Significantly enhanced temperature-dependent selectivity for NO$_2$ and H$_2$S detection based on In$_2$O$_3$ nano-cubes prepared by CTAB assisted solvothermal process

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Abstract

It is a huge challenge to develop a highly precision sensor with good selectivities for two different types of toxic gases. In this work, In$_2$O$_3$ nano-cubes, prepared using a cetyltrimethyl ammonium bromide assisted solvothermal process, were used to make gas sensors for H$_2$S and NO$_2$ detections. The In$_2$O$_3$ nano-cube based sensor exhibited a good temperature-dependent selectivity toward H$_2$S and NO$_2$. At room temperature of 25 $^\circ$C, the sensor exhibited a good selectivity towards H$_2$S with a high response (1461 for 60 ppm H$_2$S), fast response/recovery times (82 s/102 s) and a superior detection limit (0.005 ppm). Whereas at an operation temperature of 100 $^\circ$C, the sensor showed a poor sensitivity to H$_2$S, but an excellent selectivity towards NO$_2$ with a high response (336 for 100 ppm NO$_2$), fast response/recovery times (18 s/31 s) and a superior detection limit (0.001 ppm). The sensor also showed good reversibility, reproducibility and long-term stability at two optimized operation temperatures. The different sensing mechanisms for H$_2$S and NO$_2$ were discussed and the temperature dependent selectivity was explained.

Keywords: In$_2$O$_3$, nano-cube, NO$_2$, H$_2$S, gas sensor
1 Introduction

Hydrogen sulfide (H₂S) and nitrogen dioxide (NO₂) are two dangerous gases, which are daily released from vehicles and industrial processes. Because of their serious hazards to health and environment, the safe concentration limits of H₂S and NO₂ in the ambient established by American National Institute for Occupational Safety and Health (NIOSH) are 10 ppm and 1 ppm, respectively. Therefore, there are significant interests to develop gas sensors to detect for these two gases [1, 2]. The resistance type gas sensors based on metal oxides are the mostly studied ones, and the commonly reported oxides include ZnO [3, 4], In₂O₃ [5-7], WO₃ [8, 9], TiO₂[10], Fe₂O₃[11-13], SnO₂[14], CuO[15] and CeO₂[16]. Although there are many reports of either NO₂ sensors or H₂S sensors in recent years, so far there are few studies about the development of dual-function gas sensors which can efficiently detect both NO₂ and H₂S at different temperatures.

Among these metal oxides, nano-sized In₂O₃ is considered as one of the promising candidate materials to detect many hazardous gases including H₂S [17], NO₂[18], CO[19], H₂[20] and C₂H₂OH[21] etc. In particular, NO₂ or H₂S sensors based on In₂O₃ nanostructures have been frequently reported in recent years [6, 22-25]. It is well known that morphology and microstructure of these metal oxides prominently influence their sensing properties. Therefore, there are many studies to synthesize various morphologies of In₂O₃ in order to detect NO₂ or H₂S gases, including nanowires [22], nanospheres[23], nanofibers [24], nanorods[7], nanosheets [25], nanoparticles [6, 26, 27], etc. However, most of these studies are focused on sensing one specific gas of...
either NO₂ or H₂S. As far as we have searched, there is no any report to apply In₂O₃ based gas sensors for detection of both NO₂ and H₂S gases operated at different temperatures.

The objective of this paper is to synthesize In₂O₃ nano-cube sensing materials using a cetyltrimethyl ammonium bromide (CTAB) assisted solvothermal process, and then apply these nano-cubes for fabricating gas sensors to detect NO₂ and H₂S. These gas sensors exhibited good temperature-dependent selectivity and excellent sensing performance toward both H₂S and NO₂.

