



Cite this: *RSC Adv.*, 2017, 7, 23478

# Synthesis and characterization of flower-like MoO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> microstructures for highly sensitive ethanol detection†

Jie Hu, <sup>a</sup> Xiu Wang,<sup>a</sup> Meng Zhang,<sup>a</sup> Yongjiao Sun,<sup>a</sup> Pengwei Li, <sup>a</sup> Wendong Zhang,<sup>a</sup> Kun Lian,<sup>a</sup> Lin Chen<sup>\*b</sup> and Yong Chen<sup>c</sup>

Flower-like pure and Mo-loaded In<sub>2</sub>O<sub>3</sub> hierarchical microstructures were synthesized by a facile hydrothermal method. The morphology, crystal structures, and compositions of the samples were characterized by SEM, XRD, TEM, showing nanosheets with dimensions of 4 μm diameter and 25 nm thickness. Gas sensing experiments were conducted on the as-prepared MoO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> gas sensors, and the results prove that Mo-loaded In<sub>2</sub>O<sub>3</sub> gas sensors exhibit enhanced gas sensing properties at 185 °C. In particular, the 3 mol% Mo-loaded In<sub>2</sub>O<sub>3</sub> provided a high response (7 to 100 ppm ethanol), fast response and recovery time (11 s and 94 s), low detection limit (50 ppb), good selectivity and stability for ethanol detection, which is promising for low concentration ethanol detection in practical applications.

Received 2nd March 2017

Accepted 24th April 2017

DOI: 10.1039/c7ra02593a

rsc.li/rsc-advances

## 1. Introduction

In the past decades, metal oxide semiconductor (MOS) gas sensors, such as ZnO,<sup>1</sup> SnO<sub>2</sub>,<sup>2</sup> In<sub>2</sub>O<sub>3</sub>,<sup>3</sup> WO<sub>3</sub>,<sup>4</sup> Cr<sub>2</sub>O<sub>3</sub>,<sup>5</sup> CuO,<sup>6</sup> etc., have attracted tremendous attention owing to their domestic and industrial applications for detection of explosive gases, toxic gases, and volatile organic compounds (VOCs). Among them, indium oxide (In<sub>2</sub>O<sub>3</sub>), an important n-type semiconductor with a direct band gap of 3.55–3.75 eV, has been reported as the best potential gas sensing material due to its good conductivity and high stability.<sup>7–10</sup> Furthermore, In<sub>2</sub>O<sub>3</sub> has been produced in different forms of nanostructures, such as nanowires, nanospheres, nanorods, nanoporous and nanofibers, showing interesting gas sensing capabilities for various gases including nitric oxide,<sup>11</sup> methane,<sup>12</sup> ammonia,<sup>13</sup> acetone<sup>14</sup> and ethanol.<sup>15</sup>

More recently, numerous studies have demonstrated that the gas sensing properties of MOS materials are not only highly dependent on the morphology, surface to volume ratio, crystalline size, exposed surface, etc.<sup>16–18</sup> but also related to the further functionalization with other metals, graphene and so on.<sup>19–21</sup> In particular, many researchers have reported that the introducing of dopant element into In<sub>2</sub>O<sub>3</sub> sensing materials

may causes the change of crystalline structure and grain size as well as impurity levels and surface defects, which can significantly improve the gas sensing performances of In<sub>2</sub>O<sub>3</sub> gas sensors.<sup>22–24</sup> For example, Han *et al.* reported that Ce-doped In<sub>2</sub>O<sub>3</sub> gas sensors exhibited a response of 35.2 towards 100 ppm methanol, which is about 2.2 times as high as the pure In<sub>2</sub>O<sub>3</sub> gas sensor.<sup>25</sup> Zheng *et al.* have demonstrated that the response of Pt nanoparticles decorated In<sub>2</sub>O<sub>3</sub> nanofibers can reach to 1490 under 600 ppm H<sub>2</sub>S atmospheres, which is about 10 times higher than that of the pure one.<sup>26</sup> By electrospinning and subsequent calcination, Chi *et al.* have fabricated Fe<sub>2</sub>O<sub>3</sub>–In<sub>2</sub>O<sub>3</sub> nanotubes with a response of 33 to 100 ppm formaldehyde, and the obtained response is about double of the pure In<sub>2</sub>O<sub>3</sub> nanotubes.<sup>27</sup> Up to now, although considerable efforts have been focused on the study of the influence of doping unique elements to the sensing performances, to the best of our knowledge, studies of MoO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> hierarchical microstructures optimized the doping content have rarely been reported.

Herein, we report a facile method for the preparation of MoO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> flower-like hierarchical microstructures by a simple hydrothermal method. The morphology, crystalline structures, and compositions of the samples were characterized using different techniques. The gas sensing performances of pure and Mo-loaded In<sub>2</sub>O<sub>3</sub> microstructures to ethanol were investigated under different working temperatures. The results indicate that the introducing of Mo element can significantly improve the gas sensing properties of In<sub>2</sub>O<sub>3</sub>-based sensors, which can be explained by considering the change of the band structures of the samples.

<sup>a</sup>Micro and Nano System Research Center, Key Lab of Advanced Transducers and Intelligent Control System (Ministry of Education), College of Information Engineering, Taiyuan University of Technology, Taiyuan 030024, Shanxi, China. E-mail: hujie@tyut.edu.cn

<sup>b</sup>Research Center on Advanced Materials Science and Technology, Taiyuan University of Technology, Taiyuan 030024, Shanxi, China. E-mail: chenlin01@tyut.edu.cn

<sup>c</sup>Ecole Normale Supérieure, CNRS-ENS-UPMC UMR 8640, Paris 75005, France

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ra02593a

## 2. Materials and methods

### 2.1 Materials

Indium chloride tetrahydrate ( $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ ,  $\geq 97\%$ ) and ammonium molybdate tetrahydrate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ,  $\geq 99.98\%$ ) were obtained from Sigma-Aldrich (Shanghai, China). Sodium dodecyl sulfate ( $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ , SDS,  $\geq 99\%$ ) and urea ( $\text{CO}(\text{NH}_2)_2$ ,  $\geq 99\%$ ) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. The other chemical reagents were used analytical grade without any further purification.

