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# Effect of Er doping on the $\text{In}_2\text{O}_3(001)$ surface for $\text{H}_2\text{S}$ , $\text{NO}_2$ , and CO detection: a DFT study

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The impact of Erbium (Er) doping on the gas sensing performance of the  $\text{In}_2\text{O}_3(001)$  surface toward  $\text{H}_2\text{S}$ ,  $\text{NO}_2$ , and CO was rigorously investigated using density functional theory (DFT) calculations. Analysis based on adsorption energy, Bader charge transfer, and density of states (DOS) confirms that Er doping selectively enhances the surface reactivity toward  $\text{NO}_2$ . Key results demonstrate a marked improvement in  $\text{NO}_2$  binding strength: the adsorption energy increases significantly from  $-0.37$  eV on the pristine surface to  $-0.61$  eV on the Er-doped surface. This stronger chemisorption is supported by enhanced electron withdrawal from the surface by  $\text{NO}_2$ , with the charge transfer increasing from  $-0.38$  e (pristine) to  $-0.46$  e (Er-doped). Furthermore, TDOS and PDOS analyses confirm the appearance of new, strong electronic states near the Fermi level only after  $\text{NO}_2$  adsorption on the doped surface, indicating robust electron coupling. Conversely, Er doping weakens the interaction with the other test gases. For  $\text{H}_2\text{S}$ , the adsorption energy reduces from  $-0.53$  eV to  $-0.42$  eV, and charge transfer drops sharply from  $+0.40$  e to  $+0.09$  e. CO adsorption remains weak, with the energy decreasing slightly from  $-0.25$  eV to  $-0.19$  eV. These findings indicate that Er-doped  $\text{In}_2\text{O}_3(001)$  surfaces exhibit enhanced selectivity, making them highly promising candidates for selective  $\text{NO}_2$  detection.

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## 1. Introduction

The increment of industrial production has led to environmental problems, one of which is air pollution, which cannot be avoided. The source of air pollution is gaseous pollutants that are released by vehicles and industries. These can have adverse effect on human health and the environment.<sup>1</sup> The solution to this problem is precisely identifying the harmful gas pollutants present in the industrial exhaust. Gas sensors are often the usual method to detect these gases.<sup>2</sup> Metal oxide semiconductor-based gas sensors are often used to detect gases because of many features including low cost, high sensitivity, high stability, and ease of fabrication.<sup>3</sup>

Metal oxide semiconductors (MOSS) such as ZnO,  $\text{WO}_3$ ,  $\text{SnO}_2$  and  $\text{In}_2\text{O}_3$  are used as a gas sensing material in many gas sensors because of their easy fabrication process, low cost and good performance.<sup>4</sup> Among these, indium oxide ( $\text{In}_2\text{O}_3$ ) is a promising sensing material due to its high conductivity, adjustable shape and size, good catalytic properties and abundant defects.  $\text{In}_2\text{O}_3$  is an n-type metal oxide semiconductor (MOS) with a wide band gap of 3.75 eV (direct) and 2.61 eV (indirect).<sup>5</sup> Studies on various morphologies, such as nanoparticles, nanofibers, nanosheets

and nanoflowers, have been conducted for environmental pollutant gases ( $\text{NO}_2$ , CO and  $\text{H}_2\text{S}$ ) to increase sensitivity and selectivity.<sup>6</sup> Some progress has been made for pristine  $\text{In}_2\text{O}_3$ -based gas sensors to overcome the selectivity and operating temperature issue.<sup>7</sup> Doping is an efficient way to overcome these issues because a small amount of dopant may convert the non-porous structure to a porous structure and provide defect states, which is good for gas sensing.<sup>8,9</sup>

Nowadays, rare earth elements (REEs) are emerging to solve these problems because they have 4f orbitals with partially filled electrons. When a rare earth element ( $\text{RE}^{3+}$ ) is added to indium oxide ( $\text{In}_2\text{O}_3$ ), it can easily take the place of  $\text{In}^{3+}$  because of the similarity in their ionic radii. This replacement causes some strain in the crystal structure of  $\text{In}_2\text{O}_3$ .<sup>10</sup> Among them, europium (Eu) and erbium (Er) are particularly interesting for  $\text{In}_2\text{O}_3$  due to their stable trivalent oxidation state ( $\text{Eu}^{3+}/\text{Er}^{3+}$ ), which allows substitution at indium sites with minimal lattice distortion. Eu-doping has been shown to enhance charge transfer and adsorption capability, improving the surface reactivity of  $\text{In}_2\text{O}_3$  toward gas molecules. On the other hand, Er possesses a slightly smaller ionic radius and a distinct 4f electronic configuration, which can further modify the band structure and facilitate stronger interactions with adsorbed species. A study by Zhou *et al.*<sup>11</sup> reported that hydrothermally synthesized 3 wt% Ce-doped  $\text{In}_2\text{O}_3$  as compared to the pristine  $\text{In}_2\text{O}_3$  has a better response for *n*-butanol gas. They observed that 3 wt% Ce-doped  $\text{In}_2\text{O}_3$  has a response

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value of 225.3 for 100 ppm *n*-butanol gas at an optimum temperature of 320 °C, which was 3.7 times higher than that of pure In<sub>2</sub>O<sub>3</sub>. Wang *et al.*<sup>12</sup> synthesized In<sub>2</sub>O<sub>3</sub> and Er-doped In<sub>2</sub>O<sub>3</sub> nanotubes by an electrospinning method followed by calcination. They observed that the synthesized Er-doped In<sub>2</sub>O<sub>3</sub> has 4 times the response value than that of pure In<sub>2</sub>O<sub>3</sub> for 20 ppm formaldehyde (HCHO) gas at 260 °C temperature. Qin *et al.* reported that the carbon thermal reduction method was utilized for the synthesis of pure and Er-doped In<sub>2</sub>O<sub>3</sub> nanoribbons.<sup>13</sup> The Er doping in In<sub>2</sub>O<sub>3</sub> reduces the optimal temperature from 260 °C to 220 °C and also increases the sensitivity of 100 ppm ethanol from 2.4 to 4.8. It shows better selectivity towards interfering gases such as CO, H<sub>2</sub>S, HCHO and NO<sub>2</sub>. They observed that Er doping reduced the operating temperature for alcohol detection, and a fast response and recovery time were achieved for different alcohol concentrations at 220 °C. Liu *et al.* performed a DFT study to evaluate the adsorption effect of gases such as H<sub>2</sub>, CO and CH<sub>4</sub> on the In<sub>2</sub>O<sub>3</sub>(110) surface. The calculation results based on DFT indicate that intrinsic In<sub>2</sub>O<sub>3</sub> is not optimum for H<sub>2</sub>, CO and CH<sub>4</sub> adsorption, while Ag-decorated In<sub>2</sub>O<sub>3</sub> shows optimum sensing for these gases.<sup>3</sup> Chen *et al.*<sup>14</sup> reported that the Eu-doped In<sub>2</sub>O<sub>3</sub> nanobelts exhibit higher sensitivity towards H<sub>2</sub>S gas as compared to pure In<sub>2</sub>O<sub>3</sub>. They showed that Eu doping enhances the sensitivity of H<sub>2</sub>S gas by five times compared to undoped In<sub>2</sub>O<sub>3</sub>. Eu-doped In<sub>2</sub>O<sub>3</sub> exhibits better selectivity towards H<sub>2</sub>S gas with interfering gases such as CO, NO<sub>2</sub>, HCHO and ethanol at 260 °C temperature.

