

Cite this: *Mater. Adv.*, 2022,  
3, 7043

## Enhanced formaldehyde gas-sensing response based on indium oxide nanowires doped with same-valence metal cations

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Mesoporous indium oxides nanowires ( $\text{In}_2\text{O}_3$  NWs) doped with Al, Sb and La were synthesized using a nanocasting method, and then the components, microstructures and morphology were characterized. All results indicate that the doped metals are well dispersed in the  $\text{In}_2\text{O}_3$  NWs and hardly affect the NW microstructure and morphology. While the cations-doped concentration decreases greatly with the increasing radii of Al, Sb and La cations. The cation-doping not only causes the lattice distortion to improve the adsorbed oxygen on the surface, but also increases the ground-state resistance of the  $\text{In}_2\text{O}_3$  NWs. In this way, the cation-doping greatly affects the gas-sensing behavior of formaldehyde gas. Considering the resistance in air and formaldehyde gas, the  $\text{In}_{1.984}\text{La}_{0.016}\text{O}_3$  NW sensor exhibits the best gas-sensing performance of 10 ppm formaldehyde gas with a response of 39.51 at 210 °C owing to the largest radius and lowest doping content of  $\text{La}^{3+}$ .

Received 23rd June 2022,  
Accepted 24th July 2022

DOI: 10.1039/d2ma00730d

rsc.li/materials-advances

### 1. Introduction

Formaldehyde (HCHO) is the simplest aldehyde, and is a colorless irritating gas.<sup>1</sup> Long-term exposure to HCHO gas at a concentration higher than 0.1 ppm may cause serious eye irritation, a burning sensation in the throat, dyspnea, asthma-related symptoms and cancer.<sup>2</sup> Considering the health hazards to humans and animals, it is very important to monitor the concentration of HCHO gas both indoors and outdoors.<sup>3</sup> Therefore, test instruments and techniques should be well developed to detect and monitor HCHO gas in real-time.<sup>4</sup> Nowadays, gas chromatography,<sup>5</sup> high performance liquid chromatography,<sup>6</sup> colorimetry-based derivatization,<sup>7</sup> protein-based biosensing systems<sup>8</sup> and gas sensors<sup>9,10</sup> have been developed and used in formaldehyde monitoring.

Gas sensors based on metal oxide semiconductors (MOS) have been well studied and developed to detect and monitor poisonous and harmful gases.<sup>11</sup> The gas response of a MOS sensor is defined as the ratio of the resistance in target gas to that in air.<sup>12</sup> For gas sensors it is important to control the microstructure of the material, to increase the specific surface area of MOS nanostructure. Nowadays, one-dimensional MOS nanostructures are widely studied as gas-sensing mediums due to their very large surface-to-volume ratio, high specific surface area and high porosity.<sup>13–15</sup> In recent years, nanowires (NWs) have been used widely in gas sensors. For example, Wang *et al.*

synthesized mesoporous  $\text{Co}_3\text{O}_4$  NWs using a nanocasting method, and these NWs indicated an excellent gas-sensing performance for toluene gas.<sup>16</sup> Hassen *et al.* fabricated  $\text{rGO-W}_{18}\text{O}_{49}$  NWs, improving the gas-sensing response to toluene gas.<sup>17</sup> However, microstructural regulation only improves the surface area to some extent.

As is known, heterogeneous doping can effectively adjust the carrier concentration of one-dimensional MOS nanostructures.<sup>18</sup> Heterogeneous doping not only adjusts the resistance in the ground state but also causes lattice distortion of the MOS nanostructure. This lattice distortion results in more oxygen vacancies, which leads to more adsorbed oxygen on MOS nanostructures. Chen *et al.* synthesized high-valence-cation-doped NiO NWs, and the responses of the NiO NW sensor was greatly increased with doping of the high-valence donors.<sup>19</sup> Mokoena *et al.* studied a  $\text{Eu}^{3+}$ -doped NiO sensor for toluene gas detection, and the response was higher than for the NiO sensor.<sup>21</sup>

Due to its broad bandgap, low cost, low resistivity and high catalytic activity,  $\text{In}_2\text{O}_3$  nanostructures as n-type MOS have been widely investigated all over the world to improve the gas-sensing performance.<sup>22</sup> Jin *et al.* synthesized hierarchical porous  $\text{In}_2\text{O}_3$  nanospheres, the sensor for which showed better selectivity for TEA and ethanol.<sup>23</sup> Liu *et al.* prepared Sb-doped  $\text{In}_2\text{O}_3$  microstructures for acetone detection, which showed a higher response compares with  $\text{In}_2\text{O}_3$ .<sup>24</sup> Liang *et al.* synthesized Ca-doped  $\text{In}_2\text{O}_3$  nanotubes, which showed excellent selectivity and a high response toward formaldehyde.<sup>25</sup>

In order to more accurately reveal the influence of lattice distortion from cation-doping, the interference of the carrier

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concentration, morphology, average particle size and specific surface area on the gas-sensing behavior of  $\text{In}_2\text{O}_3$  nanostructures should be excluded.<sup>26</sup> In this paper, a nanocasting method and the same process conditions were used to synthesize  $\text{In}_2\text{O}_3$  NWs and cation-doped  $\text{In}_2\text{O}_3$  NWs with a similar diameter, microstructure and specific surface area. The cations  $\text{Al}^{3+}$ ,  $\text{Sb}^{3+}$  and  $\text{La}^{3+}$  were doped into the  $\text{In}_2\text{O}_3$  NWs using SBA-15 silica as a hard template. The influence of the doping content and cation radius on the microstructure and gas-sensing properties toward HCHO was investigated in detail. After optimizing the operating conditions of the  $\text{In}_2\text{O}_3$  NW gas sensors, the physical mechanism was analyzed theoretically based on the doped semiconductor theory.

## 2. Experimental

### 2.1 Synthesis of $\text{In}_2\text{O}_3$ and cation-doped $\text{In}_2\text{O}_3$ NWs

All chemicals and reagents in this study were of analytical grade and used directly without further purification. The  $\text{In}_2\text{O}_3$  NWs and Al-, Sb- and La-doped  $\text{In}_2\text{O}_3$  NWs were synthesized using mesoporous SBA-15 silica as a hard template.<sup>19</sup> Indium nitrates, aluminum chloride, antimony chloride, lanthanum nitrate and the SBA-15 powder were uniformly dissolved and dispersed in ethanol solution according to the atomic ratio of Si, *i.e.*,  $(\text{In} + \text{Al}, \text{Sb} \text{ and } \text{La}) : (\text{Al}, \text{Sb} \text{ and } \text{La}) = 2 : 1 : 0.05$ , and then *n*-hexane was added. After evaporating the above solution, the obtained powder samples were calcined at 260 °C using a muffle furnace. After washing to remove undecomposed soluble salts, the powder samples were sintered in air at 600 °C for 6 h and the SBA-15 silica was removed using a 2 M NaOH aqueous solution. Compared with the  $\text{In}_2\text{O}_3$  molecular formula, the cation-doped  $\text{In}_2\text{O}_3$  NWs were denoted as  $\text{In}_{2-x}\text{M}_x\text{O}_3$  (M = Al, Sb or La), in which *x* is the doping content calculated *via* EDS.

