MOFs-derived Co$_3$O$_4$ loaded hollow In$_2$O$_3$ nanofibers with greatly enhanced acetone sensing performance

L Zhu$^{1,*}$, X Chang$^{1,2}$ and W B Lu$^2$

$^1$School of Materials Science and Engineering, China University of Petroleum, Qingdao 266555, Shandong, People’s Republic of China
$^2$State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao 266580, Shandong, P.R. China
*Corresponding author’s e-mail: zhulei@upc.edu.cn

Abstract. In this paper, metal-organic frameworks (MOFs)-derived Co$_3$O$_4$ were easily functionalized on In$_2$O$_3$ nanofibers (NFs) by electrospinning followed a calcination at 600 °C in air. The influences of doping content, morphology, and operating temperature on the acetone sensing performances of In$_2$O$_3$ based NFs were comprehensively studied. Our results showed that the 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs exhibited outstanding acetone sensing properties at 300 °C. Exactly, it showed a high response to acetone (S~43.67 @ 100 ppm acetone), which was ∼22 times larger than that of pristine In$_2$O$_3$ NFs. On the same time, it exhibited a short response time (~13 s). The excellent acetone sensing properties of MOFs-derived Co$_3$O$_4$-In$_2$O$_3$ NFs can be explained by the formation of p-n junction between Co$_3$O$_4$ and In$_2$O$_3$. Our work offers a facile and cost-effective approach to load MOFs-derived Co$_3$O$_4$ on other metal oxides based NFs as a promising gas sensing material and shows the prospects of MOFs-derived metal oxides loaded in metal oxide NFs used for gas sensors.

1. Introduction
As a good solvent, acetone is widely used in the industry. However, acetone is extremely volatile and flammable when the concentration is over 450 mg/m$^3$ [1]. Therefore, it is necessary to explore an accurate acetone sensor. In recent years, metal oxide semiconductors (MOS), including Co$_3$O$_4$, In$_2$O$_3$, WO$_3$ have a lot of advantages, such as high chemical stability, easy mass-production and suitability for much target gases, and thus have been largely exploited and used as acetone sensors. Among them, In$_2$O$_3$ has been widely studied for the detection of both oxidizing gases and reducing gases [2]. However, the pristine In$_2$O$_3$ shows low gas response and poor selectivity. To overcome this obstacle, two main methods are adopted to enhance the gas sensing performance of In$_2$O$_3$ based sensors.

On the one hand, it is well known that the gas sensors are operated by the surface reaction of target gas on the MOS materials. Thus, the microstructural parameters of the MOS based sensing films,
including specific surface area, porosity and pore size have great influences on the sensing performance of MOS based sensors. Electrospinning has been a common method to fabricate the MOS nanofibers (NFs), which possess high gas sensing performance due to unique one dimensional structure. Such MOS NFs are made of metal oxide nanoparticles and possess high gas accessibility due to its open structures, high porosity and high aspect ratio [3].

On the other hand, various suitable catalysts and dopants have been incorporated with MOS to enhance their sensing performance, such as another metal oxides [4] and noble metals [5]. Among them, MOS are more widely used because of the low-cost and the formation of heterojunction. Recently, Metal-organic frameworks (MOFs) derived hollow and porous metal oxides have been used for gas sensing, due to their large number of reaction sites and convenient gas accessibility [6, 7].

Herein, we synthesized Co$_3$O$_4$-loaded In$_2$O$_3$ NFs (using ZIF-67 as templates) with porous hollow 1D nanostructure and Co$_3$O$_4$/In$_2$O$_3$ junctions, and investigated its acetone sensing properties. The results demonstrated that compared with pristine In$_2$O$_3$ NFs, the Co$_3$O$_4$/In$_2$O$_3$ NFs exhibited greatly enhanced acetone sensitivity. Furthermore, we discussed the mechanism for the improved acetone sensing performance.

2 Experimental Details

2.1 Synthesis of ZIF-67
Typically, 0.45 g Co(NO$_3$)$_2$·6H$_2$O (AR, 99%, Aladdin) was dispersed in 3 mL water. In the meantime, 5.5 g 2-Methylimidazole (2-MI, 99%, Sigma-Aldrich) was dispersed in 20 mL water and stirring for 20 min at 25 °C, the Co(NO$_3$)$_2$·6H$_2$O solution was added into the 2-MI solution and aged for 6 h. Afterwards, the purple precipitates were collected via centrifugation, and dried for 1 days at 80 °C in air.