2 Experimental

2.1 Preparation and characterization of In₂O₃ nano-cubes

In₂O₃ nano-cubes were prepared using the CTAB assisted solvothermal and subsequent calcination processes. Firstly, InCl₃·4H₂O of 0.440 g was dissolved into 20 ml ethanol, and NaOH of 0.6 g were dissolved into 20 ml deionized water, respectively. The above InCl₃·4H₂O ethanol solution (0.075 mol/L) and NaOH aqueous solution (0.75 mol/L) were mixed under a vigorous stirring process. CTAB of 0.273 g was added into the above mixed solution and stirred for one hour under a magnetic stirring to form a sol, which was then transferred into a Teflon-lined autoclave and placed in an oven for the solvothermal reactions at 180 °C for 12 hrs. Finally, the solvothermal product was filtered, washed and dried at 60 °C for 6 hrs to obtain In(OH)₃ powders. In₂O₃ nano-cubes were finally obtained by calcining the In(OH)₃ powder at 500 °C in air for 2 hrs.

2.2 Sample Characterization

Selected area electron diffraction (SAED) patterns and transmission electron
microscopy (TEM) images were obtained using a JEOL JEM-2100F TEM instrument with an accelerating voltage of 200 kV. Scanning electron microscope (SEM) image of the sample was obtained using an Inspect F50 SEM instrument. X-ray diffraction (XRD) patterns were obtained using a Rigaku MiniFlex II X-ray diffractometer (with a Cu Ka radiation source, 40 kV and 15 mA). An X-ray photoelectron spectroscopy (XPS, Kratos Axis-Ultra DLD apparatus) with Mg Ka radiation was used to obtain the chemical binding of different elements in the oxides. Surface area of the sample was measured based on the Brunauer-Emmett-Teller (BET) method using a Micromeritics ASAP 2020 Analyzer, measured at a temperature of −196 °C. The band gap value was measured using a diffuse reflectance spectra (DRS, UV-2101 Shimadzu), and BaSO₄ was used as the reference.

2.3 Gas sensor fabrication and measurement

Aluminum oxide ceramic tube (with a length of 4 mm and a diameter of 1 mm) with two gold electrodes on its surface was used to fabricate the gas sensor. To coat an In₂O₃ layer on the ceramic tube, 40 mg of In₂O₃ powder was dissolved in 10 ml alcohol and ultrasonically agitated for 20 min to obtain a homogeneous suspension. The In₂O₃ suspension was then dip-coated onto surface of aluminum oxide ceramic tubes until a continuous In₂O₃ film was formed. Finally, the coated sample was dried at 120 °C for 2 hrs. The thickness of the In₂O₃ layer was about 100 µm.

A Ni–Cr alloy resistive heater was placed inside the ceramic tube to control the operating temperature of the sensor. The sensor was placed inside a glass testing container of 2 liters in volume. The diluted NO₂ or H₂S gas was injected into the
container using a precision micro-injector. A Keithley 2400 SourceMeter was connected to the gold electrodes of the sensor to measure the changes of electric resistance of the sensor. The applied voltage used in the gas sensing testing system was 1 V. The response (R) of the sensor is defined as $R_{\text{air}}/R_{\text{H}_2\text{S}}$ for the reducing gas of H$_2$S, and it is defined as $R_{\text{NO}_2}/R_{\text{air}}$ for the oxidizing gas of NO$_2$, where $R_{\text{air}}$ is the electrical resistance of the sensor measured in air, $R_{\text{H}_2\text{S}}$ and $R_{\text{NO}_2}$ are the electrical resistance data measured in the diluted gases of H$_2$S or NO$_2$, respectively. After the sensor’s response was reached its largest equilibrium value, the sensor was continuously exposed to the target gas for another ~100 s in order to obtain a stable response value. The response time is defined as the time for the increase of the sensor’s response to reach 90% of its largest equilibrium value after the target gas is injected, and the recovery time is defined as the time for the decrease to 10% of the largest equilibrium value after the target gas is removed from the chamber.