### 2.2 Characterization of microstructures and gas-sensing properties

The phases, morphology and microstructures of undoped and cation-doped  $\text{In}_2\text{O}_3$  NWs were characterized *via* XRD (SmartLabSE, 3 kW, Cu target, wavelength 0.154 nm, step 0.02°),

TEM (JEOL, JEM-1400Flash, 120 kV), and EDS (HITACH, SU8010). Moreover, the bandgap and specific surface area were measured and deduced from UV-visible adsorption spectra (UV3600 Spectrophotometer) and  $\text{N}_2$  adsorption-desorption isotherms (ASAP2020 Surface Area and Porosity Analyzer, −196 °C, relative pressure of 0.06 to 0.2), respectively.

The gas-sensing tests were performed *via* static distribution using a CGS-4TPs gas-sensing measurement system with atmospheric air as the interference gas, where the relative humidity was held at about 30%. First, 2 mg  $\text{In}_2\text{O}_3$  NWs or cation-doped  $\text{In}_2\text{O}_3$  NWs and 1 ml deionized water were mixed together to form a homogeneous paste, which was brush-coated onto an  $\text{Al}_2\text{O}_3$  ceramic substrate with interdigitated Ag–Pd electrodes. The as-prepared simulated sensors were dried in air at room temperature and then aged at 350 °C for 2 h in air to improve their stability. Considering the volume of the test chamber, the volume of HCHO liquid (37–40%), ammonia water (25–28%), water, ethanol, xylene, toluene and methanol were calculated, and then the above liquid was injected into the chamber and evaporated to a gas with a concentration from 1 ppm to 15 ppm. The response for n-type  $\text{In}_2\text{O}_3$  NW sensors is defined as the ratio of the resistance in air ( $R_{\text{air}}$ ) to that in HCHO gas ( $R_{\text{gas}}$ ).<sup>13</sup>

## 3. Results and discussion

### 3.1 Microstructures and morphology of cation-doped $\text{In}_2\text{O}_3$ NWs

The phase analysis of  $\text{In}_2\text{O}_3$  and cation-doped  $\text{In}_2\text{O}_3$  NWs was performed using XRD, as shown in Fig. 1, in which all peaks are normalized according to the strongest (222) peak. The diffraction peaks of all the samples are consistent with the characteristic peaks of cubic  $\text{In}_2\text{O}_3$  (PDF#71-2194). The diffraction peaks at  $2\theta$  values of 21.65, 30.76, 35.618, 51.188 and 60.85° correspond to the (211), (222), (400), (440) and (622) facets according to the standard card. The characteristic peaks belonging to Al-, Sb- and La-based compounds are not observed. The average crystallite sizes calculated using the Scherrer equation are listed in Table 1. In order to reveal the influence of doping with different cations

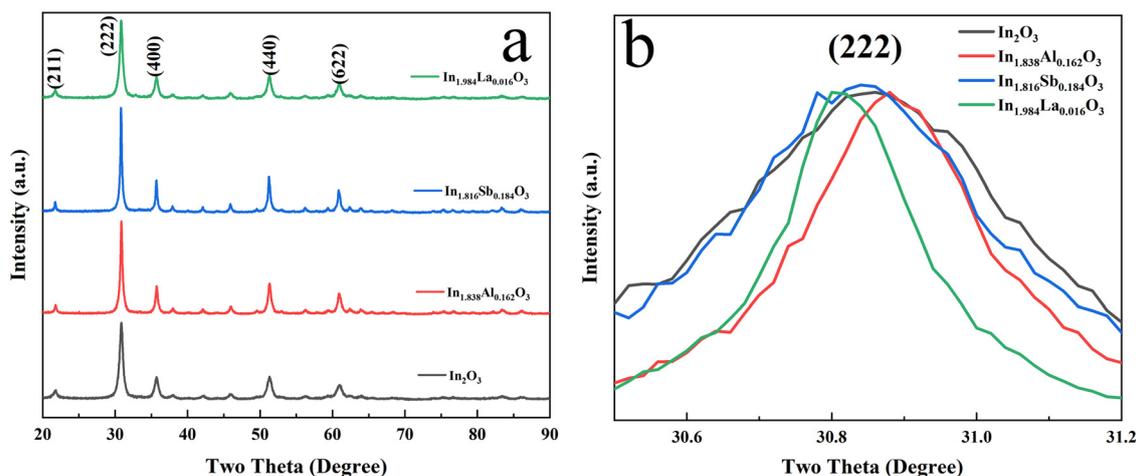


Fig. 1 Full-angle range of XRD patterns (a) and shift of the (222) peak (b) for undoped  $\text{In}_2\text{O}_3$  and cation-doped  $\text{In}_2\text{O}_3$  NWs.



**Table 1** Structural and gas-sensing parameters of In<sub>2</sub>O<sub>3</sub> and cation-doped In<sub>2</sub>O<sub>3</sub> NWs

Sample	Crystallite size (nm)	Average pore size (nm)	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	$E_g$ (eV)	Response, $S$
In <sub>2</sub> O <sub>3</sub>	17.9	6.29520	57.37	3.34	26.16
In <sub>1.838</sub> Al <sub>0.162</sub> O <sub>3</sub>	38.8	8.29376	53.55	3.39	28.73
In <sub>1.816</sub> Sb <sub>0.184</sub> O <sub>3</sub>	45.8	7.82711	49.21	3.40	19.78
In <sub>1.984</sub> La <sub>0.016</sub> O <sub>3</sub>	23.0	6.37254	57.29	3.36	39.51

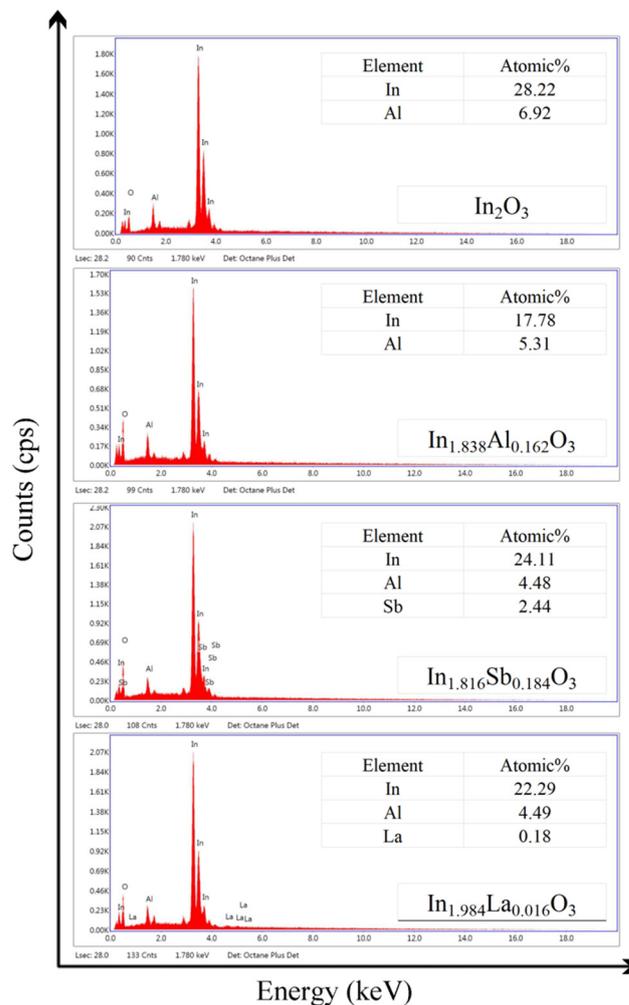
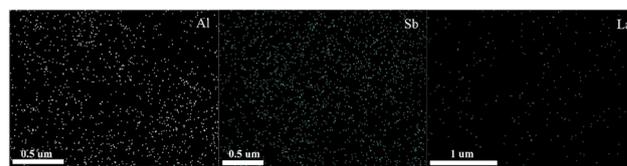
on the lattice distortion of the In<sub>2</sub>O<sub>3</sub> NWs, the (222) peaks of all the samples are enlarged and shown in Fig. 1b. Clearly, the (222) peak of the Al-doped In<sub>2</sub>O<sub>3</sub> NWs is shifted to a higher angle and the La-doped sample shifted to a lower angle, while the Sb-doped In<sub>2</sub>O<sub>3</sub> NWs are the same the In<sub>2</sub>O<sub>3</sub> NWs due to the similar radius. According to Bragg's law:

$$2d\sin\theta = \lambda \quad (1)$$

where  $d$  is the distance between parallel atomic planes,  $\lambda$  is the incident wavelength and  $\theta$  is the angle between the incident light and the crystal plane. In this way, La-doped In<sub>2</sub>O<sub>3</sub> NWs should present a higher  $d$  for the larger radius of La<sup>3+</sup> while Al-doped In<sub>2</sub>O<sub>3</sub> NWs should possess a lower  $d$  for the lower Al<sup>3+</sup> radius compared with In<sup>3+</sup> according to eqn (1). Therefore, it is concluded that Al, Sb and La were successfully doped into the In<sub>2</sub>O<sub>3</sub> lattice, which leads to the lattice distortion of the In<sub>2</sub>O<sub>3</sub> NWs.<sup>27</sup>

The components of In<sub>2</sub>O<sub>3</sub> and cation-doped In<sub>2</sub>O<sub>3</sub> NWs are characterized *via* EDS in Fig. 2. Considering the atomic percentage of all samples, cation-doped In<sub>2</sub>O<sub>3</sub> NWs can be expressed as In<sub>1.838</sub>Al<sub>0.162</sub>O<sub>3</sub>, In<sub>1.816</sub>Sb<sub>0.184</sub>O<sub>3</sub> and In<sub>1.984</sub>La<sub>0.016</sub>O<sub>3</sub> NWs, respectively. Owing to the different cation radius values of In, Al, Sb and La in the initial solution, the probability of these cations entering the mesochannels of SBA-15 is different.<sup>19</sup> The probability of entering the mesochannels decreases greatly with the increasing radius of the doped cation. As a result, the In<sub>1.838</sub>Al<sub>0.162</sub>O<sub>3</sub> and In<sub>1.816</sub>Sb<sub>0.184</sub>O<sub>3</sub> NWs present the highest doping concentration while the In<sub>1.984</sub>La<sub>0.016</sub>O<sub>3</sub> NWs show the lowest doping concentration. Moreover, Fig. 3 shows the EDS spectra of In<sub>1.838</sub>Al<sub>0.162</sub>O<sub>3</sub>, In<sub>1.816</sub>Sb<sub>0.184</sub>O<sub>3</sub> and In<sub>1.984</sub>La<sub>0.016</sub>O<sub>3</sub> NWs, indicating that Al, Sb and La are well-dispersed in the In<sub>1.838</sub>Al<sub>0.162</sub>O<sub>3</sub>, In<sub>1.816</sub>Sb<sub>0.184</sub>O<sub>3</sub> and In<sub>1.984</sub>La<sub>0.016</sub>O<sub>3</sub> NWs. It can be seen easily from the number of bright spots that the La content is the lowest while the separate Al and Sb contents are much higher.

The morphology and microstructure of In<sub>2</sub>O<sub>3</sub> and the cation-doped In<sub>2</sub>O<sub>3</sub> NWs are observed using TEM in Fig. 4. It is shown that all samples exhibit mesoporous structures and that cation doping hardly affects the microstructure of the In<sub>2</sub>O<sub>3</sub> NWs. The diameter of the nanowires is measured to be 8–9 nm and mesochannel size is about 2–3 nm.<sup>28</sup> The N<sub>2</sub> adsorption-desorption isotherms of In<sub>2</sub>O<sub>3</sub> and the cation-doped In<sub>2</sub>O<sub>3</sub> NWs are shown in Fig. 5. The curves of all samples exhibit type-IV adsorption isotherms, which are characteristic of mesoporous structures according to IUPAC. The BET surface area ( $S_{\text{BET}}$ ) and average pore size of all the samples calculated from

**Fig. 2** EDS images of In<sub>2</sub>O<sub>3</sub> and cation-doped In<sub>2</sub>O<sub>3</sub> NWs.**Fig. 3** Al, Sb and La EDS spectra of cation-doped In<sub>2</sub>O<sub>3</sub> NWs.

the N<sub>2</sub> adsorption-desorption isotherm data are given in Table 1. The specific surface area changes a little from 49.2 m<sup>2</sup> g<sup>-1</sup> to 57.4 m<sup>2</sup> g<sup>-1</sup>. The pore size distribution diagrams of all the samples are shown in the insets of Fig. 5, in which the average pore size is mainly focused around 4–5 nm.

The UV-visible absorption spectra of In<sub>2</sub>O<sub>3</sub> and the cation-doped In<sub>2</sub>O<sub>3</sub> NWs are used to calculate the bandgap ( $E_g$ ) in Fig. 6.  $E_g$  is the basis of the optical absorption spectra according to eqn (2):<sup>29</sup>

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (2)$$

where  $\alpha$  is the absorption coefficient,  $h$  is the Planck constant,  $\nu$  is the photon frequency,  $A$  is constant and  $n$  is the electronic



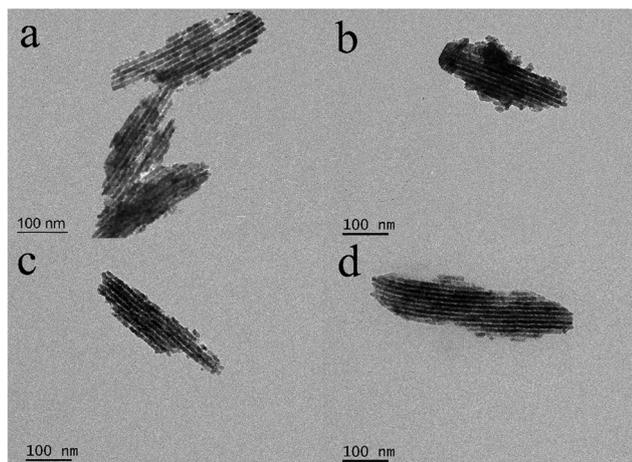


Fig. 4 TEM images of (a)  $\text{In}_2\text{O}_3$ , and (b) Al-, (c) Sb- and (d) La-doped  $\text{In}_2\text{O}_3$  NWs.

transition parameter (which is equal to 1/2 for a direct bandgap semiconductor). Since  $\alpha$  is proportional to the absorbance ( $A$ )

according to the Beer–Lambert law, the energy intercept of the curve of  $(\alpha h\nu)^2$  versus  $h\nu$  gives  $E_g$  when the linear region is extrapolated to the zero ordinate.<sup>20</sup> The  $E_g$  values of all the samples are given in Table 1, which shows that there is a small increase from 3.34 eV for the  $\text{In}_2\text{O}_3$  NWs to about 3.40 eV for the cation-doped  $\text{In}_2\text{O}_3$  NWs owing to lattice distortion.

