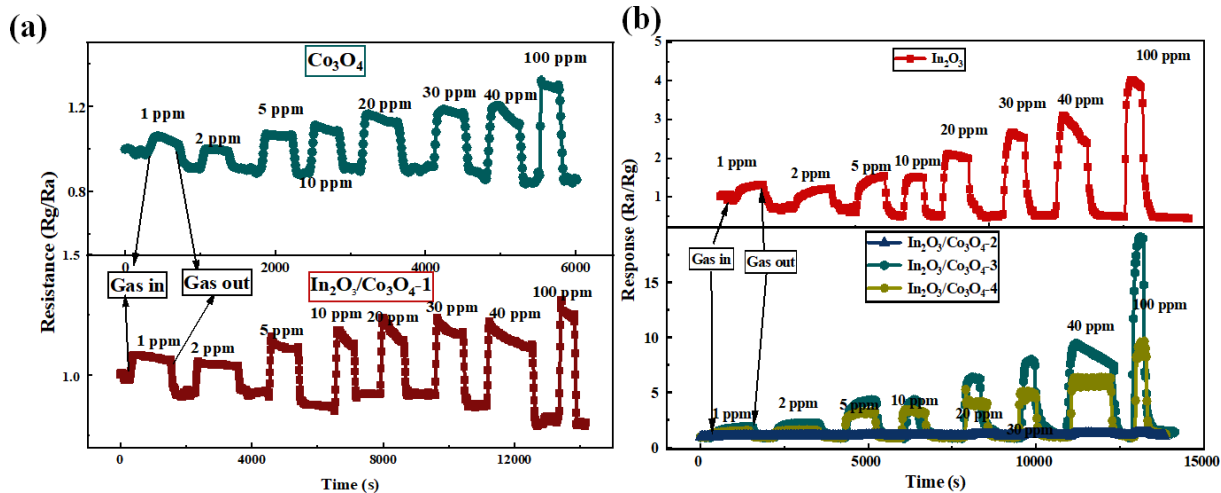


Fig. 8. Transient curves of the gas sensors based on the Co_3O_4 , In_2O_3 , $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-1$, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-2$, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-3$, and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-4$ to different acetone concentrations at 200°C

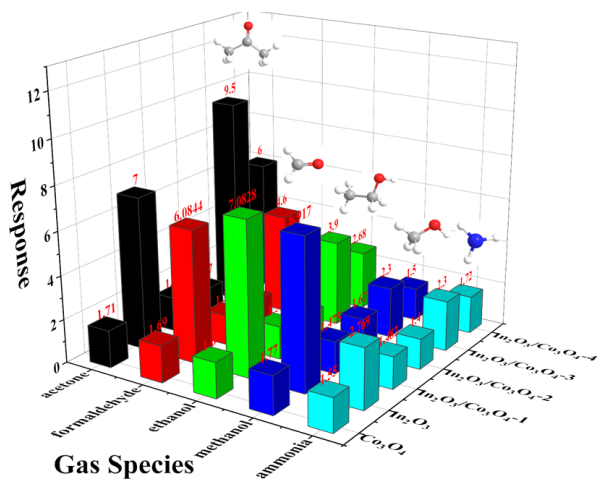


Fig. 9. Selectivity of Co_3O_4 , In_2O_3 , $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-1$, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-2$, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-3$, and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-4$ sensors

1, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-2$, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-3$, and $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-4$ sensors to four interference gases including formaldehyde, ethanol, methanol, and ammonia with a concentration of 40 ppm were examined at 200°C, as shown in Figure 9. The response values of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-3$ sensor for 40 ppm acetone, formaldehyde, ethanol, methanol, and ammonia were 9.5, 4.6, 3.9, 2.3, and 2.3, respectively. The response of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-3$ sensor to acetone is higher than the response to the other interference gases. Therefore, it can be

concluded that $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-3$ gas sensor has a good selectivity to acetone. In addition, we found that although the response value of In_2O_3 to acetone was comparable to that of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-3$, the selectivity of In_2O_3 to acetone was poor in the presence of interfering gases, especially formaldehyde, ethanol, and methanol.

