Electronic Supplementary Material

Ultratensitive H₂S gas sensors based on p-type WS₂ hybrid materials

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Resistive and field-effect transistor H₂S sensors

Table S1  Resistive and field-effect transistor H₂S sensors and their properties reported in the literature

| Method    | Sensing material                  | Sensitivity a | Operating temperature | Lowest experimental H₂S concentration | Ref.       |
|-----------|-----------------------------------|---------------|-----------------------|--------------------------------------|------------|
| Resistive | WS₂ nanowire-nanoflake hybrid     | 0.043 ppm⁻¹   | 200 °C                | 0.02 ppm                             | This work  |
| Resistive | α-Fe₂O₃ nanoparticles             | ~5.2 ppm⁻¹    | 300 °C                | 0.05 ppm                             | [1]        |
| Resistive | CuO nanosheets                    | ~3.3 ppm⁻¹    | 240 °C                | 0.03 ppm                             | [2]        |
| Resistive | Mesoporous WO₃                    | ~50 ppm⁻¹     | 250 °C                | 0.25 ppm                             | [3]        |
| Resistive | CeO₂ nanowire                     | ~2 ppm⁻¹      | Room temp.            | 0.05 ppm                             | [4]        |
| Resistive | PbS quantum dots                  | ~140 ppm⁻¹    | 135 °C                | 10 ppm                               | [5]        |
| Resistive | ZnO nanostructures                | ~0.14 ppm⁻¹   | 300 °C                | 20 ppm                               | [6]        |
| Resistive | Pt-loaded WO₃ thin films          | ~1200 ppm⁻¹   | 100 °C                | 1 ppm                                | [7]        |
| Resistive | Nanocrystalline In₂O₃−SnO₂         | ~20 ppm⁻¹     | 40 °C                 | 2 ppm                                | [8]        |
| Resistive | SnO₂ thin film                    | 0.2 ppm⁻¹     | 300 °C                | 5 ppm                                | [9]        |
| Resistive | SnO₂ nanocolumns                  | 2.8 ppm⁻¹     | 300 °C                | 5 ppm                                | [9]        |
| Resistive | SnO₂ nanocolumns decorated with Au| 22 ppm⁻¹      | 300 °C                | 5 ppm                                | [9]        |
| Resistive | SnO₂ nanocolumns decorated with Ag| 12.8 ppm⁻¹    | 300 °C                | 5 ppm                                | [9]        |
| FET       | Ultrathin Ph5T2 microplates        | 240 ppm⁻¹     | Room temp.            | 0.5 ppm                              | [10]       |
| FET       | CuPc                               | 0.004 ppm⁻¹   | Room temp.            | 100 ppm                              | [11]       |
| FET       | In₂O₃ nanowires                    | 0.41 ppm⁻¹    | Room temp.            | 1 ppm                                | [12]       |

The highest sensitivity values are calculated from the published references as the relative change of electrical resistance normalized to the corresponding H₂S concentration i.e. ΔR/(R₀·C_{H₂S}). When the electrical current values were reported, the sensitivity values were calculated from the relative change of the current at the corresponding gas concentration, i.e. ΔI/(I₀·C_{H₂S}).

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Theoretical calculations

Adsorption energy and equilibrium height

For the study of the adsorption of H2S upon WS2 monolayer, we considered four adsorption sites: the center of a hexagon (H), the center of a W–S bond (B), the top of a W atom (TW) and the top of a S atom (TS) (Figure S1). For each anchoring site we investigated three possible orientations of the H2S molecule, namely \textit{up} (the H atoms pointing away from the surface), \textit{down} (the H atoms pointing towards the slab) and \textit{par} (the bonds H–S parallel to the monolayer).

![Figure S1](image.png)  

\textbf{Figure S1} 4x4 supercell of the relaxed pristine monolayer WS2. The four adsorption sites are labelled as H (X), B (+), TW (*) and TS (o).

For each geometrical optimization of the system (supercell+molecule) we calculated the total energy. The total energies of the H2S molecule and the clean slab supercell using the same unit cell were -310.05 and -38688.53 eV respectively. The calculated adsorption energy ($E_{\text{ads}}$) and the equilibrium height ($h$) for each case are reported in Table S2.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
 & $E_{\text{ads}}$ / meV & $h$ / Å \\
\hline
H$_{\text{up}}$ & -156.509 & 3.33 \\
\hline
H$_{\text{down}}$ & \textbf{-181.365} & 2.55 \\
\hline
H$_{\text{par}}$ & -177.500 & 2.66 \\
B$_{\text{up}}$ & -172.414 & 2.97 \\
B$_{\text{down}}$ & -169.677 & 2.59 \\
B$_{\text{par}}$ & -150.301 & 2.72 \\
TW$_{\text{up}}$ & -153.173 & 3.36 \\
\hline
TW$_{\text{down}}$ & \textbf{-181.106} & 2.56 \\
\hline
TW$_{\text{par}}$ & -172.040 & 2.62 \\
TS$_{\text{up}}$ & -109.107 & 3.63 \\
TS$_{\text{down}}$ & -146.507 & 2.79 \\
TS$_{\text{par}}$ & -164.308 & 2.76 \\
\hline
\end{tabular}
\caption{Calculated adsorption energy ($E_{\text{ads}}$) and equilibrium height for the different adsorption sites of H2S molecule on pristine WS2 monolayer.}
\end{table}