### 3.2 Gas-sensing performance of cation-doped $\text{In}_2\text{O}_3$ NWs sensors

The gas-sensing behavior for 10 ppm HCHO gas of the  $\text{In}_2\text{O}_3$  and cation-doped  $\text{In}_2\text{O}_3$  NW sensors is characterized at operating temperatures from 190 to 240 °C in Fig. 7(a). For all the sensors, the response ( $S = R_{\text{air}}/R_{\text{gas}}$ ) to HCHO gas increases initially up to a maximum value at 210 °C with increasing temperature, and then decreases to some extent. This phenomenon could be attributed to the balance of the surface chemical reaction and the HCHO gas diffusion. In this way, the operating temperature was confirmed to be 210 °C for all sensors in the subsequent experiments. Comparing all sensors, the response of the  $\text{In}_{1.984}\text{La}_{0.016}\text{O}_3$  and

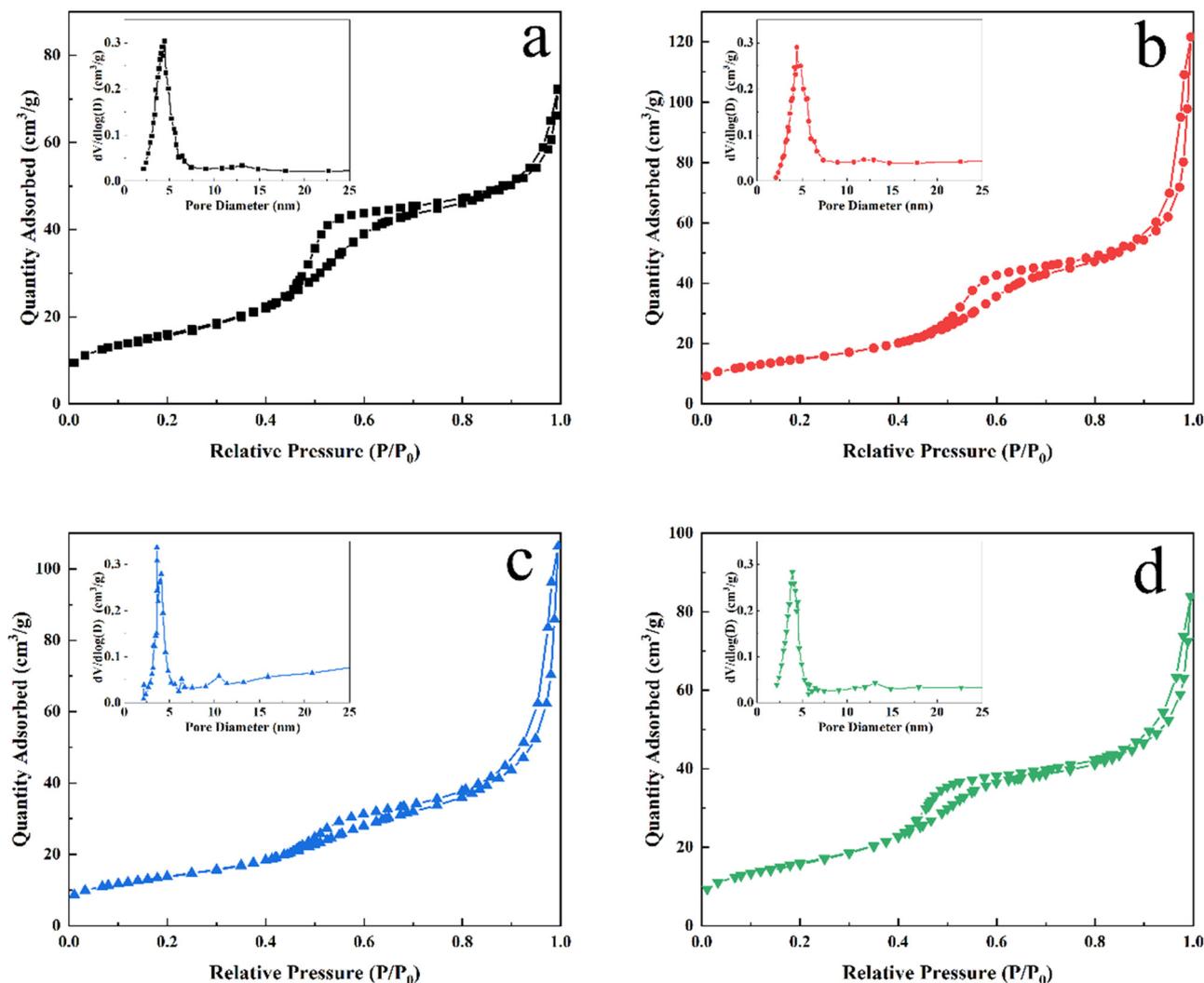


Fig. 5  $\text{N}_2$  adsorption–desorption isotherms and pore size distribution plots (inset) of (a)  $\text{In}_2\text{O}_3$ , and (b) Al-, (c) Sb- and (d) La-doped  $\text{In}_2\text{O}_3$  NWs.



