

## PAPER

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# Rare-earth-doped indium oxide nanosphere-based gas sensor for highly sensitive formaldehyde detection at a low temperature†

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Formaldehyde (HCHO) is widely viewed as a carcinogenic volatile organic compound in indoor air pollution that can seriously threaten human health and life. Thus, there is a critical need to develop gas sensors with improved sensing performance, including outstanding selectivity, low operating temperature, high responsiveness, and short recovery time, for HCHO detection. Currently, doping is considered an effective strategy to raise the sensing performance of gas sensors. Herein, various rare earth elements-doped indium oxide (RE-In<sub>2</sub>O<sub>3</sub>) nanospheres were fabricated as gas sensors for improved HCHO detection via a facile and environmentally solvothermal method. Such RE-In<sub>2</sub>O<sub>3</sub> nanosphere-based sensors exhibited remarkable gas-sensing performance, including a high selectivity and stability in air. Compared with pure, Yb-, Dy-doped In<sub>2</sub>O<sub>3</sub> and different La ratios doped into In<sub>2</sub>O<sub>3</sub>, 6% La-doped In<sub>2</sub>O<sub>3</sub> (La-In<sub>2</sub>O<sub>3</sub>) nanosphere-based sensors demonstrated a high response value of 210 to 100 ppm at 170 °C, which was around 16 times higher than that of the pure In<sub>2</sub>O<sub>3</sub> sensor, and also exhibited a detection limit of 10.9 ppb, and a response time of 30 s to 100 ppm HCHO with a recovery time of 160 s. Finally, such superior sensing performance of the 6% La-In<sub>2</sub>O<sub>3</sub> sensors was proposed to be attributed to the synergistic effect of the large specific surface area and enhanced surface oxygen vacancies on the surface of In<sub>2</sub>O<sub>3</sub> nanospheres, which produced chemisorbed oxygen species to release electrons and provided abundant reaction sites for HCHO gas. This study sheds new light on designing nanomaterials to build gas sensors for HCHO detection.

Received 9th September 2022

Accepted 11th December 2022

DOI: 10.1039/d2nr04972d

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## 1 Introduction

Formaldehyde (HCHO) is a colorless, flammable, pungent odorous volatile organic compound.<sup>1</sup> With the continuous development of industry, HCHO is widely used in textiles, furniture, and other daily necessities thanks to its excellent adhesion.<sup>2</sup> However, a narrow indoor environment is very unfavorable for the diffusion and oxidative decomposition of HCHO, which makes HCHO one of the most important components of indoor pollutants. HCHO has a pungent odor, so it can also be smelled at low concentrations. Usually people's

olfactory threshold for HCHO is 0.06–0.07 mg m<sup>-3</sup>. IARC specifically classifies HCHO as a class I carcinogen, and as a causative factor for nasopharyngeal carcinoma and leukemia.<sup>3</sup> It has been found that long-term exposure to HCHO can lead to headache, dizziness, and sensory disturbance. In addition, HCHO can also cause respiratory dysfunction and liver poisoning. In severe cases, it can lead to gene mutations.<sup>4</sup> Due to the toxicity of HCHO, the World Health Organization (WHO) has set the exposure limit of HCHO to 0.07 ppm within 30 min.<sup>3</sup> OSHA has also set an allowable exposure limit of 0.75 ppm HCHO for an 8 h workday.<sup>5</sup> Therefore, from the perspective of health and environmental protection, monitoring the concentration of HCHO in the environment is of great significance.

In recent decades, with the rapid development of the Internet of Things (IoT), many gas sensors have been developed to detect toxic and harmful gases. Sensors can give more accurate information than human senses. In particular, gas sensors based on a metal oxide semiconductor (MOS) have received extensive attention. Compared with traditional detection methods, it has the characteristics of miniaturization, low cost, easiness to manufacture, and portability.<sup>6</sup> Therefore, it

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d2nr04972d>

has important applications in monitoring human health and detecting toxic gases. At present, many metal oxide semiconductors have been reported to be used to detect HCHO, such as ZnO,<sup>7</sup> SnO<sub>2</sub>,<sup>8</sup> NiO,<sup>9</sup> and TiO<sub>2</sub>.<sup>10</sup> Among them, indium oxide (In<sub>2</sub>O<sub>3</sub>), as an n-type semiconductor with an appropriate band gap, has become a kind of sensor material with great development potential by virtue of its superior electronic and optical properties.<sup>11,12</sup> Gu *et al.* reported the synthesis of In<sub>2</sub>O<sub>3</sub> nanoparticles with excellent HCHO gas-sensing performance, whose response to 100 ppm HCHO could reach 80 at 150 °C.<sup>13</sup> This showed that In<sub>2</sub>O<sub>3</sub>-based nanomaterials have great application potential in the field of HCHO detection. However, pure In<sub>2</sub>O<sub>3</sub> still has the problems of a low response, high operating temperature, and poor selectivity, which limit its practical application.<sup>14</sup> In this regard, researchers have adopted many methods to improve the sensing performance of pure In<sub>2</sub>O<sub>3</sub>, such as by constructing two-dimensional (2D) and three-dimensional (3D) nanomaterials, forming nanocomposites, doping metal impurities, and through light excitation.<sup>15,16</sup> It has been reported that the rare earth (RE) element doping of In<sub>2</sub>O<sub>3</sub> can change the microstructure of a material, thereby effectively improving the gas-sensing properties of a material.<sup>17</sup> Thangaraj *et al.* found that doping Tb<sup>3+</sup> could effectively improve the response of In<sub>2</sub>O<sub>3</sub> nanoparticles to ethanol.<sup>18</sup> Wang *et al.* found that the response value of Nd-doped In<sub>2</sub>O<sub>3</sub> porous nanotubes to 100 ppm of HCHO was 48, which was significantly higher than that of pure In<sub>2</sub>O<sub>3</sub>.<sup>19</sup> Therefore, the doping of rare earth elements can greatly improve the gas-sensing performance of In<sub>2</sub>O<sub>3</sub>-based sensors, which gives us some inspiration for the detection of HCHO and to question whether the modification of In<sub>2</sub>O<sub>3</sub>-based sensors with rare earth elements can show better performance in the detection of HCHO. Therefore, rare earth (RE) element modification can greatly improve the gas-sensing performance of In<sub>2</sub>O<sub>3</sub>-based sensors, and at the same time has great poten-

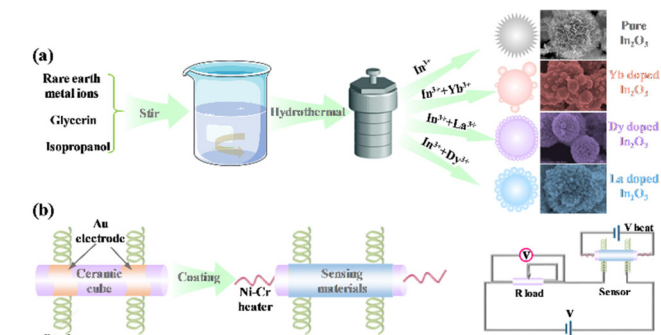


Fig. 1 Schematic diagram of the preparation of different RE-In<sub>2</sub>O<sub>3</sub> nanospheres (a) and their use in the design of a gas sensor (b).

tial in the detection of HCHO. However, to the best of our knowledge, there are relatively few studies on HCHO sensors based on RE-doped In<sub>2</sub>O<sub>3</sub> (RE-In<sub>2</sub>O<sub>3</sub>).

