SUPPORTING INFORMATION

Bidimensional Engineered Amorphous $\alpha$-SnO$_2$ interfaces: synthesis and
gas sensing response to H$_2$S and humidity

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Section S1 – Microstructure

Figure S1. Low resolution TEM images of the as exfoliated SnSe$_2$ flake (a) and SnSe$_2$ annealed at: 250 °C 1 week (b), 250 °C two weeks (c) and 250 °C two weeks + 280 °C one week (d).
**Figure S2.** (a) High-resolution SEM of a representative as-exfoliated SnSe$_2$ flake; (b) lateral size distribution of the SnSe$_2$ flakes.

**Figure S3.** HRTEM of as-exfoliated flakes with thicknesses measured on the red circles by means of EELS technique.
Section S2 – Gas sensing

Figure S4. Dynamic electrical responses in dry air at (a) 25 °C, (b) 50 °C and (c) 75 °C OT to H₂O in the range 10-80% RH (all @25 °C); (d) log/log calibration plots of Relative humidities from 10% to 80% @ 25°C at 25, 50, 75 and 100 °C OT

Figure S5. Long-term stability of the resistance to (a) 1 ppm H₂S and (b) 40% RH @ 25°C over a period one year (with associated standard deviations calculated over a set of 5 consecutive measurements carried at the end of each week.)
Figure S6. Dynamic electrical responses at 100°C OT to H$_2$S (400 ppb - 1.5 ppm) with 60% RH (a) and 80% RH (b) as interfering gases.

Figure S7. Adsorption and desorption times of 1.5 ppm H$_2$S calculated at different RH% from 0 to 80% @ 25°C and 100°C OT.

Section S3 – Calculation of the low detection limit (LDL) and calibration lines to assess sensitivity

Gas sensor sensitivity (SS) is represented by the slopes of the calibrating line lines obtained by plotting in a log-log scale (Rg/Ra)$_{H_2S}$ as function of increasing H$_2$S gas concentrations. According to the IUPAC definition, the lowest detection limit (LDL) of a sensor can be estimated starting from experimental data, according to:

$$LDL_{ppm} = 3 \frac{rms_{noise}}{slope}$$

where “slope” represents the slope of the linear fitting of the logarithm of relative response vs. the logarithm of the concentration. For the calculation of the $rms_{noise}$, ten points at baseline (i.e. baseline
before gas exposure) of the sensor were considered and fitted by a fifth order polynomial equation. Then, $\text{rms}_{\text{noise}}$ was calculated as

$$
\text{rms}_{\text{noise}} = \sqrt{\frac{(R_i - R)^2}{N}}
$$

where $N$ is the number of points, $R_i$ are the experimental data points, and $R$ is the calculated value from the fifth order polynomial fitting.

In our case, for $\text{H}_2\text{S}$, the noise and slope values of the sensor were 0.04 and 0.55 ppm$^{-1}$ respectively, giving an LDL value of the $\text{H}_2\text{S}$ sensor of about $0.21 \pm 0.1$ ppm.

Table S1. Calculated $\text{H}_2\text{S}$ limit of detection (LOD) of the $\alpha$-SnO$_2$ at different RH content (@ 25°C) and 100°C OT

| Test Conditions | H$_2$S LOD [ppb] |
|-----------------|------------------|
| Dry air         | 210              |
| 40% RH          | 280              |
| 60% RH          | 360              |
| 80% RH          | 380              |
**Section S4 – Computational Methods**

*Computational procedure & validation of the model*

The modeling of the amorphous $\alpha$-SnO$_2$ NS (Figure S8) has been inspired by that of amorphous TiO$_2$ ones,$^{25,35}$ while the anchoring mechanisms of H$_2$S molecule stem from a chemisorbed and physisorbed (molecular) model, related to H$_2$S adsorption on stable crystalline rutile SnO$_2$ surfaces.$^{25}$ Specifically, we considered 4 initial guesses, i.e. chemisorbed H$_2$S (with one broken H—S bond) on top of: (i) a 4-fold and (ii) a 5-fold Sn at the surface of a-SnO$_2$ NS and physisorbed H$_2$S still on top of a (iii) 4-fold and a (iv) 5-fold Sn at the surface of $\alpha$-SnO$_2$ NS. The overall physisorption and chemisorption attack mechanisms are sketched in Figure S8a,b, respectively. Besides the physisorbed configuration mode (a), in the chemisorbed attack (b), the H atom resulting from the H—S bond-breaking of the H$_2$S molecule saturates an oxygen atom at the surface.