### 2.2 Preparation of flower-like Mo-loaded $\text{In}_2\text{O}_3$ microstructure

In a typical process, 1.2 mmol of  $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ , 3.6 mmol of SDS and 6 mmol of urea were dissolved into 72 mL of deionized (DI) water. After that, different amounts of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (0, 1, 3 and 5 mol%) were added into the mixed solution with vigorous stirring for 30 min at room temperature. Then, the obtained solution was transferred into a 72 mL Teflon-lined stainless steel autoclave, sealed tightly, maintained at  $120^\circ\text{C}$  for 12 h. After cooled to room temperature naturally, the precipitates were collected by centrifugation and then washed with DI water and ethanol for several times. The fine powders were obtained after dried at  $80^\circ\text{C}$  for 24 h in oven. Finally, the samples were calcined in a muffle furnace at  $600^\circ\text{C}$  for 3 h, and the calcined products were then collected for further analyses. For convenience, the molar ratio of Mo/In (0, 1, 3 and 5 mol%) were defined as  $\text{Mo}_0\text{In}$ ,  $\text{Mo}_1\text{In}$ ,  $\text{Mo}_3\text{In}$  and  $\text{Mo}_5\text{In}$ , respectively.

### 2.3 Characterization

The crystal phase and crystallinity of as-synthesized products were analyzed by X-ray diffraction (XRD, Haoyuan, China) with  $\text{Cu K}\alpha_1$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the range of  $20\text{--}80^\circ$ . The morphology and structure of Mo-loaded  $\text{In}_2\text{O}_3$  were observed by using scanning electron microscope (SEM, JSM-7001F, Japan) and transmission electron microscopic (TEM, JEOL-2010F, Japan) at an accelerating voltage of 10 kV and 200 kV, respectively. The element compositions of the samples were characterized by the energy dispersive X-ray spectroscopy (EDS, Bruker) and the chemical state was investigated by X-ray photoelectron spectroscopy (XPS, Thermo Electron, U.K.) with monochromatic  $\text{Al K}\alpha$  (1486.6 eV) irradiation.

### 2.4 Fabrication and measurement of gas sensor

The fabrication process of Mo-loaded  $\text{In}_2\text{O}_3$  gas sensors can be described as follows. The obtained powders were firstly mixed with terpineol and ethyl cellulose (weight ratio 2 : 8 : 1) to form symmetrical slurry. Then, the slurry was carefully coated on the surface of alumina ceramic tube as sensing film with a pair of Au electrodes and Pt wires (Fig. 1(a)). Subsequently, the sensing element was dried at  $80^\circ\text{C}$  for 10 h in air and annealed at  $600^\circ\text{C}$  for 2 h to improve the mechanical strength. After that, a small Ni-Cr wire ( $\sim 45 \Omega$ ) was inserted into the alumina tube as heater to control the operating temperature of the sensor. After soldered on the pedestal (Fig. 1(b)), the gas sensor was aged at

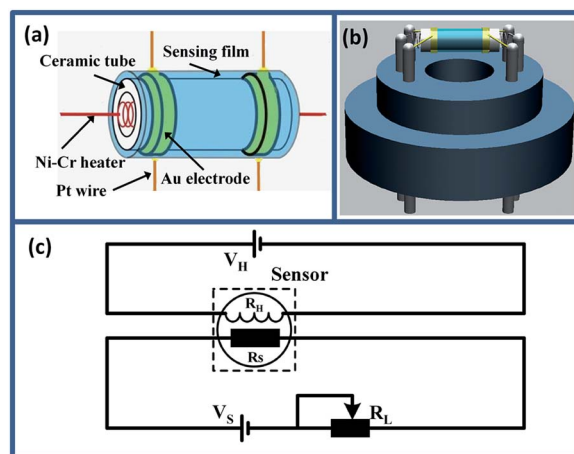


Fig. 1 (a) Schematic illustration of gas sensing element. (b) The 3D schematic diagram of gas sensor. (c) The working principle of the electrical circuit for measuring the as-prepared gas sensors.

5 V for 3 days in air to improve the long-term stability and repeatability.

The gas sensing properties of as-prepared sensors were measured using CGS-1TP intelligent analysis system (Elite, Beijing, China), and all the measures were performed under the controlled relative humidity (RH)  $30\% \pm 5\%$ . Fig. 1(c) shows the schematic diagram of the electrical circuit for measuring the pure and Mo-loaded  $\text{In}_2\text{O}_3$  gas sensors. In the measuring electric circuit of gas sensor, the heating voltage ( $V_H$ ) is used to control the working temperature by heating the Ni-Cr wire. The load resistor ( $R_L$ ) is connected in series with the as-fabricated gas sensor. The circuit voltage  $V_S$  is 5 V, and the output voltage ( $V_{\text{out}}$ ) is the terminal voltage of the load resistor  $R_L$ . During the gas sensing experiments, the gas sensors were placed into the testing chamber (18 L), and the target gas was injected into the chamber using microsyringe. The response was defined as the ratio of the resistance in air to the resistance in target gas ( $R_a/R_g$ ). The response and recovery time was expressed as the time taken for the sensor to reach 90% of the total resistance change in the case of adsorption and desorption, respectively.

## 3. Results and discussion

### 3.1 Morphology and structure analysis

Fig. 2(a) depicts the XRD pattern of Mo-loaded  $\text{In}_2\text{O}_3$  microstructures with different concentrations of Mo after calcination. The measured results show that all the diffraction peaks are matched well with  $\text{In}_2\text{O}_3$  (JCPDS File no. 06-0416), and no other characteristic peaks can be found in the spectrum of samples, which indicates the high purity of the final products. Meanwhile, there is also no apparent peak of Mo can be detected, which is possibly due to the low concentration of Mo in the sample. Fig. 2(b) exhibits the magnified image of the peak (440) for as-synthesized  $\text{In}_2\text{O}_3$  microstructures. It can be found that all the diffraction peaks are slightly shift to a higher angle, which might be due to lattice strain by the formation of  $\text{Mo}^{6+}$



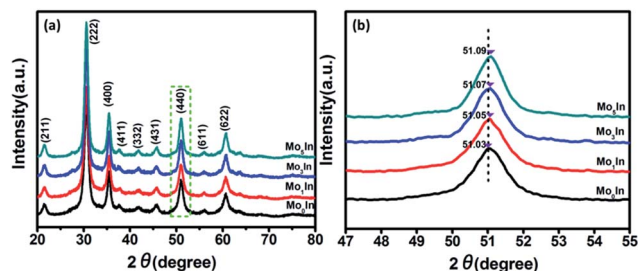


Fig. 2 (a) X-ray diffraction patterns of as-synthesized microstructures. (b) High magnification of the (440) peaks.

ions (the ionic radius of  $\text{Mo}^{6+}$  (0.59 Å) is smaller than that of  $\text{In}^{3+}$  (0.8 Å) in the loaded  $\text{In}_2\text{O}_3$  microstructures).<sup>28</sup> The similar results have been reported in previous works.<sup>29–31</sup> In addition, Fig. S1 (ESI S1†) illustrates the XRD patterns of as-synthesized samples before calcination, and the results indicate that the pure and Mo-loaded  $\text{In}_2\text{O}_3$  samples can be obtained after calcination in a muffle furnace at 600 °C in air atmosphere.