2.2 Preparation of Co$_3$O$_4$-In$_2$O$_3$ NFs
The Co$_3$O$_4$-In$_2$O$_3$ NFs were prepared by electrospinning followed by calcination. In(NO$_3$)$_3$·xH$_2$O (99.9%, Aladdin) and ZIF-67 (total weight of 0.2 g) were dispersed in a mixed solution of 2.21 g ethanol and 2.21 g DMF (Sinopharm Chemical Reagent Co. Ltd), and stirring for 1 h at 25 °C. The weight ratios of ZIF-67 were 0, 10 wt%, 20 wt% and 30 wt%, respectively. Afterwards, 0.4 g PVP was injected into above solution and then stirring for 10 h. Subsequently, using a 20-gauge stainless steel needle, the prepared solution was injected into a 5 mL plastic syringe and electro-spun for 4 h. The flow rate was set as 1 mL/h and the applied voltage from needle to the collection roller was set as 18 kV. After that, the obtained NFs were dried for half of the day at 60 °C in air. In order to remove the PVP, convert the In(NO$_3$)$_3$ to the In$_2$O$_3$ and convert the ZIF-67 to the Co$_3$O$_4$, the dried NFs were heated at 600 °C for 3 h in air.

2.3 Samples fabrication and acetone sensing measurement
The 20 mg above-obtained samples were dispersed into 10 mL deionized water to prepare solution. And then we dropped 10 μL solution on the Pt interdigitated electrodes. Afterwards, the In$_2$O$_3$ NFs based sensing layers on the substrate were dried at 120 °C for 20 min. Finally, all samples were aged in the air for 2 h at 400 °C, which could be used to improve the stability and reproducibility of obtained samples. The process steps in the fabrication of our In$_2$O$_3$ based sensors and the gas-sensing
test platform are illustrated in Figure 1.

![Figure 1. The schematic diagram of the gas-sensing test system and fabrication of In$_2$O$_3$ based sensors.](image)

The acetone sensing characteristics were carried out by a commercial gas detection apparatus. The detection apparatus consists of electrical signal testing system, resistive-type heater system and gas flow controlled system. Using four computer-driven digital mass flow controllers, the gas concentration was controlled by changing the mixing ratio of standard acetone (acetone in N$_2$, Qingdao Ai Ruo Gas Co. Ltd) and synthetic air. The total constant gas flow was set as 1 L/min. The response was calculated by $S = R_a/R_g$, where $R_g$ represents the resistance of the sensors when exposed to the target gas and $R_a$ represents the resistance of the sensors in the background atmosphere.

2.4 Characterization of the samples
To investigate the crystallographic structure of samples, X-ray diffraction (XRD) was conducted through Cu-K$_\alpha$ radiation ($\lambda = 1.5406$ Å) in a wide angle range (2θ = 10–90°). The samples’ surface morphology and microstructures were characterized by transmission electron microscope (TEM; JEM-2100) and scanning electron microscopy (SEM; Hitachi S-4800). The chemical composition and states were studied through X-ray photoelectron spectroscopy (XPS, ULVAC-PHI5000). The specific surface areas of the NFs were investigated using the Brunauer-Emmett-Teller (BET) method (TriStar 3020).