![Figure S8.](image)

*Figure S8.* Sketch of the initially considered attacks. H$_2$S (a) physisorbed and (b) chemisorbed on the amorphous SnO$_2$ surface. The two schemes do not consider the coordination, 4-fold or 5-fold, of Sn atom.

Corresponding H$_2$S molecule’s adsorption energies ($E_{ads}$) on the amorphous surface has been computed according to the following equation:

$$E_{ads} = E_{surf \_H2S} - (E_{surf} + E_{H2S}) \quad (S1)$$

where $E_{surf \_H2S}$, $E_{surf}$, and $E_{H2S}$ are the energy of the final system with the hydrogen sulfide molecule anchored on the $\alpha$-SnO$_2$ NS surface, of a single optimized molecule of H$_2$S, and of the optimized initial clean $\alpha$-SnO$_2$ NS respectively. Remarkably, the adsorption energies calculated with Eq. (S1) for (i-iv) H$_2$S anchoring are all quantitatively endothermic (i.e. $E_{ads} > 0$) with the molecularly adsorbed ones (Figure S8a) more unstable than the chemisorbed systems (Figure S8b), partly supporting previously reported data for H$_2$S adsorbed on SnO$_2$ rutile (110) surface.$^{45}$ Such unexpected result was further investigated considering the occurrence of other different geometries obtained by thermalizing the initially calculated (i-iv) metastable systems at 300 K, by means of short AIMD runs and subsequently re-optimizing some representative trajectories for each system.
at the DFT level (0 K, PAW/PBE). Following this procedure, we found three exothermic geometries, all chemisorbed, whose structural features are discussed in the main text. Accordingly, adsorption energies ($E_{\text{ads}}$) shown in Table 3 refer to (i) values obtained by thermalizing (300 K, AIMD) and re-optimizing (0 K, DFT) only products (i.e., precisely the term $E_{\text{surf, H}_2\text{S}}$ only in Eq. (S1)), (ii) values (in brackets) obtained by thermalizing (300 K, AIMD) and re-optimizing (0 K, DFT) for the sake of consistency both products and reactants of the anchoring (i.e., both $E_{\text{surf, H}_2\text{S}}$ and $E_{\text{surf}}$ terms in Eq. (S1)). Notably, $E_{\text{ads}}$ values, despite being smaller for the latter case, show a consistent trend (exothermic), attesting no significant changes in the adsorption thermodynamics (i.e., by thermalizing or not the clean $a$-SnO$_2$ at 300 K before the DFT optimization), a result that in this case can be ascribed to a temperature-driven saturation of dangling bonds initially present in the amorphous layers.

As for the case of H$_2$S, in this study we additionally thermalized water chemisorbed structure with short AIMD runs at 300 K, further re-optimizing at DFT level some trajectories of relevance, yielding no significant structural differences by comparing the combined AIMD+DFT computations with previous DFT ones.

**Theoretical setup**

Geometry optimization of the free-standing amorphous layer of SnO$_2$ and of the H$_2$S/$a$-SnO$_2$ anchored systems was performed by means of Density Functional Theory (DFT)-based simulations as implemented in the Vienna Ab-initio Simulation Package (VASP) code. We similarly employed the projector augmented wave (PAW) method along with the generalized gradient approximation exchange–correlation functional as parametrized by Perdew–Burke–Ernzerhof (PBE). The DFT-D3 dispersion correction was also used to include the van der Waals interactions. We selected plane-wave cutoff energy of 600 eV. All the structures were optimized until the forces on all atoms were smaller than 0.04 eV/Å.
Starting from the initially optimized structure of bulk $\alpha$-SnO$_2$ (192 atoms, 64 Sn, 128 O, $3 \times 3 \times 3 \Gamma$-centered k-point sampling of the Brillouin Zone (see ref.[5s] for further details) we have added a large amount of vacuum (~15 Å) along the three directions to assemble the nanosheets (NSs) and prevent accordingly spurious interactions among the replicas in the non-periodic directions. We corrected all the slabs for the possible residual dipole still along the non-periodic directions and fully re-optimized both lattice parameters and ionic positions in all the systems investigated, finding that the most stable orientation is the one where the non-periodic direction is oriented along the c-axis (see Figure S9). NS in-plane optimized lattice parameters are $a = 13.17$ and $b = 13.37$ Å, respectively. The initial anchoring systems reported in the sketch in Figure S8 are thus optimized at the PAW/PBE level of theory. As mentioned, the initially obtained i-iv systems (described in the main text) are all endothermic.