3 Results and discussion

3.1 Microstructural analysis
Fig. 1 XRD patterns of samples before and after calcination at 500 °C in air.

XRD patterns of samples before and after calcination at 500 °C are shown in Fig. 1. All the diffraction peaks of the samples before the calcination are corresponding to In(OH)$_3$ crystal structure (JCPDS Card No. 16-0161). After calcined at 500 °C, the In(OH)$_3$ was transformed into cubic In$_2$O$_3$ crystal (JCPDS Card No. 06-0416). No other characteristic peaks of impurities were detected, indicating that the pure In$_2$O$_3$ was obtained after calcination at 500 °C. According to Scherrer equation, the estimated average crystal size of the In$_2$O$_3$ is ~48.4 nm.
Fig. 2 (a) SEM and (b) TEM images of the In$_2$O$_3$ nano-cubes (the inset in b is its corresponding SAED pattern).

SEM and TEM images of In$_2$O$_3$ are shown in Fig. 2, and another low-magnification TEM image is presented in the Fig. S1 in the Supporting Information. It can be seen that the In$_2$O$_3$ sample is mainly composed of many nano-cubes, although there are also tiny amount of nano-rods. The average diameter of In$_2$O$_3$ nano-cubes was estimated to be ~50 nm, which is consistent with the calculated average size from XRD analysis. The SAED pattern (see the inset in Fig. 2b) can be indexed to cubic phase of In$_2$O$_3$, indicating its highly crystalline structure. Based on the BET analysis from the nitrogen adsorption isotherm, the obtained BET surface area of the In$_2$O$_3$ nano-cubes is 11.96 m$^2$·g$^{-1}$. In$_2$O$_3$ is a wide band-gap semiconductor material, and its optical bandgap changes with its size and shape, especially when it is in a nanoscale structure. The DRS result of the In$_2$O$_3$ nano-cubes is shown in Fig. 3. The obtained optical band-gap (E$_g$) is ~3.37 eV, which is similar to the value reported in literature [28].
Fig. 3. The diffuse reflectance spectrum of the In$_2$O$_3$ nano-cubes.

Fig. 4. XPS spectra of the In$_2$O$_3$ nano-cubes: (a) In 3d and (b) O 1s.

XPS spectra of the In$_2$O$_3$ nano-cubes are shown in Fig. 4. In the XPS spectrum of In 3d (see in Fig. 4a), the binding energy peaks at 443.9 and 451.5 eV are attributed to In 3d$_{5/2}$ and In 3d$_{3/2}$ of In$^{3+}$ ions, respectively, which proves the formation of In$_2$O$_3$ [22]. Two peaks are observed in the O 1s spectrum, in which the peak at 529.5 eV is corresponding to the O$^{2-}$ ions in the crystal lattice of the In$_2$O$_3$, and the peak at 531.4 eV is corresponding to the chemisorbed oxygen ions on the surface of In$_2$O$_3$ [27]. Based on the calculation result of XPS integral area, the surface atomic ratio of the In and O is 37:63, which means that there is a high concentration of oxygen ions on the surface of In$_2$O$_3$ nano-cubes. Furthermore, the atomic content of chemisorbed oxygen ions was as high as 20.8% in the total oxygen atoms, indicating that there are plenty of
chemisorbed oxygen ions on the surface.

3.2 Gas sensing properties

3.2.1 NO₂ gas sensing properties

![Graph showing response of In₂O₃ nano-cubes based gas sensor to NO₂ at different operating temperatures.](image)

Fig. 5. (a) Response values of the In₂O₃ nano-cubes based gas sensor to 30 ppm of NO₂ at different operating temperatures, and (b) response values to different gases operated at the operating temperature of 100 °C.

The I-V curves of the gas sensor based on In₂O₃ nano-cubes measured at 25 °C and 100 °C (see the Fig. S2 in the Supporting Information) show a linear behavior. This is a typical phenomenon of Ohmic contact behavior. It was previously reported that the contact of the In₂O₃ with the Au electrodes normally has a Schottky contact behavior [29, 30]. However, in this study, the electrical resistance generated between the In₂O₃ nano-cubes (normally with the Ohmic contact behavior) is much larger than that between the In₂O₃ and Au electrode. Therefore, the I-V curves of this In₂O₃ gas sensor exhibit an Ohmic behavior, rather than a typical Schottky contact behavior [16]. When the temperature is increased from 25 °C to 100 °C, the resistance of gas sensor is decreased from 782 KΩ to 175 KΩ.