As shown in Figure 10A, the lower detection limit of the $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-3$ sensor was 0.7 ppm with a response value of 1.14, and the response/recovery time of the $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-3$ sensor to 0.7 ppm acetone at 200°C was 21 s/51 s. In order to explore the stability of the sensor, a periodic test of 10 ppm acetone gas was carried out for $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-3$ at 200°C. The test interval was 30 days and lasted for 5 months, as shown in Figure 10B. It can be seen from the figure that the sensitivity of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-3$ sensor has a small fluctuation, but the amplitude is small, indicating that the sensor has good stability and can meet the actual demand. A comparison of the sensing performance of various In_2O_3 -based sensing materials and preparation processes is given in Table 1. The results show that the $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-3$ sensor has lower operating temperature and higher gas response values. The structural features, including hollow interiors, porous surfaces and micropore size, give the $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4-3$ a higher surface adsorption sites and more efficient gas diffusion of

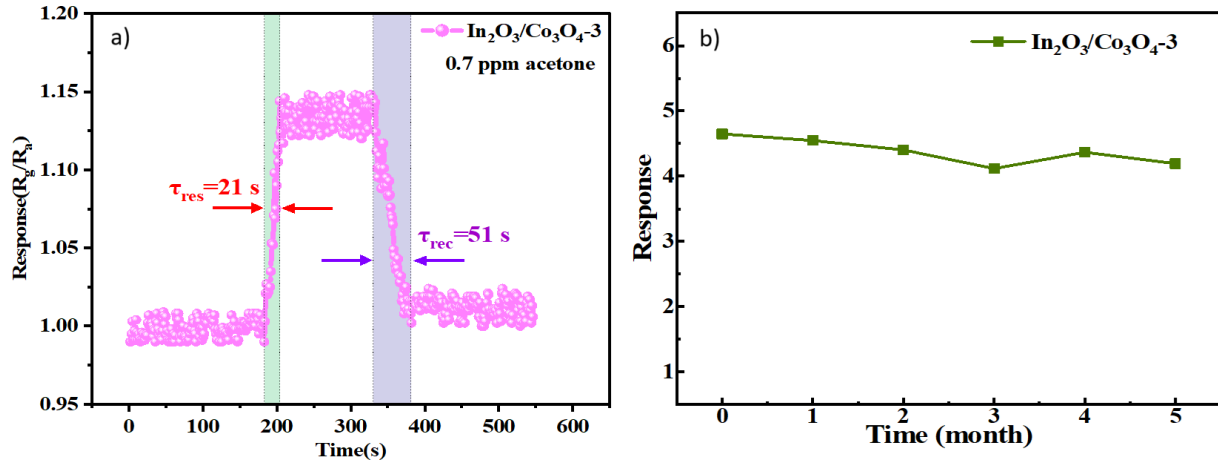


Fig. 10. (a) Response and recovery curve of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4\text{-3}$ to 0.7 ppm acetone at 200°C; (b) Long term stability of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4\text{-3}$ toward 10 ppm acetone over a period of 5 months at an operating temperature of 200°C

Table 1. Comparative analysis of sensor performance and preparation processes based on In_2O_3 sensing materials

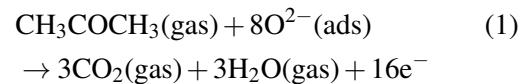
Sensor materials	Fabrication method	Operating temperature (°C)	Response/ppm	References
$\text{SnO}_2/\text{In}_2\text{O}_3$	Thermal evaporation	300	1.05/100	[29]
In_2O_3 microsphere	Solvothermal method	250	36/20	[30]
In_2O_3	facile solution route	260	8.60/100	[31]
$\text{Bi}_2\text{O}_3/\text{In}_2\text{O}_3$	one-step process	200	17.7/200	[32]
Co_3O_4	electrospinning	200	1.71/40	This work
In_2O_3	electrospinning	200	7/40	This work
$\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4\text{-3}$	Double-jet electrospinning	200	9.5/40	This work

oxygen and target gases, which may facilitate its enhanced response [28]. In addition, the process of preparing $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4\text{-3}$ materials using double-jet electrospinning is simple, convenient and low cost.