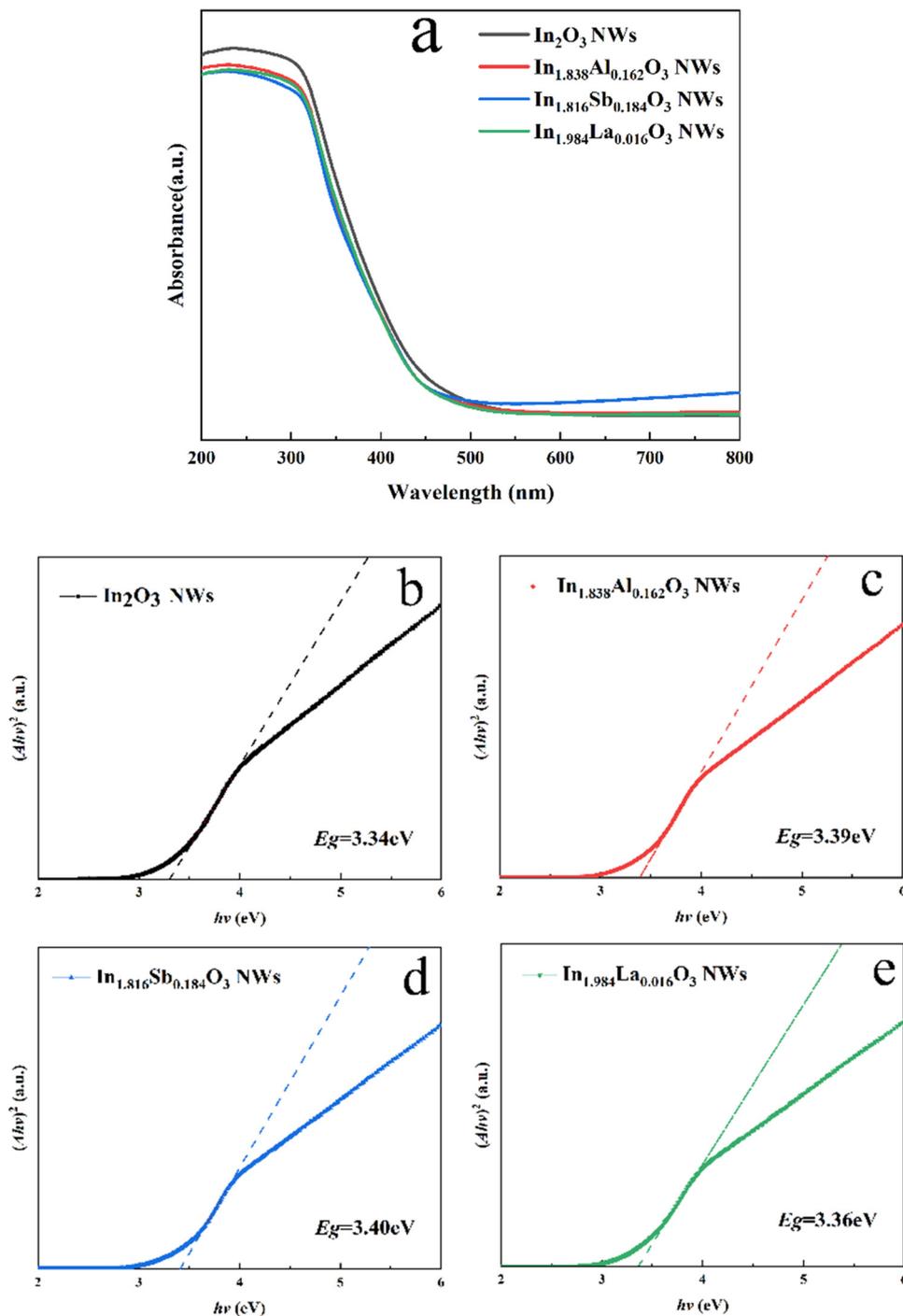


Fig. 6 UV-vis spectrum of (a)  $\text{In}_2\text{O}_3$  and the cation-doped  $\text{In}_2\text{O}_3$  NWs; and (b–e) plots of  $(Ah\nu)^2$  versus  $h\nu$  for (b)  $\text{In}_2\text{O}_3$ , and the (c) Al-, (d) Sb- and (e) La-doped  $\text{In}_2\text{O}_3$  NWs.

$\text{In}_{1.838}\text{Al}_{0.162}\text{O}_3$  NWs sensor is higher than that of the  $\text{In}_2\text{O}_3$  NW sensor, while the  $\text{In}_{1.816}\text{Sb}_{0.184}\text{O}_3$  NWs sensor shows the lowest response to HCHO gas at 210 °C. The change in resistance for  $\text{In}_2\text{O}_3$  and the cation-doped  $\text{In}_2\text{O}_3$  NW sensors to 10 ppm HCHO gas at 210 °C is given in Fig. 7(b), for which the resistance values in air and HCHO gas are also listed in Table 2. Owing to the electron-depletion layer at the shell of  $\text{In}_2\text{O}_3$  NWs in air from adsorbed oxygen,  $R_{\text{air}}$  for all the sensors is much larger than  $R_{\text{gas}}$ .

Furthermore, the differences in the resistance are relatively large due to the thickness differences of all the sensors. The  $R_{\text{air}}$  values of all the sensors at the different operating temperatures are given in Fig. 7(c), in which  $R_{\text{air}}$  decreases with the increasing temperature. The response and recovery time are defined as the time required for a change in the resistance to reach 90% of the equilibrium value after HCHO is injected and then removed. The response time for  $\text{In}_2\text{O}_3$  and the cation-doped  $\text{In}_2\text{O}_3$  NWs



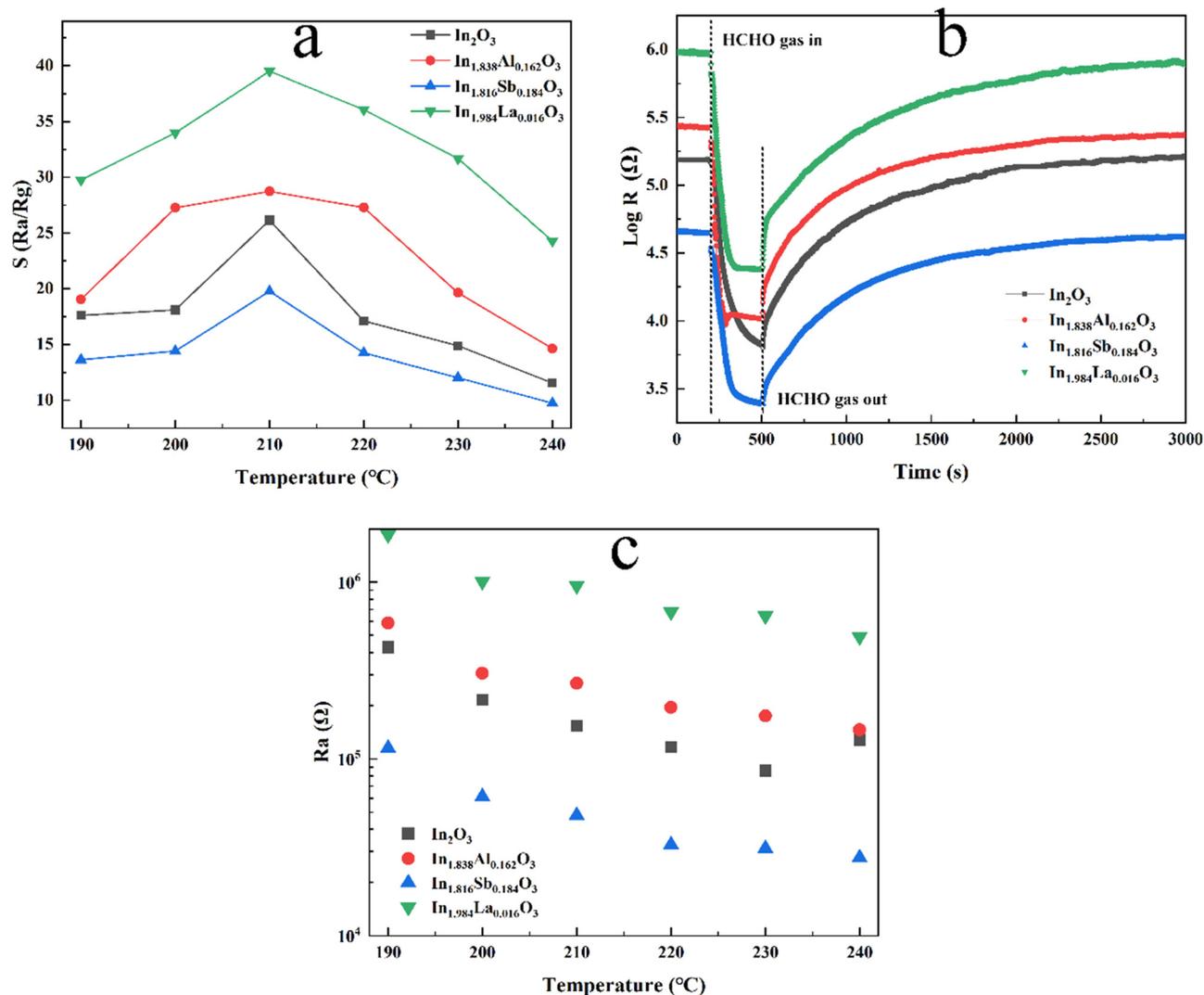


Fig. 7 (a) Response of  $In_2O_3$  and Al-, Sb- and La-doped  $In_2O_3$  NW sensors to 10 ppm HCHO gas at different operating temperatures; (b) response and recovery curves of all the sensors to 10 ppm HCHO gas at 210  $^{\circ}C$ ; and (c)  $R_{air}$  values for all sensors at the different operating temperatures.