As can be observed in Table S2 there are two anchoring positions that show a more marked stability. These are the H and TW sites with adsorption energy of $\sim$ -181 meV. However, we could not appreciate significant differences between the determined electronic structures in both more stable sites, which allowed us to perform all the calculations from the H anchoring position in order to simulate the interaction of H2S with the hybrid...
material. Subsequently, we have structurally optimized the adsorption of H₂, CO, NO and NH₃ upon the WS₂ supercell. As a starting point, we placed the gas molecules in the most stable orientation determined using LDA [13], i.e. TW, H, B and H respectively. The most favorable configurations according to our results are reported in Figures S2-S5.

**Figure S2**  Relaxed geometries for H₂ adsorbed on pristine monolayer WS₂. (left) Top and (right) side view of the most favorable DFT/PBE-D2 relaxed geometries for H₂ adsorbed on pristine monolayer WS₂. The S, W and H atoms are depicted by the yellow, pink and white spheres, respectively.

**Figure S3**  Relaxed geometries for CO adsorbed on pristine monolayer WS₂. (left) Top and (right) side view of the most favorable DFT/PBE-D2 relaxed geometries for CO adsorbed on pristine monolayer WS₂. The S, W, C and O atoms are depicted by the yellow, pink, black and red spheres, respectively.

**Figure S4**  Relaxed geometries for NO adsorbed on pristine monolayer WS₂. (left) Top and (right) side view of the most favorable DFT/PBE-D2 relaxed geometries for NO adsorbed on pristine monolayer WS₂. The S, W, N and O atoms are depicted by the yellow, pink, blue and red spheres, respectively.

**Figure S5**  Relaxed geometries for NH₃ adsorbed on pristine monolayer WS₂. (left) Top and (right) side view of the most favorable DFT/PBE-D2 relaxed geometries for NH₃ adsorbed on pristine monolayer WS₂. The S, W, N and H atoms are depicted by the yellow, pink, blue and white spheres, respectively.
The adsorption energies are -57.4 meV (H₂), -84.7 meV (CO), -509.3 meV (NO) and -171.7 meV (NH₃). The calculated $E_{\text{ads}}$ are in good qualitative agreement with the ones calculated within LDA: -75 meV (H₂), -127 meV (CO), -206 meV (NO) and -216 meV (NH₃) [13]. The exception is the case of NO, which we properly describe using spin-polarized calculations, whereas LDA results for NO [13] were incorrectly calculated at the spin-paired level. On the other hand, if we compare quantitatively, one can observe the smaller binding energy for all the studied gases determined within GGA+vdW, which is consistent with the general trend towards underbinding (overbinding) typical of GGA(LDA) [14].

**Electronic structure**

![Figure S6](image1.png)

**Figure S6**  Calculated electronic band structure and density of states of H₂ adsorbed on monolayer WS₂. The sky blue line represent the projection of the local density of states of the H₂ gas molecule.

![Figure S7](image2.png)

**Figure S7**  Calculated electronic band structure and density of states of CO adsorbed on monolayer WS₂. The pink line represent the projection of the local density of states of the CO gas molecule.
Figure S8  Calculated electronic band structure and density of states of NO adsorbed on monolayer WS$_2$. The red (spin up) and purple (spin down) lines represent the projection of the local density of states of the NO gas molecule.

Figure S9  Calculated electronic band structure and density of states of NH$_3$ adsorbed on monolayer WS$_2$. The blue line represent the projection of the local density of states of the NH$_3$ gas molecule.

Figure S10  Valence electronic density differential plot with an isosurface value of 0.0004 e/Bohr$^3$. Blue (red) depicts electron accumulation (depletion) regions, respectively. Reorganization of the electronic density in H$_2$S molecule upon adsorption and electron accumulation at the interface are visible. However, this density redistribution is small in absolute terms and moreover Bader charge analysis predicts no net electron transfer between H$_2$S and WS$_2$ slab.
Table S3  Comparison of the calculated charge transfer from PBE-D2 and LDA for the different gas species adsorbed on pristine monolayer WS₂. Positive values mean transfer from WS₂ to adsorbate.

| Gas      | GGA - This work | LDA [13] |
|----------|----------------|----------|
| H₂       | 0.004          | 0.002    |
| CO       | 0.003          | 0.022    |
| NO       | 0.008          | 0.018    |
| NH₃      | -0.017         | -0.061   |
| H₂S      | 0.005          | -        |
| H₂S (bilayer) | 0.002          | -        |

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