The novelty of the present study lies in providing a comparative mechanistic understanding of gas adsorption on rare earth element (REE)-doped In<sub>2</sub>O<sub>3</sub> surfaces. The present study explores Er and Eu-doped In<sub>2</sub>O<sub>3</sub> systems for gas-sensing applications at the DFT level, which have not been previously explored. Earlier DFT studies on In<sub>2</sub>O<sub>3</sub> mainly focused on pristine and transition metal-doped surfaces and their analysis was limited to single gas adsorption. In contrast, our DFT investigation systematically examines the adsorption behaviour of multiple gases (H<sub>2</sub>S, NO<sub>2</sub>, and CO), analysing adsorption energies, charge density differences (CDD), and density of states (DOS). All calculations were performed using Quantum Espresso on a hexagonal In<sub>2</sub>O<sub>3</sub> unit cell (space group *R* $\bar{3}c$ ). Compared with previous theoretical investigations on In<sub>2</sub>O<sub>3</sub> surfaces, the present DFT study provides several distinctive contributions. First, the (001) surface of In<sub>2</sub>O<sub>3</sub> was chosen, which is less explored but exhibits high surface reactivity relevant for gas sensing applications. Second, the study systematically examines the influence on the electronic structure and gas adsorption properties of rare-earth element Er. Third, a comparative analysis of H<sub>2</sub>S, NO<sub>2</sub>, and CO adsorption is performed to elucidate NO<sub>2</sub> selectivity based on adsorption energy, charge density difference, and DOS evolution. This approach provides atomistic insight into how the Er dopant modulates surface reactivity and charge transfer characteristics, thereby guiding towards a more reliable rare-earth-element-doped In<sub>2</sub>O<sub>3</sub> gas sensor.

## 2. Computational details

### 2.1. Software and parameters

Quantum Espresso (QE) software, based on density functional theory (DFT), was employed for the computational work. The Perdew–Burke–Ernzerhoff (PBE) functional was used in these calculations to treat the exchange–correlation inside the general gradient approximation (GGA), while ultrasoft pseudopotentials were used to characterise the electron–ion interactions.<sup>15</sup> In the current work, the energy cut-offs of 50 and 450 Ryd for the wave functions and charge densities were used to calculate the band structure and other parameters. All calculations were performed using a  $2 \times 2 \times 2$  *k*-point mesh, except DOS, which, after optimisation, employed a dense *k*-point grid ( $6 \times 6 \times 2$ ). Similar *k*-point sampling ( $2 \times 2 \times 1$ ) was successfully used for 60-atom In<sub>2</sub>O<sub>3</sub>(110) surface models employing DFT-D2 methods, demonstrating the reliability of the present setup.<sup>3</sup> To determine the surface reliability, different In<sub>2</sub>O<sub>3</sub> surfaces were employed but the In<sub>2</sub>O<sub>3</sub>(001) surface gave the best results. For each structure, a vacuum layer of 15 Å was created along the *z*-direction to remove interference from nearby layers.

### 2.2. Surface model

We chose the In<sub>2</sub>O<sub>3</sub> hexagonal crystal system for this work. This hexagonal unit cell of In<sub>2</sub>O<sub>3</sub> is made up of 12 In and 18 O atoms, with lattice parameters of  $a = b = 5.5162$  Å and  $c = 14.5911$  Å, which is equivalent to the experimental value.<sup>16</sup> The In<sub>2</sub>O<sub>3</sub>(001) surface was selected for this study. It is represented by a  $2 \times 2 \times 1$  In<sub>2</sub>O<sub>3</sub> supercell, which is cleaved by the plane 001 which contains 120 atoms. Furthermore, the cell width was reduced from 1 to 0.5 to obtain the In<sub>2</sub>O<sub>3</sub>(001) two-layer surface with a total of 60 atoms. For the defect In<sub>2</sub>O<sub>3</sub> surfaces one was replaced by one rare earth element Er. All structures were optimized without and with the adsorbate gas molecules (CO, NO<sub>2</sub>, and H<sub>2</sub>S) as shown in Fig. 1. The relaxed structure represents that the Er-doping creates a more compact structure. After NO<sub>2</sub> gas molecule adsorption, the compact behaviour is reduced.