sensors is 80 s, 33 s, 77 s and 50 s, respectively. The response time of the cation-doped  $In_2O_3$  NWs sensors is shorter than for the  $In_2O_3$  NW sensor. This should be attributed to the destruction of the periodic potential field for cation doping, which facilitates the diffusion of molecular oxygen.<sup>40</sup>

The influence of the HCHO gas concentration from 1 ppm to 15 ppm on the response of  $In_2O_3$  and the cation-doped  $In_2O_3$  NW sensors at 210  $^{\circ}C$  is also discussed in Fig. 8(a). It was seen that the response of all the sensors increases with the HCHO

gas concentration. HCHO gas first reacts with the adsorbed oxygen, and re-injects the extracted electrons back to the shell of  $In_2O_3$  and the cation-doped  $In_2O_3$  NWs. As the result, the resistance decreases greatly when in HCHO gas. The higher the HCHO gas concentration, the lower is the resistance value of all the sensors. Therefore, the response to HCHO gas increases greatly with the HCHO gas concentration for all sensors. Moreover, the relationship between the response ( $S$ ) and the HCHO gas concentration ( $C$ ) can be expressed in eqn (3) as:

$$S = a(C)^b + 1 \quad (3)$$

where  $a$  and  $b$  are constants.<sup>29</sup> Based on the data in Fig. 8(a),  $a$  and  $b$  can be calculated using eqn (3). The above equation can therefore be rewritten as:

$$\log(S - 1) = b \log(C) + \log(a). \quad (4)$$

In this way, the relationship between  $\log(S - 1)$  and  $\log(C)$  is plotted in Fig. 8(b) for  $In_2O_3$  and the cation-doped  $In_2O_3$  NW

Table 2 Resistance values of all sensors in air and 10 ppm HCHO gas at 210  $^{\circ}C$

Sample	$R_{air}$ ( $\Omega$ )	$R_{gas}$ ( $\Omega$ )
$In_2O_3$ NWs	153 644	6650
$In_{1.838}Al_{0.162}O_3$ NWs	267 635	10 389
$In_{1.816}Sb_{0.184}O_3$ NWs	47943	2424
$In_{1.984}La_{0.016}O_3$ NWs	954 557	24 202



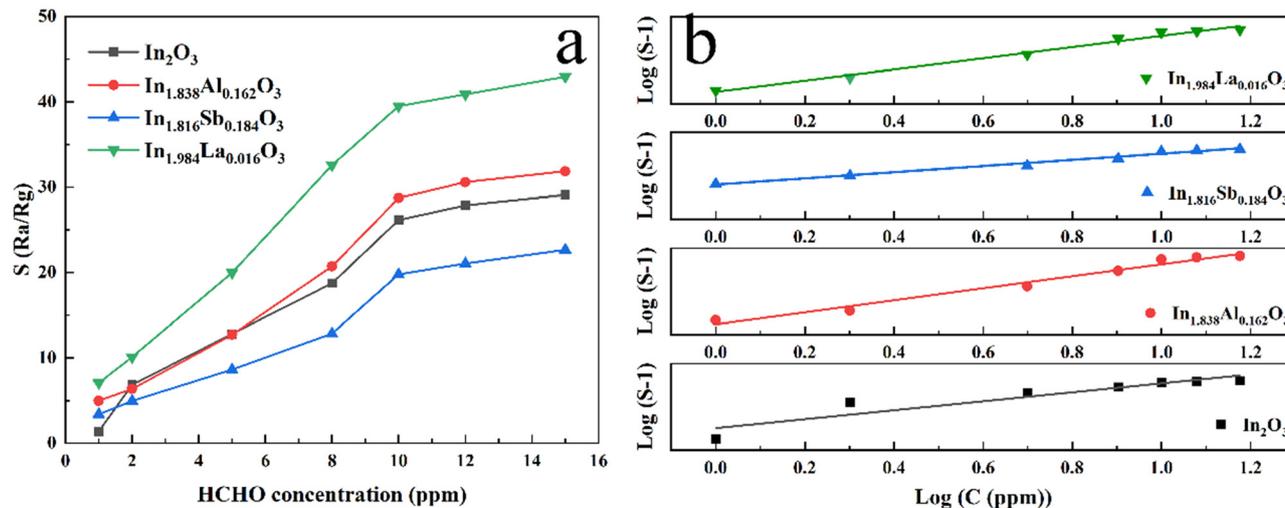


Fig. 8 Concentration-dependent response curves (a) and the predicted concentration-response curves (b) for  $\text{In}_2\text{O}_3$  and the cation-doped  $\text{In}_2\text{O}_3$  NW sensors to HCHO gas at 210 °C.

sensors, in which the response exhibits a good linear relationship with the HCHO gas concentration. Therefore, the HCHO gas concentration can be easily predicted according to the response value, indicating an excellent application in practice.

Furthermore, the selectivity of all the sensors towards 10 ppm ethanol, ammonia gas (ammonia water changed to ammonia gas after evaporation), water vapor, xylene, toluene, methanol and HCHO gases at 210 °C are given in Fig. 9(a). All sensors exhibit a much smaller response to water vapor than that of HCHO gas, indicating that the influence of humidity on the gas-sensing performance can be ignored. Clearly, the response to HCHO gas presents the highest value of all the gases, which indicates the excellent selectivity of the sensor to HCHO gas. In order to investigate the stability of  $\text{In}_2\text{O}_3$  and the cation-doped  $\text{In}_2\text{O}_3$  NW sensors, the response to 10 ppm HCHO gas was tested 5 times at 210 °C, as shown in Fig. 9(b).

The response of all the sensors hardly changes, indicating the long-term stability of  $\text{In}_2\text{O}_3$  and the cation-doped  $\text{In}_2\text{O}_3$  NWs. Compared with the work of other researchers, the response to HCHO gas using the different gas-sensing media is listed in Table 3, in which the  $\text{In}_{1.984}\text{La}_{0.016}\text{O}_3$  NW sensor presents one of the highest responses to 10 ppm HCHO gas with an  $S$  value of about 40.

