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# Solution-processed In<sub>2</sub>Se<sub>3</sub> nanosheets for ultrasensitive and highly selective NO<sub>2</sub> gas sensors†

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In this work, we demonstrate that solution-processed In<sub>2</sub>Se<sub>3</sub> nanosheets exhibit exceptional selectivity and sensitivity to NO<sub>2</sub> gas, making them a promising candidate for gas detection systems. Theoretical simulations and surface-science experiments reveal the unique surface properties of In<sub>2</sub>Se<sub>3</sub> nanosheets, which prevent physisorption of oxygen, carbon monoxide, and carbon dioxide, making them remarkably stable towards oxidation and CO-poisoning. Moreover, we show that NO<sub>2</sub> molecules adsorb stably on In<sub>2</sub>Se<sub>3</sub> nanosheets, particularly on Se vacancies, even at high temperatures. The coadsorption of water further enhances NO<sub>2</sub> sticking on the In<sub>2</sub>Se<sub>3</sub> surface, making it an ideal material for gas sensing applications in humid and harsh environments. The fabricated In<sub>2</sub>Se<sub>3</sub> gas sensors exhibit excellent and reversible sensing response to NO<sub>2</sub> gas, with a limit of detection of 5 ppb at 300 °C, and a highly selective response to NO<sub>2</sub> compared to other gases and volatile organic compounds. Our sensors outperform other two-dimensional (2D) semiconductors, metal oxides, and their heterostructures, thanks to the unique surface properties of In<sub>2</sub>Se<sub>3</sub> nanosheets. Importantly, the number of layers and termination of the surface almost have no impact on the sensing performance of In<sub>2</sub>Se<sub>3</sub>, which is advantageous for practical applications. The high sensitivity, selectivity, and stability of In<sub>2</sub>Se<sub>3</sub> nanosheets make them an exciting platform for the fabrication of high-performance gas sensors, particularly in harsh environments, such as industrial settings or outdoor monitoring. Moreover, our solution processing approach enables scalable production of the sensors. Additionally, their unique surface properties make them an attractive candidate for developing complex composite nanostructures with tailored gas sensing characteristics for various applications.

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## 1 Introduction

Air quality monitoring has become increasingly important, due to industrialization and global warming issues.<sup>1–5</sup> Various

approaches have been developed for detecting toxic and hazardous gaseous compounds in the air, including chemoresistive gas sensors based on metal-oxide semiconductors.<sup>6–10</sup> These sensors are popular, due to their small size and easy operation mechanism, whereby changes in electrical parameters of metal oxides are used as a sensing signal, based on the adsorption of gas molecules on their surface.<sup>6–8,11–18</sup> However, to ensure high sensitivity, the sticking coefficient for the adsorption of gases on their surface should be maximized, while keeping the absolute value of the adsorption energy not too high to ensure adsorption/desorption of analytes. Moreover, the presence of different gaseous and volatile organic compounds in the air can cause variations in the conductance (or resistance) of metal oxides, affecting their selectivity to a specific analyte. These challenges continue to impact the sensitivity and selectivity of conventional chemical gas sensors, highlighting the need for novel functional materials to meet modern requirements.

Recently, 2D semiconductors have drawn attention for their large surface area, unique charge transport, and surface physicochemical properties, which make them promising candidates for gas sensing.<sup>19–22</sup> However, their performance in gas sensing

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is not yet comparable to that of metal oxides in terms of sensitivity, selectivity, response/recovery time, and long-term stability. Despite this, the wide range of 2D semiconductors<sup>23,24</sup> has not fully explored for gas sensing.

Among the various 2D semiconductors,  $\text{In}_2\text{Se}_3$  is particularly noteworthy. It is III–VI semiconductor with a direct bandgap<sup>25</sup> and weak van der Waals interlayer bonds. In the past,  $\text{In}_2\text{Se}_3$  has been studied for its capabilities as a broadband light absorber<sup>26</sup> and phase-change<sup>27,28</sup> material, with potential applications in broadband photodetection,<sup>25,29–31</sup> solar cells,<sup>32</sup> non-volatile memories,<sup>33,34</sup> and ferroelectric devices.<sup>35–37</sup> At room temperature,  $\text{In}_2\text{Se}_3$  exists in five stable phases:  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\kappa$ ,<sup>27,31,38–44</sup> with  $\alpha$ - $\text{In}_2\text{Se}_3$  having also two differently stacked polymorphs (2H and 3R<sup>44,45</sup>). Phase transitions between different structures can be induced through pressure and heating, making it a significant material for phase-change memories.<sup>27,42,44</sup> However, the layered 2D structure only appears in the  $\alpha$  and  $\beta$  phases.<sup>29</sup>

Here, we report on the fabrication of novel gas sensors based on solution-processed  $\text{In}_2\text{Se}_3$  nanosheets, showing superb selectivity and sensitivity for the detection of  $\text{NO}_2$ . The fabricated  $\text{In}_2\text{Se}_3$  gas sensors exhibit excellent and reversible sensing response to  $\text{NO}_2$  gas, with a limit of detection of 5 ppb at 300 °C, and a highly selective response to  $\text{NO}_2$  compared to other gases and volatile organic compounds. Theoretical simulations and experiments reveal the unique surface properties of  $\text{In}_2\text{Se}_3$  nanosheets, which prevent physisorption of oxygen, carbon

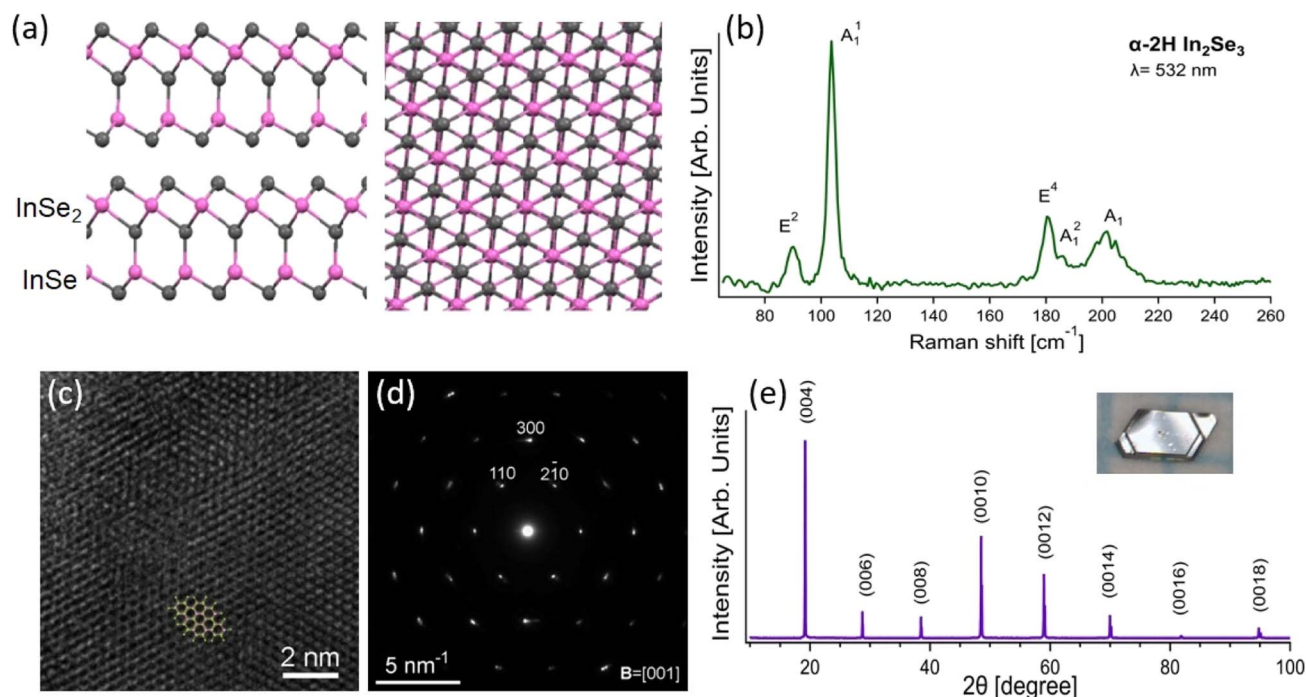
monoxide, and carbon dioxide, making them remarkably stable towards oxidation and CO-poisoning. These findings make  $\text{In}_2\text{Se}_3$  nanosheets an exciting platform for the fabrication of high-performance gas sensors in harsh environments.