The adsorption energy was calculated by the quantitative analysis of gas molecule interaction with the In<sub>2</sub>O<sub>3</sub>(001) surface by the following equation<sup>17,18</sup>

$$\Delta E_{\text{adsorption}} = E_{\text{surface+gas molecule}} - E_{\text{surface}} - E_{\text{gas molecule}} \quad (1)$$

where,  $\Delta E_{\text{adsorption}}$ ,  $E_{\text{surface+gas molecule}}$ ,  $E_{\text{surface}}$  and  $E_{\text{gas molecule}}$  represent the adsorption energy, total energy of the surface with a gas molecule, total energy of the surface, and total energy of the gas molecule, respectively. The adsorption energy of defect/doped surfaces was calculated by eqn (2)

$$\Delta E_{\text{adsorption}} = E_{\text{defect surface+gas molecule}} - E_{\text{defect surface}} - E_{\text{gas molecule}} \quad (2)$$

where  $\Delta E_{\text{adsorption}}$ ,  $E_{\text{defect surface+gas molecule}}$ ,  $E_{\text{defect surface}}$  and  $E_{\text{gas molecule}}$  represent the adsorption energy, total energy of the defect/doped surface with a gas molecule, total energy of



Fig. 1 Optimized geometries of (a) the pure In<sub>2</sub>O<sub>3</sub>(001) surface, (b) Er-doped In<sub>2</sub>O<sub>3</sub>(001) surface, and adsorption of H<sub>2</sub>S, NO<sub>2</sub>, and CO molecules on the top In atom site of (c), (e) and (g) pure and (d), (f) and (h) Er-doped In<sub>2</sub>O<sub>3</sub>(001) surfaces, respectively. The arrows indicate the adsorption distances between the surface atoms and the gas molecules. The 15 Å scale bar represents the vacuum region introduced along the z-direction to prevent interlayer interactions.

the defect surface, and total energy of the gas molecule, respectively.

### 3. Results and discussion

#### 3.1. Adsorption energy analysis

The strength of the adsorbate's binding to the substrate (pure and Er-doped In<sub>2</sub>O<sub>3</sub>(001)) is commonly indicated by adsorption energy. The total energy of the adsorption system will be less than the sum of the energies of the substrate and the adsorbate if the adsorption is thermodynamically favourable, leading to a negative adsorption value. The physisorption and chemisorption processes can be identified by the magnitude of the adsorption energies.<sup>19</sup>

The adsorption energies of H<sub>2</sub>S, NO<sub>2</sub> and CO were calculated on both pristine and Er-doped In<sub>2</sub>O<sub>3</sub> surfaces using eqn (1) and (2). The adsorption energies were calculated for different Er-doped sites in In<sub>2</sub>O<sub>3</sub>. Among them, the configuration in which the first Er atom replaced the first indium (In) atom on the In<sub>2</sub>O<sub>3</sub>(001) upper surface was found to be the most favourable. The adsorption energy for NO<sub>2</sub>, Er-doping significantly enhanced the adsorption strength (from −0.379 eV to −0.61 eV) (as shown in Table 1), indicating improved sensing potential. However, for H<sub>2</sub>S and CO, the adsorption strength slightly decreased upon Er incorporation. The decrease in H<sub>2</sub>S adsorption energy (−0.53 eV to −0.42 eV) remains within an acceptable sensing range, suggesting moderate sensing capability. CO adsorption energies remained weak in both cases (−0.25 eV to −0.19 eV), indicating poor interaction with surfaces. These findings suggest that Er-doping on the In<sub>2</sub>O<sub>3</sub> surface increases the adsorption of the NO<sub>2</sub> molecule while

Table 1 Adsorption energies and charge transfer values through Bader charge analysis for pure and Er-doped In<sub>2</sub>O<sub>3</sub>(001) surfaces

| S. no. | Gases            | Adsorption energy (eV)                            |   | Charge transfer values                            |   |
|--------|------------------|---|---|---|---|
|        |                  | Pure In <sub>2</sub> O <sub>3</sub> (001) surface | Er-doped In <sub>2</sub> O <sub>3</sub> (001) surface | Pure In <sub>2</sub> O <sub>3</sub> (001) surface | Er-doped In <sub>2</sub> O <sub>3</sub> (001) surface |
| 1.     | NO <sub>2</sub>  | −0.37   | −0.61   | −0.3855e  | −0.4596e  |
| 2.     | H <sub>2</sub> S | −0.53   | −0.42   | +0.4053e  | +0.0927e  |
| 3.     | CO               | −0.25   | −0.19   | +0.0312e  | +0.0711e  |

diminishing the adsorption of H<sub>2</sub>S and CO molecules. This suggests that erbium (Er) doping selectively enhances the sensitivity of In<sub>2</sub>O<sub>3</sub> toward NO<sub>2</sub>.

#### 3.2. Bader charge analysis

Bader charge analysis was employed to evaluate the effect of Er doping on the In<sub>2</sub>O<sub>3</sub> surface. The pure and Er-doped In<sub>2</sub>O<sub>3</sub> surfaces exhibit noticeable difference in Bader charge, attributed to the incorporation of the Er-dopant. While the lower surface layers show minimal variation, significant changes are observed in the upper surface atoms where the doping is introduced. These changes indicate that the Er dopant modifies the surface electronic structure and charge distribution of the In<sub>2</sub>O<sub>3</sub> surface.

Also, Bader charge analysis was performed to evaluate the charge transfer between gas molecules and the surfaces (In<sub>2</sub>O<sub>3</sub> and Er-doped In<sub>2</sub>O<sub>3</sub>). The charge transfer results indicate distinct gas adsorption behaviours for the pure and Er-doped In<sub>2</sub>O<sub>3</sub> systems. The net charge transfer values for gas molecules

on  $\text{In}_2\text{O}_3$  and Er-doped  $\text{In}_2\text{O}_3$  surfaces were examined through the following equation:

$$\Delta Q = Q_a - Q_b \quad (3)$$

where,  $\Delta Q$ ,  $Q_a$  and  $Q_b$  represent the net charge transfer, charge on the gas molecule after adsorption and charge on the gas molecule before adsorption (isolated gas molecule).<sup>20</sup>

For  $\text{H}_2\text{S}$ , the pure  $\text{In}_2\text{O}_3$  surface shows a significantly higher charge transfer (+0.4053 e) than the Er-doped surface (+0.0927 e), suggesting stronger adsorption on the undoped material. Conversely, for  $\text{NO}_2$ , the Er-doped  $\text{In}_2\text{O}_3$  surface exhibits a more negative charge transfer (−0.4596 e) as compared to the pure  $\text{In}_2\text{O}_3$  surface (−0.3855 e), implying enhanced electron donation, and thus stronger adsorption upon doping. The CO molecule, however, exhibits very low charge transfer performance for both the surfaces  $\text{In}_2\text{O}_3$  and Er-doped  $\text{In}_2\text{O}_3$ , +0.0312 e, +0.0711 e, respectively. The CO molecule interaction reduces slightly on the Er- $\text{In}_2\text{O}_3$  surface. This indicates that a weak physisorption process occurs for the CO gas molecule. The charge transfer values are consistent with the results of adsorption energy. These findings reveal that Er-doping improves the  $\text{NO}_2$  sensing selectivity, while a pure  $\text{In}_2\text{O}_3$  surface is more favourable for  $\text{H}_2\text{S}$  gas detection.