Ab-Initio Molecular Dynamics (AIMD) simulations $^{14s}$ have been accordingly performed to better shed light on the anchoring mechanism. In particular, short runs of 5 ps (2.5 ps for equilibration, 2.5 ps for production) have been performed on the initially DFT optimized anchoring geometries in a canonical ensemble (NVT) at $T = 300$ K and with a timestep of 0.5 fs. $^{14s}$ A significant trajectory after 5 ps is thus extracted for each anchored system which is once more fully re-optimized @PAW/PBE. Finally, we have computed the Bader charge distribution associated with H$_2$S absorption for each structure of interest by means of the Bader code. $^{15s-18s}$
Figure S8. Optimized geometry of the three NSs obtained adding vacuum on top of (a) the (100), (b) the (010), and (c) the (001) direction of the initially optimized bulk $\alpha$-SnO$_2$. For each structure the energy per formula unit relative to the most stable one, (c) is similarly reported. [Mauve: Sn; Red: Oxygen atoms].

Section S5 – Experimental Section

Synthesis of amorphous $\alpha$-SnO$_2$

SnSe$_2$ crystals (Ossila – UK) were exfoliated in NMP (N-Methyl-2-pyrrolidone, Sigma-Aldrich) solvent by means of Sonication-Assisted Liquid Phase Exfoliation (LPE). The dispersion was sonicated at 25 °C using a Sonics VC 505 working at 20 kHz and 400 W for 3 hours and subsequently centrifuged to remove the solvent. Flakes were then redispersed in ethanol, spin-coated over Si$_3$N$_4$ (at 1500 rpm for 30 s) substrates, and successively annealed in static air at 250 °C for two weeks.

Materials characterization

Microstructure was investigated by SEM imaging (Gemini FESEM 500) working at an accelerating voltage of 2 kV, and by TEM, HRTEM and SAED performed using Jeol JEM 2010F (Jeol Ltd., Tokyo, Japan) operating at 200 kV. Thermogravimetric (TG) and differential thermal (DTA) analyses of exfoliated SnSe$_2$ were carried out in air in Air and in N$_2$ atmospheres using LINSEIS L81-I at a heating rate at 5 °C/min from 25 °C to 1050 °C. XPS spectra were collected using a PHI 1257 spectrometer equipped with monochromatic Al Kα source (hv =
1486.6 eV) and operating at a spectral resolution of 250 meV. Grazing Incidence X-Ray Diffraction (GI-XRD) was performed by XRD-PAN Analytical X’Pert Pro using Cu Kα1 radiation (λ = 1.5406 Å) in parallel geometry using an incident angle of 0.8°.

**Gas sensing measurements**

Thin films were prepared by spin coating 50 μL of centrifuged dispersion containing 2D SnSe2 nanosheets over Si3N4 substrates provided with Pt finger type electrodes (30 micron apart) on front side and heater on backside and mounted inside a Teflon test chamber (500 cm3) to measure resistance variations (Agilent 34970A). Thin films were in situ annealed at 250 °C in dry air for two weeks to yield amorphous α-SnO2, while in “operando” monitoring the variation of the baseline resistance as previously reported28. After baseline resistance stabilization, films were exposed to H2S and humidity at different concentrations in the temperature range 25–150 °C. Different H2S concentrations in the range 400 ppb - 1.5 ppm were obtained by diluting in dry air certified H2S gas mixture (5 ppm in air) using mass flow controllers (MKS 147) with a constant flow rate of 500 sccm/min. Distinct relative humidity’s (RH%) were obtained by mixing dry air with saturated water vapor air and RH% content monitored before injection at a temperature of 25 °C (Thermo-Hygrometer AHTD-625). The following definitions were applied in gas sensing measurements: (BLR), Baseline Resistance represented by the sensor’s electrical resistance in air at equilibrium; sensor’s signal or Relative Response, the relative resistances changes RR = R_{Air}/R_{Gas} for a given concentration of gases; (S), Sensor Sensitivity, the slope of the calibration curve in the log-log sensitivity plot; (τ_{ADS}, τ_{DES}) adsorption and desorption times, the time needed to reach 90% of the resistance value at equilibrium after adsorption and desorption of the analyte.
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