Density Functional Theory Analysis of Gas Adsorption on Monolayer and Few Layer Transition Metal Dichalcogenides: Implications for Sensing

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Abstract

First principles calculations are performed to compare the adsorption of CO, NH$_3$, NO, and NO$_2$ molecules on monolayer, bilayer, and heterobilayer MoS$_2$ and WS$_2$, using van der Waals corrected density functional theory. Only minor differences are demonstrated for the adsorption behaviors of the monolayer and bilayer systems despite fundamental differences in the electronic structure (direct versus indirect band gap). We also show that NO$_2$ binds stronger to the sensor materials than the other gas molecules, resulting in enhanced charge transfer. Adsorption of paramagnetic NO and NO$_2$ has significant impact on the electronic states, in contrast to adsorption of non-magnetic CO and NH$_3$.

Keywords: sensor, gas, transition metal dichalcogenide, adsorption, first principles

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I. INTRODUCTION

Metal oxides are conventional gas sensing materials with high sensitivity at low cost [1–5]. However, they often require high operating temperatures, about 200-500 °C, causing issues of power consumption and safety [6, 7]. Development of gas sensing materials with high sensitivity that can operate at room temperature therefore is of great importance, for example in areas such as human health, agriculture, and industry [8–11]. In this context, two-dimensional materials are attractive candidates, particularly transition metal dichalcogenides (MoS$_2$, WS$_2$, etc.), as they provide a wide range of band gap sizes [12–14]. Gas sensing by two-dimensional materials typically exploits charge transfer processes that modify the resistance after exposure to gas molecules [15]. For example, a field effect transistor based on monolayer MoS$_2$ can provide excellent detection limits of 1 ppm for NH$_3$ and 20 ppb for NO$_2$ [16]. monolayer MoSe$_2$ has been used to sense NH$_3$ with a detection limit of 50 ppm [17]. A field effect transistor based on graphene for sensing CO, NH$_3$, NO$_2$, and H$_2$O at room temperature has been discussed in Ref. [18], sensing of NH$_3$ and NO$_2$ by monolayer MoS$_2$ has been studied by in-situ photoluminescence spectroscopy in Ref. [19], and it has been demonstrated that monolayer MoS$_2$ supported on SiO$_2$/Si substrate provides selective response to electron donor analytes [20].

While the preparation of monolayer transition metal dichalcogenides is expensive, few layer films provide also high surface-to-volume ratios and can be obtained by scalable methods [21]. However, in contrast to the direct band gaps of monolayer transition metal dichalcogenides, bilayers and few layer films reproduce the main features of the bulk band structures (in particular the indirect band gap nature) [22, 23]. Because of this fundamental difference in the electronic structure, it cannot be predicted whether the excellent gas sensing properties of monolayer transition metal dichalcogenides are inherited by few layer films. Density functional theory previously has been used to investigate the adsorption of gas molecules on monolayer MoS$_2$ [24], monolayer WS$_2$ [25], and monolayer MoS$_2$/WS$_2$ in-plane heterojunctions [26]. In the present study, we perform a systematic first principles investigation to establish the adsorption behavior of prototypical gas molecules (CO, NH$_3$, NO, and NO$_2$) on MoS$_2$ and WS$_2$, comparing the monolayer geometry (direct band gaps) to few layer films (which we represent by bilayers, as these already realize indirect band gaps). We also discuss results for MoS$_2$/WS$_2$ heterobilayers. Adsorption energies, Bader charges, and
electronic band structures are used to describe the molecule-sensor interaction.

II. COMPUTATIONAL METHODS

We use spin-polarized density functional theory as implemented in the Vienna Ab-initio Simulation Package [27] with the generalized gradient approximation for the exchange-correlation potential (Perdew-Burke-Ernzerhof parametrization). The plane wave energy cutoff is set to 500 eV, the van der Waals interaction is described by the DFT-D2 method [28], and the Brillouin zone is sampled on $3 \times 3 \times 1$ k-meshes. Moreover, the adsorption energy of gas molecules,

$$E_a = E[\text{sensor}] + E[\text{molecule}] - E[\text{sensor+molecule}],$$

is calculated from the total energies before and after adsorption. Positive values imply that adsorption is energetically favorable. We use hexagonal $4 \times 4 \times 1$ supercells (lattice constant 12.73 Å) of monolayer MoS$_2$ and WS$_2$, consisting of 48 atoms, and periodic boundary conditions with a 15 Å vacuum slab added in the $c$-direction. bilayers and heterobilayers are constructed for different stacking configurations (96 atoms per supercell). It turns out that location of the S atoms of one layer on top of the Mo/W atoms of the other layer minimizes the total energy, in agreement with previous reports [29–31]. This stacking configuration therefore is used throughout our study. Structural optimizations are conducted by the conjugate gradient method until the changes in the total energy and atomic forces decline below $10^{-6}$ eV and $5 \times 10^{-3}$ eV Å$^{-1}$, respectively. The charge transfers between the gas molecules and sensor materials are calculated by Bader charge analysis [32].