## 2 Results and discussion

### 2.1 Atomic structure

The atomic structure of  $\alpha$ - $\text{In}_2\text{Se}_3$  consists of non-covalently bonded  $\text{In}_2\text{Se}_3$  units (Fig. 1a), each composed of two covalently bonded  $\text{InSe}_2$  and  $\text{InSe}$  sub-units. The  $\text{InSe}_2$  sub-unit displays an atomic structure similar to the 1T-structural phase of other diselenides, such as  $\text{MoSe}_2$  (ref. 46 and 47) and  $\text{VSe}_2$ ,<sup>48,49</sup> while the  $\text{InSe}$  sub-unit has an atomic structure, that can be described as an  $\text{InSe}_2$  sub-layer missing Se atoms from one side. The In-terminated side of the  $\text{InSe}$  sub-layer is covalently bonded with Se atoms of the  $\text{InSe}_2$  sub-layer, resulting in two different terminations corresponding to  $\text{InSe}_2$  or  $\text{InSe}$  sub-layers on the surface. The surface termination type can only be recognized by side view (Fig. 1a), while, in the case of the monolayer, both sides are available for adsorption.

Single crystals of  $\text{In}_2\text{Se}_3$  were grown by chemical vapour transport (see Methods) and their phase was determined by Raman spectroscopy (Fig. 1b) and X-ray diffraction (XRD, Fig. 1e) to be  $\alpha$ -2H, belonging to the  $P6_3mc$  space group, which differs from the  $\alpha$ -3R phase ( $R3m$  space group). The spectroscopic fingerprint of the  $\alpha$ -2H phase is the  $E^2$  phonon at



**Fig. 1** Structural and spectroscopic characterization of  $\alpha$ -2H  $\text{In}_2\text{Se}_3$ . (a) Side and top view of a single crystal of  $\alpha$ -2H  $\text{In}_2\text{Se}_3$ , where grey and pink balls represent Se and In atoms, respectively. (b) Raman spectrum of  $\alpha$ -2H  $\text{In}_2\text{Se}_3$  acquired with  $\lambda = 532$  nm, with the corresponding assignment of each Raman-active mode. Prior studies were consulted for the mode assignments.<sup>37,44,50</sup> (c) High-resolution transmission electron microscopy (HRTEM) image, showing atomic-level details of the crystal structure (taken at the bottom-right side of the box in Fig. 3b), with an overlaid atomic model of the  $\alpha$ -2H  $\text{In}_2\text{Se}_3$  crystal in a [001] projection. (d) Selected area electron diffraction (SAED) pattern, demonstrating the single-crystalline nature of the sample. (e) X-ray diffraction (XRD) pattern of an  $\alpha$ -2H  $\text{In}_2\text{Se}_3$  single crystal, with an inset photograph of the crystal as grown.



$\sim 88 \text{ cm}^{-1}$ , which is missing in the 3R phase.<sup>51,52</sup> Transmission electron microscopy (TEM) characterization further supports this assignment (HR-TEM in Fig. 1c and small-area electron diffraction in Fig. 1d).

## 2.2 Surface chemical reactivity

To assess the oxidation resistance of  $\alpha\text{-In}_2\text{Se}_3$ , we modelled the physisorption and the following decomposition of molecular oxygen ( $\text{O}_2$ ) on different terminations of  $\alpha\text{-In}_2\text{Se}_3$ . Firstly, we calculated the formation energies for Se vacancies. The formation of the single Se vacancy in the  $\text{InSe}_2$  termination requires energies as high as 191 and 189  $\text{kJ mol}^{-1}$  for bulk and monolayer, respectively. In the case of the  $\text{InSe}$  termination, the formation of the single Se vacancy corresponds to energy costs of 102 and 183  $\text{kJ mol}^{-1}$  for bulk and monolayer, respectively. Therefore, the presence of Se vacancies appears to be unavoidable.

Calculations (see Table 1) indicate that in the absence of Se vacancies, adsorption and further decomposition of molecular oxygen would be energetically unfavorable even at zero temperature. Increasing temperature enhances the contribution from entropy, making the physisorption of molecular oxygen on defect-free  $\alpha\text{-In}_2\text{Se}_3$  less favorable. However, the presence of Se vacancies is crucial, as, in defective  $\alpha\text{-In}_2\text{Se}_3$ , the physisorption and further chemical decomposition of oxygen molecules is an exothermic process for both terminations in bulk and in monolayer. The physisorption of molecular oxygen on Se vacancies is stable even at 400 °C. Similar calculations were performed for water adsorption on various surfaces of bulk and monolayer  $\alpha\text{-In}_2\text{Se}_3$ , and results of the calculations (see Table 1) demonstrate that physical adsorption of water is stable only at Se vacancies in the  $\text{InSe}$ -terminated surface of bulk or monolayer  $\alpha\text{-In}_2\text{Se}_3$ . Therefore, only some defective sites of bulk and monolayer  $\alpha\text{-In}_2\text{Se}_3$  will be oxidized, even after prolonged storage in ambient conditions.

To validate theoretical predictions on the chemical stability of  $\alpha\text{-In}_2\text{Se}_3$ , we conducted near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) experiments on bulk crystals exposed to  $\text{O}_2$  and  $\text{H}_2\text{O}$  with a total dose of  $10^{10} \text{ L}$  ( $1 \text{ L} = 10^{-6} \text{ Torr s}$ ). The Se-3d core level of the as-cleaved sample (Fig. 2) has a binding energy (BE) of  $\sim 55.0 \text{ eV}$ , and a minor component related to Se(0) is present at BE of  $\sim 55.7 \text{ eV}$ . The In-3d core levels (Fig. 2) exhibit a single peak with the  $J = 5/2$  component located at BE =  $\sim 446 \text{ eV}$ , congruent with previous reports for  $\text{In}_2\text{Se}_3$ .<sup>53,54</sup> Notably, exposure to  $10^{10} \text{ L}$  of oxygen and water did not cause any change in both In-3d and Se-3d core levels, indicating the superior oxidation resistance of bulk  $\text{In}_2\text{Se}_3$ .

## 2.3 $\text{In}_2\text{Se}_3$ nanosheets

To maximize surface area, we produced nanosheets of  $\text{In}_2\text{Se}_3$  by liquid-phase exfoliation, with an average lateral size of  $\sim 450 \text{ nm}$  (see the distribution in Fig. 3c) and an average thickness of  $\sim 15 \text{ nm}$  (see the distribution in Fig. 3e). The selected area electron diffraction (SAED) pattern in Fig. 1d suggests a certain mosaicity around the  $[001]$  hexagonal axis, as indicated by the presence of elongated diffraction peaks. The six-fold symmetry

of the HRTEM pattern corresponds to the  $[001]$  zone axis orientation, while the step-like grey contrast confirms the decreasing thickness, given by the diminishing number of overlapped structural foils towards the crystal border. The outermost border of the grain consists of a thin ( $\sim 2.5 \text{ nm}$ ) amorphous layer, resulting from surface oxidation. Actually, the surface oxidation became relevant for the case of exfoliated nanosheets, because of the presence of vacancy sites, which promote surface oxidation, in agreement with the theoretical results in Table 1. We assessed the stability of exfoliated  $\text{In}_2\text{Se}_3$  nanosheets by synchrotron-based X-ray photoemission electron microscopy (XPEEM), which allows the acquisition of XPS spectra with nanoscale spatial resolution. The binding energy of In-4d and Se-3d is  $\sim 18.2$  and  $54.3 \text{ eV}$  (Fig. 3h), respectively, consistent with previous reports for  $\text{In}_2\text{Se}_3$ .<sup>55,56</sup> Additionally, the In-4d spectra have a secondary component located at  $\sim 18.5 \text{ eV}$  related to indium oxide,<sup>57–59</sup> as highlighted in the HRTEM image in Fig. 3f.