3 Results and discussion

3.1 Structure characterization of the Co$_3$O$_4$-In$_2$O$_3$ NFs
Firstly, we investigated the phase composition and crystal structure of the samples by XRD measurement. Figure 2 illustrates the XRD patterns of pure In$_2$O$_3$ NFs and Co$_3$O$_4$ doped In$_2$O$_3$ NFs. As shown in Figure 2 (a), the peaks of the pure In$_2$O$_3$ NFs could be well indexed to crystal structure of In$_2$O$_3$ (JCPDS: 06-0416) [2]. Besides, it can be confirmed that the In(NO$_3$)$_3$ is totally converted to In$_2$O$_3$ after calcination, due to that no other diffraction peaks are observed. Figure 2 (b-d) shows the XRD pattern of 10, 20, 30 wt% Co$_3$O$_4$-In$_2$O$_3$. It is shown that the characteristic peaks of both In$_2$O$_3$ and Co$_3$O$_4$ can be observed. Besides, these two peaks matches well with the cubic In$_2$O$_3$ and the cubic Co$_3$O$_4$ (JCPDS: 43-1003) [8]. The peaks around 2θ = 36.84°, 59.35° and 65.23° are indexed to the (311), (511) and (440) planes of crystal Co$_3$O$_4$, demonstrating that the ZIF-67 are totally converted into...
The peaks of Co$_3$O$_4$ are weak in Co$_3$O$_4$-In$_2$O$_3$ NFs, probably resulting from that the quantity of ZIF-67 is too little. In addition, it is obvious that with increasing ZIF-67 doping content, the intensity of the diffraction peaks of Co$_3$O$_4$ increases while the intensity of the diffraction peaks of In$_2$O$_3$ decreases.

The morphology and size of the as-prepared ZIF-67 crystals were characterized by SEM. From Figure 3 (a) and (b), it is shown that ZIF-67 crystals are typical polyhedrons and the sizes of them are from tens to hundreds nanometers. The SEM images of pure In$_2$O$_3$ NFs and 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs are shown in Figure 3 (c) and (e), respectively. The diameter of all In$_2$O$_3$ based NFs are about 100–200 nm and they are composed of strings of tiny nanoparticles after heat treatment at 600 °C. It is observed that the surface of pure In$_2$O$_3$ NFs is smooth and the heating treatment results in a thick-walled tubular structure, which is well correlated with the TEM result in Figure 3 (d). The inset picture in Figure 3 (d) shows the selected area electron diffraction (SAED) patterns of pure In$_2$O$_3$ NFs. It is shown that the In$_2$O$_3$ NFs consists of a series of concentric rings, indicating the In$_2$O$_3$ NFs possess high crystallinity. Compared with the pristine In$_2$O$_3$ NFs, the 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs shown in Figure 3 (e) and (f) have larger surface-to-volume ratios and higher porosity because the ultra-thin walled tubular structures and numerous microporous on it. Due to that this 1D hollow NFs structures possess highly porous morphology, the acetone molecules can easily get inside and react with sensing materials. The SAED pattern of 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs is similar with that of the pure In$_2$O$_3$ NFs and reveals polycrystalline nature of In$_2$O$_3$ and Co$_3$O$_4$ nanoparticles. The HRTEM image of In$_2$O$_3$ NFs illustrates that the lattice-fringes spacing is 0.292 nm, which is corresponding to the In$_2$O$_3$ (222) crystallographic planes (see Figure 3 (g)).[9] From Figure 3 (h), it can be observed that both crystalline In$_2$O$_3$ and Co$_3$O$_4$ nanoparticles are included in 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs. Besides, the lattice fringes spacing of 0.292 nm and 0.467 nm are corresponding to the (222) plane of the In$_2$O$_3$ and (111) plane of the Co$_3$O$_4$, respectively. Therefore, it is sure that the In(NO$_3$)$_3$ and ZIF-67 are totally converted to In$_2$O$_3$ and Co$_3$O$_4$ after heat treatment, which is consistent with the XRD results.

![Figure 2. XRD patterns of (a) pure In$_2$O$_3$ NFs, (b) 10 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs, (c) 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs, (d) 30 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs.](image)
3.2 Acetone sensing performance