### 3.3. Analysis of charge density difference (CDD) plot

In the CDD plot, the individual isolated system's charge densities are subtracted from the adsorbed entire system's charge density. It reflects the charge redistribution caused by the interaction between gas molecules and the material's surfaces. The CDD provides information about charge accumulation and depletion around surfaces and gas molecules. The CDD plot is obtained by the given formula:<sup>21,22</sup>

$$\Delta\rho = \rho_{\text{surface+gas molecule}} - \rho_{\text{isolated surface}} - \rho_{\text{isolated gas molecule}} \quad (4)$$

where  $\Delta\rho$ ,  $\rho_{\text{surface+gas molecule}}$ ,  $\rho_{\text{isolated surface}}$  and  $\rho_{\text{isolated gas molecule}}$  represent the charge density difference, charge density of the gas molecule adsorbed surface, charge density without a gas molecule, and charge density of an isolated gas molecule, respectively.

The CDD plots for the intrinsic  $\text{In}_2\text{O}_3(001)$  surface and Er-doped  $\text{In}_2\text{O}_3(001)$  surface upon adsorption of gases  $\text{H}_2\text{S}$ ,  $\text{NO}_2$  and CO are shown in Fig. 2. The CDD plot gives a qualitative analysis of Bader charge analysis. For  $\text{H}_2\text{S}$  gas, the CDD plot of  $\text{In}_2\text{O}_3$  and Er-doped  $\text{In}_2\text{O}_3$  shows a delocalized distribution of charges between the surface and gas molecule. In CDD plots, the yellow colour indicates the charge accumulation while cyan colour indicates the charge depletion.<sup>23</sup> The Bader charge transfer of +0.4053 e for  $\text{H}_2\text{S}$  on the  $\text{In}_2\text{O}_3$  surface indicates that the gas molecules donate electrons from the surface. In the corresponding CDD plot, cyan lobes appear around the  $\text{H}_2\text{S}$  molecule, confirming charge depletion, while yellow lobes on the surface (at the lower surface around the In and O atoms) indicate charge accumulation (as shown in Fig. 2(a)). This indicates a sign of electron transfer from the gas molecule to the surface. Similar behaviour is observed for the Er-doped  $\text{In}_2\text{O}_3$  surface, but charge transfer reduces to 0.09 e, which is reflected by light yellow and cyan colours. For  $\text{NO}_2$  gas absorption, the CDD plot exhibits both yellow (accumulation) and cyan (depletion) lobes around the  $\text{NO}_2$  molecule and the Er-doped  $\text{In}_2\text{O}_3$  surface, indicating localized charge redistribution.<sup>24</sup> However, Bader charge analysis reveals a net negative charge transfer to the gas molecule, confirming that  $\text{NO}_2$  withdraws electrons from the surface and acts as an electron acceptor.<sup>25</sup> For  $\text{H}_2\text{S}$  adsorption on pure and Er-doped  $\text{In}_2\text{O}_3$  surfaces, the lobes are not localized at one atom, which reflects surface wide interaction

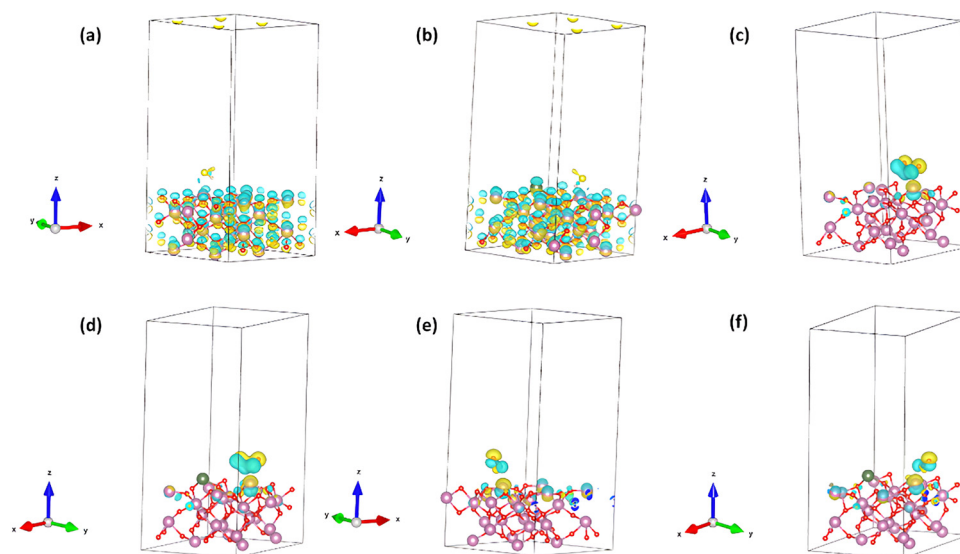


Fig. 2 CDD plots of (a), (c) and (e) pure and (b), (d) and (f) Er-doped  $\text{In}_2\text{O}_3(001)$  surfaces after gas adsorption: (a) and (b)  $\text{H}_2\text{S}$ , (c) and (d)  $\text{NO}_2$ , and (e) and (f) CO. Pink, red, and dark green spheres represent indium (In), oxygen (O), and erbium (Er) atoms, respectively. Blue, brown, white, and black spheres denote nitrogen (N), sulphur (S), hydrogen (H), and carbon (C) atoms, respectively. The yellow and cyan regions indicate charge accumulation and depletion, respectively. The colour bar represents the variation from charge accumulation (yellow) to charge depletion (cyan).

and indicates a physisorption process. The charge redistribution indicates electron donation from the CO molecule to the surface, confirming n-type behaviour.