The responses of the gas sensor to 30 ppm NO₂ gas at different temperatures from 25
to 300 °C were measured. According to the response/recovery curves (see the Fig. S3 in Supporting Information), the response values were calculated and the results are shown in Fig. 5a. The sensor exhibits a good response to NO₂ at different temperatures, and the maximum response value of 176 is obtained at 100 °C. Therefore, the optimum operation temperature for the NO₂ gas of this gas sensor should be 100 °C. Generally it is preferred that the detection of NO₂ should be operated at a lower temperature, better at room temperature [31]. Therefore, in the following studies, the sensing tests using the In₂O₃ nano-cubes based gas sensor were performed at both 25 °C and 100 °C.

To investigate the NO₂ selectivity of the In₂O₃ nano-cubes based gas sensor, its responses to different gases (including NH₃, H₂, CO, ethanol, H₂S and NO₂) were tested at the operating temperature of 100 °C. From the results shown in Fig. 5b, the gas sensor shows a high response value to 30 ppm of NO₂. However, it shows little response values to other tested gases of NH₃, H₂, CO and ethanol with a concentration of 100 ppm. For the 30 ppm of H₂S gas, the response value is 56, which is much less than that for NO₂. Therefore, the gas sensor shows a good NO₂ gas selectivity at the operating temperature of 100 °C.

Fig. 6. (a) Response/recovery curves and (b) response value of the In₂O₃ nano-
cubes based gas sensor to different concentrations of NO₂ from 100 ppm to 1 ppm at room temperature.

Fig. 6a shows the response/recovery curves of the In₂O₃ nano-cubes based gas sensor exposed to different concentrations of NO₂ from 100 ppm to 1 ppm at room temperature. This gas sensor shows a good reversibility at room temperature. Its response values are dependent on the NO₂ concentration (as shown in Fig 6b). For 100 ppm of NO₂, the response value is 60.4, and the response and recovery times are 49 s and 197 s, respectively. The detection limit of this sensor is 1 ppm when operated at room temperature.

Figs. 7 (a) and (b) Response/recovery curves of the In₂O₃ nano-cubes based gas sensor to NO₂ with different concentrations from 100 ppm to 0.001 ppm at 100 °C, (c) the repeated response/recovery curves to 30 ppm of NO₂ by successively testing at
100℃, (d) the response value to different concentrations of NO\textsubscript{2} at 100℃.

Figs. 7 shows the NO\textsubscript{2} sensing performance of the In\textsubscript{2}O\textsubscript{3} sensor measured at 100℃. The gas sensor shows a good reversibility for the NO\textsubscript{2} detection. When the measurement temperatures are increased from 25℃ to 100℃, the response values are increased and the response/recovery times of the sensor are decreased remarkably. For example, when exposed to 100 ppm NO\textsubscript{2} at 100℃, the response value of the sensor is increased to 336, and the response and recovery times are decreased to 18 s and 31 s, respectively. It is also worthy to mention that even for 0.001 ppm of NO\textsubscript{2}, the sensor still shows an obvious response of 1.2. Therefore, this In\textsubscript{2}O\textsubscript{3} sensor show a high sensitivity, fast response/recovery, and a low detection limit for the NO\textsubscript{2} at the working temperature of 100℃. After the sensor is successively tested in 30 ppm of NO\textsubscript{2} for four times, the response/recovery curves (shown in Fig. 7c) exhibit good reproducibility.

Table 1 Comparisons of NO\textsubscript{2} sensing properties of In\textsubscript{2}O\textsubscript{3} gas sensor in this work with those reported in literature.