## 2.4 Gas sensing with $\text{In}_2\text{Se}_3$ nanosheets

To assess the suitability of  $\text{In}_2\text{Se}_3$  for gas sensing, we used DFT calculations. Firstly, we modelled physisorption of various analytes on the surfaces of bulk and monolayer  $\alpha\text{-In}_2\text{Se}_3$ , with and without Se vacancies. Calculations (see Table 1) indicate that adsorption of molecular hydrogen is stable only at temperatures below 150 K, even at defect sites. At higher temperature, adsorption of  $\text{H}_2$  on  $\alpha\text{-In}_2\text{Se}_3$  is metastable. The differential enthalpy of physisorption of water molecules is larger than for hydrogen molecule, especially for adsorption on Se vacancies. For example, the values for adsorption of  $\text{H}_2\text{O}$  and  $\text{H}_2$  on Se vacancies in  $\text{InSe}_2$  side of monolayer are  $-38.8$  and  $-11.7 \text{ kJ mol}^{-1}$ , respectively. However, at the temperatures used in sensing experiments (above 200 °C), adsorption of water is also metastable. Regarding CO and  $\text{CO}_2$ , their adsorption on  $\alpha\text{-In}_2\text{Se}_3$  surfaces is metastable at 200 °C and unstable at 300 °C. The differential Gibbs free energies for both CO and  $\text{CO}_2$  were calculated to be above  $+10 \text{ kJ mol}^{-1}$  for these temperatures. Notably, the physisorption of  $\text{NO}_2$  exhibits a significantly different behaviour compared to other analyzed substances. Firstly, the differential enthalpy of adsorption of  $\text{NO}_2$  is negative, even for defect-free substrates (as seen in Table 1), and its magnitude is larger than for the other considered analytes. This dissimilarity for  $\text{NO}_2$  is related to the charge transfer between the analyte and substrate, with visible changes in the electronic structure and significant charge redistribution at the interface (as demonstrated in Fig. 4a and b). It is worth noting that even visible changes in charge densities (Fig. 4b) do not provide qualitative changes in the electronic structure in the vicinity of the Fermi energy (Fig. 4c).

The adsorption of  $\text{NO}_2$  on  $\alpha\text{-In}_2\text{Se}_3$  is less stable with increasing temperature (the differential Gibbs free energy increases up to  $11.1 \text{ kJ mol}^{-1}$ ). However, up to 300 °C, the adsorption of  $\text{NO}_2$  on both terminations of bulk and monolayer of  $\alpha\text{-In}_2\text{Se}_3$  is stable on Se vacancies with differential Gibbs free energies below  $-50 \text{ kJ mol}^{-1}$ , or metastable on defect-free regions. Further increasing of the temperature up to 400 °C



**Table 1** Differential enthalpy and Gibbs free energies at different temperatures for various surface terminations of bulk/monolayer of  $\alpha$ -In<sub>2</sub>Se<sub>3</sub>. Calculated energy costs of oxygen molecule decomposition are shown in parentheses. Negative values indicate exothermic processes, while positive values indicate endothermic processes

| Termination of $\alpha$ -In <sub>2</sub> Se <sub>3</sub> | $\Delta H$ [kJ mol <sup>-1</sup> ] | $\Delta G$ [kJ mol <sup>-1</sup> ] |               |               |
|--|------------------------------------|------------------------------------|---------------|---------------|
|  |                                    | 200 °C                             | 300 °C        | 400 °C        |
| <b>O<sub>2</sub></b>                                     |                                    |                                    |               |               |
| InSe <sub>2</sub>  | +11.1 (+136.9)/+91.3 (+52.7)       | +29.3/+109.5                       | +33.2/+113.4  | +37.0/+117.2  |
| InSe <sub>1,9</sub>                                      | -102.6 (-108.1)/-173.9<br>(-213.6) | -84.4/-155.7                       | -80.5/-151.8  | -76.7/-147.9  |
| InSe   | +6.6 (+40.9)/+18.6 (+125.4)        | +24.8/+36.8                        | +28.7/+40.7   | +32.5/+44.5   |
| InSe <sub>0,9</sub>                                      | -68.8 (-61.9)/-0.4 (-86.2)         | -50.6/+17.8                        | -46.7/+21.7   | -42.8/+25.5   |
| <b>H<sub>2</sub>O</b>                                    |                                    |                                    |               |               |
| InSe <sub>2</sub>  | -10.3/-12.8                        | +39.4/+36.9                        | +49.9/+47.4   | +60.4/+57.9   |
| InSe <sub>1,9</sub>                                      | -21.3/-36.8                        | +28.6/+12.9                        | +38.9/+23.4   | +50.4/+33.9   |
| InSe   | -13.1/-13.8                        | +36.6/+35.9                        | +47.1/+46.4   | +57.6/+56.9   |
| InSe <sub>0,9</sub>                                      | -60.9/-54.1                        | -11.2/-4.4                         | -0.2/+6.1     | +9.8/+16.6    |
| <b>CO</b>  |                                    |                                    |               |               |
| InSe <sub>2</sub>  | +14.2/-5.7                         | +31.9/+12.0                        | +51.4/+31.5   | +57.9/+38.0   |
| InSe <sub>1,9</sub>                                      | -22.4/-19.9                        | -4.7/-2.2                          | + 14.8/+ 17.3 | + 21.3/+ 23.8 |
| InSe   | -9.5/-7.2                          | +8.2/+10.5                         | +27.7/+30.0   | +34.2/+35.5   |
| InSe <sub>0,9</sub>                                      | -44.3/-23.4                        | -26.6/-5.7                         | -7.1/+ 13.8   | -0.6/+ 20.3   |
| <b>H<sub>2</sub></b>                                     |                                    |                                    |               |               |
| InSe <sub>2</sub>  | -4.3/-5.0                          | +8.7/+8.0                          | +11.6/+10.9   | +14.4/+13.7   |
| InSe <sub>1,9</sub>                                      | +1.2/-11.7                         | +14.2/+1.3                         | +17.1/+4.2    | +19.9/+7.0    |
| InSe   | +7.3/-5.0                          | +18.0/+8.0                         | +23.2/+10.9   | +26.0/+13.7   |
| InSe <sub>0,9</sub>                                      | -1.3/-0.5                          | +9.7/+10.5                         | +14.6/+15.4   | +17.4/+18.2   |
| <b>CO<sub>2</sub></b>                                    |                                    |                                    |               |               |
| InSe <sub>2</sub>  | -17.4/-3.2                         | +8.1/+22.3                         | +13.5/+27.7   | +18.9/+33.1   |
| InSe <sub>1,9</sub>                                      | -28.4/-23.4                        | -2.9/+ 2.1                         | + 2.5/+ 7.5   | + 7.9/+12.9   |
| InSe   | -16.6/-2.7                         | +8.9/+22.8                         | +14.3/+28.2   | +27.4/+33.6   |
| InSe <sub>0,9</sub>                                      | -47.5/-23.4                        | -22.0/+ 2.1                        | -16.6/+ 7.5   | -11.2/+12.9   |
| <b>NO<sub>2</sub></b>                                    |                                    |                                    |               |               |
| InSe <sub>2</sub>  | -47.2/-31.3                        | +5.3/+21.2                         | +16.6/+32.3   | 27.5/+43.4    |
| InSe <sub>2</sub> + H <sub>2</sub> O                     | -71.7/-33.3                        | -19.2/+19.2                        | -8.1/+30.3    | +3.0/+41.4    |
| InSe <sub>1,9</sub>                                      | -111.3/-126.7                      | -58.8/-74.2                        | -47.7/-63.1   | -36.5/-51.9   |
| InSe   | -40.3/-2.7                         | +40.2/+49.8                        | +20.3/+60.9   | +34.4/+72.0   |
| InSe + H <sub>2</sub> O                                  | -87.7/-139.2                       | -35.2/-86.7                        | -23.9/-75.4   | -13.0/-64.5   |
| InSe <sub>0,9</sub>                                      | -194.5/-120.5                      | -142.0/-68.0                       | -130.9/-56.9  | -119.7/-45.7  |
| <b>(CH<sub>3</sub>)<sub>2</sub>CO (acetone)</b>          |                                    |                                    |               |               |
| InSe <sub>2</sub>  | -25.7/-25.3                        | +25.9/+26.3                        | +36.8/+37.2   | +47.7/+48.1   |
| InSe <sub>1,9</sub>                                      | -50.7/-57.3                        | +0.9/-5.7                          | +11.8/+5.2    | +22.7/+16.1   |
| InSe   | +32.8/+29.6                        | +84.4/+81.2                        | +95.3/+92.1   | +106.2/+103.0 |
| InSe <sub>0,9</sub>                                      | -35.0/-58.8                        | +16.6/-7.2                         | +27.5/+3.7    | +38.4/+14.6   |
| <b>C<sub>2</sub>H<sub>5</sub>OH (ethanol)</b>            |                                    |                                    |               |               |
| InSe <sub>2</sub>  | -19.3/-17.7                        | +19.7/+21.3                        | +27.9/+29.5   | +36.2/+37.8   |
| InSe <sub>1,9</sub>                                      | -55.2/-57.2                        | -16.2/-18.2                        | -7.9/-10.0    | +0.3/-1.7     |
| InSe   | -4.4/-20.6                         | +34.6/+18.4                        | +42.8/+26.6   | +51.1/+34.9   |
| InSe <sub>0,9</sub>                                      | -99.7/-136.7                       | -60.7/-97.7                        | -52.4/-89.5   | -44.2/-81.2   |
| <b>NH<sub>3</sub></b>                                    |                                    |                                    |               |               |
| InSe <sub>2</sub>  | +190.3/+183.1                      | +235.2/+228.0                      | +244.7/+237.5 | +254.2/+247.0 |
| InSe <sub>1,9</sub>                                      | -73.9/-74.1                        | -29.0/-29.2                        | -19.5/-19.7   | -10.0/-10.2   |
| InSe   | -58.4/-57.7                        | -13.5/-12.8                        | -4.0/-3.3     | +5.5/+6.2     |
| InSe <sub>0,9</sub>                                      | -67.8/-77.5                        | -22.9/-32.6                        | -13.4/-23.1   | -3.9/-13.6    |
| <b>H<sub>2</sub>S</b>                                    |                                    |                                    |               |               |
| InSe <sub>2</sub>  | -11.3/-13.3                        | +29.9/+27.3                        | +38.6/+36.6   | +47.3/+44.3   |