### 3.4. Band structure analysis of $\text{In}_2\text{O}_3(001)$ and Er-doped $\text{In}_2\text{O}_3(001)$ surfaces

The band structure plots of pure and Er-doped  $\text{In}_2\text{O}_3$  surfaces are shown in Fig. 3. The band structure analysis confirms that both the pure and Er-doped  $\text{In}_2\text{O}_3$  exhibit a direct band gap.<sup>26</sup> The Er-doping increases the band gap of the  $\text{In}_2\text{O}_3$  surface compared to the bulk  $\text{In}_2\text{O}_3$  system.<sup>27</sup> The band gap value increases from 0.11 eV to 0.17 eV. For the Er-doped  $\text{In}_2\text{O}_3$  surface the band structure in the conduction band is denser than the pure  $\text{In}_2\text{O}_3$  surface, which reflects the presence of defect surfaces after doping. Also, the Fermi energy level slightly shifts towards the conduction band. The changes in band structure reflect the change in electronic properties of the material. Also, the calculated band gaps for pure and doped  $\text{In}_2\text{O}_3$  surfaces are very small, indicating near-metallic behaviour. Despite this, the adsorption of gas molecules ( $\text{H}_2\text{S}$ ,  $\text{NO}_2$ , and CO) can still modulate surface electronic properties through charge transfer, producing a measurable sensing response. Er doping slightly increases the band gap by introducing localized states near the Fermi level, which enhances charge transfer interactions and improves gas-sensing performance. It should also be noted that DFT calculations using local or gradient-corrected exchange–correlation potentials are known to severely underestimate the band gap of semiconducting materials.<sup>15</sup> Therefore, while the absolute band gap values appear smaller, the relative trends and electronic structure changes remain physically meaningful, supporting the proposed sensing mechanism governed primarily by surface charge redistribution rather than large band gap modulation (discussed in Section 4).

### 3.5. Density of states (TDOS and PDOS) analysis

For further confirmation, DOS and PDOS analyses have been conducted. The density of states (DOS) and partial density of states (PDOS) have been evaluated for the surface before adsorption of gas molecules and after adsorption of gas molecules.

The total density of states and partial density of states for the pure  $\text{In}_2\text{O}_3(001)$  surface are shown in Fig. 4(a). It indicates that in TDOS the main contribution is due to the oxygen atoms, while a minor contribution is observed from the indium (In)

atoms. Valence band states have concentrated DOS peaks while the conduction band region exhibits low intensity of DOS peaks. Also, band gaps are observed in between the highest occupied state and lower unoccupied state indicating its semi-conducting behaviour. For Er-doped  $\text{In}_2\text{O}_3$ , the DOS contribution of Er is mainly from the p and d orbitals (as shown in Fig. 4(b)). The contribution of Er is observed only in the conduction band, indicating the creation of new states or defect surfaces. These defects are useful for gas sensing applications.

After  $\text{H}_2\text{S}$  adsorption on the  $\text{In}_2\text{O}_3(001)$  surface, the DOS peak intensity decreases from the  $\text{In}_2\text{O}_3(001)$  surface, indicating an interaction between the surface and  $\text{H}_2\text{S}$  gas molecule (as shown in Fig. 4(c)). The partial DOS (PDOS) of indium (In) atoms enhances after  $\text{H}_2\text{S}$  adsorption, suggesting a strong interaction between the  $\text{In}_2\text{O}_3(001)$  surface and  $\text{H}_2\text{S}$  molecule. Oxygen atoms contribute significantly to the total DOS (TDOS), similar to the  $\text{In}_2\text{O}_3(001)$  surface. The PDOS contributions from hydrogen (H) and sulphur (S) atoms are also observed in Fig. 4(d). However, after Er doping into the  $\text{In}_2\text{O}_3(001)$  surface, the PDOS contributions from hydrogen (H) and sulphur (S) atoms decrease, indicating that the interaction between  $\text{H}_2\text{S}$  and the surface is weakened due to Er incorporation (as shown in Fig. 4(d)). Additionally, the TDOS and PDOS of oxygen atoms increase, and the Er contribution appears mainly in the conduction band region. This suggests that Er doping reduces the strength of  $\text{H}_2\text{S}$  on the  $\text{In}_2\text{O}_3$  surface.

Also, in  $\text{NO}_2$  adsorption, the valence band is dominated by oxygen (O) PDOS with O 2p states. The nitrogen (N) contribution is seen at energies just above 2 eV, which indicates that  $\text{NO}_2$  introduces molecular orbitals in the conduction band region, without strongly disturbing the valence band (as shown in Fig. 4(e)). Any significant DOS peaks are not observed exactly at the Fermi level, indicating low charge transfer from pure  $\text{In}_2\text{O}_3$  to  $\text{NO}_2$ . This suggests physisorption or weak chemisorption of  $\text{NO}_2$  on the surface. For the Er- $\text{In}_2\text{O}_3(001)$  surface after adsorption of  $\text{NO}_2$  a large DOS peak is observed right at the Fermi level, mainly contributed by Er and N (as shown in Fig. 4(f)).<sup>28</sup> The alteration of TDOS and PDOS peaks after adsorption of a  $\text{NO}_2$  molecule indicates that the electronic structure changes. The overall electronic structure is altered, and the interaction is stronger than that of pure  $\text{In}_2\text{O}_3$ , indicating strong adsorption of gas molecules.

After adsorption of CO gas molecules on the  $\text{In}_2\text{O}_3$  and Er-doped  $\text{In}_2\text{O}_3$  surface the changes in TDOS and PDOS are

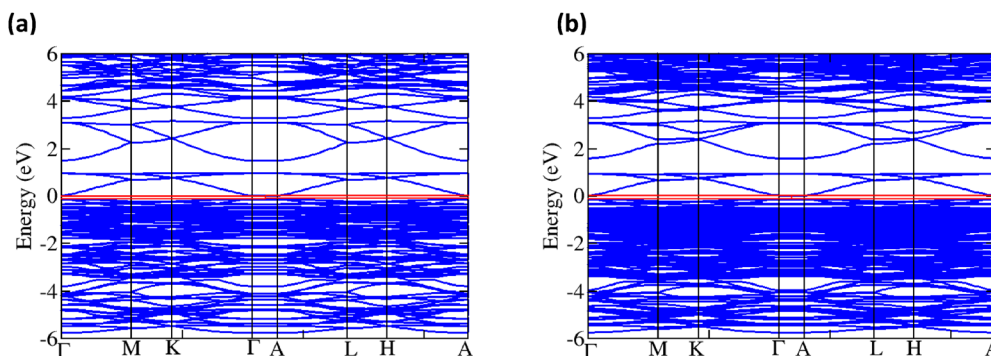


Fig. 3 Band structure for the (a) pure  $\text{In}_2\text{O}_3(001)$  surface and (b) Er-doped  $\text{In}_2\text{O}_3(001)$  surface.