In this work, we prepared various RE-element-doped In<sub>2</sub>O<sub>3</sub> (RE-In<sub>2</sub>O<sub>3</sub>) nanospheres by a simple and environmentally friendly solvothermal method (Fig. 1a) and studied the doping effect of different REs and doped lanthanum (La) ratios on the gas-sensing performances of In<sub>2</sub>O<sub>3</sub> sensors for HCHO detection (Fig. 1b). Through comparing the structure, gas response, and detection limit, RE-In<sub>2</sub>O<sub>3</sub> nanospheres were found to effectively improve the sensing performance of In<sub>2</sub>O<sub>3</sub>, with lanthanum-doped In<sub>2</sub>O<sub>3</sub> (La-In<sub>2</sub>O<sub>3</sub>) nanospheres exhibiting the optimized performance with high response values of 210 to 100 ppm at 170 °C, a detection limit of 10.9 ppb, and outstanding selectivity and stability. Further compared with doping 3% and 9% La into In<sub>2</sub>O<sub>3</sub>, the 6% La-In<sub>2</sub>O<sub>3</sub>-based sensor possessed the best gas-sensing properties. These results were attributed to the fact that the incorporation of RE elements into nanospheres can enlarge the specific surface area and enhance surface oxygen vacancies on the surface of the In<sub>2</sub>O<sub>3</sub> nanospheres.<sup>20</sup> Therefore, RE-In<sub>2</sub>O<sub>3</sub> could be expected to be a strong candidate for the detection of HCHO in practice.



Houjuan Zhu

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Her research focuses on the design and synthesis of various nanomaterials, including two-dimensional nanosheets, transition metal dichalcogenides quantum dots, and semiconducting polymer nanoparticles, in bioimaging, cancer therapy, antibacterial, biosensing, and photocatalysis.

## 2 Experimental

All the chemical reagents in the experiments were of analytical grade and used as received without further purification.

### 2.1 Preparation of pure and RE-doped In<sub>2</sub>O<sub>3</sub> nanospheres

A typical synthesis was as follows: In (NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O (0.5 g) and 6 mol% (LaCl<sub>3</sub>·6H<sub>2</sub>O, DyCl<sub>3</sub>·6H<sub>2</sub>O, YbCl<sub>3</sub>·6H<sub>2</sub>O) solution were respectively dispersed in 48 mL of isopropanol and stirred for 30 min. Subsequently, 16 g of glycerin was added to the aforementioned solution and stirred for 1 h. The above solution was then transferred to an autoclave and heated at 180 °C for 6 h, and then the autoclave was cooled to room temperature. The reacted mixture was centrifuged at 8000 rpm and washed 3–5 times with distilled water and absolute ethanol to obtain a solid product, followed by drying at 80 °C for 12 h. The pro-

ducts were heated from room temperature to 350 °C at a rate of 5 °C min<sup>-1</sup> under an air atmosphere to produce RE-In<sub>2</sub>O<sub>3</sub>.

## 2.2 Characterization of RE-In<sub>2</sub>O<sub>3</sub> nanospheres

The powder X-ray diffraction patterns were obtained using a Rigaku Ultima IV system (Cu K $\alpha$ ,  $\lambda$  = 1.54051 Å) in the range of 5°–80° at room temperature. The morphological and elemental composition were observed by field emission scanning electron microscopy (FE-SEM, JEOL) along with elemental mapping. Nitrogen (N<sub>2</sub>) adsorption–desorption isotherms were collected at 77 K on an ASAP 2460 instrument (Micromeritics). The surface areas were determined by the Brunauer–Emmett–Teller (BET) method. The element compositions were characterized by X-ray photoelectron spectroscopy (XPS) on a Thermo Escalab 250 electron spectrometer using Al K irradiation.

## 2.3 Fabrication of a gas sensor device based on RE-In<sub>2</sub>O<sub>3</sub> nanospheres

The preparation process of the RE-In<sub>2</sub>O<sub>3</sub> sensor device was as follows. First, the synthetic sample was mixed with a certain amount of deionized water in an agate mortar to form a uniform slurry, and then was coated with ceramics. The film was formed by drying at natural temperature. A Ni–Cr heating wire was inserted into the ceramic tube as a heater, and the working temperature was controlled by controlling the heating current. It was then welded to a black hexagonal base. Finally, it was put on an AS-20 sensor aging stage and aged for 10 h under 115 mA heating current. A schematic diagram of the RE-In<sub>2</sub>O<sub>3</sub> sensor is shown in Fig. 1b. The Ni–Cr heating wire was inserted into the ceramic tube as the heater, and the optimal operating temperature was controlled by controlling the heating current.

## 2.4 Gas-sensing measurements

The working principle and sensing performance of the sensor were tested with the gas-sensing analysis system. In the gas-sensing experiment, when the relative humidity of the air was about 50% (in Maoming City, Guangdong Province, the relative humidity is usually high), the air was used as the background gas. Liquid volume calculation software (Elite. Tech.) was used to calculate the volume of liquid with the required concentration injected into the gas chamber, and then the right amount of liquid was injected into the evaporating dish set in the gas chamber with a microsyringe, and then evaporated completely at a temperature higher than its boiling point. The response of the sensor is defined as  $S = R_a/R_g$ , where  $R_a$  represents the resistance of the sensor in the air atmosphere, and  $R_g$  represents the resistance of the sensor in the target gas.

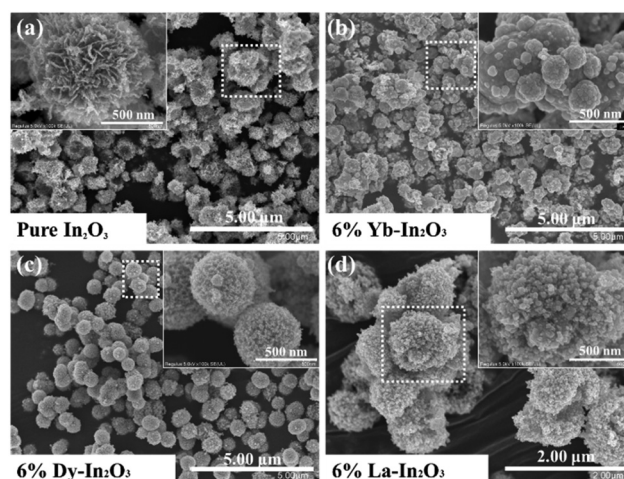
# 3 Results and discussion

## 3.1 Structural and morphological characterization

RE-In<sub>2</sub>O<sub>3</sub> nanospheres and pure In<sub>2</sub>O<sub>3</sub> were fabricated using a mixture of RE ions and glycerine as a precursor solution by a simple one-step solvothermal method, as presented in Fig. 1a.

The morphologies and microstructures of the as-synthesized RE-In<sub>2</sub>O<sub>3</sub> nanospheres and pure In<sub>2</sub>O<sub>3</sub> were studied by scanning electron microscopy (SEM). As shown in Fig. 2a, pure In<sub>2</sub>O<sub>3</sub> showed irregular nanoflowers with good monodispersity and uniformity formed by the self-assembly of nanosheets composed of small nanospheres. With the doping of RE elements, the morphology of RE-In<sub>2</sub>O<sub>3</sub> changed into a relatively uniform large nanosphere assembled from small nanospheres, as depicted in Fig. 2(b–d). It was evident that no other morphologies could be found from the panoramic SEM images, showing a high yield of these nanostructures. From the enlarged SEM images in Fig. 2(b–d), different-sized small nanospheres were observed to grow on the surface of a big nanosphere. These adjacent nanospheres were in contact with each other, enabling the gas to migrate to the internal space of the material, thereby increasing the response of the material to HCHO vapor. Also, the sizes of the small nanospheres were found to decline with the doped rare earth elements changing from Yb, to La, to Dy, making RE-In<sub>2</sub>O<sub>3</sub> materials with different improved gas-sensing performances for HCHO detection.