The morphological characteristics of the as-synthesized hierarchical flower-like samples were observed by SEM. Fig. 3(a) shows the SEM image of flower-like  $\text{In}_2\text{O}_3$  microstructures, and the average diameter of microspheres is about 4 μm assembled with numerous nanosheets. Fig. 3(c) and (d) exhibits the SEM image of 3 mol% Mo-doped  $\text{In}_2\text{O}_3$  samples, and the thickness of the nanosheet is only 25 nm from the inset image (Fig. 3(d)). It seems that the introduction of Mo element has no obvious influence on the morphology of samples, as shown in Fig. S2 (ESI S2†). Meanwhile, in order to investigate the composition, the EDS was performed on the sample of  $\text{Mo}_3\text{In}$ , and the measured peaks of In, O and Mo are all corresponding well with the standard spectrum diagram, which confirms the existence of Mo element in sample. Moreover, the 3 mol% Mo-loaded  $\text{In}_2\text{O}_3$  sample was further confirmed using the elemental mapping. From the Fig. 3(f)–(i), we can found that the spatial distribution of the In, O and Mo elements exhibits spherical microstructure, which indicates the uniform distributions of Mo element on the sample.

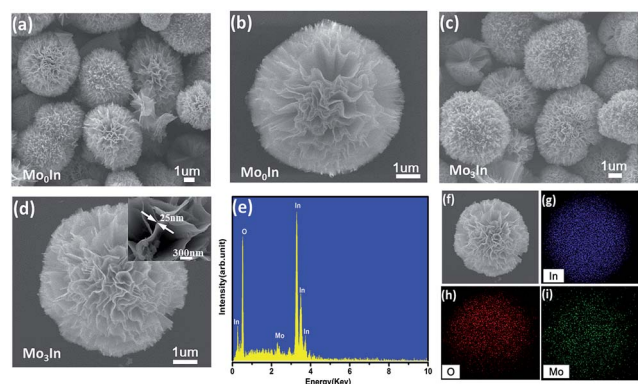


Fig. 3 SEM images of as-synthesized flower-like hierarchical microstructures, (a and b)  $\text{Mo}_0\text{In}$ , (c and d)  $\text{Mo}_3\text{In}$ . (e) EDS spectrum of  $\text{Mo}_3\text{In}$ . (f–i) Elemental mapping images of In, O and Mo element, respectively.

To further investigate the structural features of Mo-loaded  $\text{In}_2\text{O}_3$  microstructures, TEM and HRTEM combined with the selected area electron diffraction (SAED) techniques were conducted on the sample of  $\text{Mo}_3\text{In}$ . Fig. 4(a) shows the low magnification image of nanosheet, and the lattice fringes can be clearly observed in the high magnification image as Fig. 4(b). The lattice plane spacing was calculated with a periodic value of 0.253 nm and 0.292 nm corresponding to the (400) and (222) plane of  $\text{In}_2\text{O}_3$  (Fig. 4(c) and (d)), respectively. Fig. 4(e) illustrates the corresponding SAED pattern of sample. The diffraction circles can be indexed to the (211), (400), (422), (440) and (622) planes of the flower-like  $\text{In}_2\text{O}_3$  microstructure, which indicates the as-synthesized  $\text{In}_2\text{O}_3$  microstructures is polycrystalline. However, it seems that there is no diffraction circle of Mo element, which is possibly due to the low concentration of Mo element in the sample.

In order to determine the surface elements and chemical states of Mo-loaded  $\text{In}_2\text{O}_3$  sample, the XPS measurements were performed on the  $\text{Mo}_3\text{In}$  microstructures. The XPS spectra were calibrated with respect to the binding energy of the C 1s peak at 284.6 eV and deconvolution with the Casa XPS software. Fig. 5(a) illustrates XPS survey spectra of  $\text{Mo}_3\text{In}$  microstructures, the elements of In, N, O and Mo can be clearly detected in the sample. Fig. 5(b) exhibits the high resolution XPS spectrum of In 3d state, which indicates the peaks located at 443.78 eV and 451.38 eV correspond to the In 3d<sub>5/2</sub> and In 3d<sub>3/2</sub>, respectively. The peak separation between In 3d<sub>5/2</sub> and In 3d<sub>3/2</sub> is 7.6 eV, which suggests that In element exists principally in the form of  $\text{In}^{3+}$  in sample. From the XPS spectra of O 1s in Fig. 5(c), two peaks centered at 529.28 eV and 530.98 eV can be observed in the sample. The peak located at 529.28 eV can be assigned to the lattice oxygen in the as-synthesized product structure embraced by indium and molybdenum, and the peak at 530.98 eV can be ascribed to the oxygen defects in the metal oxide regions.<sup>32,33</sup> The Mo 3d spectra (Fig. 5(d)) shows two peaks of the binding energy at 232.63 eV and 235.78 eV, which is associated with the Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub> on the surface of sample, separately.<sup>34,35</sup> Meanwhile, the crystal phase of  $\text{MoO}_3$  can be further confirmed

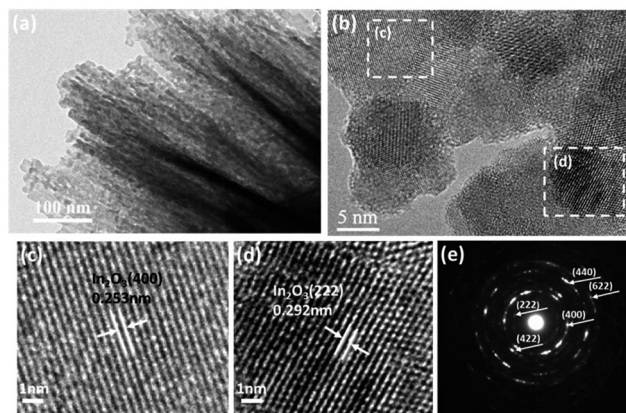


Fig. 4 (a) TEM image of  $\text{Mo}_3\text{In}$  nanosheets. (b) HRTEM image of  $\text{Mo}_3\text{In}$ . (c and d) The enlarged HRTEM images of the marked areas, and (e) the corresponding SAED pattern.