3.3. Gas sensing mechanism

The gas-sensing mechanism of MOSs is generally explained by the electron depletion layer theory. In this study, when the $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ gas sensor was exposed to air, the oxygen molecules were adsorbed on the surface of MOSs material. These adsorbed oxygen molecules captured free electrons to be converted to the ionized oxygen species O_{ads} (O_2^- , O^- , O^{2-}), as shown in Figure 11A, where “ads” is the abbreviation for adsorbed. The electron depletion layers and hole accumulation layers were formed around the surface of MOSs grains.

Upon exposure to acetone gas, CO_2 , and H_2O are formed as follows [33]:



For a single In_2O_3 sensor, oxygen molecules in the air at room temperature are converted into adsorbed oxygen ions on the surface of the indium oxide material, forming an electron depletion layer. There are a lot of $\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$ homogeneous junctions between indium oxide grains in this material. According to the carrier concentration formula for the n-type indium oxide sensor, most of the carriers in the material are negatively charged electrons. The electron concentration formula is shown as follows:

$$n = n_i \exp\left(\frac{E_F - E_i}{kT}\right) \quad (2)$$

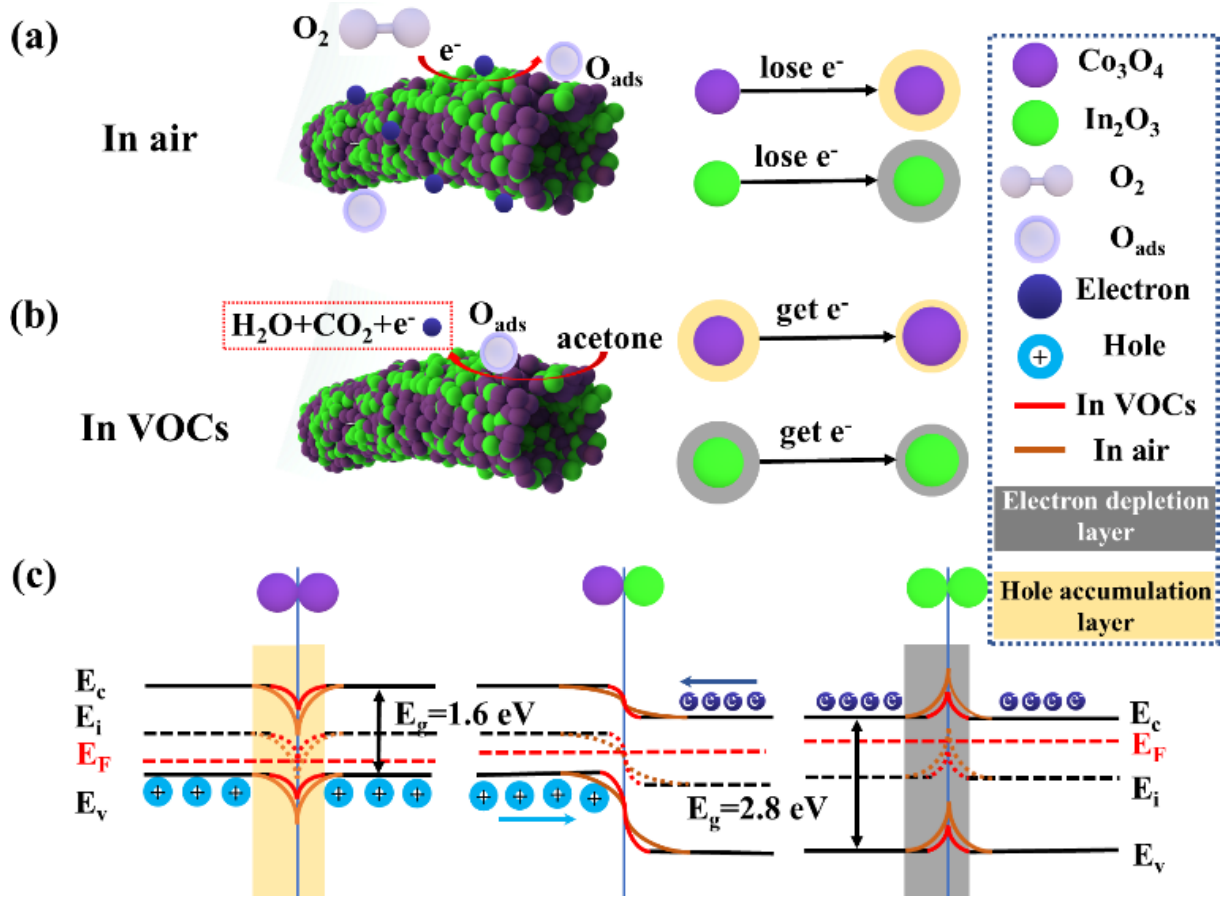


Fig. 11. Sensing mechanism of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ (a) in air and (b) in VOCs, and (c) energy band diagram of $\text{Co}_3\text{O}_4/\text{Co}_3\text{O}_4$, $\text{Co}_3\text{O}_4/\text{In}_2\text{O}_3$ and $\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$ grains

Where n is the electron concentration, n_i is the intrinsic carrier concentration, E_F is the Fermi level, E_i is the intrinsic Fermi level as the reference level, k is the Boltzmann constant, and T is the thermodynamic temperature. When In_2O_3 particles are in the air, ionized oxygen is adsorbed on the particle surface and electrons are lost, leading to a decrease in the conduction band electron concentration. According to Formula 2, E_i increases and bends upward, leading to an increase in barrier height. When exposed to a reducing gas such as acetone, a large number of electrons will be released into the material due to the reaction in Formula 1. When electrons are released, the electron concentration increases, so E_i decreases and the barrier height in the air decreases, as shown in Figure 11C. Similarly, for Co_3O_4 sensors, according to formula 3, when Co_3O_4 particles are in the air, E_i

bends downward, and the barrier height in the air is higher than that of VOCs.