Table 1 (Contd.)

| Termination of $\alpha$ -In <sub>2</sub> Se <sub>3</sub> | $\Delta H$ [kJ mol <sup>-1</sup> ] | $\Delta G$ [kJ mol <sup>-1</sup> ] |             |             |
|--|------------------------------------|------------------------------------|-------------|-------------|
|  |                                    | 200 °C                             | 300 °C      | 400 °C      |
| InSe <sub>1.9</sub>                                      | -36.3/-15.9                        | +4.9/+25.3                         | +13.6/+34.0 | +22.3/+42.6 |
| InSe   | -25.6/-26.8                        | +15.6/+14.4                        | +24.3/+23.1 | +33.0/+31.7 |
| InSe <sub>0.9</sub>                                      | -67.8/-47.0                        | -26.6/-5.8                         | -17.9/+2.9  | -9.3/+11.5  |

corresponds to stable adsorption of NO<sub>2</sub> only at Se vacancies. The calculated differential Gibbs free energies of the adsorption of NO<sub>2</sub> at 400 °C on Se vacancies in  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> monolayers are -51.9 and -45.7 kJ mol<sup>-1</sup> for InSe<sub>1.9</sub> and InSe<sub>0.9</sub> terminations, respectively.

In<sub>2</sub>Se<sub>3</sub>-based NO<sub>2</sub> gas sensors are designed to work in the ambient atmosphere, *i.e.*, in the presence of coadsorbed molecules, especially water (based on results in Table 1). Calculations for adsorption of NO<sub>2</sub> on defect-free surfaces of bulk and monolayer  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> with pre-adsorbed single water molecule (InSe<sub>2</sub> + H<sub>2</sub>O and InSe + H<sub>2</sub>O in Table 1) indicate that pre-adsorption of water decreases the differential enthalpy of adsorption for all considered surfaces. In the presence of pre-adsorbed water, the differential Gibbs free energy of the adsorption of NO<sub>2</sub> on InSe-terminated surface of  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> is negative even at 400 °C (-13.0 and -64.5 kJ mol<sup>-1</sup> for bulk and monolayer, respectively). Moderate doping by pre-adsorbed water molecules increases the substrate's affinity for NO<sub>2</sub>, which corresponds to a decrease of the differential enthalpy of adsorption. This contribution from charge transfer in the energetics of physisorption overcomes the energy cost of small distortions of the substrate (about 10 kJ per supercell), caused

by the formation of non-covalent substrate-analyte bonds. A similar effect is also observed for both terminations of  $\alpha$ -In<sub>2</sub>Se<sub>3</sub>.

As regards volatile organic compounds (VOC), calculations (Table 1) show that the adsorption of acetone and ethanol is more stable than hydrogen but less stable than nitrogen dioxide. Explicitly, the lowest values of the differential Gibbs free energy of the adsorption at 200 °C are -142.0 kJ mol<sup>-1</sup> for NO<sub>2</sub>, +0.9 kJ mol<sup>-1</sup> for acetone, -60.7 kJ mol<sup>-1</sup> for ethanol, -10.0 kJ mol<sup>-1</sup> for NH<sub>3</sub>, -9.3 kJ mol<sup>-1</sup> for H<sub>2</sub>S, and +8.7 kJ mol<sup>-1</sup> for H<sub>2</sub>. Notably, despite the larger size of ethanol and acetone, both molecules demonstrate preferential adsorption on Se vacancies. Thus, we can propose that, at higher temperatures, some minor amount of adsorbed NO<sub>2</sub> molecules leave adsorption sites (especially, Se vacancies). Subsequently, these sites could be occupied by VOC molecules, as well as by the molecules with small size and negative adsorption energy such as NH<sub>3</sub> and H<sub>2</sub>S. The cause of this high selectivity to adsorption of the NO<sub>2</sub> on  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> is the combination of the small size and the peculiar polarization of these molecules. Robust electrostatic interactions between negatively charged Se centres (see Fig. 4a and b) on the surface and positively charged nitrogen significantly decrease the differential enthalpy of the

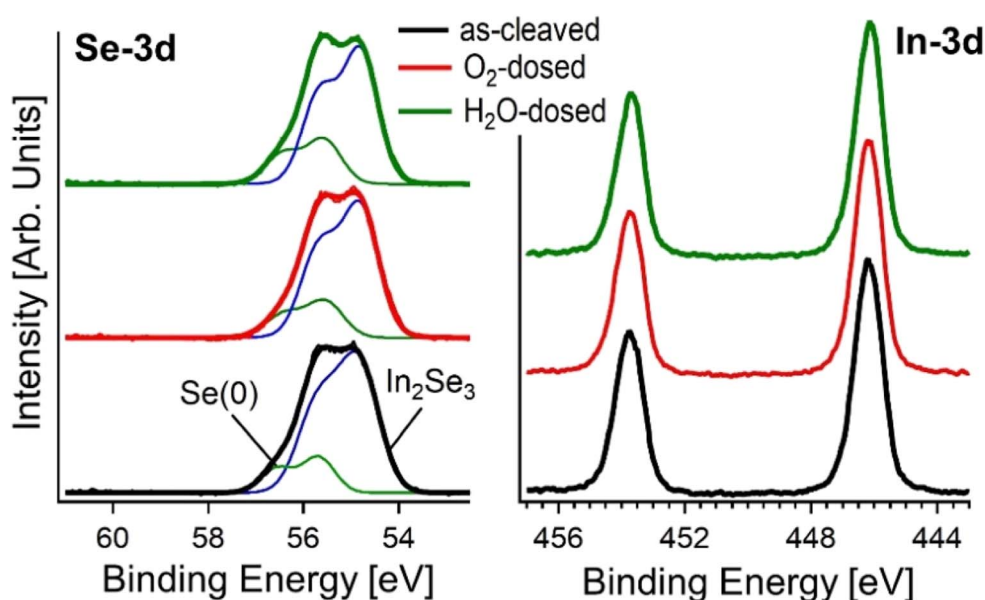


Fig. 2 X-ray photoelectron spectroscopy (XPS) spectra of Se-3d and In-3d core levels for the as-cleaved surface of the bulk crystal of  $\alpha$ -In<sub>2</sub>Se<sub>3</sub>, and after exposure to 10<sup>10</sup> L of O<sub>2</sub> and H<sub>2</sub>O.