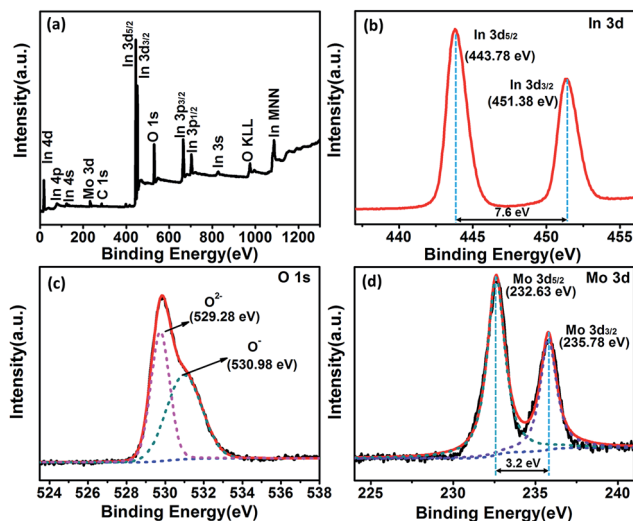


Fig. 5 XPS spectra of the as-synthesized  $\text{Mo}_3\text{In}$ . (a) Full survey scan spectrum, (b) In 3d, (c) O 1s and (d) Mo 3d, respectively.

on account of the two peaks separation of 3.2 eV, and it indicates the successful introduction of  $\text{MoO}_3$  in the sample, which consists well with the results of XRD and the elemental mapping of EDS.

### 3.2 Gas sensing performance

As we all know, the operating temperature is most important parameter for a metal oxide semiconductor gas sensor, and the gas response is highly influenced by the working temperature. In order to determine the optimum operating temperature of as-prepared gas sensors, the responses of gas sensors were measured under different operating temperatures varying from 110 °C to 285 °C. As shown in Fig. 6, it can be clearly observed that the responses of all the gas sensors initially increase with temperature rising and reaching the maximum at 185 °C, and then decrease with further increasing of the operating temperature. Therefore, the optimum working temperature is chosen

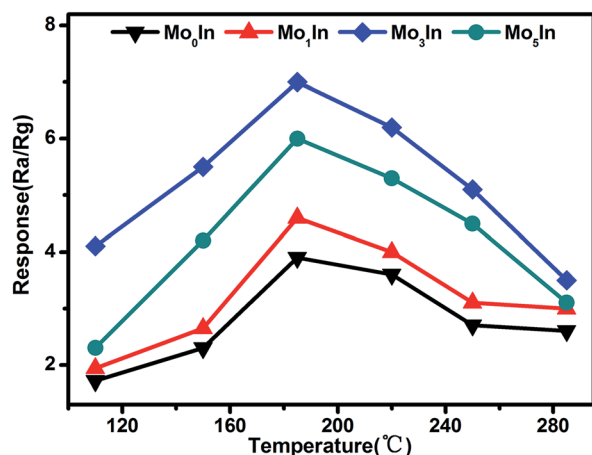


Fig. 6 Response of as-prepared gas sensors upon exposure to 100 ppm ethanol at different working temperatures.

as 185 °C, which is applied in all the following investigation of gas sensing performance. For the 'increase–maximum–decrease' tendency of gas response, which could be attributed to the reason as following: when the operating temperature is too low, the absorbed ethanol molecules can't be activated enough to overcome the activation energy barrier to react with the absorbed oxygen species. However, when the operating temperature enhances too much, some absorbed oxygen species maybe escape away before the reaction.<sup>36,37</sup> Meanwhile, the measured results also demonstrate that Mo-loaded  $\text{In}_2\text{O}_3$  gas sensors exhibit significant enhanced gas response than pure one, which could be ascribed to the introduction of Mo element. Moreover, the  $\text{Mo}_3\text{In}$  gas sensor shows the highest gas response, which is about two times higher than that of pure one. The measured results prove that appropriate  $\text{MoO}_3$  loading can significantly improve the gas sensing performances of  $\text{In}_2\text{O}_3$  gas sensors, which was demonstrated in our experimental results. However, excessive amount of  $\text{MoO}_3$  in the samples will reduce the amount of oxygen adsorption and reactive sites, which will suppress the gas sensing properties of gas sensors.<sup>38</sup>

At the same time, the reversibility of Mo-loaded  $\text{In}_2\text{O}_3$  gas sensors were also investigated under different operating temperatures, Fig. 7 shows the corresponding resistance curves of sensors to 100 ppm ethanol under different operating temperatures. The results show that the resistance values of all the as-prepared gas sensors decrease sharply after exposure to ethanol gas, and recovery to the initial value when exposed in fresh air, which exhibit excellent reversibility. Fig. S3 (ESI S3†)

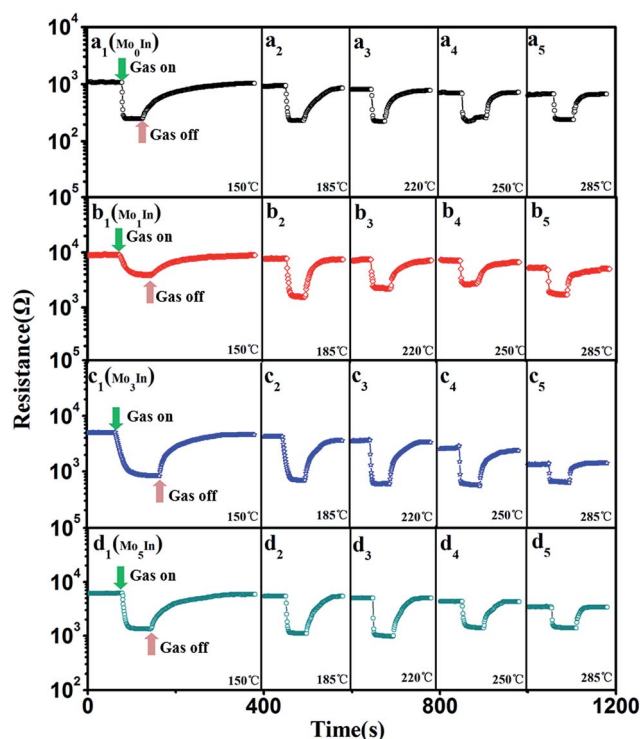


Fig. 7 Resistance of as-prepared  $\text{In}_2\text{O}_3$  gas sensors to 100 ppm ethanol under different operating temperatures, (a)  $\text{Mo}_0\text{In}$ , (b)  $\text{Mo}_1\text{In}$ , (c)  $\text{Mo}_3\text{In}$ , (d)  $\text{Mo}_5\text{In}$ .

presents the detailed initial resistance of as-prepared gas sensors under different operating temperature. It is worth noting that the resistance of gas sensors decreased with the increasing of the operating temperature, and the  $\text{Mo}_1\text{In}$  gas sensor exhibits the highest resistance than other sensors under different operating temperature.