$$p = n_i \exp\left(\frac{E_i - E_F}{kT}\right) \quad (3)$$

In $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$, due to the contact between p-type Co_3O_4 grains and n-type In_2O_3 grains, there are a large number of p- Co_3O_4 /n- In_2O_3 heterostructures besides homogeneous p- Co_3O_4 /p- Co_3O_4 and n- In_2O_3 /n- In_2O_3 . The Fermi energy levels of n- In_2O_3 and p- Co_3O_4 are different. The electrons flow from n- In_2O_3 ($W_f=5.0$ eV, $E_g=2.8$ eV) [34] to p- Co_3O_4 ($W_f=6.1$ eV, $E_g=1.6$ eV) [35], forming an electron transfer until the Fermi energy level is balanced by the Fermi energy level balance effect [36, 37]. Therefore, the formation of p-n heterostructures in the composites additionally increases the width of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ heterostruc-

ture depletion layer. In reducing gas atmosphere, as shown in Figure 11B, due to the release of electrons, the net decrease of the width of the depletion layer becomes larger, which improves gas-sensing performance.

4. Conclusions

In conclusion, $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanofibers with a hollow structure were prepared by electrospinning and calcining with homopolar double nozzles. The morphology, structure and gas-sensing characteristics of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -based nanocomposites with different molar ratios was studied, and the growth mechanism of the hollow structure of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanofibers was also analyzed. The gas-sensing test showed that with the increase of indium oxide content in the composite system, the conductive type of the composite changed from p-type to n-type, and when the molar ratio of the two was equal, it was in a critical state of response. Therefore, the conductive type of the composite can be controlled by controlling the content of indium oxide, which provides some experimental reference for the controllable preparation of materials. The enhanced response of $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -3 sensors is related to the formation of n- In_2O_3 /n- In_2O_3 and p- Co_3O_4 /p- Co_3O_4 homojunction and n- In_2O_3 /p- Co_3O_4 heterojunction. The stability of sensor devices based on $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ heterojunction structure is up to five months or more. The high stability and simple preparation process make $\text{In}_2\text{O}_3/\text{Co}_3\text{O}_4$ -based sensor devices more capable of meeting the requirements of modern detection processes and more suitable for practical applications than similar materials.

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