To preliminarily understand the chemical elemental distribution in these nanostructures, elemental mapping was further performed of the RE-In<sub>2</sub>O<sub>3</sub> nanospheres and pure In<sub>2</sub>O<sub>3</sub> and the results are shown in Fig. 3. As expected, In (green) and O (cyan) elements could be clearly detected in the selected area of both the pure In<sub>2</sub>O<sub>3</sub> nanoflowers and RE-In<sub>2</sub>O<sub>3</sub> nanospheres, showing the successful formation of In<sub>2</sub>O<sub>3</sub> nanostructures. Besides this, Yb (red), Dy (violet), and La (blue) elements could also be observed and were homogeneously distributed and showed no apparent element separation or aggregation in Yb-In<sub>2</sub>O<sub>3</sub> (Fig. 3h), Dy-In<sub>2</sub>O<sub>3</sub> (Fig. 3l), or La-In<sub>2</sub>O<sub>3</sub> (Fig. 3p), respectively. These findings indicated that the RE (La, Yb, and Dy) dopants were effectively bound to the surface of the In<sub>2</sub>O<sub>3</sub> sensing materials. Furthermore, to further show the chemical composition of the pure In<sub>2</sub>O<sub>3</sub> and RE-In<sub>2</sub>O<sub>3</sub>



**Fig. 2** SEM images of pure-In<sub>2</sub>O<sub>3</sub> nanoflowers (a), Yb-In<sub>2</sub>O<sub>3</sub> nanospheres (b), Dy-In<sub>2</sub>O<sub>3</sub> nanospheres (c), and La-In<sub>2</sub>O<sub>3</sub> nanospheres (d).



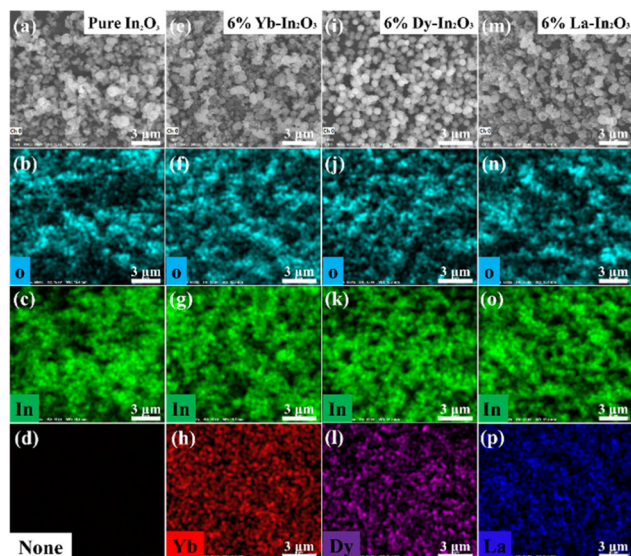


Fig. 3 FESEM images and elemental mapping images of pure  $\text{In}_2\text{O}_3$  nanoflowers (a–d),  $\text{Yb-In}_2\text{O}_3$  nanospheres (e–h),  $\text{Dy-In}_2\text{O}_3$  nanospheres (i–l), and  $\text{La-In}_2\text{O}_3$  nanospheres (m–p), scale bar: 3  $\mu\text{m}$ .

nanospheres, the corresponding electron dispersive spectroscopy (EDS) was used to analyze their element amounts (Fig. S1†). Obviously, the EDS spectra showed that there were oxygen (O) and indium (In) in both the pure  $\text{In}_2\text{O}_3$  and RE- $\text{In}_2\text{O}_3$  nanospheres, as well as the presence of Yb, Dy, and La in the corresponding RE-doped  $\text{In}_2\text{O}_3$  nanostructures, which was consistent with the results from the element mapping. In addition, the ratios of the doped RE elements and In element in the 6%  $\text{La-In}_2\text{O}_3$ , 6%  $\text{Yb-In}_2\text{O}_3$ , and 6%  $\text{Dy-In}_2\text{O}_3$  were respectively about 6.04%, 6.26%, and 6.06%, showing that there were no additional pollutants in the synthesized samples.

To explore the crystalline structure of these  $\text{In}_2\text{O}_3$  nanostructures, the X-ray diffraction (XRD) spectra for all the samples were determined. From Fig. 4a, it could be clearly observed that the XRD peaks for pure  $\text{In}_2\text{O}_3$  and RE- $\text{In}_2\text{O}_3$  were a little wide and strong, suggesting their relatively good crystallinity. It was notable that the major diffraction peaks of all the samples were located at around  $21.50^\circ$ ,  $30.58^\circ$ ,  $37.69^\circ$ ,  $39.81^\circ$ ,  $40.80^\circ$ ,  $45.69^\circ$ ,  $51.02^\circ$ , and  $60.67^\circ$ , corresponding to the (211),

(222), (411), (420), (422), (431), (440), and (622) lattice planes, respectively, which were in good agreement with the peaks of cubic-phase  $\text{In}_2\text{O}_3$  (JCPDS Card No. 71-2194). In addition, the RE- $\text{In}_2\text{O}_3$  nanospheres did not show obvious impurity peaks, indicating that the doping of RE elements did not generate the RE oxide crystal phase, or significantly damage the cubic structure of  $\text{In}_2\text{O}_3$ .

At the same time, according to the calculation by the Scherrer formula in eqn (1),<sup>21</sup> where  $\lambda$  is the X-ray wavelength (1.54056 Å), and  $\theta$  and  $\beta$  are respectively the Bragg diffraction angle and the peak width at half maximum. With the doping of RE elements, the average grain sizes of  $\text{Dy-In}_2\text{O}_3$ ,  $\text{La-In}_2\text{O}_3$ , and  $\text{Yb-In}_2\text{O}_3$  were calculated to be respectively 15.06, 15.46, and 22.14 nm, which were higher than that of pure  $\text{In}_2\text{O}_3$  (8.23 nm), as shown in Table 1, indicating the incorporation of RE ions could effectively prevent the grain growth of  $\text{In}_2\text{O}_3$ . Furthermore, the ion radii of  $\text{Yb}^{3+}$ ,  $\text{Dy}^{3+}$ , and  $\text{La}^{3+}$  were respectively 0.868, 0.912, and 1.032 Å, which were all larger than that of  $\text{In}^{3+}$  (0.81 Å). With the introduction of these RE ions into the  $\text{In}_2\text{O}_3$  lattice, the lattice positions of  $\text{In}^{3+}$  were replaced to induce an increase in the interplanar spacing ( $d$ ) of  $\text{In}_2\text{O}_3$  lattice.<sup>22</sup> In detail, the variations in RE- $\text{In}_2\text{O}_3$  were investigated through calculating the lattice constant and microstrain ( $\epsilon$ ) (Table 1), which were determined by eqn (2) and (3).

$$D = \frac{0.89 \times \lambda}{\beta \times \cos \theta} \quad (1)$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + l^2 + k^2}} \quad (2)$$

$$2\epsilon = \Delta d / 2d \quad (3)$$

It can be observed from Table 1 that the lattice constant was increased to a certain extent when doping in RE ions, which may be attributed to higher radius of the doping ions and aliovalent substitution. Apart from this, the microstrain ( $\epsilon$ ) was also found to be gradually increase. This could be due to the lattice contraction resulting from the lattice constant, finally causing structural defects in the RE- $\text{In}_2\text{O}_3$  nanospheres.