The response and recovery time are also important sensing characteristics of a gas sensor. Fig. 8(a) illustrates the response/recovery curves of as-prepared  $\text{In}_2\text{O}_3$  gas sensors to 100 ppm ethanol vapor at 185 °C. It can be clearly observed that the response of gas sensor increases fast and reach to the stable value when exposed to ethanol. However, after the pumping ethanol gas away, the sensor response slowly returned to its initial value. At optimized operating temperature (185 °C), the measured response and recovery time for  $\text{Mo}_3\text{In}$  sensor is about 11 s and 94 s, respectively. Fig. 8(b) displays the detailed information of response and recovery times for the as-prepared  $\text{In}_2\text{O}_3$  gas sensors. From the measured curves, it can be clearly observed that the response time is ranged from 9 s to 12 s for 100 ppm ethanol vapor, whereas the recovery time varied from 68 s to 94 s. The results demonstrate that the response time is much shorter than the recovery time for all the gas sensors. Meanwhile, the response and recovery values as a function of operating temperature to 100 ppm ethanol for all the gas sensors are shown in Fig. S4 (ESI S4†). Compared with the lower temperature, we can find that all the as-fabricated  $\text{In}_2\text{O}_3$  gas sensors exhibit faster response and recovery times at higher temperature.

To further evaluate the gas sensing properties of as-prepared sensors, the dynamic response transient characteristics were conducted on  $\text{In}_2\text{O}_3$  gas sensors under different concentrations of ethanol (1–800 ppm) at 185 °C, as shown in Fig. 9(a). When exposed to ethanol, the responses of all the gas sensors increase fast with the increasing concentration of ethanol. Meanwhile, it is noteworthy that the  $\text{Mo}_3\text{In}$  gas sensor exhibits the highest response compared with others gas sensors, which indicates the enhanced gas sensing properties. Fig. 9(b) illustrates the response plots of  $\text{In}_2\text{O}_3$  gas sensors *versus* ethanol concentration in the range of 1–800 ppm at optimum working temperature. It is obvious that the response values of gas sensors grow with the increasing concentration of ethanol (1–200 ppm). However, the responses of gas sensors exhibit the tendency of plateau as further increase the concentration of ethanol vapour. This phenomenon can be explained as follows: with the

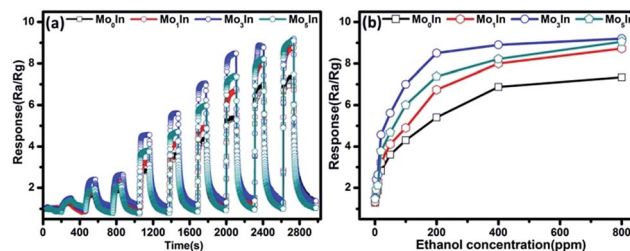


Fig. 9 (a) Dynamic response transient of the gas sensor to different concentrations of ethanol at 185 °C. (b) Responses *versus* ethanol concentration for  $\text{In}_2\text{O}_3$  gas sensors at 185 °C.

increasing concentration of ethanol, the response of gas sensor was determined by the surface reaction rate. Because there are insufficient adsorption sites, the response easily presents the status of saturation, and the similar results have been reported in previous literatures.<sup>22,38</sup> Fig. S5 (ESI S5†) displays the real time resistance curves of as-prepared sensors toward different concentrations of ethanol vapour (1–800 ppm). It can be clearly observed that the resistance of the pure and Mo-loaded  $\text{In}_2\text{O}_3$  gas sensors drastically decreased upon exposure to ethanol vapour and rapidly increased when the gas was removed. Furthermore, the resistance of  $\text{Mo}_3\text{In}$  gas sensor can return to its original value after a response and recovery cycle comparing with  $\text{Mo}_0\text{In}$  sensor, which indicates the good stability of  $\text{Mo}_3\text{In}$  sensor.

In order to assess the detection limit, the gas sensing experiments were conducted on the as-fabricated gas sensors to low concentrations (50–500 ppb) of ethanol vapour under the optimum operating temperature. Fig. 10 depicts the transient response of gas sensors sequentially exposed to 50 ppb, 100 ppb, 200 ppb, 300 ppb, 400 ppb and 500 ppb ethanol at 185 °C, respectively. The measured responses of all the gas sensors show an obvious increase with the increasing concentration of

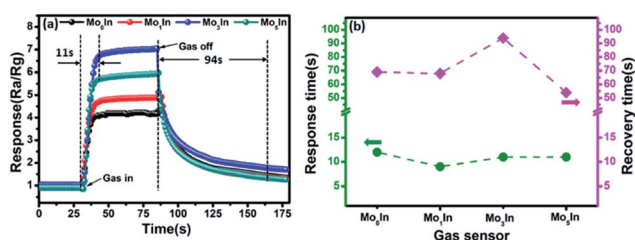


Fig. 8 (a) Dynamic response–recovery behavior of  $\text{In}_2\text{O}_3$  gas sensors toward 100 ppm ethanol at 185 °C, (b) response/recovery time of  $\text{In}_2\text{O}_3$  gas sensors to 100 ppm ethanol at 185 °C.

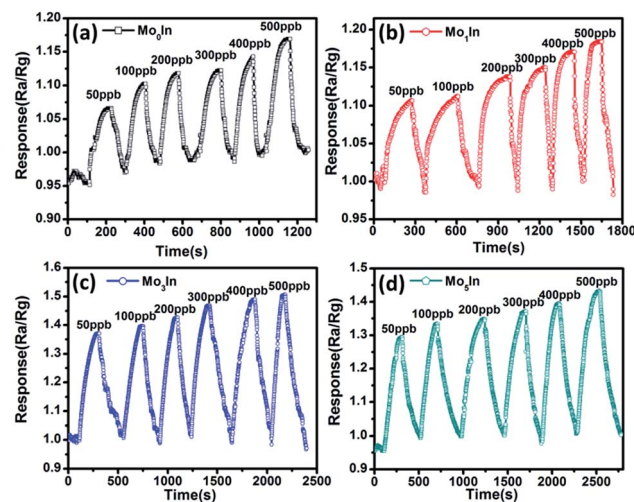


Fig. 10 Dynamic response curves of as-prepared gas sensors to low concentrations of ethanol (50–500 ppb) at 185 °C, (a)  $\text{Mo}_0\text{In}$ , (b)  $\text{Mo}_1\text{In}$ , (c)  $\text{Mo}_2\text{In}$ , (d)  $\text{Mo}_3\text{In}$ .



ethanol. Meanwhile, Fig. S6 (ESI S6†) illustrates the response curves of gas sensors to low concentrations of ethanol, and the measured results demonstrate that the introduction of Mo element can significantly improve the gas sensing performance. Especially, the Mo<sub>3</sub>In sensor exhibits the highest gas response, and the measured response can reach to 1.5 even for 500 ppb ethanol. In addition, the obtained detection limit of Mo<sub>3</sub>In sensor can down to 50 ppb, which indicates that the as-prepared Mo<sub>3</sub>In gas sensor has a potential for lower concentration of ethanol detection.