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<tr>
<td>Pd-In\textsubscript{2}O\textsubscript{3} nanowire</td>
<td>300℃</td>
<td>3</td>
<td>3.4</td>
<td>60 s/365 s</td>
<td>3</td>
<td>[22]</td>
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<tr>
<td>In\textsubscript{2}O\textsubscript{3} nanosphere</td>
<td>120℃</td>
<td>0.5</td>
<td>217.5</td>
<td>148 s/72 s</td>
<td>0.01</td>
<td>[23]</td>
</tr>
<tr>
<td>In\textsubscript{2}O\textsubscript{3} Nanoparticle</td>
<td>300℃</td>
<td>1.2</td>
<td>1.09</td>
<td>120 s/39 s</td>
<td>0.5</td>
<td>[26]</td>
</tr>
<tr>
<td>Pd-In\textsubscript{2}O\textsubscript{3}</td>
<td>135℃</td>
<td>50</td>
<td>4080</td>
<td>120 s/90 s</td>
<td>0.5</td>
<td>[32]</td>
</tr>
<tr>
<td>Ni-doped In\textsubscript{2}O\textsubscript{3}</td>
<td>58℃</td>
<td>0.5</td>
<td>178</td>
<td>9 min/~10 min</td>
<td>0.01</td>
<td>[33]</td>
</tr>
<tr>
<td>In\textsubscript{2}O\textsubscript{3} nanorod bundle</td>
<td>100℃</td>
<td>1</td>
<td>87</td>
<td>177 s/152 s</td>
<td>0.04</td>
<td>[34]</td>
</tr>
<tr>
<td>In\textsubscript{2}O\textsubscript{3}–graphene</td>
<td>25℃</td>
<td>30</td>
<td>8.25</td>
<td>4 min/24 min</td>
<td>5</td>
<td>[35]</td>
</tr>
<tr>
<td>In\textsubscript{2}O\textsubscript{3} microcube</td>
<td>60℃</td>
<td>30</td>
<td>1884</td>
<td>~300 s/~200 s</td>
<td>0.5</td>
<td>[5]</td>
</tr>
<tr>
<td>In\textsubscript{2}O\textsubscript{3} microsphere</td>
<td>250℃</td>
<td>20</td>
<td>37</td>
<td>5 s/20 s</td>
<td>5</td>
<td>[36]</td>
</tr>
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</table>
Table 1 summarizes the reported NO$_2$ sensing properties of various In$_2$O$_3$ based gas sensors from literature. Compared with most of these reported sensors, the In$_2$O$_3$ nano-cube based gas sensor developed in this study shows a lower working temperature, higher response values and the lowest detection limit. Furthermore, the response/recovery times are also much shorter than most of other In$_2$O$_3$ based NO$_2$ gas sensors reported in literature.

### 3.2.2 H$_2$S gas sensing properties

![Graph showing response of In$_2$O$_3$ nano-cubes to H$_2$S at different temperatures and to different gases.](image)

Fig. 8 (a) Response values of In$_2$O$_3$ nano-cubes based gas sensor to 5 ppm of H$_2$S at different operating temperatures, and (b) response values to different gases operated at room temperature of 25 $\square$.

To obtain the optimum operation temperature to H$_2$S, we have measured the response/recovery curves of the In$_2$O$_3$ sensor to 5 ppm H$_2$S from 25 $\square$ to 300 $\square$ (see...
the Fig. S4 in Supporting Information). The response values are shown in Fig. 8a. The sensor exhibits a significantly high response to H₂S when measured at room temperature, whereas the response value is gradually decreased with the increase in the operating temperature above 25 °C. Therefore, the optimum operation temperature for the H₂S gas is 25 °C.

At room temperature, the responses of the In₂O₃ based sensor to different gases (including NH₃, H₂, CO, NO₂, ethanol and H₂S) were tested. From the results shown in Fig. 8b, the sensor shows a high response of 639 to 5 ppm of H₂S. Whereas it shows little responses to other tested gases. Therefore, the In₂O₃ nano-cube based gas sensor has a good H₂S selectivity at room temperature.

![Graph showing response/recovery curves and response values of the In₂O₃ nano-cubes based gas sensor to H₂S gas with different concentrations from 60 ppm to 0.005 ppm.](image)

Fig. 9. (a) Response/recovery curves and (b) response values of the In₂O₃ nano-cubes based gas sensor to H₂S gas with different concentrations from 60 ppm to 0.005 ppm.
ppm at room temperature, (c) repeated response/recovery curves of five time exposure
to 20 ppm of H2S gas by successively testing the sensor.