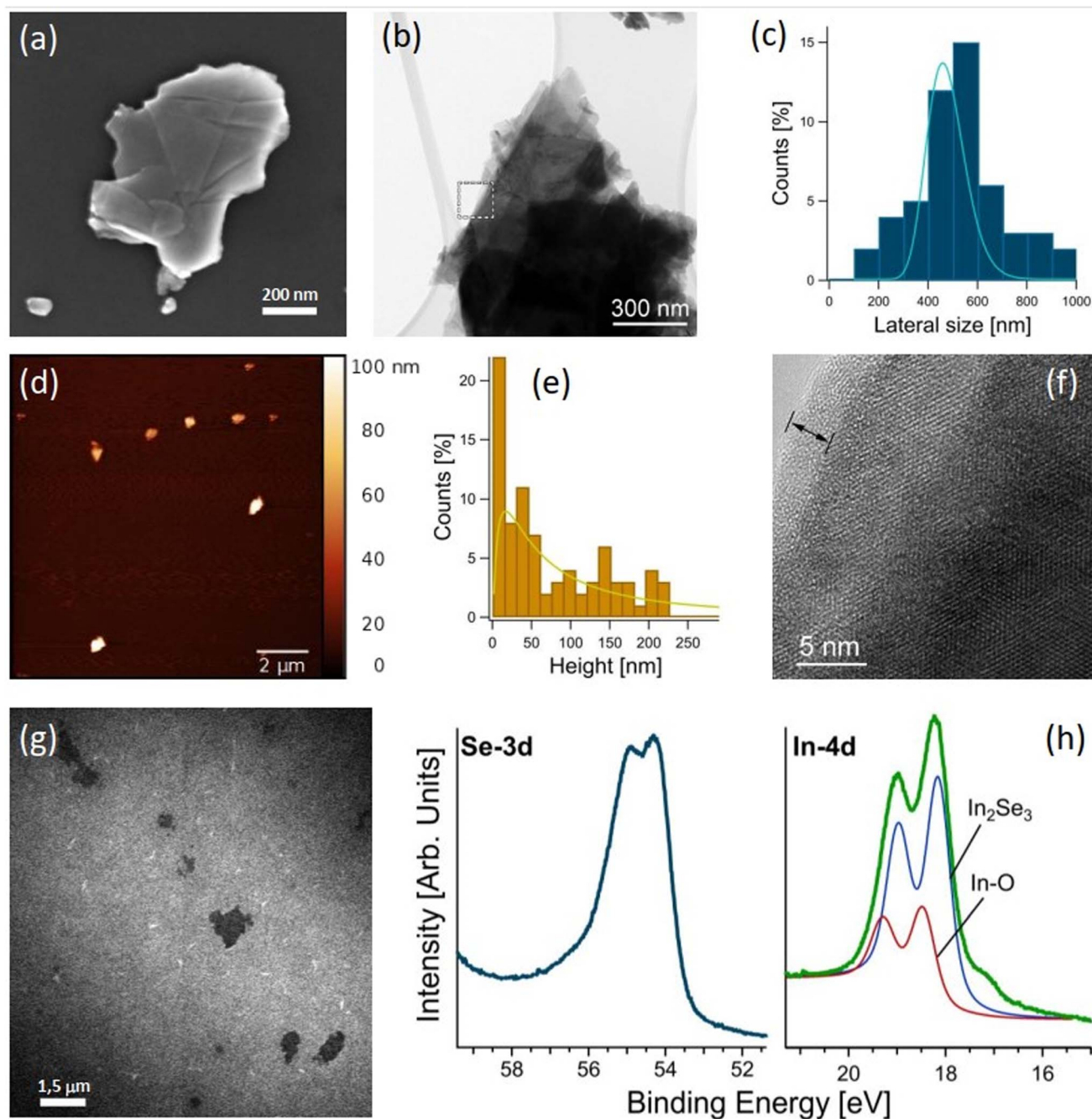


Fig. 3 Structural and morphological characterization of exfoliated  $\text{In}_2\text{Se}_3$  nanosheets. (a) SEM and (b) TEM images showing the typical morphology of  $\text{In}_2\text{Se}_3$  flakes. (c) Lateral size distribution obtained from a large dataset of SEM images. (d) AFM image of  $\text{In}_2\text{Se}_3$  flakes showing their thickness. (e) Thickness distribution obtained from AFM measurements. (f) HRTEM image of a thin area at the edge of the nanosheet. (g) XPEEM image at the In-4d core level. (h)  $\mu$ -XPS spectra in the region of Se-3d and In-4d core levels. Photon energy was 110 and 70 eV, respectively.

adsorption. The small size of  $\text{NO}_2$  leads to a decrease of the energy cost of distortion of the substrate caused by the formation of non-covalent bonds, which is extremely important for the material with a peculiar surface structure. Contrarily,  $\beta$ - $\text{In}_2\text{Se}_3$  has a much more rigid surface and it has an inherently lower selectivity in the adsorption of reactants (see ESI, Table S3†).

Recently, other theoretical predictions have proposed  $\text{In}_2\text{Se}_3$  as a suitable platform for gas sensing.<sup>60,61</sup> However, a careful

inspection of these works evidences the presence of severe inconsistencies, which led to misleading conclusions. Specifically, in ref. 60, analyte adsorption was considered only at Se sites of the  $\alpha$ - $\text{In}_2\text{Se}_3$  surface, which are usually unfavourable for adsorption. This led to calculated values of the differential enthalpies of adsorption that were positive and indicative of unstable adsorption. On the other hand, ref. 61 recognized more appropriate adsorption sites for CO, NO, and  $\text{NO}_2$  on  $\beta$ - $\text{In}_2\text{Se}_3$ , but claimed its superiority with respect to  $\alpha$ - $\text{In}_2\text{Se}_3$  based



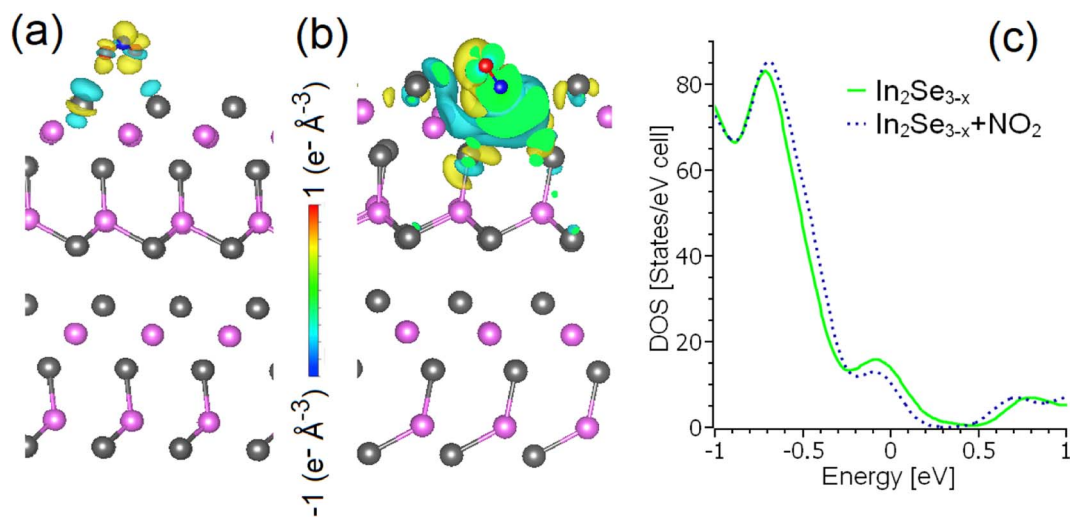


Fig. 4 Changes in the charge density distribution following the adsorption of  $\text{NO}_2$  on the (a)  $\text{InSe}_2$ - and (b)  $\text{InSe}_{1.9}$ -terminated surfaces of  $\alpha$ - $\text{In}_2\text{Se}_3$ , along with (c) the total densities of states of  $\alpha$ - $\text{In}_2\text{Se}_{3-x}$  before and after physisorption of  $\text{NO}_2$  on one Se vacancy in the  $\text{InSe}_{1.9}$ -terminated surface.

on the incorrect choice of adsorption sites in ref. 60. Additionally, the reported (i) adsorption energies, (ii) charge transfers, and (iii) changes in electronic structure for CO and  $\text{NO}_2$  on  $\beta$ - $\text{In}_2\text{Se}_3$  in ref. 61 are rather close. To resolve the issue related to the presence of controversial reports, systematic calculations for adsorption of species under consideration were carried out for both bulk and monolayer  $\beta$ - $\text{In}_2\text{Se}_3$ . Results of the calculations (see ESI, Table S3†) demonstrate that even at 400 °C stable adsorption of  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , ethanol, acetone, CO, and  $\text{CO}_2$  should occur even on defects-free surfaces of  $\beta$ - $\text{In}_2\text{Se}_3$ . Accordingly,  $\beta$ - $\text{In}_2\text{Se}_3$  cannot be considered neither as CO-tolerant nor as material sensitive to some special compounds.<sup>60,61</sup>