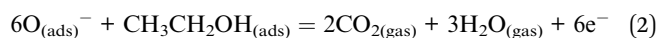
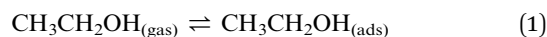
The selectivity is another key parameter for gas sensor, which is also crucial for practical application. Fig. 11(a) displays the responses of pure and Mo-loaded In<sub>2</sub>O<sub>3</sub> gas sensors to various gases under the concentration of 100 ppm at 185 °C including ethanol, methanol, methane, carbon monoxide and hydrogen. It is noted that the as-prepared In<sub>2</sub>O<sub>3</sub> gas sensors exhibit higher responses to ethanol compared with other testing gases. Meanwhile, the measured response of Mo-loaded In<sub>2</sub>O<sub>3</sub> gas sensors to ethanol are significantly larger than that of pure In<sub>2</sub>O<sub>3</sub> gas sensor, which prove the gas sensing performances of In<sub>2</sub>O<sub>3</sub> has been effectively enhanced by Mo loading.

For practical applications, gas sensors not only need to present high response and good selectivity to the target gases, but also ensure excellent their long-term reliability. Therefore, the long-term stability experiments were conducted on the as-fabricated In<sub>2</sub>O<sub>3</sub> gas sensors toward 100 ppm of ethanol over a total period of 90 days, as shown in Fig. 11(b). It is clearly shown that the maximal deviations of the responses for all the In<sub>2</sub>O<sub>3</sub> gas sensors are less than 10% toward ethanol, which exhibit the excellent stability of sensors.

### 3.3 Gas-sensing mechanism

It is well known that In<sub>2</sub>O<sub>3</sub> is an n-type semiconducting chemiresistive oxide sensor material. The gas sensing mechanism for the In<sub>2</sub>O<sub>3</sub> gas sensor was explained on the basis of an interaction mechanism for the adsorption of ethanol onto In<sub>2</sub>O<sub>3</sub> microstructures. As an electron donor, In<sub>2</sub>O<sub>3</sub> can provide electrons because of the existence of oxygen vacancy (V<sub>O</sub>) in the gas sensing material.<sup>39–41</sup> When In<sub>2</sub>O<sub>3</sub> gas sensor exposed to fresh air, the oxygen molecules in air will be adsorbed on the surface of In<sub>2</sub>O<sub>3</sub> through capturing free electrons from conduction band and form reactive oxygen species such as O<sup>2−</sup>, O<sub>2</sub><sup>−</sup> and O<sup>−</sup>,

leading to the creation of a depletion region and the increase of the resistance.<sup>21,22,26</sup> When exposed to reducing gas like ethanol in this work, the ethanol gas molecules react with the reactive oxygen ions as the following reactions:<sup>15,42</sup>



As shown in the reactions (1) and (2), the trapped electrons are released back to the conduction band of the In<sub>2</sub>O<sub>3</sub>. This reaction causes the resistance of the In<sub>2</sub>O<sub>3</sub> gas sensor decrease and induces the gas sensing.

For the Mo-loaded In<sub>2</sub>O<sub>3</sub> microstructures (Fig. 12(a)), the enhancement of gas response can be attributed to the reasons as follows: on the one hand, there is a synergetic effect on gas target due to that both In<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub> are n-type semiconducting metal oxide materials, and this effect has also been found in other composites.<sup>43,44</sup> Fig. 12(b) and (c) illustrates the partial enlarged section of the MoO<sub>3</sub>–In<sub>2</sub>O<sub>3</sub> junction after exposure to fresh air and ethanol, respectively. It is clearly seen that the reactions happened at the section of MoO<sub>3</sub> are the same as what on the surface of In<sub>2</sub>O<sub>3</sub>, which have a positive effect for the response of gas sensor. On the other hand, the improvement of gas response can be ascribed to the formation of n–n homotype heterojunction structure between In<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub>.<sup>45–47</sup> As show in Fig. 12(d) and (e), the band gap of In<sub>2</sub>O<sub>3</sub> ( $E_g = 3.75$  eV) is higher than that of MoO<sub>3</sub> ( $E_g = 3.15$  eV), and electrons are transported from MoO<sub>3</sub> to In<sub>2</sub>O<sub>3</sub>, leading to the formation of an accumulation layer and a depletion layer at the interface of In<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub>, respectively. The subsequent oxygen adsorption makes the accumulation layer depleted in air, resulting in a further increase of resistance. Compared with pure In<sub>2</sub>O<sub>3</sub> gas sensor, the larger change of resistance for MoO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> composite material can be measured upon exposure to fresh air and ethanol, which results in the improvement of the sensing properties.

Furthermore, the high selectivity of gas sensor to ethanol could be explained in the following reasons: for one thing, the

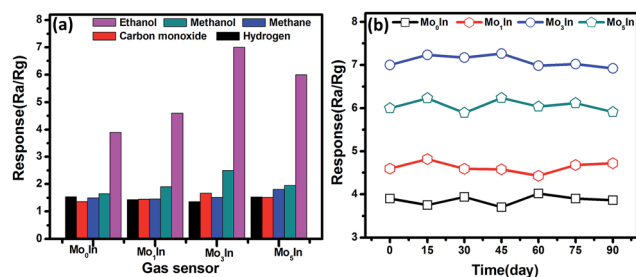


Fig. 11 (a) Response of as-prepared In<sub>2</sub>O<sub>3</sub> gas sensors to 100 ppm various gases at 185 °C. (b) The long term stability of In<sub>2</sub>O<sub>3</sub> gas sensors to 100 ppm ethanol.