In addition, the interaction between the doping ratios of the RE elements with the  $\text{In}_2\text{O}_3$  lattice was investigated by XRD. As depicted in Fig. 4b, no change was observed in the

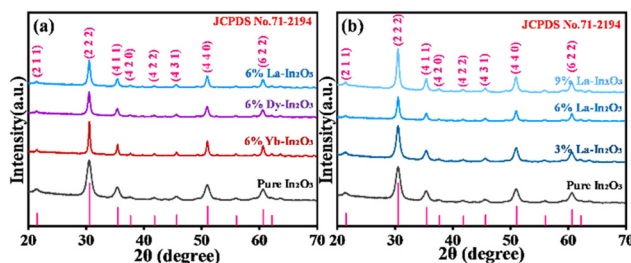


Fig. 4 XRD patterns of (a) pure  $\text{In}_2\text{O}_3$  and 6% RE- $\text{In}_2\text{O}_3$  and (b) 0%, 3%, 6%, and 9%  $\text{La-In}_2\text{O}_3$ .

Table 1 Grain sizes, lattice constants, and microstrains of all the samples

Samples	Grain size, $D$ (nm)	$\lambda$ (Å)	Lattice constant, $a = b = c$ (Å)	$d_{222}$ (Å)	Microstrain, $\epsilon$ (%)
Pure $\text{In}_2\text{O}_3$	8.23	1.54056	10.1348	2.925664	
6% $\text{Yb-In}_2\text{O}_3$	22.14	1.54056	10.13545	2.925852	0.003197605
6% $\text{Dy-In}_2\text{O}_3$	15.06	1.54056	10.14128	2.927537	0.031976739
3% $\text{La-In}_2\text{O}_3$	10.34	1.54056	10.14178	2.927681	0.034439011
6% $\text{La-In}_2\text{O}_3$	15.46	1.54056	10.14188	2.927707	0.034886698
9% $\text{La-In}_2\text{O}_3$	13.07	1.54056	10.14328	2.928113	0.041809892

diffraction peaks with increasing the La doping ratios when comparing the major peaks of the four samples, thus showing no influence of the La doping ratio on the crystal  $\text{In}_2\text{O}_3$  lattice. Also, from Table 1, the average grain sizes of  $\text{La-In}_2\text{O}_3$  all increased, which effectively inhibited the grain growth of  $\text{In}_2\text{O}_3$  with the incorporation of 3%, 6%, and 9% of  $\text{La}^{3+}$ , being a maximum at 6% doping, which may be one reason behind this structure having the best gas-sensing performance. Furthermore, with the doping ratios of  $\text{La}^{3+}$  increasing from 0 to 9%, the interplanar spacing, lattice constants, and micro-strain all increased. Such phenomena could be explained from the greater introduction of  $\text{La}^{3+}$ , which led to more aliovalent substitution of  $\text{In}^{3+}$  by  $\text{La}^{3+}$  with a larger radius, also inducing more lattice distortion and contraction in the  $\text{In}_2\text{O}_3$  lattice, and thus generating more structural defects in  $\text{La-In}_2\text{O}_3$ .

To further study the internal architectures,  $\text{N}_2$  adsorption-desorption isotherm curves for the pure  $\text{In}_2\text{O}_3$  and  $\text{RE-In}_2\text{O}_3$  nanospheres were applied. As shown in Fig. S2,<sup>†</sup> the isotherms for the four samples presented with type V shapes, which clearly showed that all the  $\text{In}_2\text{O}_3$  samples had mesoporous features according to the IUPAC classification. Moreover, the specific surface areas of the pure  $\text{In}_2\text{O}_3$ ,  $\text{Yb-In}_2\text{O}_3$ ,  $\text{Dy-In}_2\text{O}_3$ , and  $\text{La-In}_2\text{O}_3$  nanospheres tested by BET were 37.71, 68.80, 52.13, and 70.77  $\text{m}^2 \text{g}^{-1}$ , respectively. The large specific surface area of such composites is an important factor for an adsorbed target gas because of the ability to support abundant reaction sites for facilitating gas molecular diffusion, consequently inducing improved gas-sensing performance.

To identify the chemical composition and valence states of the oxygen species of the pure  $\text{In}_2\text{O}_3$  and  $\text{RE-In}_2\text{O}_3$  NPs, X-ray photoelectron spectroscopy (XPS) was employed. All the binding energies were charge corrected with reference to the 284.5 eV for the C 1s line.<sup>23</sup> In particular, as shown in the magnified corresponding O 1s spectra of the pure  $\text{In}_2\text{O}_3$  and  $\text{RE-In}_2\text{O}_3$  in Fig. 5a, the chemical state of oxygen and the relative concentration of different oxygen states were analyzed by high-resolution XPS. It was obvious that the O 1s XPS spectra of the four samples were deconvoluted into two separate peaks by the best fitting, where the peak at a lower binding energy of  $529.5 \pm 0.3$  eV was attributed to the crystal lattice oxygen ( $\text{O}_\text{L}$ ) and the one at the position of  $531.1 \pm 0.2$  eV ( $\text{O}_\text{V}$ ) was ascribed to oxygen adsorbed on the surface of  $\text{In}_2\text{O}_3$ .<sup>24,25</sup> The corresponding area ratios of each component peak represented the contents of the two oxygen species in these samples, as shown in Fig. 5b. Clearly, the doping of RE elements was observed to significantly change the surface concentration of these oxygen species on the surface. It was acknowledged that the chemisorbed oxygen ( $\text{O}_\text{V}$ ) acted as an electron donor and played a significant role in the detection of gas. The proportion of  $\text{O}_\text{V}$  in the  $\text{RE-In}_2\text{O}_3$  nanospheres from the doping of Yb to La gradually increased from 51.72% to 72.81%, and they were all higher than that of the pure  $\text{In}_2\text{O}_3$  nanoflowers, indicating that the doping of RE elements into the  $\text{In}_2\text{O}_3$  lattice facilitated the increased adsorbed oxygen, thus improving the gas-sensing performance. This phenomenon may be related to the improved moisture resistance of metal oxides by doping metal