Theoretical results on gas sensing were validated by tests after having fabricated gas sensors, following methods discussed in the corresponding section. Fig. 5a reports the response of  $\alpha$ - $\text{In}_2\text{Se}_3$  towards 1 ppm of  $\text{NO}_2$  at the operating temperatures of 100–400 °C. The response values of the material were calculated as the relative variation of its electrical resistance (eqn (1)), where  $R_0$  is the baseline resistance value of the sensor in air, and  $R_f$  is the steady state value of its resistance in the presence of  $\text{NO}_2$  gas.

$$S = \frac{(R_f - R_0)}{R_0} = \frac{\Delta R}{R_0} \quad (1)$$

Fabricated  $\alpha$ - $\text{In}_2\text{Se}_3$  sensors had a high response ( $S = 73.0$ ) to  $\text{NO}_2$  at 200 °C, with a slightly higher response ( $S = 73.7$ ) at 250 °C. However, the sensing response of  $\alpha$ - $\text{In}_2\text{Se}_3$  decreased with increasing operating temperature, reaching its lowest value ( $S = 2.7$ ) at 400 °C. These experimental findings were consistent with the DFT calculations, which indicated that the adsorption of  $\text{NO}_2$  on  $\alpha$ - $\text{In}_2\text{Se}_3$  was stable at Se vacancies and metastable at defect-free zones at  $\leq 300$  °C, while it was stable only at Se vacancies at an operating temperature of 400 °C. Moreover, we

found that the conductance of  $\alpha$ - $\text{In}_2\text{Se}_3$  did not fully recover to its baseline after the gas sensing tests at 200 and 250 °C.

We also measured the conductance variation associated with the exposure to different concentrations of  $\text{NO}_2$  and found a reversible sensing response at 300 °C (Fig. 5b). Specifically,  $\text{NO}_2$  as an oxidizing gas was adsorbed on the surface of  $\alpha$ - $\text{In}_2\text{Se}_3$ , trapping electrons from its surface and reducing the density of charge carriers, leading to a reduction of the conductance of the sensing structure. The temperature increase to 300 °C enhanced the desorption of  $\text{NO}_2$ , ensuring the recovery of the sensor conductance to its baseline value. Therefore, the optimal operating temperature of  $\alpha$ - $\text{In}_2\text{Se}_3$ -based sensors was 300 °C. Table S1 in the ESI† reports the response of the material to different concentrations of  $\text{NO}_2$  at 300 °C. Furthermore, the conductance reduction of the structure after the injection of each concentration of  $\text{NO}_2$  into the test chamber and its recovery to the initial stage (Fig. 5b) indicated the n-type sensing behavior of  $\alpha$ - $\text{In}_2\text{Se}_3$ . The response variation of the fabricated sensor depending on the concentration of  $\text{NO}_2$  (Fig. 5c) indicated that  $\alpha$ - $\text{In}_2\text{Se}_3$  was suitable for providing quantification analysis of the analyte gas.

Moreover,  $\alpha$ - $\text{In}_2\text{Se}_3$  displays high sensitivity ( $S = 9.8$ ) towards 200 ppb of  $\text{NO}_2$ , which is particularly significant, considering the health risks associated with short-term exposure to  $\text{NO}_2$  gas. Based on research findings, the occupational exposure limit for  $\text{NO}_2$  gas should not exceed 5 ppm.<sup>62</sup> Our study highlights the critical sensitivity of  $\alpha$ - $\text{In}_2\text{Se}_3$ -based sensors to low concentrations of  $\text{NO}_2$ , making it a promising candidate for real-life applications. To estimate the limit of detection (LOD) of the  $\alpha$ - $\text{In}_2\text{Se}_3$  sensor, we used a power law function to fit the experimental data (ESI, Fig. S1b†). The LOD for the structure is approximately 5 ppb  $\pm$  5%.

The humidity level is another crucial factor that can affect the functionality of chemiresistive gas sensors. Therefore, we investigated the electrical and sensing properties of  $\alpha$ - $\text{In}_2\text{Se}_3$  at



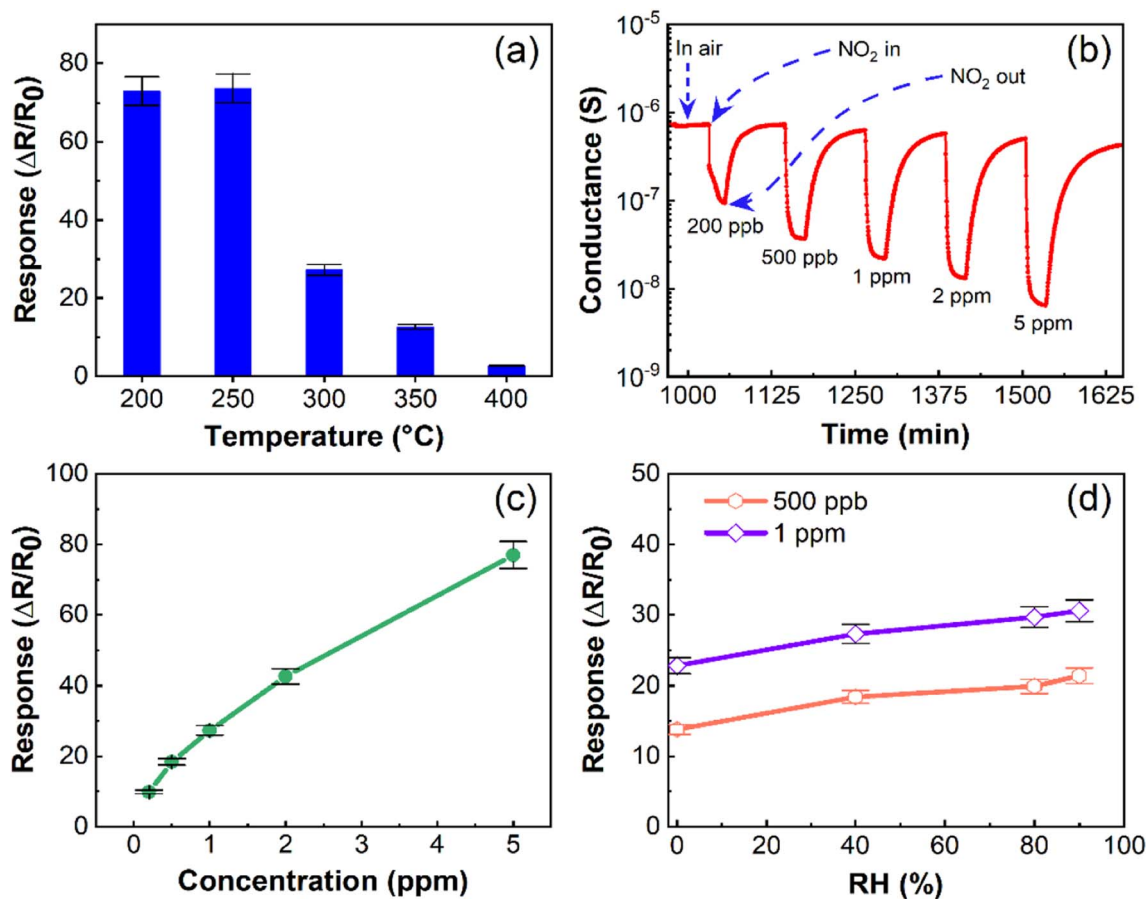


Fig. 5 Gas sensing performance of  $\alpha$ -In<sub>2</sub>Se<sub>3</sub>. (a) Response of  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> to 1 ppm NO<sub>2</sub> as a function of operating temperature (RH = 40% in the test chamber). (b) Dynamic response of  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> to different concentrations of NO<sub>2</sub> (200 ppb to 5 ppm) at 300 °C. (c) Response of  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> to NO<sub>2</sub> concentrations ranging from 0.2 to 5.0 ppm at an operating temperature of 300 °C. (d) Response of  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> to 500 ppb and 1 ppm NO<sub>2</sub> at various humidity levels (dry air, 40%, 60%, 80%, and 90% RH).