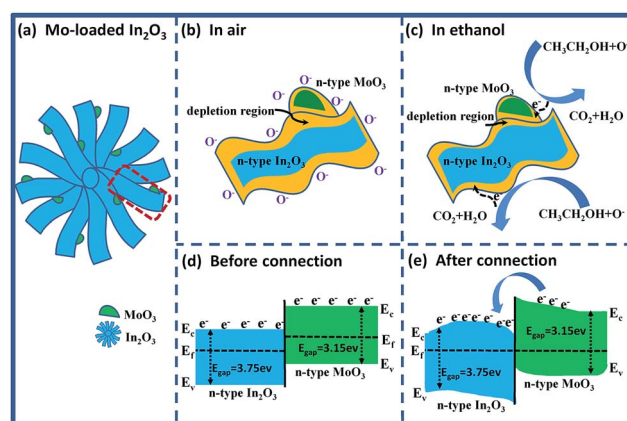
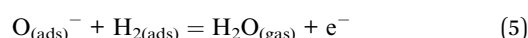
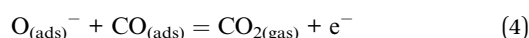
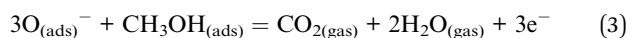


Fig. 12 (a) Schematic diagram of Mo-loaded In<sub>2</sub>O<sub>3</sub> microstructures, (b and c) Mo-loaded In<sub>2</sub>O<sub>3</sub> microstructures exposed in air and ethanol, (d and e) energy band of Mo-loaded In<sub>2</sub>O<sub>3</sub> microstructures before and after connection, respectively.





stability of compound is greatly affected by the bond energy. The higher the bond energy, the harder the bond breaks. It is well known that the bond strengths of C-H, C-C, C=O, H-H and O-H are 411, 345, 748.2, 436, 462 kJ mol<sup>-1</sup>, respectively,<sup>48</sup> which indicates that the ethanol is relatively unstable due to the lowest bond energy of C-C in ethanol. Compared with these detected gases (methanol, methane, carbon monoxide, hydrogen), the higher reducing ability of ethanol results in the significant response. For another thing, many previous works have been reported that the gas sensing response of basic oxides was improved in terms of the reactive functional group or the complex molecular structure such as ethanol.<sup>49,50</sup> An electron-liberate theory was used to elucidate the experimental results (for instance, methanol, hydrogen and carbon monoxide). The reactions can be expressed as follows:<sup>51,52</sup>



Form the reactions (2)–(5), it is clearly seen that the ethanol gas can release more electrons under the same concentration comparing with other gases, which could be the other way to explain the better selectivity to ethanol.

## 4. Conclusions

Flower-like MoO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> microstructures with different contents of Mo element were synthesized by hydrothermal method. Characterization results showed that the obtained flower-like microstructure were about 4 μm in size and composed of numerous nanosheets. Comparing with pure In<sub>2</sub>O<sub>3</sub> gas sensor, the Mo-loaded In<sub>2</sub>O<sub>3</sub> gas sensors exhibits better gas sensing performance for ethanol detection, including high response, fast response and recovery time, low detection limit, good selectivity and stability. This improvement could be attributed to synergetic effect as well as the n–n homotype heterojunction structure between In<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub>, which provide sufficient active surfaces. However, excessive amount of MoO<sub>3</sub> in the samples will suppress the detection sensibility of In<sub>2</sub>O<sub>3</sub>. In particular, optimization of the Mo content in the In<sub>2</sub>O<sub>3</sub> hierarchical microstructures has proved that the optimum Mo load should be about 3 mol% ensuring the best gas sensing properties of the ethanol sensor.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (51205274), Higher school science and technology innovation project of Shanxi (2016137), Natural Science of Shanxi Province (2016011039), Talent project of Shanxi Province (201605D211036), Science and Technology Major Project of the Shan Xi Science and Technology Department (20121101004), Key Disciplines Construction in Colleges and Universities of Shanxi ([2012]45).

## Notes and references

- H. J. Zhang, R. F. Wu, Z. W. Chen, G. Liu, Z. N. Zhang and Z. Jiao, *CrystEngComm*, 2012, **14**, 1775–1782.
- F. Song, H. L. Su, J. J. Chen, W. J. Moon, W. M. Lau and D. Zhang, *J. Mater. Chem.*, 2012, **22**, 1121–1126.
- L. L. Liu, S. C. Li, X. Guo, L. Y. Wang, L. Liu and X. S. Wang, *J. Mater. Sci.: Mater. Electron.*, 2016, **27**, 5153–5157.
- X. Q. An, J. C. Yu, Y. Wang, Y. M. Hu, X. L. Yu and G. J. Zhang, *J. Mater. Chem.*, 2012, **22**, 8525–8531.
- H. Liu, X. W. Du, X. R. Xing, G. X. Wang and S. Z. Qiao, *Chem. Commun.*, 2012, **48**, 865–867.
- A. Aslani and V. Oroojpour, *Phys. B*, 2011, **406**, 144–149.
- C. H. Feng, W. Li, C. Li, L. H. Zhu, H. F. Zhang, Y. Zhang, S. P. Ruan, W. Y. Chen and L. X. Yu, *Sens. Actuators, B*, 2012, **166**, 83–88.
- X. M. Zou, J. L. Wang, X. Q. Liu, C. L. Wang, Y. Jiang, Y. Wang, X. H. Xiao, J. C. Ho, J. C. Li, C. Z. Jiang, Y. Fang, W. Liu and L. Liao, *Nano Lett.*, 2013, **13**, 3287–3292.
- H. X. Yang, L. Liu, H. Liang, J. J. Wei and Y. Z. Yang, *CrystEngComm*, 2011, **13**, 5011–5016.
- H. Zhao, H. X. Dong, L. N. Zhang, X. W. Wang and H. Q. Yang, *Mater. Chem. Phys.*, 2011, **130**, 921–931.
- C. S. Rout, K. Ganesh, A. Govindaraj and C. N. R. Rao, *Appl. Phys. A*, 2006, **85**, 241–246.
- Y. Cao, J. Zhao, X. X. Zou, P. P. Jin, H. Chen, R. Q. Gao, L. J. Zhou, Y. C. Zou and G. D. Li, *RSC Adv.*, 2015, **5**, 5424–5431.
- S. Elouali, L. G. Bloor, R. Binions, I. P. Parkin, C. J. Carmalt and J. A. Darr, *Langmuir*, 2012, **28**, 1879–1885.
- X. H. Sun, H. M. Ji, X. L. Li, S. Cai and C. M. Zheng, *Mater. Lett.*, 2014, **120**, 287–291.
- S. An, S. Park, H. Ko, C. Jin, W. I. Lee and C. Lee, *J. Phys. Chem. Solids*, 2013, **74**, 979–984.
- M. Hashimoto, S. Ujiiie and A. Mori, *Adv. Mater.*, 2003, **15**, 797–800.
- Y. F. Hao, G. W. Meng, C. H. Ye and L. D. Zhang, *Cryst. Growth Des.*, 2005, **5**, 1617–1621.
- T. Gao and T. H. Wang, *J. Cryst. Growth*, 2006, **290**, 660–664.
- Y. J. Sun, Z. T. Zhao, P. W. Li, G. Li, Y. Chen, W. D. Zhang and J. Hu, *Appl. Surf. Sci.*, 2015, **356**, 73–80.
- W. Yang, P. Wan, X. D. Zhou, J. M. Hu, Y. F. Guan and L. Feng, *ACS Appl. Mater. Interfaces*, 2014, **6**, 21093–21100.
- X. W. Li, J. Y. Liu, H. Guo, X. Zhou, C. Wang, P. Sun, X. L. Hu and G. Y. Lu, *RSC Adv.*, 2015, **5**, 545–551.
- X. P. Shen, L. J. Guo, G. X. Zhu, C. Y. Xi, Z. Y. Ji and H. Zhou, *RSC Adv.*, 2015, **5**, 64228–64234.
- X. Y. Lai, P. Li, T. L. Yang, J. C. Tu and P. Xue, *Scr. Mater.*, 2012, **67**, 293–296.
- W. W. Chen, Y. K. Liu, Z. J. Qin, Y. M. Wu, S. H. Li and P. Ai, *Sensors*, 2015, **15**, 29950–29957.
- D. Han, P. Song, S. Zhang, H. H. Zhang, Q. Xu and Q. Wang, *Sens. Actuators, B*, 2015, **216**, 488–496.
- W. Zheng, X. F. Lu, W. Wang, Z. Y. Li, H. N. Zhang, Z. J. Wang, X. R. Xu, S. Y. Li and C. Wang, *J. Colloid Interface Sci.*, 2009, **338**, 366–370.