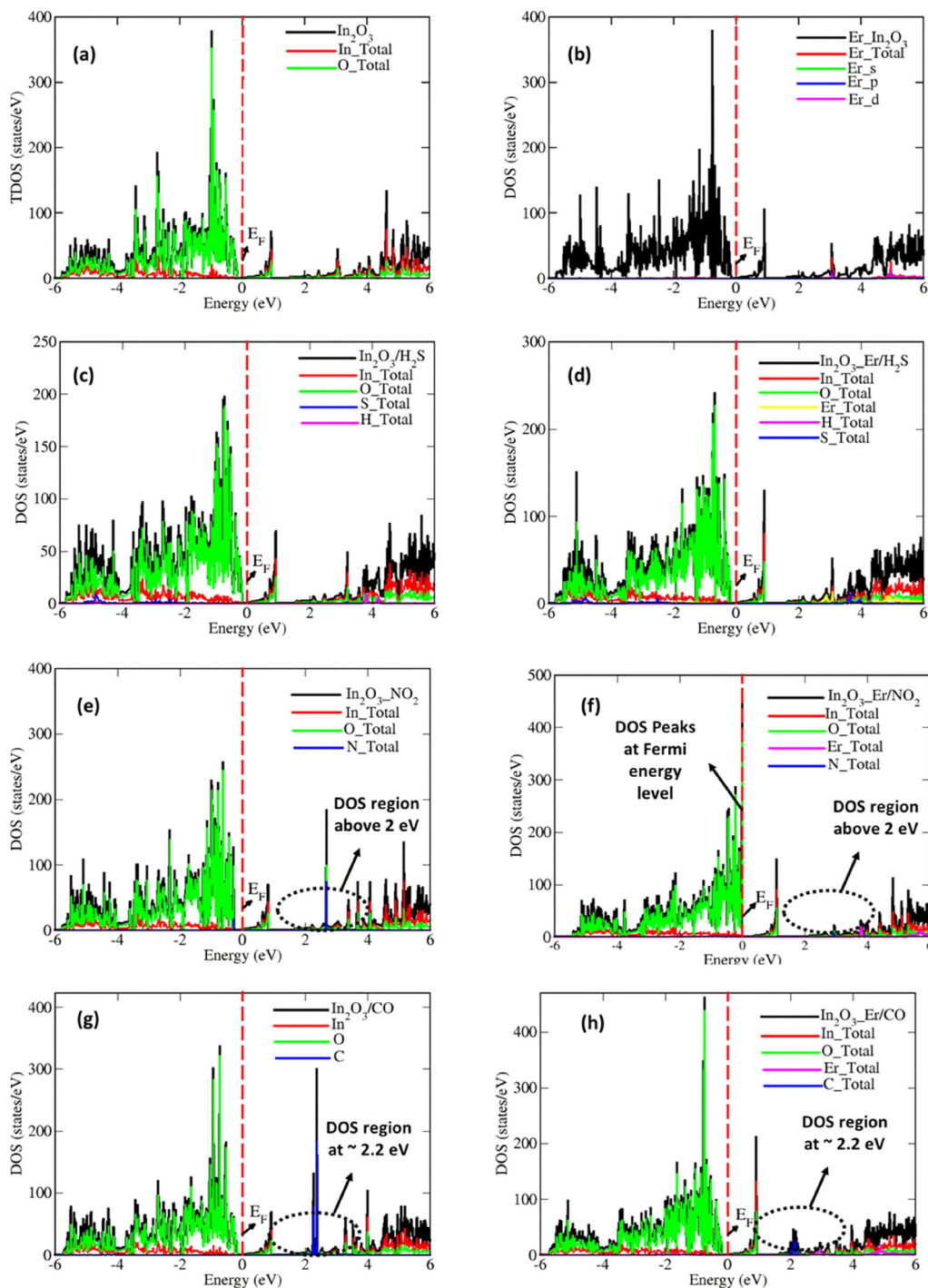


Fig. 4 Total and partial density of states (DOS and PDOS) of (a), (c), (e) and (g) pure and (b), (d), (f) and (h) Er-doped  $\text{In}_2\text{O}_3(001)$  surfaces: (a) and (b) without gas adsorption, (c) and (d) after  $\text{H}_2\text{S}$  adsorption, (e) and (f) after  $\text{NO}_2$  adsorption, and (g) and (h) after  $\text{CO}$  adsorption. The red dotted line indicates the Fermi energy level.

slightly modified. The carbon (C) related sharp peak at  $\sim 2.2$  eV represents the CO molecular orbital contribution (as shown in Fig. 4(g)). This state lies well above the Fermi level, suggesting weak electronic interaction and minimal charge transfer between CO and the  $\text{In}_2\text{O}_3$  surface. There being no new states near the Fermi level indicates physisorption or weak chemisorption of CO on pure  $\text{In}_2\text{O}_3$ . The band gap is preserved,

with no significant mid-gap state formation. For the Er-doped  $\text{In}_2\text{O}_3$  surface the C-related peak at  $\sim 2.2$  eV becomes slightly broader and less intense, and new states appear closer to the Fermi level, indicating a stronger interaction than in the undoped system (as shown in Fig. 4(h)). Some Er-related states overlap with the O and C contributions, especially just below and above the Fermi level. This suggests hybridization and possible weak charge

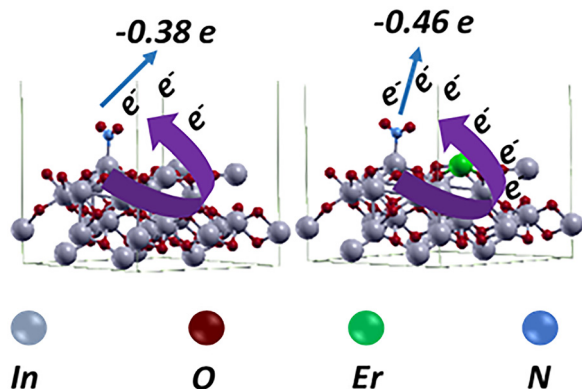


Fig. 5  $\text{NO}_2$  gas sensing mechanism diagram on both the pure and Er-doped  $\text{In}_2\text{O}_3$  surfaces.

transfer. However, the change is not as significant as observed with  $\text{NO}_2$  adsorption, indicating that Er doping enhances the CO interaction only slightly, likely weak chemisorption.