Fig. 9a shows the response/recovery curves of the In2O3 based gas sensor to different
concentrations of H2S at room temperature. The sensor shows a steady baseline in air
before and after the sensing tests, meaning that the sensor has good reversibility for the
H2S detection. Fig. 9b shows the response/recovery curves of the sensor exposed to 20
ppm H2S after successively tested for five times. The gas sensor exhibits almost same
response/recovery curves with the same response value of 1126 in all five repeated tests,
indicating that the gas sensor has a good reproducibility. The response values of the
sensor are shown in Fig. 9c. It can be seen that the response values are increased with
the increase of the concentration of H2S. The response value to 60 ppm H2S is as large
as 1461 with the response/recovery times of 82 s/102 s. In addition, the gas sensor still
has an obvious response value of 1.8 when the concentration of H2S is as low as 0.005
ppm. Therefore, the In2O3 nano-cube based gas sensor has not only a high response, but
also a superior detection limit to H2S.

Table 2 compares the H2S sensing properties of In2O3 gas sensor in this work with
those reported in the literature. Compared with most of the reported gas sensors, the gas
sensor developed in this study shows the highest response value, except for the Mg-
In2O3 nanotubes based sensor reported in Ref [40]. Although the Mg-In2O3 sensor
shows a higher response value, a full recovery of its signals is difficult to achieve [38].
Furthermore, the In2O3 sensor in this study has the lowest detection limit as listed in
Table 2.
Table 2 Comparisons of H$_2$S sensing properties of In$_2$O$_3$ based gas sensor in this work with those reported in literature.

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<tr>
<td>In$_2$O$_3$ porous film</td>
<td>300</td>
<td>50</td>
<td>30</td>
<td>16 s/30 s</td>
<td>1</td>
<td>[17]</td>
</tr>
<tr>
<td>CuO-In$_2$O$_3$ nanofiber</td>
<td>150</td>
<td>5</td>
<td>9170%*</td>
<td>~200 s/no recovery</td>
<td>0.4</td>
<td>[24]</td>
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<tr>
<td>V-In$_2$O$_3$ nanofiber</td>
<td>90</td>
<td>50</td>
<td>13.9</td>
<td>15 s/18 s</td>
<td>1</td>
<td>[41]</td>
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<td>Eu-In$_2$O$_3$ nanobelts</td>
<td>260</td>
<td>100</td>
<td>5.74</td>
<td>11 s/13 s</td>
<td>5</td>
<td>[42]</td>
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<tr>
<td>Mg-In$_2$O$_3$ nanotube</td>
<td>130</td>
<td>10</td>
<td>1959.77</td>
<td>~75 s/no recovery</td>
<td>-</td>
<td>[40]</td>
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<tr>
<td>In$_2$O$_3$/WO$_3$ composite</td>
<td>150</td>
<td>10</td>
<td>143</td>
<td>5.5 min/16 min</td>
<td>0.5</td>
<td>[43]</td>
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<td>In$_2$O$_3$ whisker</td>
<td>25</td>
<td>10</td>
<td>30</td>
<td>4 min/2 h</td>
<td>0.2</td>
<td>[44]</td>
</tr>
<tr>
<td>In$_2$O$_3$ nanoparticle</td>
<td>25</td>
<td>2</td>
<td>200%*</td>
<td>30 min/5 min</td>
<td>0.02</td>
<td>[27]</td>
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<tr>
<td>PVA-In$_2$O$_3$ film</td>
<td>25</td>
<td>1</td>
<td>1.9</td>
<td>~5 min/31 min</td>
<td>0.5</td>
<td>[45]</td>
</tr>
<tr>
<td>In$_2$O$_3$/CuO nanofiber</td>
<td>25</td>
<td>100</td>
<td>2.23</td>
<td>5.3 s/--</td>
<td>1</td>
<td>[46]</td>
</tr>
<tr>
<td>In$_2$O$_3$ nanotube</td>
<td>25</td>
<td>50</td>
<td>320.14</td>
<td>45 s/127 s</td>
<td>1</td>
<td>[47]</td>
</tr>
<tr>
<td>In$_2$O$_3$ nano-cubes</td>
<td>25</td>
<td>60</td>
<td>1461</td>
<td>82 s/102s</td>
<td>0.005</td>
<td>This work</td>
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* Response = ($R_a$ - $R_g$)/$R_a$ × 100%.