In order to investigate the gas sensing performance of Co$_3$O$_4$-In$_2$O$_3$ NFs, we monitored the samples’ resistance from 200 °C to 400 °C. Subsequently, to investigate the optimum working temperature and optimum Co$_3$O$_4$ doping concentration, we carried out acetone sensing test of all samples to 100 ppm acetone at different working temperatures. It can be seen in Figure 4 (a) that the acetone response of pure In$_2$O$_3$ NFs and 10 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs increases with increasing temperature. Besides, the optimal temperature of acetone response is 400 °C. In addition, the 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs exhibited the best sensing property among them at 300 °C and the optimal temperature of 30 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs is 250 °C. So the optimum working temperature and optimum Co$_3$O$_4$ doping concentration is 300° C and 20 wt%, respectively. The response characteristic curves of pure and 20 wt% Co$_3$O$_4$ loaded In$_2$O$_3$ NFs are shown in Figure 4 (b), it is indicated that the 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs is much more sensitive to acetone than the unloaded one and the reproducibility of the sensing response is great. The resistance of them decreases when exposed to acetone and the acetone response for them is 38.75 and 1.67, respectively. Figure 4 (c) represents the dynamic acetone sensing characteristics of pure In$_2$O$_3$ NFs and 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs at 5-100 ppm and 300 °C. The gas responses of 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs are about 43.67, 28.99, 15.75, 6.41 and 4.17 to 100, 50, 25, 10 and 5 ppm acetone, respectively. The acetone response of 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs (S = 43.67 @ 100 ppm) was 22 times higher compared with that of pure In$_2$O$_3$ NFs (S = 1.99 @ 100 ppm). Moreover, the responses of pristine In$_2$O$_3$ NFs toward 5-100 ppm acetone are very low (< 2) and the 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs have a good stability. Figure 4 (d) shows that at the same working temperature, the $R_a$ of In$_2$O$_3$ based NFs dramatically increases with increasing Co$_3$O$_4$ doping content, which means that the Co$_3$O$_4$/In$_2$O$_3$ p-n heterojunctions are successfully built. In$_2$O$_3$ is a natural n-type semiconductor and Co$_3$O$_4$ is an natural p-type semiconductor with an indirect band gap of 1.6~2.2 eV. Besides, the work function of In$_2$O$_3$ and Co$_3$O$_4$ are 5.1 eV and 6.3 eV, respectively. When the Co$_3$O$_4$ nanoparticles interact with In$_2$O$_3$, electrons can transfer from In$_2$O$_3$ to the Co$_3$O$_4$ nanoparticles, and a potential barrier is formed at the Co$_3$O$_4$/In$_2$O$_3$ interface. The thickness of electron depletion layer of In$_2$O$_3$ NFs increases due to the forming of p-n junctions. Therefore, the resistance of In$_2$O$_3$ based NFs increases. In addition, the
resistance of In$_2$O$_3$ based NFs sensors decrease with increasing temperature, which is in agreement with its semiconducting nature.

**Figure 4.** (a) Histogram plots of gas response of all samples to 100 ppm acetone at temperature from 200 °C to 400 °C, (b) the response characteristic curves of pure In$_2$O$_3$ and 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs, (c) typical response-recovery characteristic of pure In$_2$O$_3$ and 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs to different concentrations of acetone at 300 °C, (d) the resistance change of all samples in air at different temperatures.

**Figure 5.** (a) Response/recovery time of 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs to 100 ppm acetone at temperature ranging from 200 °C to 400 °C, (b) gas response of 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs towards acetone in various concentrations at 300 °C.

Apart from gas response, the response/recovery time is also an important factor to evaluate the sensing properties of gas sensors. The response time can be defined as the time it takes from $R_g$ to $R_g + 90\% \times (R_a - R_g)$ and the recovery time can be defined as the time it takes from $R_a$ to $R_a - 90\% \times (R_a - R_g)$. Figure 5 (a) shows the response time of the 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs to 100 ppm acetone decreases a lot from 183.88 s at 200 °C to 23.53 s at 250 °C and stabilizes at ~13 s over 300 °C. In addition, the recovery time keeps decreasing from 271.61 s to 54.56 s with increasing temperature from 200 °C to 400 °C.
Figure 5 (b) shows the gas response of 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs versus acetone concentrations from 5 to 1600 ppm at 300 °C. It is found that the sensitivity increases rapidly with the acetone concentration goes up between 5 to 100 ppm, and then almost follows a linear increase with further increasing acetone concentration, indicating that the determination of acetone gas concentration is feasible.