III. RESULTS AND DISCUSSION

The favorable adsorption sites of the gas molecules are taken from previous studies on monolayer MoS$_2$ [24] and monolayer WS$_2$ [25]. The relaxed structures obtained after adding one CO, NH$_3$, NO, or NO$_2$ molecule to monolayer MoS$_2$ are shown in Figure 1(left). Qualitatively the same structures are found for adsorption on monolayer WS$_2$. We obtain for the CO, NH$_3$, NO, NO$_2$ molecules distances of 3.48, 3.28, 3.15, 3.25 Å from monolayer MoS$_2$ and distances of 3.43, 3.28, 3.14, 3.21 Å from monolayer WS$_2$, respectively. The computed
FIG. 1. Top and side views of relaxed monolayer (left) and bilayer (right) MoS$_2$ with different molecules adsorbed (white: H, black: C, blue: N, red: O, yellow: S, pink: Mo/W). Qualitatively the same structures are obtained for WS$_2$. Band structures are given for adsorption on both MoS$_2$ and WS$_2$. Corresponding results for the pristine materials are shown on top.

adsorption energies of the gas molecules on monolayer MoS$_2$ and WS$_2$ are summarized in Figure 2. It turns out that they are systematically higher on monolayer WS$_2$ than on monolayer MoS$_2$, in agreement with previous results [33]. We find that CO, NH$_3$, NO, and NO$_2$ donate 0.01 (0.04), 0.06 (0.05), 0.00 (−0.03), and −0.11 (−0.07) electrons to monolayer MoS$_2$ (WS$_2$), respectively. According to Figure 2, all gas molecules are physisorbed on monolayer MoS$_2$ and WS$_2$, where the slightly enhanced adsorption energy of NO$_2$ corresponds to the observation of higher charge transfer to the sensor material. The C atom of CO, N atoms of NH$_3$ and NO, and O atom of NO$_2$ point towards the sensor material. We find that the band gaps of monolayer MoS$_2$ and WS$_2$ amount to 1.66 and 1.79 eV, respectively, matching
FIG. 2. Comparison of the adsorption energies obtained for adsorption of CO, NH$_3$, NO, and NO$_2$ molecules on monolayer, bilayer, and heterobilayer MoS$_2$ and WS$_2$.

well with earlier reports [24, 25]. According to the band structures given in Figure 1(left) with respect to the valence band maximum (VBM), the valence and conduction bands are hardly affected by the adsorption of non-magnetic CO and NH$_3$, while the adsorption of paramagnetic NO and NO$_2$ on monolayer MoS$_2$ (WS$_2$) introduces two (three) and one (one) flat impurity bands inside the band gap, respectively.

Figure 1(right) shows the relaxed structures obtained after adsorption of the gas molecules on bilayer MoS$_2$. Qualitatively the same structures are found for adsorption on bilayer WS$_2$. In addition, the same molecular orientations are favorable as on the monolayers. It turns out that the same adsorption sites are energetically favorable for the bilayers as for the monolayers. In addition, the distances of the CO, NH$_3$, NO, NO$_2$ molecules from bilayer MoS$_2$ (3.46, 3.29, 3.16, 3.26 Å) and bilayer WS$_2$ (3.42, 3.27, 3.14, 3.23) are almost identical to those reported above for the monolayers. Corresponding adsorption energies are given in Figure 2. Bilayer WS$_2$ provides systematically stronger interaction than bilayer MoS$_2$. In addition, for each molecule the interaction is stronger on the bilayers than on the monolayers. For bilayer MoS$_2$ (WS$_2$) we find that CO, NH$_3$, NO, and NO$_2$ donate −0.03 (0.03), 0.00 (0.02), −0.02 (−0.01), and −0.08 (−0.07) electrons, respectively. The band gaps of bilayer MoS$_2$ and WS$_2$ amount to 1.22 (indirect) and 1.31 eV (indirect), respectively, in agreement
FIG. 3. Top and side views of relaxed MoS$_2$/WS$_2$ heterobilayers with different molecules adsorbed on the MoS$_2$ side (white: H, black: C, blue: N, red: O, yellow: S, pink/grey: Mo/W). Qualitatively the same structures are obtained for adsorption on the WS$_2$ side of the heterobilayer. Band structures are given for adsorption on both the MoS$_2$ and WS$_2$ sides of the heterobilayer. Corresponding results for the pristine heterobilayer are shown on top.

with Ref. [31]. According to Figure 1(right), the adsorption of non-magnetic CO and NH$_3$ has no relevant influence on the conduction and valence bands, while the adsorption of paramagnetic NO and NO$_2$ on bilayer MoS$_2$ (WS$_2$) introduces two (three) and one (one) flat impurity bands inside the band gap, respectively.