its optimal operating temperature under varying relative humidity (RH) levels in the test chamber. The conductance behavior at 300 °C, as shown in Fig. S1a in the ESI,† indicates that the conductance is slightly higher at 40% RH compared to dry air conditions. However, significant variations were not observed at higher RH levels (40–90%). Fig. 5d displays the response of  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> towards 500 ppb and 1 ppm of NO<sub>2</sub> as a function of RH concentration. As RH increased from 0 (dry air) to 40% in the test chamber, the response towards 500 ppb and 1 ppm of NO<sub>2</sub> increased by 25% and 17%, respectively. At 90% RH, the response towards 500 ppb and 1 ppm of NO<sub>2</sub> was 14% and 11% higher than at 40% RH, respectively. These results suggest that  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> exhibits stable electrical and sensing performance at different RH levels, particularly in the range of 40–90%, corresponding to real-life conditions. These slight variations in the response of the sensor to increasing the concentration of RH in the chamber are due to the dissociation of water molecules on the surface of the sensing material resulting in the formation of hydroxyl groups, which may provide additional electrons.<sup>63</sup> However, the co-adsorption of water molecules and other gaseous compounds on a semiconductor is a complex mechanism and varied depending on the working conditions of the sensor. Furthermore, at relatively

high operating temperatures the effect of water molecules is reduced due to their evaporation.<sup>64</sup>

It is also worth noting that our theoretical model predicts that water molecule adsorption on the material is metastable above 200 °C (Table 1). Therefore, the weak enhancement in electrical conductance and sensor response at high RH levels aligns with theoretical predictions.

To evaluate the performance for NO<sub>2</sub> sensing, we compared  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> with other sensors based on 2D semiconductors (SnS<sub>2</sub>,<sup>65</sup> Sb<sub>2</sub>Se<sub>3</sub>,<sup>66</sup> N-doped In<sub>2</sub>S<sub>3</sub>,<sup>67</sup> black phosphorus,<sup>68</sup> reduced graphene oxide<sup>69</sup>), graphitic carbon nitride,<sup>70</sup> metal oxides (In<sub>2</sub>O<sub>3</sub> nanoparticles,<sup>71,72</sup> SnO<sub>2</sub> nanowires<sup>73</sup>), and various heterostructures (SnO<sub>2</sub>/SnSe<sub>1.7</sub>,<sup>74</sup> In<sub>2</sub>O<sub>3</sub>/SnS<sub>2</sub>,<sup>75</sup> SnO<sub>2</sub>/SnS<sub>2</sub>,<sup>76</sup> SnSe<sub>2</sub>/SnO/SnSe,<sup>77</sup> In<sub>2</sub>O<sub>3</sub> nanoparticles/SnO<sub>2</sub> nanowires<sup>73</sup>). The comparative analysis highlights the superior suitability of  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> compared to state-of-the-art materials, with significantly higher sensing response and lower LOD than all other above-mentioned systems. Additionally, while water adsorption is unfavorable on  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> surfaces, it is energetically favorable at near-room temperature on the surfaces of all other above-mentioned systems, leading to detrimental effects on their gas-sensing properties.



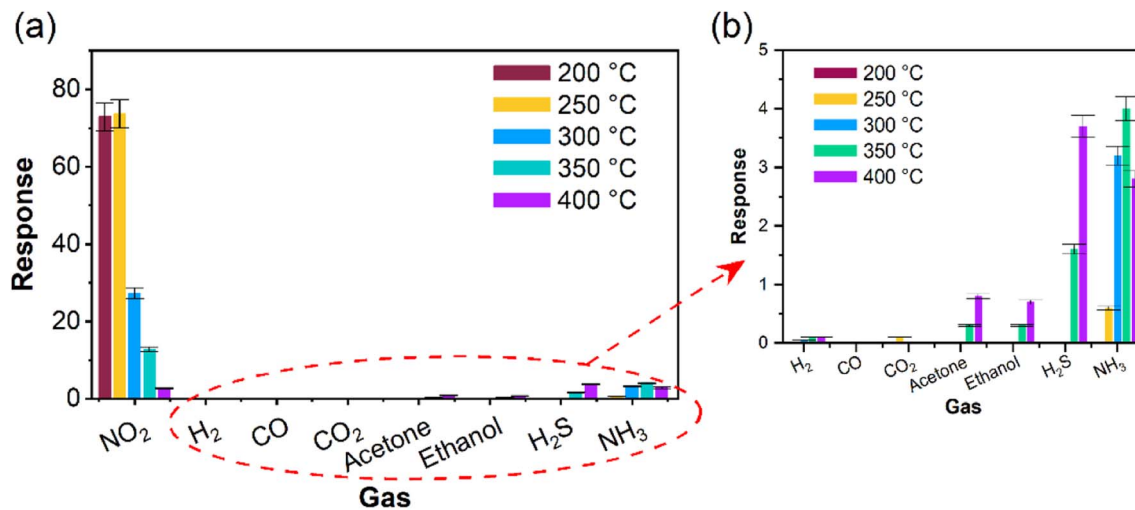


Fig. 6 Gas sensing performance of  $\alpha$ -In<sub>2</sub>Se<sub>3</sub>. (a) Response of the material to 1 ppm of NO<sub>2</sub>, 25 ppm of H<sub>2</sub> and CO, 5 ppm of acetone and ethanol at temperatures, 2 ppm of H<sub>2</sub>S and 5 ppm of NH<sub>3</sub> ranging from 200 to 400 °C. (b) Magnified section of panel (a), showing the response values of  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> towards H<sub>2</sub>, CO, acetone, and ethanol.

To ensure that  $\alpha$ -In<sub>2</sub>Se<sub>3</sub>-based sensors are selective towards the target gas (NO<sub>2</sub>) and not affected by other interfering gases, we investigated the selectivity of  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> towards different gaseous and volatile organic compounds. Fig. 6 illustrates the response of the material to NO<sub>2</sub>, H<sub>2</sub>, CO, (CH<sub>3</sub>)<sub>2</sub>CO (acetone), C<sub>2</sub>H<sub>5</sub>OH (ethanol), H<sub>2</sub>S, and NH<sub>3</sub> at the operating temperatures of 200–400 °C. The response value towards reducing gases was calculated using eqn (2), where  $G_0$  is the conductance of  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> in air and  $G_f$  is the steady-state value of sensor conductance in the presence of gas.

$$\frac{(G_f - G_0)}{G_0} = \frac{\Delta G}{G_0} \quad (2)$$

$\alpha$ -In<sub>2</sub>Se<sub>3</sub> exhibited an excellent selective response to NO<sub>2</sub>. Moreover, the material was found to be insensitive to 25 ppm of CO, 800 ppm of CO<sub>2</sub>, 2 ppm of H<sub>2</sub>S, and 5 ppm of acetone and ethanol, it had a very weak response (0.06) to 25 ppm of H<sub>2</sub> and a significantly lower response value (3.2) to 5 ppm of NH<sub>3</sub> compared to the 1 ppm of NO<sub>2</sub> (27.3) at its optimum operating temperature of 300 °C.

It is worth noting that H<sub>2</sub>, acetone, ethanol, H<sub>2</sub>S, and NH<sub>3</sub> adsorption induced small changes in the electronic structure of the material, while CO<sub>2</sub> caused a weak change at relatively low temperatures and CO did not affect the electronic structure of the sensor. However, the NO<sub>2</sub> sensing response of the material was remarkably high, owing to the negative differential enthalpy of the adsorption of NO<sub>2</sub> and the larger magnitude of the enthalpy of NO<sub>2</sub> adsorption compared to other gaseous and volatile compounds (as shown in Table 1). This exceptional selective response is attributed to the strongest binding energy for NO<sub>2</sub>. Our theoretical simulations are consistent with the experimental results, supporting our findings. Moreover, the gas sensing tests after two months show that the  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> has stable performance for the detection of NO<sub>2</sub> (ESI, Fig. S2†). For

the sake of completeness, we also report in ESI, Fig. S3† the conductance as a function of time dependence for In<sub>2</sub>Se<sub>3</sub>-based sensors at 300 °C.