3.3 Acetone sensing mechanism

As illustrated in Figure 6, the enhanced gas sensing properties of the MOFs derived Co$_3$O$_4$ loaded In$_2$O$_3$ NFs can be explained by p-n heterojunctions theory. According to the reported literatures [5, 10], the work function and band gap of In$_2$O$_3$ (Co$_3$O$_4$) are 5.1 eV (6.3 eV) and 3.6 eV (2.07 eV), respectively. When Co$_3$O$_4$ is combined with In$_2$O$_3$, since the Fermi level of them is different, the holes transfer from p-type Co$_3$O$_4$ to n-type In$_2$O$_3$ while the electrons transfer from n-type In$_2$O$_3$ to p-type Co$_3$O$_4$. Then, an equalization of the Fermi level is formed, and the depletion layer thickness of In$_2$O$_3$ NFs increases and the initial resistance of Co$_3$O$_4$-In$_2$O$_3$ NFs increases significantly compared to that of pure In$_2$O$_3$ NFs. It is beneficial for acetone gas sensor to have a high resistance, resulting from that a small number of adsorbed acetone gas can lead to the large resistance changes during acetone sensing [11]. Furthermore, the existence of heterojunction could improve the gas sensing properties due to more active sites [12, 13]. Based on the reasons above, MOFs-derived Co$_3$O$_4$ in In$_2$O$_3$ NFs can greatly improve the acetone sensing properties.

![Figure 6. The schematic diagram of acetone sensing mechanisms of Co$_3$O$_4$-In$_2$O$_3$ NFs.](image)

4. Conclusion

In summary, the MOFs-derived Co$_3$O$_4$ nano-grains are homogeneously dispersed on the wall of In$_2$O$_3$ NFs through electrospinning followed by calcination. It is found that the In$_2$O$_3$ based NFs consists of tiny nanoparticles strings and their average diameters are in the range from 100 nm to 200 nm. The existence of p-n (Co$_3$O$_4$-In$_2$O$_3$) heterojunctions significantly improve acetone-sensing performance. The response of 20 wt% Co$_3$O$_4$-In$_2$O$_3$ NFs (S = 43.67 @ 100 ppm) is ~22 times larger than that of pristine In$_2$O$_3$ NFs (S = 1.99 @ 100 ppm) at the optimal working temperature of 300 °C. These results confirm that loading MOFs-derived metal oxides in 1D metal oxide NFs through electrospinning is an efficient way to fabricate superior 1D metal oxide based gas sensors.

Acknowledgments
This work is supported by the Natural Science Foundation of China (11374372), the Natural Science Foundation of Shandong Province (ZR2018BEM033), Taishan Scholar Foundation (ts20130929), Fundamental Research Funds for the Central Universities (18CX02022A, 18CX02187A).

Reference
[1] Xiong Y, Zhu Z. Y, Ding D G, Lu W B and Xue Q Z 2018 Appl. Surf. Sci. 443 114.
[2] Prim A, Pellicer E, Rossinyol E, Peiró F, Cornet A and Morante J R 2007 Adv. Funct. Mater. 17 2957.
[3] Zhang C L and Yu S H 2014 Chem. Soc. Rev. 43 4423.
[4] Kim H J, Jeong H M, Kim T H, Chung J H, Kang Y C and Lee J H 2014 ACS Appl. Mater. Inter. 6 18197.
[5] Xing R Q, Li Q L, Xia L, Song J, Xu L, Zhang J H, Xie Y and Song H W 2015 Nanoscale 7 13051.
[6] Li W H, Wu X F, Han N, Chen J Y, Qian X H, Deng Y Z, Tang W X and Chen Y F 2016 Sens. Actuators B: Chem. 225 158.
[7] Xu L, Dong B, Wang Y, Bai X, Liu Q and Song H W 2010 Sens. Actuators B: Chem. 147 531.
[8] Wen Z, Zhu L P, Mei W M, Hu L, Li Y G, Sun L W, Cai H and Ye Z Z 2013 Sens. Actuators B: Chem. 186 172.
[9] Liang X S, Jin G X, Liu F M, Zhang X S, An S S, Ma J and Lu G Y 2015 Ceram. Int. 41 13780.
[10] Jang J S, Koo W T, Choi S J and Kim I D 2017 J. Am. Chem. Soc. 139 11868.
[11] Wang C, Li X, Wang B, Ma J, Cao Y, Sun Y and Lu G Y 2014 RSC Adv. 4 18365.
[12] Xiong Y, Zhu Z Y, Guo T C, Li H and Xue Q Z 2018 J. Hazard. Mater. 353 290.
[13] Feng C H, Li X, Ma J, Sun Y F, Wang C, Sun P, Zheng J and Lu G Y 2015 Sens. Actuators B: Chem. 209 622.