### 3.3 Gas-sensing mechanism of cation-doped $\text{In}_2\text{O}_3$ NW sensors

For  $\text{In}_2\text{O}_3$  and the cation-doped  $\text{In}_2\text{O}_3$  NWs in air, the higher surface area adsorbed more oxygen molecules on the surface. The adsorbed oxygen molecules extract electrons from the surface shell and become  $\text{O}^-$  at 210 °C to form an electron-depletion layer.<sup>38</sup> As a result, the shell resistance in air ( $R_{\text{shell(air)}}$ ) increases dramatically owing to the high surface area

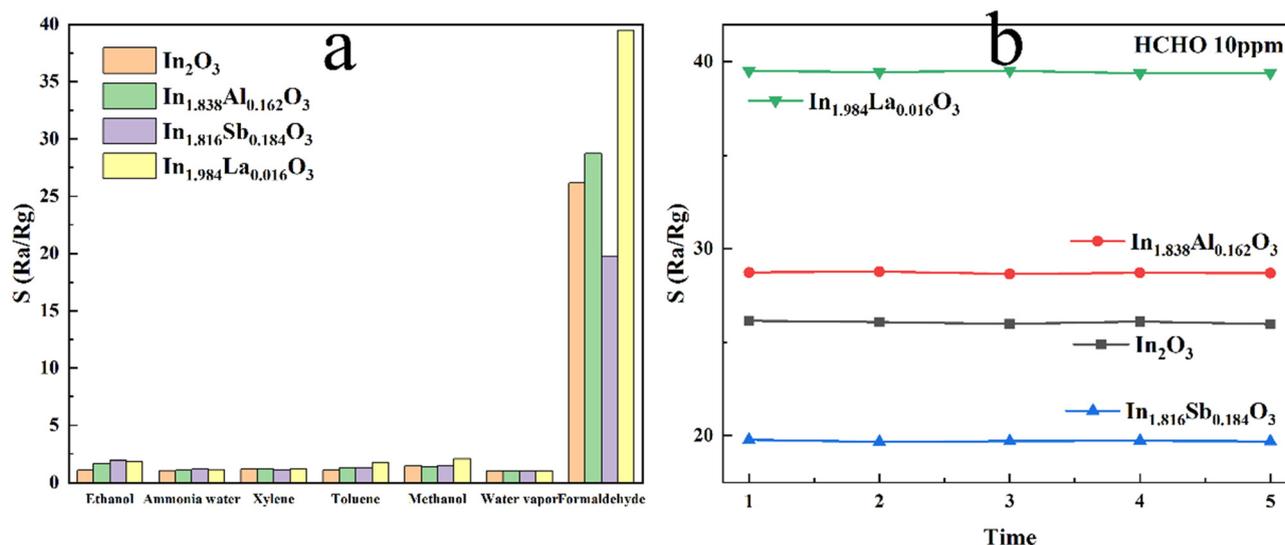


Fig. 9 Selectivity (a) and long-term stability (b) of  $\text{In}_2\text{O}_3$  and the cation-doped  $\text{In}_2\text{O}_3$  NW sensors.



Table 3 HCHO gas-sensing properties of the different sensing media

Sensing material	HCHO			Ref.
	$T_{\text{sens}}$ (°C)	concentration (ppm)	$S$	
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> particles	270	500	23	30
ZnSnO <sub>3</sub> cubic	180	30	25	31
rGO/ZnSnO <sub>3</sub> microspheres	110	10	12	32
In <sub>2</sub> O <sub>3</sub> @rGO nanocubes	225	25	88	33
WO <sub>x</sub> /In <sub>2</sub> O <sub>3</sub> nanosheets	170	100	25	34
SnO <sub>2</sub> nanowires	270	10	2.45	35
Er-doped porous In <sub>2</sub> O <sub>3</sub> nanotubes	260	20	12	36
2 at% Al-doped ZnO	320	50	6.8	37
In <sub>1.984</sub> La <sub>0.016</sub> O <sub>3</sub> NWS	210	10	39.51	This work

of the mesoporous structures. The more adsorptive O<sup>-</sup> that are present, the thicker electron-depletion layer, as shown in Fig. 10. When HCHO gas is injected, the HCHO gas molecules prefer to react with O<sup>-</sup> at the surface. The adsorptive O<sup>-</sup> decreases with the increasing HCHO gas concentration and more and more electrons are re-injected back to the shell of In<sub>2</sub>O<sub>3</sub> and the cation-doped In<sub>2</sub>O<sub>3</sub> NWS.  $R_{\text{gas}}$  hardly changes without the adsorbed O<sup>-</sup> at the extreme high concentration of HCHO gas. As a result,  $R_{\text{gas}}$  decreases and the response increases with the HCHO gas concentration.

The conduction pathway for n-type In<sub>2</sub>O<sub>3</sub> NWS is equivalent to a series circuit of the core resistance ( $R_{\text{core}}$ ) and shell resistance ( $R_{\text{shell}}$ ).<sup>29</sup> In this way, the response can be rewritten as follows in eqn (5):

$$S = \frac{R_{\text{air}}}{R_{\text{gas}}} = \frac{R_{\text{core}} + R_{\text{shell(air)}}}{R_{\text{core}} + R_{\text{shell(gas)}}} = 1 + \frac{R_{\text{shell(air)}} - R_{\text{shell(gas)}}}{(R_{\text{core}} + R_{\text{shell}})_{\text{gas}}} = 1 + \frac{\Delta R_{\text{shell(air-gas)}}}{R_{\text{(gas)}}} \quad (5)$$

If a higher response is wanted,  $\Delta R_{\text{shell(air-gas)}}$  should be big enough and  $R_{\text{gas}}$  should be small as much as possible. The same-valent Al<sup>3+</sup>, Sb<sup>3+</sup> and La<sup>3+</sup> ions that are substituted for In<sup>3+</sup> in the In<sub>2</sub>O<sub>3</sub> NWS hardly change the carrier concentration of the In<sub>1.816</sub>Sb<sub>0.184</sub>O<sub>3</sub>, In<sub>1.838</sub>Al<sub>0.162</sub>O<sub>3</sub> and In<sub>1.984</sub>La<sub>0.016</sub>O<sub>3</sub> NWS compared with the undoped In<sub>2</sub>O<sub>3</sub> NWS. Furthermore, the In<sub>2</sub>O<sub>3</sub>, In<sub>1.838</sub>Al<sub>0.162</sub>O<sub>3</sub>, In<sub>1.816</sub>Sb<sub>0.184</sub>O<sub>3</sub> and In<sub>1.984</sub>La<sub>0.016</sub>O<sub>3</sub> NWS are synthesized using SBA-15 silica as a hard template under the same chemical conditions and calcination temperature, so the microstructures, morphology and defects of all the samples should be similar. Only in this way can the influence of the

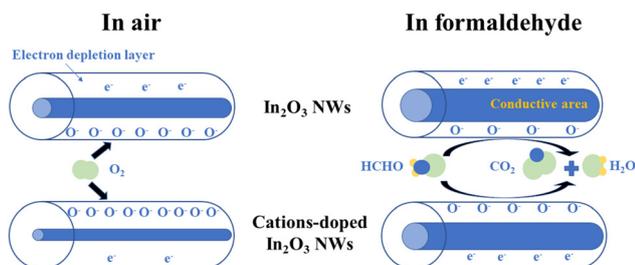


Fig. 10 Theoretical schematic of the electron-depletion layer for In<sub>2</sub>O<sub>3</sub> and the cation-doped In<sub>2</sub>O<sub>3</sub> NWS in air and formaldehyde.