3.2.3 Stability of the In$_2$O$_3$ nano-cubes based gas sensor

In order to investigate the long-term stability of the In$_2$O$_3$ sensor, its responses to both H$_2$S and NO$_2$ were repeatedly tested in a month at their different optimum operation temperatures, and the results are shown in Fig. 10. The fluctuations of the response value to 20 ppm of H$_2$S and 30 ppm of NO$_2$ are lower than 3%, indicating that the In$_2$O$_3$ based gas sensor have a good stability for detection of both NO$_2$ and H$_2$S gases.
Fig. 10 Stability of the In$_2$O$_3$ nano-cube based gas sensor with repeated tests of H$_2$S and NO$_2$ in a month.

3.3 Gas sensing mechanisms

For the n-type semiconductor materials such as In$_2$O$_3$, the mechanism for NO$_2$ and H$_2$S gas sensing are all related to the surface controlled reaction mechanisms as reported in References [27, 39]. In air, oxygen molecules are absorbed on the surfaces of In$_2$O$_3$ nano-cubes, and they capture free electrons from the In$_2$O$_3$ to form chemisorbed oxygen ions (such as O$^{2-}$, O$^-$ and O$_2^-$) [48]. This process will result in formation of an electron-depletion layer on the surface of In$_2$O$_3$ nano-cube, and thus increase the gas sensor’s resistance. These types of chemisorbed oxygen ions are dependent on the operation temperature of the gas sensor. When the temperature is lower than 100 $^\circ$C, the chemisorbed oxygen ions are O$_2^-$, whereas they are mainly O$^-$ at an operation temperature from 100 $^\circ$C to 300 $^\circ$C [48].

Effect of temperature on the sensing property is strongly related to the surface processes of adsorption, reaction and desorption. At the operation temperature below 100 $^\circ$C, after the In$_2$O$_3$ sensor is exposed in NO$_2$, the NO$_2$ molecules can be easy
absorbed on the surface of In$_2$O$_3$, and then result in the following reactions [49-51]:

\[
\text{NO}_2(g) + e^- \rightarrow \text{NO}_2(\text{ads})^- \tag{1}
\]

\[
\text{NO}_2(g) + O_2^- (\text{ads}) + 2e^- \rightarrow \text{NO}_2^- (\text{ads}) + 2O^- \tag{2}
\]

However, the above reactions are not easily triggered (less energy favorite) and the desorption of NO$_2^-$ is also slow in the recovery process. This should be reason why the response/recovery times are quite long as shown in Fig. S3. Also the response is very low at low temperatures.

When the temperature is increased to 100 $^\circ$C, the absorbed NO$_2$ molecules will react with the chemisorbed O$^-$ according to the following reaction equation [51]:

\[
\text{NO}_2^- (\text{ads}) + O^- (\text{ads}) + 2e^- \leftrightarrow \text{NO}_2(g) + 2O^2^- (\text{ads}) \tag{3}
\]

At such a temperature, thermal energy of the NO$_2$ molecules is high enough, and can overcome the activation energy barrier of the reaction. More NO$_2$ molecules can react with the chemisorbed O$^-$ species. Because the above reaction will trap free electrons from the conduction band of In$_2$O$_3$ nano-cubes, the electron concentration on the surface of the In$_2$O$_3$ nano-cubes will be reduced. The thickness of electron-depletion layer region is decreased, and consequently the resistance of the sensor is increased. Therefore, the sensor's sensitivity is increased.