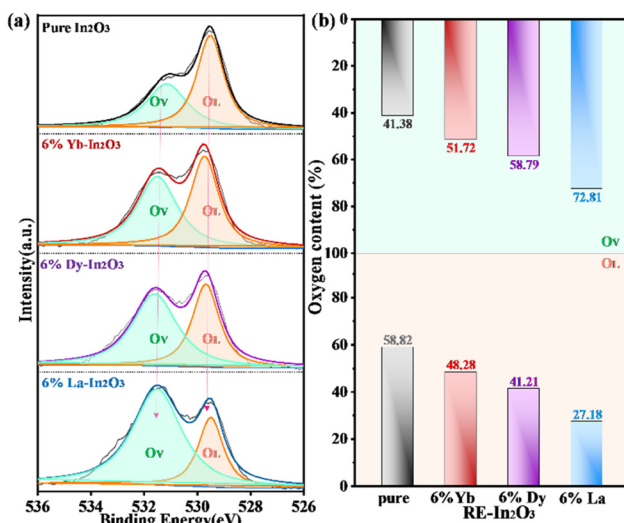


Fig. 5 O 1s high-resolution XPS spectra of the pure  $\text{In}_2\text{O}_3$ ,  $\text{RE-In}_2\text{O}_3$  nanospheres,  $\text{O}_\text{V}$ : chemisorbed oxygen;  $\text{O}_\text{L}$ : crystal lattice oxygen. (b) Relative contents of  $\text{O}_\text{V}$  and  $\text{O}_\text{L}$  in oxygen species of the pure  $\text{In}_2\text{O}_3$ ,  $\text{RE-In}_2\text{O}_3$  nanospheres.

elements<sup>26,27</sup> and the abundant reaction sites supported by the nanosphere structure with a large specific surface area. Specially, among these  $\text{RE-In}_2\text{O}_3$  nanospheres,  $\text{La-In}_2\text{O}_3$  significantly increased the highest content of  $\text{O}_\text{V}$  accompanied with the highest content of lattice oxygen ( $\text{O}_\text{L}$ ) being reduced, which may also be the main reason for the  $\text{La-In}_2\text{O}_3$  sensor having the best sensing performance for HCHO.<sup>28</sup>

### 3.2 Gas-sensing properties of $\text{RE-In}_2\text{O}_3$

The optimum working temperature is an important factor for a material's surface state during measuring the gas-sensing performance. To determine the optimal operating temperature of the nanoparticle sensor based on pure  $\text{In}_2\text{O}_3$  and  $\text{RE-In}_2\text{O}_3$ , we investigated the response of the four sensors to 100 ppm of HCHO to obtain the optimum working temperature (Fig. 6a). As displayed in Fig. 6b, the four sensors showed similar behaviors at different temperatures from 120 °C to 300 °C, where the response values of the four sensors increased with the increase in the working temperature until reaching the maximum value. This may be ascribed to the fact that it was hard for the adsorbed HCHO molecules to get enough thermal energy to react with the oxygen species at lower working temperature, following which the molecular motion could accelerate with the working temperature increasing. Thus, we could clearly see in Fig. 6b that the response values of the pure  $\text{In}_2\text{O}_3$  and  $\text{Yb-In}_2\text{O}_3$  sensors reached the maximum at 220 °C, while the maximum was at 170 °C for  $\text{La-In}_2\text{O}_3$  and  $\text{Dy-In}_2\text{O}_3$ . However, as the temperature increased further, the response value started to decrease, which was mainly because the desorption rate of HCHO was higher than the adsorption rate, and thus there was a large ratio of HCHO gas overflow.<sup>16,29</sup> Compared with the pure  $\text{In}_2\text{O}_3$  and other  $\text{RE-In}_2\text{O}_3$ , the response value of  $\text{La-In}_2\text{O}_3$  to 100 ppm HCHO at 170 °C

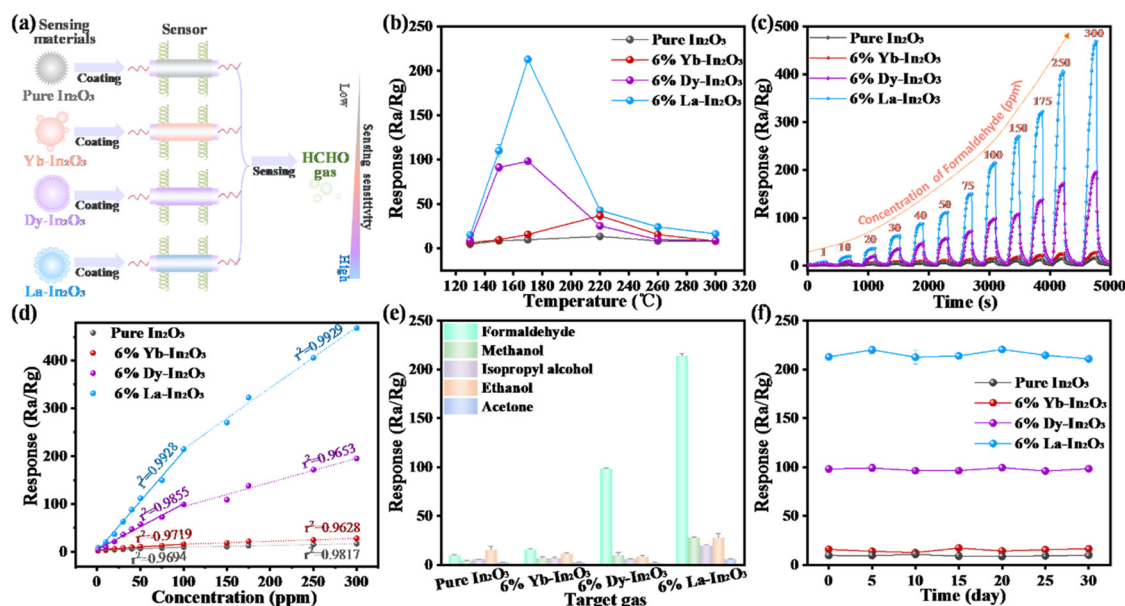
reached the best maximum at about 210, indicating the promotion effect of doping RE elements.

The dynamic response/recovery curves of the pure  $\text{In}_2\text{O}_3$  and RE- $\text{In}_2\text{O}_3$  sensors with the concentration of HCHO increasing from 1 to 300 ppm are shown in Fig. 6c. It could be seen that the response of both the pure  $\text{In}_2\text{O}_3$  and RE- $\text{In}_2\text{O}_3$  sensors gradually increased with the increase in HCHO concentration, and the response enhancement to HCHO increased from the pure  $\text{In}_2\text{O}_3$  sensor to the La- $\text{In}_2\text{O}_3$  sensor. Correspondingly, the curve of the responses in the concentration range of HCHO for these sensors at 170 °C was also investigated, as shown in Fig. 6d. These sensors displayed a stepwise distribution as the HCHO concentration increased from 1 to 300 ppm, and there was a good linear relationship for the four sensors for their sensor response and HCHO concentration from 1 to 100 ppm and from 100 to 300 ppm. Obviously, among these sensors, the slopes of the straight lines for the 6% La- $\text{In}_2\text{O}_3$  gas-sensing material were the largest in the two concentration ranges, implying that the 6% La- $\text{In}_2\text{O}_3$  sensor exhibited the highest sensitivity and the best gas-sensing properties. The selectivity is another critical prerequisite for gas sensors. Thus, the selectivity of the pure  $\text{In}_2\text{O}_3$  and RE- $\text{In}_2\text{O}_3$  sensors for a variety of gases, including ethanol, HCHO, isopropanol, acetone, and methanol, at 170 °C was further investigated. From Fig. 6e, it could be clearly seen that all the sensors had a higher response to HCHO gas over other gases, and RE- $\text{In}_2\text{O}_3$  possessed a higher response to HCHO compared with the pure  $\text{In}_2\text{O}_3$ . By contrast, the response value of La- $\text{In}_2\text{O}_3$  to HCHO gas over various gases was the highest, showing the excellent selectivity of RE- $\text{In}_2\text{O}_3$  toward HCHO at

the optimum working temperature. This result may indicate that the energy that was needed when various gas molecules reacted with adsorbed oxygen during the surface reaction process of the sensing materials may have existed at the appropriate resource levels. However, when this energy could not be obtained enough at lower temperature or of the gas got away from the surface of the sensing materials under the higher temperature, the preferred gas response could not be reached. Apparently, HCHO gas herein was more easily adsorbed and reacted on the surface of the RE- $\text{In}_2\text{O}_3$  sensors, especially the La- $\text{In}_2\text{O}_3$  sensors. Furthermore, continuous gas response measurements were also performed on the pure  $\text{In}_2\text{O}_3$  and RE- $\text{In}_2\text{O}_3$  sensors to study the long-term stability of the sensor, as shown in Fig. 6f. Obviously, the response values for the four sensors did not change even within 30 days, suggesting the outstanding long-term stability of the  $\text{In}_2\text{O}_3$ -based sensors, paving the foundation for HCHO sensing.