## 4. Gas sensing mechanism

Bader charge analysis was used to elucidate the adsorption mechanism of  $\text{NO}_2$  on  $\text{In}_2\text{O}_3$ . On the pure  $\text{In}_2\text{O}_3$  surface,  $\text{NO}_2$

exhibits a negative charge transfer of  $-0.38 e$ , indicating electron withdrawal from the n-type metal oxide. Upon erbium (Er) doping, the charge transfer becomes more negative ( $-0.46 e$ ), evidencing stronger electron extraction by  $\text{NO}_2$ . This enhanced electron withdrawal widens the surface depletion layer and increases the sensor resistance in comparison to the Er-doped surface. Consistent with this, the electronic-structure picture is that  $\text{NO}_2$  introduces acceptor-like states near the Fermi level more strongly in Er-doped  $\text{In}_2\text{O}_3$ , promoting chemisorption and greater carrier depletion (as shown in Fig. 5). Therefore, erbium (Er) doping tunes the surface electronic environment to favour  $\text{NO}_2$  adsorption and response, predicting higher selectivity to  $\text{NO}_2$  compared with the undoped material.

## 5. Future scope

In the present study, the electronic structure and gas adsorption behaviour of Er-doped  $\text{In}_2\text{O}_3$  surfaces were thoroughly investigated for  $\text{H}_2\text{S}$ ,  $\text{NO}_2$  and CO gases. To expand on this research, future studies could explore the adsorption characteristics of Eu-doped  $\text{In}_2\text{O}_3$  surfaces. Preliminary DFT calculations (Bader charges and DOS calculations as shown below) on Eu-doped  $\text{In}_2\text{O}_3$  without gas adsorption have already been performed, revealing notable changes in the electronic structure compared to Er doping.

Table 2 Bader charge of the respective In, Er\_1, Eu\_1 and O atoms for  $\text{In}_2\text{O}_3(001)$ , Er-doped  $\text{In}_2\text{O}_3(001)$ , and Eu-doped  $\text{In}_2\text{O}_3(001)$  systems

| Atoms                |      | Bader charge  |  | Bader charge   |  | Bader charge   |  |
|----------------------|------|---|--|--|--|--|--|
| In, O, Er_1 and Eu_1 |      | Pure $\text{In}_2\text{O}_3(001)$ surface (In1 to In12) | Pure $\text{In}_2\text{O}_3(001)$ surface (In13 to In24) | Er-doped $\text{In}_2\text{O}_3(001)$ surface (In1 (replaced In1 from Er_1) to In12) | Er-doped $\text{In}_2\text{O}_3(001)$ surface (In13 to In24) | Eu-doped $\text{In}_2\text{O}_3(001)$ surface (In1 (replaced In1 from Eu_1) to In12) | Eu-doped $\text{In}_2\text{O}_3(001)$ surface (In13 to In24) |
| In1                  | In13 | 1.725   | 1.725  | Er_1(2.06)   | 1.710  | Eu_1(2.04)   | 1.709  |
| O1                   | O17  | -1.185  | -1.185   | -1.191   | -1.275   | -1.192   | -1.261   |
| O2                   | O18  | -1.186  | -1.186   | -1.277   | -1.191   | -1.262   | -1.191   |
| O3                   | O19  | -1.187  | -1.187   | -1.192   | -1.195   | -1.191   | -1.195   |
| In2                  | In14 | 1.855   | 1.854  | 1.861  | 1.861  | 1.862  | 1.860  |
| In3                  | In15 | 1.869   | 1.869  | 1.874  | 1.873  | 1.871  | 1.872  |
| O4                   | O20  | -1.245  | -1.245   | -1.248   | -1.245   | -1.242   | -1.245   |
| O5                   | O21  | -1.246  | -1.246   | -1.245   | -1.250   | -1.244   | -1.250   |
| O6                   | O22  | -1.245  | -1.245   | -1.245   | -1.243   | -1.244   | -1.242   |
| In4                  | In16 | 1.867   | 1.867  | 1.887  | 1.866  | 1.888  | 1.865  |
| In5                  | In17 | 1.856   | 1.856  | 1.856  | 1.856  | 1.856  | 1.856  |
| O7                   | O23  | -1.138  | -1.138   | -1.137   | -1.138   | -1.137   | -1.138   |
| O8                   | O24  | -1.139  | -1.139   | -1.138   | -1.139   | -1.138   | -1.139   |
| O9                   | O25  | -1.137  | -1.137   | -1.136   | -1.137   | -1.136   | -1.137   |
| In6                  | In18 | 1.537   | 1.537  | 1.533  | 1.533  | 1.533  | 1.533  |
| In7                  | In19 | 1.725   | 1.725  | 1.707  | 1.708  | 1.705  | 1.708  |
| O10                  | O26  | -1.185  | -1.185   | -1.191   | -1.188   | -1.192   | -1.189   |
| O11                  | O27  | -1.186  | -1.186   | -1.193   | -1.188   | -1.193   | -1.189   |
| O12                  | O28  | -1.188  | -1.187   | -1.277   | -1.918   | -1.264   | -1.192   |
| In8                  | In20 | 1.854   | 1.854  | 1.854  | 1.863  | 1.852  | 1.861  |
| In9                  | In21 | 1.869   | 1.869  | 1.872  | 1.867  | 1.871  | 1.865  |
| O13                  | O29  | -1.245  | -1.245   | -1.248   | -1.244   | -1.248   | -1.244   |
| O14                  | O30  | -1.246  | -1.246   | -1.245   | -1.248   | -1.245   | -1.248   |
| O15                  | O31  | -1.245  | -1.245   | -1.248   | -1.245   | -1.248   | -1.245   |
| In10                 | In22 | 1.867   | 1.867  | 1.866  | 1.866  | 1.866  | 1.865  |
| In11                 | In23 | 1.856   | 1.856  | 1.856  | 1.856  | 1.856  | 1.857  |
| O16                  | O32  | -1.138  | -1.138   | -1.138   | -1.138   | -1.138   | -1.139   |
| O17                  | O33  | -1.139  | -1.139   | -1.139   | -1.139   | -1.140   | -1.139   |
| O18                  | O34  | -1.137  | -1.137   | -1.137   | -1.137   | -1.138   | -1.137   |
| In12                 | In24 | 1.537   | 1.537  | 1.533  | 1.534  | 1.533  | 1.533  |

Er\_1 and Eu\_1 are the dopants replaced by first indium (In) atom.