lattice distortion caused by cation doping on the gas-sensing performance of the In<sub>1.816</sub>Sb<sub>0.184</sub>O<sub>3</sub>, In<sub>1.838</sub>Al<sub>0.162</sub>O<sub>3</sub> and In<sub>1.984</sub>La<sub>0.016</sub>O<sub>3</sub> NW sensors be truly revealed. As is known, cation-doping leads to lattice distortion of the In<sub>2</sub>O<sub>3</sub> NWs for the different cation radii, resulting in a change in the oxygen vacancy concentration or chemical state of the adsorbed ions on the surface.<sup>39</sup> At the same time, cation doping causes destruction of the periodic potential field, making the In<sub>2</sub>O<sub>3</sub> lattice more open, which facilitates the diffusion of molecular oxygen through the In<sub>2</sub>O<sub>3</sub> lattice.<sup>40</sup>

The radii of Al<sup>3+</sup> (0.0535 nm) and La<sup>3+</sup> (0.1032 nm) present a larger difference with that of In<sup>3+</sup> (0.080 nm), whereas Sb<sup>3+</sup> (0.076 nm) possesses a similar radius to In<sup>3+</sup>.<sup>41</sup> Doping with the large La<sup>3+</sup> radius causes the largest lattice distortion for the In<sub>1.984</sub>La<sub>0.016</sub>O<sub>3</sub> NW lattice whereas doping with Al<sup>3+</sup> and Sb<sup>3+</sup>, which have a smaller radius than La<sup>3+</sup>, bring about a smaller lattice distortion, as shown in schematic diagram in Fig. 11. Moreover, the cation-doped In<sub>2</sub>O<sub>3</sub> NWs present the similar specific surface areas with a value of about 50 m<sup>2</sup> g<sup>-1</sup>, which possesses the similar adsorbed oxygen owing to the mesoporous structures.<sup>42</sup> As shown in Fig. 10, the larger lattice distortion results in more oxygen vacancies, which leads to the more adsorbed oxygen on the surface of the cation-doped In<sub>2</sub>O<sub>3</sub> NWS.<sup>22</sup> It was reported that rare-earth doping increases the surface alkalinity, which further improves the adsorbed oxygen of the In<sub>1.984</sub>La<sub>0.016</sub>O<sub>3</sub> NWS.<sup>43</sup> The more adsorbed oxygen leads to a larger change of  $\Delta R_{\text{shell(air-gas)}}$  according to eqn (5) for the In<sub>1.984</sub>La<sub>0.016</sub>O<sub>3</sub> NWS sensor.

Moreover, cation-doping generates the lattice distortion of the In<sub>1.816</sub>Sb<sub>0.184</sub>O<sub>3</sub>, In<sub>1.838</sub>Al<sub>0.162</sub>O<sub>3</sub> and In<sub>1.984</sub>La<sub>0.016</sub>O<sub>3</sub> NWS, which scatters the electron transport and increases the  $R_{\text{gas}}$  value. The cation-doping content increases from In<sub>1.984</sub>La<sub>0.016</sub>O<sub>3</sub> to In<sub>1.838</sub>Al<sub>0.162</sub>O<sub>3</sub> and In<sub>1.816</sub>Sb<sub>0.184</sub>O<sub>3</sub> NWS, leading to the highest  $R_{\text{gas}}$  for the In<sub>1.816</sub>Sb<sub>0.184</sub>O<sub>3</sub> NWS and the lowest  $R_{\text{gas}}$  for the In<sub>1.984</sub>La<sub>0.016</sub>O<sub>3</sub> NWS. According to eqn (5), the response of all the sensors to HCHO gas increases from 19.78 for In<sub>1.816</sub>Sb<sub>0.184</sub>O<sub>3</sub> to 26.16 for In<sub>2</sub>O<sub>3</sub>, 28.73 for In<sub>1.838</sub>Al<sub>0.162</sub>O<sub>3</sub> and 39.51 for In<sub>1.984</sub>La<sub>0.016</sub>O<sub>3</sub>. La-doping not only improves the adsorbed oxygen on the surface of the In<sub>2</sub>O<sub>3</sub> NW sensor but also increases  $R_{\text{gas}}$ . Compared with the In<sub>2</sub>O<sub>3</sub>, In<sub>1.816</sub>Sb<sub>0.184</sub>O<sub>3</sub> and In<sub>1.838</sub>Al<sub>0.162</sub>O<sub>3</sub> NW

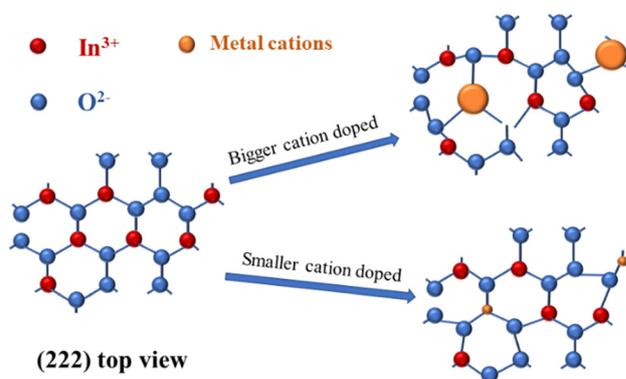


Fig. 11 Schematic diagram of lattice distortion for In<sub>2</sub>O<sub>3</sub> and the cation-doped In<sub>2</sub>O<sub>3</sub> NWS.



sensors, the  $\text{In}_{1.984}\text{La}_{0.016}\text{O}_3$  NW sensor presents the highest response owing to the larger lattice distortion and the lowest doping content.

## 4. Conclusions

Mesoporous  $\text{In}_2\text{O}_3$  and cation-doped  $\text{In}_2\text{O}_3$  NWs have been synthesized using a nanocasting method. Different metals (Al, Sb and La) have been introduced to study the influence on the sensing performance. The characterization results show that both cation-doped  $\text{In}_2\text{O}_3$  and undoped  $\text{In}_2\text{O}_3$  NWs have a long-range-order mesoporous structure with a high specific surface area. All sensors present the best gas-sensing performance at the optimal working temperature of 210 °C, and the response of the La-doped  $\text{In}_2\text{O}_3$  NWs reaches the maximum value of 39.51 for 10 ppm HCHO gas. The cation doping not only brings about lattice distortion to improve the adsorbed oxygen on the surface but also increases the ground-state resistance of the  $\text{In}_2\text{O}_3$  NWs. Rare-earth doping increases the surface alkalinity, improving the sensor response towards HCHO. La-doping increases both the adsorbed oxygen and the lattice distortion of La-doped  $\text{In}_2\text{O}_3$  NWs, and is responsible for the highly enhanced HCHO gas-sensing performance of the  $\text{In}_{1.984}\text{La}_{0.016}\text{O}_3$  NWs sensor.

## Conflicts of interest

The authors declare that they have no conflict of interest.

## Acknowledgements

This work was supported by the Natural Science Foundation of Zhejiang Province (LY16E030004 and LY20E020011) and the National Natural Science Foundation of China (U1809216).

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