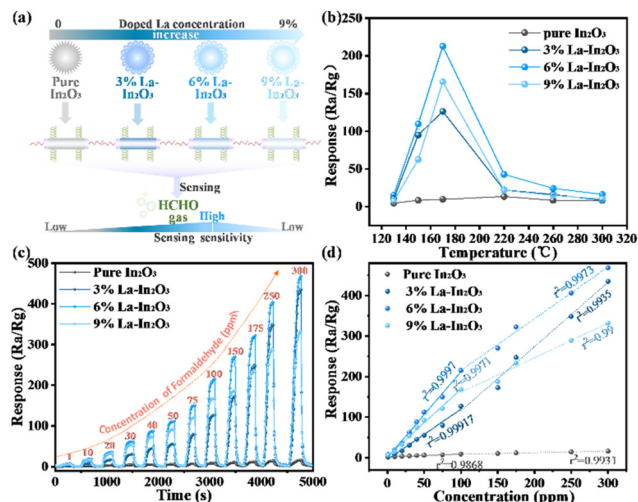
### 3.3 Gas-sensing performance of La- $\text{In}_2\text{O}_3$

According to above-mentioned results, the La- $\text{In}_2\text{O}_3$  sensor exhibited the best gas-sensing performance for HCHO gas compared with the other RE- $\text{In}_2\text{O}_3$  sensors, such as the lowest operating temperature, and the highest sensitivity and selectivity. Therefore, we further studied the gas-sensing performance of the La- $\text{In}_2\text{O}_3$  sensor in detail (Fig. 7a). The response of the four La- $\text{In}_2\text{O}_3$  sensors with doping 0%, 3%, 6%, 9% La to 100 ppm HCHO at different operating temperatures were studied, as shown in Fig. 7b. As can be seen, the optimum operating temperature of La- $\text{In}_2\text{O}_3$  was 170 °C, and the response value of the 6% La- $\text{In}_2\text{O}_3$  sensor (about 210) was the



**Fig. 6** (a) Diagram for sensing HCHO by the RE- $\text{In}_2\text{O}_3$  nanosphere-based gas sensor. (b) Response of the four sensors based on pure  $\text{In}_2\text{O}_3$  and RE- $\text{In}_2\text{O}_3$  to 100 ppm HCHO at different operating temperatures. (c) Response of the four sensors based on pure  $\text{In}_2\text{O}_3$  and RE- $\text{In}_2\text{O}_3$  to HCHO with different concentrations (1–300 ppm) at an operating temperature of 170 °C. (d) Response curves of these gas sensors towards different HCHO concentrations. (e) Response of the four sensors based on pure  $\text{In}_2\text{O}_3$  and RE- $\text{In}_2\text{O}_3$  to 100 ppm of different gases. (f) Response versus time curves for assessing the stability of the sensors upon exposure to 100 ppm HCHO.





**Fig. 7** (a) Schematic illustration showing La-In<sub>2</sub>O<sub>3</sub> doped with different levels for HCHO sensing. (b) Response of the four sensors based on *x* La-In<sub>2</sub>O<sub>3</sub> (*x* = 0%, 3%, 6%, 9%) to 100 ppm HCHO at different operating temperatures. (c) Typical responses of the two sensors based on *x* La-In<sub>2</sub>O<sub>3</sub> (*x* = 0%, 3%, 6%, 9%) La-In<sub>2</sub>O<sub>3</sub> in the HCHO concentration range of 1–300 ppm at 170 °C. (d) Linear relationship between the response and HCHO concentration from 1 to 300 ppm.

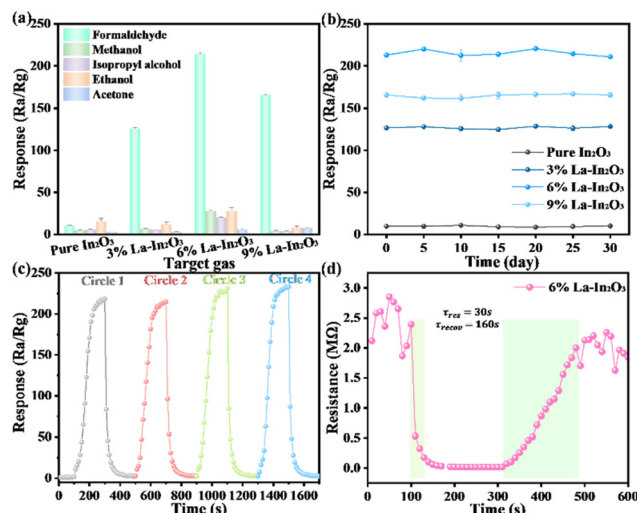
highest, which was nearly 1.68, 1.29, and 16 times that of the 3%, 9% La-In<sub>2</sub>O<sub>3</sub> sensor and pure In<sub>2</sub>O<sub>3</sub> sensor (about 13), respectively. Therefore, 6% was considered as the best doping ratio of La-In<sub>2</sub>O<sub>3</sub>. To display the dynamic response curves of the four 0%, 3%, 6%, 9% La-In<sub>2</sub>O<sub>3</sub>-based sensors to 100 ppm HCHO, the relationship between their response values and the concentration of HCHO were investigated. Fig. 7c displays that the response values of the four sensors increased with the HCHO concentration increasing in the range from 1 to 300 ppm and that the 6% La-In<sub>2</sub>O<sub>3</sub> sensors exhibited the best response enhancement. At the same time, the response linearity is an important criterion for the success of sensors. A good response linearity could give the sensor the ability to perform quantitative detection. From Fig. 7d, a linear relationship between the HCHO concentration and the response of the four La-In<sub>2</sub>O<sub>3</sub> sensors at 170 °C could be observed. It was not difficult to find that a good linearity of these sensors could be obtained in the HCHO concentration ranges of 1–100 ppm and 100–300 ppm respectively. The slopes and the *R*<sup>2</sup> values are shown in Table S1,<sup>†</sup> indicating the high correlation and good linear relationship. Also, the theoretical detection limit (TDL) of the gas sensors could be calculated by the following formula (eqn (4)).<sup>30</sup>

$$\text{TDL} = \frac{3 \text{ rms}_{\text{noise}}}{\text{slope}} \quad (4)$$

where *rms*<sub>noise</sub> and slope respectively represent the root mean square error of the baseline and the slope value of the linear curve. So, it could be calculated that the TDLs of the 3%, 6% and 9% La-In<sub>2</sub>O<sub>3</sub> sensors were respectively 18.7, 10.9, and 14.0 ppb, which were all lower than that of the Yb-In<sub>2</sub>O<sub>3</sub> sensor