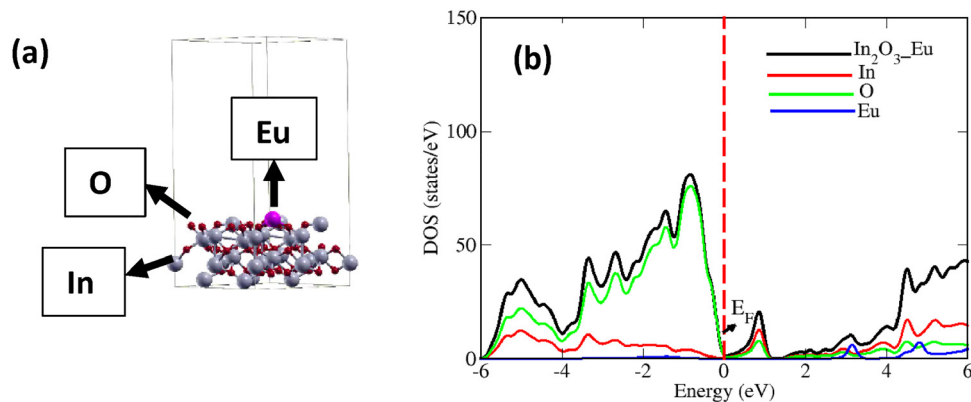


Fig. 6 (a) Optimized geometry of Eu-doped In<sub>2</sub>O<sub>3</sub> obtained from DFT calculations. (b) Corresponding total and partial density of states (TDOS and PDOS) of the Eu-doped In<sub>2</sub>O<sub>3</sub>(001) surface.

Bader charge analysis was conducted to evaluate the effect of Er and Eu doping on the In<sub>2</sub>O<sub>3</sub>(001) surface. In the doped systems, the Er and Eu atoms exhibit Bader charges of 2.06 e and 2.04 e, respectively (as shown in Table 2), indicating partial electron donation to the surrounding lattice. This electron redistribution alters the local electronic environment, which can influence gas adsorption behaviour. Notably, nearby oxygen atoms (O1, O2) show charges of  $-1.275$  and  $-1.277e$ , respectively, which are more negative than the pure system ( $-1.185$  and  $-1.186e$ ). For Eu-doping, O1 and O2 also become more negative ( $-1.261$  and  $-1.262e$ ). These results indicate localized electron accumulation around the oxygen atoms, possibly due to the higher electronegativity and ionic character of the dopants compared to indium (In) atoms. The indium (In) atoms remain largely unaffected across all systems, indicating structural stability.

The optimized structure of Eu-doped In<sub>2</sub>O<sub>3</sub> is shown in Fig. 6(a). The TDOS and PDOS of Eu-doped In<sub>2</sub>O<sub>3</sub> are shown in Fig. 6(b). The contribution in the DOS structure near the Fermi level indicates the presence of defect states introduced by Eu doping. The peak around  $\sim 0.85$  eV likely corresponds to the hybridization between O 2p states and indium (In) atoms (as shown in Fig. 6(b)). The observed band gap is useful for the enhancement in the electrical conductivity, which is crucial in sensing applications.

## 6. Limitation

While DFT calculations provide results at 0 K and consider only static adsorption energies, these results provide crucial atomistic-level insight into gas-surface interactions that cannot be directly accessed experimentally. In real sensor operation, factors such as temperature, adsorption/desorption kinetics, and desorption energy barriers influencing sensitivity, selectivity, and recovery are also involved. Nevertheless, the calculated adsorption energies, Bader charge transfer, and electronic structure reveal how Er-doping modulates surface reactivity and enhances NO<sub>2</sub> adsorption. These predictive insights serve

as a reliable guideline for experimental optimisation, helping to identify promising dopants, surface sites, and gas-specific interactions prior to costly sensor fabrication. Therefore, even without explicitly including kinetic/thermal effects, the present study offers valuable mechanistic understanding that complements and guides future investigations.

## 7. Conclusion

The effect of rare earth element (Er) doping in In<sub>2</sub>O<sub>3</sub> for gas sensing applications was investigated. DFT calculations were performed to analyse the sensing behaviour of H<sub>2</sub>S, NO<sub>2</sub> and CO gas on both pristine and Er-doped In<sub>2</sub>O<sub>3</sub>(001) surfaces. The gas sensing behaviour was evaluated through adsorption energy, Bader charge analysis, charge transfer, TDOS and PDOS analysis. The main conclusions are as follows:

(I) Er-doping significantly alters the adsorption energy for gas molecules. For H<sub>2</sub>S, the adsorption energy is stronger or more favourable for the pristine surface ( $-0.53$  eV) while for the Er-doped surface it is less negative ( $-0.42$  eV), indicating reduced interaction. For the CO molecule, a slight decrease is observed (from  $-0.25$  to  $-0.19$  eV). In contrast, the adsorption energy for the NO<sub>2</sub> molecule enhances from  $-0.37$  to  $-0.61$  eV upon Er doping, indicating enhanced interaction and suggesting that the Er-doped In<sub>2</sub>O<sub>3</sub>(001) surface is more favourable for selective NO<sub>2</sub> gas detection.

(II) Bader charge analysis supports these observations. For H<sub>2</sub>S gas, charge transfer decreases from  $+0.40$  e (pristine) to  $+0.09$  e (Er-doped surface) and for CO the changes are minor. However, for NO<sub>2</sub>, charge transfer increases from  $-0.38$  e (pristine) to  $-0.46$  e (Er-doped), confirming stronger interaction upon doping.

(III) Band structure results indicate changes in the electronic structure after Er doping, reflecting the impact of dopant states.

(IV) TDOS and PDOS analyses reveal that after NO<sub>2</sub> adsorption on the Er-doped In<sub>2</sub>O<sub>3</sub> surface, new states appear near the Fermi energy, indicating strong electronic interaction.

## Conflicts of interest

The authors declare that they have no known financial or non-financial conflicts of interest that could have appeared to influence the work reported in this paper.

## Data availability

The datasets generated and analyzed during the current study, including input and output files from Quantum Espresso calculations, are available from the corresponding author on reasonable request.

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