### 3 Conclusions

In summary, our study has successfully demonstrated the exceptional sensing performance of In<sub>2</sub>Se<sub>3</sub> nanosheets towards NO<sub>2</sub> gas. The material exhibits high selectivity and sensitivity to NO<sub>2</sub>, with a LOD of only 5 ppb at an operating temperature of 300 °C. The theoretical simulations and experimental measurements indicate that the unique selectivity of In<sub>2</sub>Se<sub>3</sub> towards NO<sub>2</sub> is attributed to the negative differential enthalpy of NO<sub>2</sub> adsorption, as well as the larger magnitude of the enthalpy of NO<sub>2</sub> adsorption compared to other gases and VOC.

We also found that the interaction between the In<sub>2</sub>Se<sub>3</sub> and H<sub>2</sub>, acetone, ethanol, CO, and CO<sub>2</sub> is metastable at high operating temperatures. NO<sub>2</sub> is stably adsorbed on the In<sub>2</sub>Se<sub>3</sub> nanosheets even at high temperatures, especially on Se vacancies. Furthermore, theoretical simulations demonstrate that the chemical properties of In<sub>2</sub>Se<sub>3</sub> are independent of the number of layers and termination of the surface, indicating its scalability and potential for practical applications.

The stability of In<sub>2</sub>Se<sub>3</sub> towards oxidation and CO-poisoning was also confirmed by XPS measurements and theoretical simulations. The scalability and stability of the material towards oxidation and CO-poisoning, as well as its unique selectivity towards NO<sub>2</sub>, suggest that it could be used in gas detection systems for harsh environments, such as industrial settings, where other gas sensors may fail. Additionally, our sensors are highly scalable due to the solution-based processing approach, which enables the fabrication of large-area devices, making them ideal for practical gas sensing applications, as an example for the development of complex composite nanostructured sensors. We anticipate that our findings will



contribute to the advancement of gas sensing technology and inspire further studies on  $\text{In}_2\text{Se}_3$  and related materials. The various unique features of  $\text{In}_2\text{Se}_3$ -based sensors could potentially open up new opportunities for the development of gas sensing devices with tailored properties.

## 4 Methods

### 4.1 Single-crystal growth

$\text{In}_2\text{Se}_3$  single crystals were grown by a chemical vapor transport method. In pieces (99.99%) and Se pellets (99.99%) in a stoichiometric ratio of 2:3 with additional iodine (99.9%, 5 mg  $\text{cm}^{-3}$ ) were sealed in an evacuated silica ampoule (170 mm in length and 16 mm in inner diameter). Then, the ampoule was heated in a two-zone tubular furnace. The reactant zone was slowly heated up ( $\sim 12$  h) to 900 C, while the other end was set to 750 C. The entire growth process was maintained for 300 h, followed by a naturally cooling process down to room temperature. Black plate-like crystals with typical dimensions of  $5 \times 5 \times 0.03$  mm<sup>3</sup>. The crystal structure was characterized using powder XRD (Bruker D2) with Cu-K $\alpha$  radiation. The single crystal quality and crystallization directions were identified by the Laue diffraction method (Photonic Science).

### 4.2 Liquid-phase exfoliation and production of nanosheets

To produce a fine powder,  $\text{In}_2\text{Se}_3$  crystals were meticulously ground using a mortar. Following this, 0.03 grams of the resulting  $\text{In}_2\text{Se}_3$  powder were dispersed in 10 milliliters of isopropyl alcohol (IPA). This dispersion was then subjected to a three-hour sonication process in a temperature-controlled bath sonicator, ensuring that the temperature remained below 20 °C. After sonication, the sample underwent centrifugation at 1000 rpm, effectively separating the exfoliated flakes from any unexfoliated material. Finally, the supernatant was collected and prepared for subsequent analysis.

### 4.3 Fabrication and characterization of sensors

$\text{Al}_2\text{O}_3$  substrates with dimensions of 2 mm  $\times$  2 mm  $\times$  0.75 mm were cleaned in acetone and ethanol using an ultrasonic bath and then were washed with distilled water. Platinum (Pt) interdigitated electrodes (ESI, Fig. S4†) were deposited on the surface of the substrates using radiofrequency (13.56 MHz) magnetron sputtering for electrical measurements. To perform sensing characterization of the prepared  $\alpha\text{-In}_2\text{Se}_3$  layers at different operating temperatures, a Pt meander was deposited on the backside of the  $\text{Al}_2\text{O}_3$  substrates as a heater. To perform the sensing measurements, a flow-through system was used, where a stream of synthetic air/analyte gas mixture (constant flow, 0.3 L  $\text{min}^{-1}$ ) passed through the test chamber. The level of RH in the chamber during the measurements was kept under the control using a humidity sensor. A detailed description of the configuration of the chemoresistive sensing device and gas test system was reported in our previous works.<sup>78,79</sup>

$\text{In}_2\text{Se}_3$  layers were dispersed in isopropanol at a concentration of 3 mg  $\text{mL}^{-1}$ . The prepared dispersion was drop cast on the surface of  $\text{Al}_2\text{O}_3$  substrates. A high-precision dispenser

(Gilson Company, Inc, USA) was used for drop casting. The electrical conductance of the fabricated sensors was stabilized at each operating temperature for 10 h, and then the analyte gas with the desired concentration was injected into the test chamber. The conductance value of the sensing structures was monitored by the volt-ampere method. The applied voltage for the measurements was 1 V.

### 4.4 TEM

Sample was prepared for TEM experiments by dripping a liquid suspension containing  $\alpha\text{-In}_2\text{Se}_3$  nanosheets onto the TEM grid, provided with a lacey carbon membrane. Experiments were carried out a JEM ARM200F TEM operating at 200 kV.

### 4.5 XPS

A NAP-XPS apparatus at the Charles University in Prague, Czech Republic, equipped with a Scienta R3000 hemispherical electron analyzer and Al K $\alpha$  X-ray source, was used for *in situ* measurements for bulk crystals exposed to gases in NAP conditions.

The XPEEM measurement took place at the PEEM end-station within the MAXPEEM Beamline at MAX IV Laboratory in Lund, Sweden. The sample was prepared through drop casting and subsequently dried in an ultra-high vacuum (UHV) environment for 4 hours at 350 °C. The experiment utilized a linearly polarized photon beam at perpendicular incidence angles. No beam-induced damage was observed throughout the process.

### 4.6 DFT calculations

The atomic structure, energetics of various configurations, and interactions were studied by DFT using the QUANTUM-ESPRESSO code<sup>80</sup> with GGA-PBE,<sup>81</sup> taking into account van der Waals-like forces correction.<sup>82</sup> Ultrasoft pseudopotentials<sup>83</sup> were used for all simulations, with energy cutoffs of 55 and 400 Ry for the plane-wave expansion of the wave functions and the charge density, respectively. Physisorption enthalpies were also calculated by the standard formula:

$$\Delta H_{\text{phys}} = [E_{\text{subst+mol}} - (E_{\text{subst}} + E_{\text{mol}})],$$

where  $E_{\text{subst}}$  is the total energy of the substrate and  $E_{\text{mol}}$  is the energy of the single molecules of the selected species in an empty box. In the case of water adsorption, only the gaseous phase was considered. Decomposition energy was defined as the difference between the total energy of the system with an adsorbed molecule and the total energy of same system after decomposition on the surface. For physisorption, the differential Gibbs free energy at given temperature was also evaluated using the formula:

$$\Delta G = \Delta H - T\Delta S,$$

where  $T$  is the temperature and  $\Delta S$  is the change of entropy of the adsorbed molecule. The change in entropy  $\Delta S$  was



estimated considering the gas  $\rightarrow$  liquid transition using the standard formula:

$$\Delta S = \Delta H_{\text{vaporisation}}/T,$$

where  $\Delta H_{\text{vaporization}}$  is the measured enthalpy of vaporization.

To test the technical parameters, we performed an optimization of the atomic structure of bulk  $\text{In}_2\text{Se}_3$ . Good convergence between the theoretical and experimental lattice parameters was achieved only for a rather large value of the energy cut-off. For simulations of the surface of the bulk crystal and monolayer, we used a  $3 \times 3$  supercell. For the simulation of the bulk, we used an  $\alpha\text{-In}_2\text{Se}_3$  bilayer with fixed lattice parameters obtained in the calculations for bulk. Only atomic positions were optimized. This type of calculation imitates the effect of the rigid sub-surface bulk part of the crystal on the structure and properties of surface layers. To simulate a flexible monolayer, optimization of the lattice parameters and atomic positions was performed.

## Conflicts of interest

There are no conflicts to declare.

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