(183 ppb) and Dy-In<sub>2</sub>O<sub>3</sub> (24.0 ppb) sensor. The result showed that the 6% La-In<sub>2</sub>O<sub>3</sub> sensors possessed the lowest TDL, and the TDLs for the La-In<sub>2</sub>O<sub>3</sub> and Dy-In<sub>2</sub>O<sub>3</sub> sensors both met the international standard for the indoor detection of the HCHO concentration (70 ppb).<sup>31</sup>

In the actual working environment, there are often multiple gases at the same time, so the selectivity of the sensor to HCHO gas is very important. To demonstrate the selectivity of the La-In<sub>2</sub>O<sub>3</sub> sensors, the cross-selectivity of the four sensors under the same conditions to several typical gases, including ethanol, HCHO, acetone, isopropanol, and methanol were tested (Fig. 8a). Apparently, it could be seen that the sensors based on the 3%, 6%, and 9% La-In<sub>2</sub>O<sub>3</sub> samples showed a higher response to HCHO than the other gases compared to pure In<sub>2</sub>O<sub>3</sub>. Noted that there was no obvious response for both the La-In<sub>2</sub>O<sub>3</sub> and pure In<sub>2</sub>O<sub>3</sub> sensors to these contrasted gases. These results indicated the excellent selectivity of the La-In<sub>2</sub>O<sub>3</sub> sensors to HCHO gas, laying the foundation for future HCHO testing in practice. Additionally, good stability is conducive to the long-term use of the sensor in practical work. The stability of the sensor based on La-In<sub>2</sub>O<sub>3</sub> nanospheres was tested every five days for one month, as shown in Fig. 8b. It can be seen from the figure that the response of the four sensors to 100 ppm HCHO at 170 °C still kept constant without significant drift even within 30 days, proving the outstanding long-time stability of the four sensors. Simultaneously, the influence of humidity on the response of the La-In<sub>2</sub>O<sub>3</sub> sensors was also studied (Fig. S3<sup>†</sup>). There were no obvious effects on the response of the sensor to HCHO under a relative humidity of 30%–60%. However, it was found that when the relative humidity increased further from 70% to 90% RH, the response began to sharply drop from about 189 to 10. Note that when the humidity was close to 100%, the sensor had almost no



**Fig. 8** (a) Response of *x* La-In<sub>2</sub>O<sub>3</sub> (*x* = 0%, 3%, 6%, 9%) to 100 ppm of different gases. (b) Response time curves for the stability of the four sensors upon exposure to 100 ppm HCHO. (c) Cyclic response curve of the sensor and (d) the dynamic response–recovery curves of the sensor based on 6% La-In<sub>2</sub>O<sub>3</sub> nanospheres.

response. Also, the good reproducibility of a sensor plays an important role in gas sensing. Thus, the continuous reproducibility of the sensor based on 6% La-In<sub>2</sub>O<sub>3</sub> nanospheres was further investigated. As shown in Fig. 8c, no matter whether exposed to HCHO vapor or air, the response value of this sensor was relatively stable even after four cycles, indicating that the sensor had good reproducibility and reversibility. The dynamic response characteristics of the sensor based on 6% La-In<sub>2</sub>O<sub>3</sub> nanospheres at 170 °C were studied. Fig. 8d obviously displays that this sensor had a continuous and intact response–recovery curve with a short response time of 30 s and recovery time of 160 s for 100 ppm HCHO, respectively.

Lastly, some nanomaterials have been designed for HCHO detection so far. So a comparison of the gas-sensing performance of several MOS-based gas sensors for detecting HCHO was performed and the results are briefly summarized in Table 2.<sup>32–38</sup> In consideration of all the gas-sensing properties, such as optimal working temperature, response value, sensi-

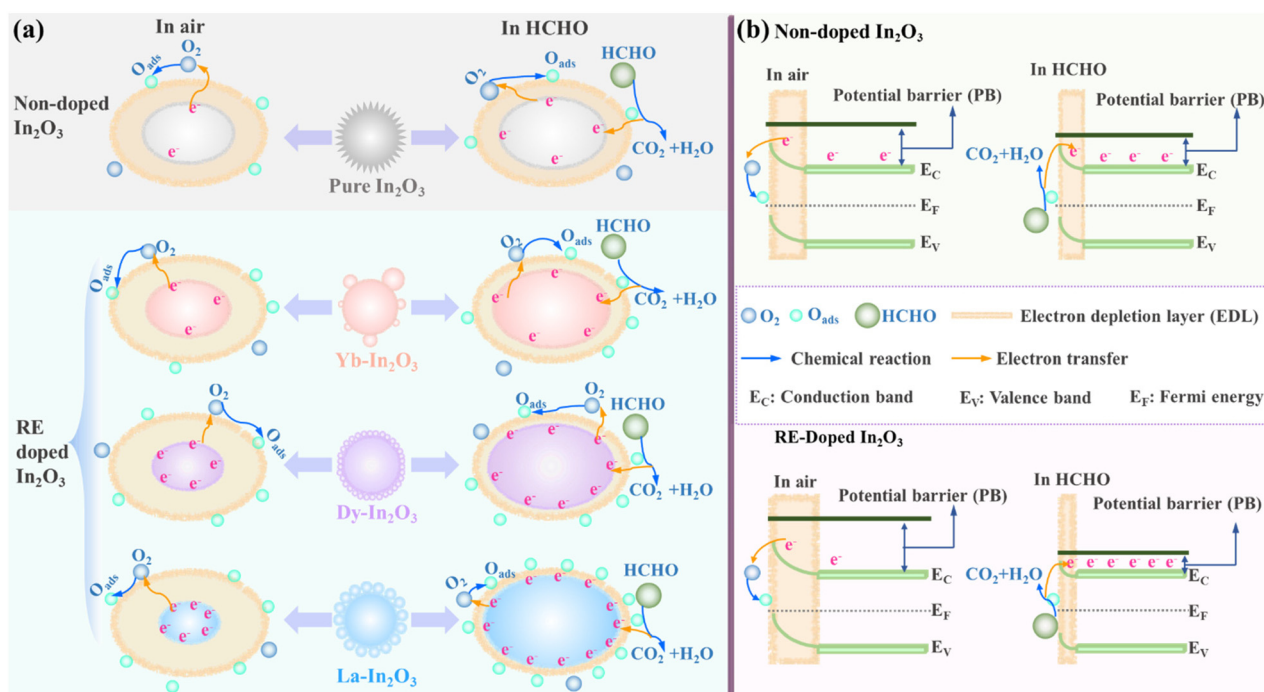
tivity, and selectively, the 6% La-In<sub>2</sub>O<sub>3</sub> sensor in our work exhibited a relatively better HCHO detection performance compared with the other MOS-based gas sensors. Note that the superior gas response of the RE-In<sub>2</sub>O<sub>3</sub> was closely related to the RE element dopant.