However, when the operation temperature is increased further above 100 $^\circ$C, the absorbed NO$_2$ molecules will be significantly reduced. Their reactions with the surface chemical-absorbed oxygen species will be reduced, thus decreasing the sensitivity of the gas sensor.

When the gas sensor is exposed to be H$_2$S gas at room temperature, the chemisorbed


O$_2^-$ ions on the surfaces of In$_2$O$_3$ will react with the H$_2$S molecules as described using the following reaction [52]:

$$H_2S(g) + 3/2O_2^-_{(ads)} \leftrightarrow H_2O(g) + SO_2(g) + 3/2e^-$$  \hspace{1cm} (4)

Consequently, electrons will be released to the electron-deletion region on the In$_2$O$_3$ surface, which will reduce the electrical resistance of the sensor. In addition, the sulfuration process of In$_2$O$_3$ at room temperature is also responsible for the decrease of the sensor’s electrical resistance [53]. The H$_2$S molecules can react with In$_2$O$_3$ to form In$_2$S$_3$ on the surface of In$_2$O$_3$ nano-cubes according to the following equations [54]:

$$In_2O_3(s) + 3H_2S(g) \rightarrow In_2S_3(s) + 3H_2O(g) \hspace{1cm} (\Delta G = -1318.6 \text{ kJ mol}^{-1})$$  \hspace{1cm} (5)

$$In_2S_3(s) + 9/2O(g) \rightarrow In_2O_3(s) + 3SO_2(g) \hspace{1cm} (\Delta G = -1318.6 \text{ kJ mol}^{-1})$$  \hspace{1cm} (6)

The Gibbs free energy changes ($\Delta G$) of the chemical reactions (5) and (6) are −161.7 and −1318.6 kJ mol$^{-1}$ at 25 $^\circ$C, respectively. This means that these two chemical reactions are spontaneously occurring with the consideration of thermodynamics. The sulfuration of In$_2$O$_3$ in H$_2$S gas (e.g. formation of In$_2$S$_3$) and the desulfuration of In$_2$S$_3$ in air can happen at room temperature. This has been proved by Xu et al using Raman spectrum [54]. Because the formed In$_2$S$_3$ has a higher conductivity than In$_2$O$_3$, the electrical resistance will be remarkably increased, thus resulting in a significant response.

With the increase of temperature above room temperature, the $\Delta G$ value of chemical reaction (5) will be increased. This indicates that the sulfuration reaction will be restricted, and less In$_2$S$_3$ will be formed on the surface of In$_2$O$_3$. As a result, the sensitivity to the H$_2$S will be significantly decreased.
Clearly, the reaction of the oxidizing gas of NO\(_2\) with the chemisorbed oxygen ions on the sensor’s surface will release electrons into In\(_2\)O\(_3\). On the contrary, the reaction of reducing gas of H\(_2\)S with the chemisorbed oxygen ions will extract electrons from the In\(_2\)O\(_3\). Therefore, the electrical resistance of the In\(_2\)O\(_3\) based gas sensor will be increased when exposed to NO\(_2\), but it will be decreased when exposed to H\(_2\)S. Therefore, the gas sensor exhibits totally opposite changes in resistance values when exposed to NO\(_2\) and H\(_2\)S, respectively, which allows the sensor to easily distinguish these two gases.

4 Conclusions

In summary, the In\(_2\)O\(_3\) nano-cubes were synthesized using the CTAB assisted solvothermal method, and then used to fabricate a dual-function NO\(_2\) and H\(_2\)S gas sensor. At room temperature of 25 °C, the gas sensor exhibited a good selectivity towards H\(_2\)S gas. When the operating temperature was increased to 100 °C, the sensitivity to H\(_2\)S was decreased dramatically, but it showed an excellent selectivity towards NO\(_2\) gas at this temperature. This gas sensor has high response, fast response/recovery time, good reversibility and repeatability, and superior low detection limits in detection of both of NO\(_2\) and H\(_2\)S gases. Therefore, the In\(_2\)O\(_3\) nano-cubes based gas sensor should be very promising in detection of both the NO\(_2\) and H\(_2\)S gases at low operating temperature.

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