- 27 X. Chi, C. B. Liu, L. Liu, S. C. Li, H. Y. Li, X. B. Zhang, X. Q. Bo and H. Shan, *Mater. Sci. Semicond. Process.*, 2014, **18**, 160–164.
- 28 S. S. Farvid, M. Hegde and P. V. Radovanovic, *Chem. Mater.*, 2013, **25**, 233–244.
- 29 J. Hu, F. Q. Gao, Z. T. Zhao, S. B. Sang, P. W. Li, W. D. Zhang, X. T. Zhou and Y. Chen, *Appl. Surf. Sci.*, 2016, **363**, 181–188.
- 30 S. S. Yi, J. B. Cui, S. Li, L. J. Zhang, D. J. Wang and Y. H. Lin, *Appl. Surf. Sci.*, 2014, **319**, 230–236.
- 31 N. R. Yogamalar and A. C. Bose, *J. Alloys Compd.*, 2011, **509**, 8493–8500.
- 32 A. Gurlo, N. Barsan, U. Weimar, M. Ivanovskaya, A. Taurino and P. Siciliano, *Chem. Mater.*, 2003, **23**, 4377–4383.
- 33 Q. Liu, W. Zhang, R. Liu and G. B. Mao, *Eur. J. Inorg. Chem.*, 2015, **5**, 845–851.
- 34 C. Tao, S. P. Ruan, X. D. Zhang, G. H. Xie, L. Shen, X. Z. Kong, W. Dong, C. X. Liu and W. Y. Chen, *Appl. Phys. Lett.*, 2008, **93**, 193307.
- 35 J. Swiatowska-Mrowiecka, S. de Diesbach, V. Maurice, S. Zanna, L. Klein, E. Briand, I. Vickridge and P. Marcus, *J. Phys. Chem. C*, 2008, **112**, 11050–11058.
- 36 Y. D. Zhang, Z. Zheng and F. L. Yang, *Ind. Eng. Chem. Res.*, 2010, **49**, 3539–3543.
- 37 F. Li, S. J. Guo, J. L. Shen, L. Shen, D. M. Sun, B. Wang, Y. Chen and S. P. Ruan, *Sens. Actuators, B*, 2017, **238**, 364–373.
- 38 C. Q. Ge, C. S. Xie and S. Z. Cai, *Mater. Sci. Eng., B*, 2007, **137**, 53–58.
- 39 C. S. Rout, K. Ganesh, A. Govindaraj and C. N. R. Rao, *Appl. Phys. A*, 2006, **85**, 241–246.
- 40 L. Liao, H. B. Lu, J. C. Li, H. He, D. F. Wang, D. J. Fu and C. Liu, *J. Phys. Chem. C*, 2007, **111**, 1900–1903.
- 41 S. Xu, J. Gao, L. L. Wang, K. Kan, Y. Xie, P. K. Shen, L. Li and K. Y. Shi, *Nanoscale*, 2015, **7**, 14643–14651.
- 42 T. T. Wang, S. Y. Ma, L. Cheng, J. Luo, X. H. Jiang and W. X. Jin, *Sens. Actuators, B*, 2015, **216**, 212–220.
- 43 P. Sun, Y. X. Cai, S. S. Du, X. M. Xu, L. You, J. Ma, F. M. Liu, X. S. Liang, Y. F. Sun and G. Y. Lu, *Sens. Actuators, B*, 2013, **182**, 336–343.
- 44 B. P. J. de Lacy Costello, R. J. Ewen, N. M. Ratcliffe and P. S. Sivanand, *Sens. Actuators, B*, 2003, **92**, 159–166.
- 45 P. Li, H. Q. Fan and Y. Cai, *Sens. Actuators, B*, 2013, **185**, 110–116.
- 46 W. L. Zang, Y. X. Nie, D. Zhu, P. Deng, L. L. Xing and X. Y. Xue, *J. Phys. Chem. C*, 2014, **118**, 9209–9216.
- 47 W. Zeng, T. M. Liu and Z. C. Wang, *Phys. E*, 2010, **43**, 633–638.
- 48 X. F. Chu, S. M. Liang, W. Q. Sun, W. B. Zhang, T. Y. Chen and Q. F. Zhang, *Sens. Actuators, B*, 2010, **148**, 399–403.
- 49 J. Q. Xu, J. J. Han, Y. Zhang, Y. A. Sun and B. Xie, *Sens. Actuators, B*, 2008, **132**, 334–339.
- 50 H. Men, P. Gao, B. B. Zhou, Y. J. Chen, C. L. Zhu, G. Xiao, L. Q. Wang and M. L. Zhang, *Chem. Commun.*, 2010, **46**, 7581–7583.
- 51 P. Song, Q. Wang and Z. X. Yang, *Sens. Actuators, B*, 2011, **156**, 983–989.
- 52 P. Song, H. H. Zhang, D. Han, J. Li, Z. X. Yang and Q. Wang, *Sens. Actuators, B*, 2014, **196**, 140–146.