### 3.4 Gas-sensing mechanism of RE-In<sub>2</sub>O<sub>3</sub> nanospheres

In<sub>2</sub>O<sub>3</sub> nanomaterials, as an n-type semiconductor with electron carriers, are acknowledged to be a conventional chemiresistor sensing material with an easily noted change of their electrical features derived from the surface reaction of In<sub>2</sub>O<sub>3</sub>. According to the current gas-sensing theory of In<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub> generally detect a gas *via* changing its resistance value through the surface adsorbed oxygen and reaction between gas molecules and the surface electron. As presented in the HCHO-sensing diagram of Fig. 9a, when pure In<sub>2</sub>O<sub>3</sub> nanoflowers were exposed in air at low temperature, the oxygen molecules were absorbed on their surface to produce different chemisorbed oxygen

**Table 2** Comparison of the sensing performance of HCHO sensors based on MOS nanostructures

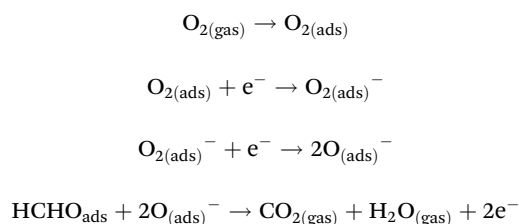
Sensing materials	Structure	HCHO concentration (ppm)	Temperature (°C)	Response ( $R_a/R_g$ )	Ref.
6% La-In <sub>2</sub> O <sub>3</sub>	Nanosphere	100	170	210	This work
In <sub>2</sub> O <sub>3</sub>	Nanoparticle	100	230	80	13
SnO <sub>2</sub> /In <sub>2</sub> O <sub>3</sub>	Hetero-nanofiber	50	375	18.9	32
NiO	Ordered mesoporous nanoparticle	380	300	20.6	33
Ag-loaded In <sub>2</sub> O <sub>3</sub>	Sunflower-like nanostructure	50	240	20.6	34
Pd-SnO <sub>2</sub>	Hollow nanofiber	100	160	18.8	35
SnO <sub>2</sub>	Mesoporous microtube	100	200	37	36
Pd-SnO <sub>2</sub>	Nanocrystals	100	260	85	37
Ag-LaFeO <sub>3</sub>	Nanofiber	5	230	4.8	38



**Fig. 9** (a) Schematic mechanism for sensing HCHO by RE-doped In<sub>2</sub>O<sub>3</sub> and (b) illustration of their corresponding bands.



species ( $Q_{\text{ads}}$ ), including  $\text{O}^{2-}$ ,  $\text{O}$ , and  $\text{O}_2^-$ , via capturing the free electrons ( $e^-$ ) from the conduction band of  $\text{In}_2\text{O}_3$ . It should be noted that an electron-depletion layer (EDL) on the surface of  $\text{In}_2\text{O}_3$  would be formed due to the decreased carrier level and increased resistance. To specially introduce this process in to the electronic structure, the corresponding upward band mechanism is schematically illustrated in Fig. 9b. Notably, a potential barrier (PB) between the air and electrons was also generated in the present situation, except for the EDL. When exposed to HCHO gas, the chemisorbed oxygen species ( $Q_{\text{ads}}$ ) could react with HCHO molecules adsorbed on the sensor surface to release electrons into the conductance band of  $\text{In}_2\text{O}_3$ , leading to a decline in the EDL thickness, resistance (Fig. 9a) and PB (Fig. 9b). It should be noted that  $\text{In}_2\text{O}_3$ 's resistance value will revert to its initial resistance value within a certain time when  $\text{In}_2\text{O}_3$  is put back in to air, showing the superior stability and reusability of  $\text{In}_2\text{O}_3$  as a gas sensor. The possible interaction between  $\text{O}_{\text{ads}}$  and HCHO can be described by the following chemical equations.



With the doping of RE elements into  $\text{In}_2\text{O}_3$  nanomaterials, the HCHO-sensing performances of RE- $\text{In}_2\text{O}_3$  nanospheres were observed to be greatly improved compared to pure  $\text{In}_2\text{O}_3$  nanoflowers, which could possibly be attributed to the following two aspects, as described in Fig. 9. First, the nanosphere structure enabled the  $\text{In}_2\text{O}_3$  nanomaterials to have a large specific surface area, leading to abundant reaction sites. Such a change promotes the electron-transfer process and accelerates the surface reaction of the nanospheres, thus inducing a rapid change in the resistance, finally causing an enhanced gas-sensing response. Second, the incorporated RE ions could replace  $\text{In}^{3+}$  as a donor to realize an enhancement in the surface oxygen vacancies in  $\text{In}_2\text{O}_3$ , thus having an effective influence on the adsorption behavior. It is well-known that more oxygen vacancies in crystal structures can cause more free electrons, which can be captured and thus can significantly affect the gas-sensing performances. According to XPS analysis, the introduction of RE elements into the crystal structure could lead to abundant adsorbed oxygen, thus promoting surface reactions to finally produce improved gas-sensing features. Additionally, with doping various RE elements from Yb, to Dy, to La into  $\text{In}_2\text{O}_3$ , the HCHO-sensing properties of La- $\text{In}_2\text{O}_3$  were found to be the best, which was mainly may due to the more defect oxygens generated from the more chemisorbed oxygen species ( $\text{O}_{\text{ads}}$ ). Based on the same reason, the maximum absorbed oxygen endowed the 6% La- $\text{In}_2\text{O}_3$  sensor with the optimum response to the target gas in comparison with the 3% La- $\text{In}_2\text{O}_3$  and 9% La- $\text{In}_2\text{O}_3$ .

## 4 Conclusions

In summary, rare earth elements-doped indium oxide (RE- $\text{In}_2\text{O}_3$ ) nanospheres were prepared by respectively doping Yb, Dy, or La ions into  $\text{In}_2\text{O}_3$  using a facile solvothermal strategy and these were further designed as gas sensors for HCHO detection with improved gas-sensing performance. Such RE- $\text{In}_2\text{O}_3$  gas sensors exhibited high stability in air at RT. and selectivity for HCHO in mixtures of five gases, namely ethanol, HCHO, isopropanol, acetone, and methanol. In addition, the 6% La- $\text{In}_2\text{O}_3$  based sensor was found to possess the best gas-sensing properties in comparison with that of pure  $\text{In}_2\text{O}_3$ , Yb- $\text{In}_2\text{O}_3$ , Dy- $\text{In}_2\text{O}_3$ , as well as La- $\text{In}_2\text{O}_3$  with 3% and 9% La. In particular, the 6% La- $\text{In}_2\text{O}_3$  nanospheres were demonstrated to not only have a low detection limit of 10.9 ppb, a response time of 30 s to 100 ppm HCHO with a recovery time of 160 s, but also demonstrated a high response value of 210 to 100 ppm at 170 °C, which was around 16 times higher than that of the pure  $\text{In}_2\text{O}_3$  sensor. Finally, these results were mainly due to the synergistic effect of the large specific surface area and enhanced surface oxygen vacancies on the surface of the  $\text{In}_2\text{O}_3$  nanospheres, which produced chemisorbed oxygen species to release electrons and provided abundant reaction sites for HCHO gas. This study shows the huge potential of RE- $\text{In}_2\text{O}_3$  nanospheres in gas-sensing application toward HCHO.

## Author contributions

X. Y. M. and L. Yu performed the sensing investigations and analyzed the data. X. L. verified all the experimental data and draft. H. J. Z. performed the chemical, XRD, electronic XPS studies, analyzed the data and drafted the manuscript with contributions from all authors. Z. B. L., E. Y. Y., X. J. L. and S. H. W. reviewed and edited the manuscript. All authors discussed the experimental results and commented on the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (U21A20290, 82001957), the Guangdong Basic and Applied Basic Research Foundation (2022A1515011656).

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