For comparison with the monolayers and bilayers, we also study a MoS$_2$/WS$_2$ heterobilayer. The interlayer distance in the heterobilayer turns out to be 6.16 Å, in agreement with
TABLE I. Adsorption energies (in meV) of CO, NH$_3$, NO, and NO$_2$ on the sensor materials under consideration, compared to literature results for selected two-dimensional materials.

<table>
<thead>
<tr>
<th>Method</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>monolayer MoS$_2$</td>
<td>This work</td>
</tr>
<tr>
<td>monolayer WS$_2$</td>
<td>This work</td>
</tr>
<tr>
<td>bilayer MoS$_2$</td>
<td>This work</td>
</tr>
<tr>
<td>bilayer WS$_2$</td>
<td>This work</td>
</tr>
<tr>
<td>MoS$_2$/WS$_2$ heterobilayer, MoS$_2$ side</td>
<td>This work</td>
</tr>
<tr>
<td>MoS$_2$/WS$_2$ heterobilayer, WS$_2$ side</td>
<td>This work</td>
</tr>
<tr>
<td>monolayer MoS$_2$</td>
<td>LDA [24]</td>
</tr>
<tr>
<td>monolayer MoS$_2$</td>
<td>GGA [24]</td>
</tr>
<tr>
<td>monolayer WS$_2$</td>
<td>GGA [25]</td>
</tr>
<tr>
<td>Graphene</td>
<td>GGA [35]</td>
</tr>
<tr>
<td>h-BN</td>
<td>LDA [36]</td>
</tr>
<tr>
<td>MoS$_2$/WS$_2$ in-plane heterojunction</td>
<td>LDA [26]</td>
</tr>
<tr>
<td>MoS$_2$/WS$_2$ in-plane heterojunction</td>
<td>GGA [26]</td>
</tr>
<tr>
<td>MoS$_2$/WS$_2$ in-plane heterojunction</td>
<td>DFT-D2 [26]</td>
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Ref. [34]. Figure 3 shows the structures obtained for adsorption of the molecules on the MoS$_2$ side of the heterobilayer. Adsorption on the WS$_2$ side of the heterobilayer results in qualitatively the same structures. Again the C atom of CO, N atoms of NH$_3$ and NO, and O atom of NO$_2$ point towards the sensor material. The distances between the closest atoms of the gas molecules and sensor material turn out to be 3.48, 3.29, 3.24, and 3.25 Å (3.41, 3.27, 3.14, and 3.22 Å) for CO, NH$_3$, NO, and NO$_2$ adsorbed on the MoS$_2$ (WS$_2$) side of the heterobilayer, respectively. The corresponding adsorption energies, see Figure 2, are higher for adsorption on the WS$_2$ than on the MoS$_2$ side. We find that CO, NH$_3$, NO, and NO$_2$ donate 0.01 (−0.01), 0.09 (0.03), −0.00 (−0.05), and −0.04 (−0.13) electrons to the MoS$_2$ (WS$_2$) side of the heterobilayer, respectively. According to Figure 3, the pristine MoS$_2$/WS$_2$ heterobilayer is a semiconductor with a band gap of 1.09 eV (indirect), in agreement with Ref. [31], which is smaller than obtained for both monolayers and both bilayers. The band
structures given in Figure 3 for adsorption of the different molecules on the MoS$_2$ and WS$_2$ sides of the heterobilayer again indicate that the valence and conduction bands are not significantly affected by the adsorption of non-magnetic CO and NH$_3$, while the adsorption of paramagnetic NO and NO$_2$ introduces two and one flat impurity bands inside the band gap, respectively. The behavior thus is the same as in the cases of monolayer and bilayer MoS$_2$.

The adsorption energies of Figure 2 follow the orders NO$_2 >$ NH$_3 >$ NO > CO and bilayer > heterobilayer > monolayer. A comparison of the obtained values to previous results for various two-dimensional materials is given in Table I. Significant differences of our findings to the results of Refs. [24] and [25] for monolayer MoS$_2$ and WS$_2$ show the importance of considering the van der Waals interaction. The fact that bilayers and heterobilayers provide higher adsorption energies than monolayers is a consequence of the interlayer interaction. The binding energy (total energy of the bilayer/heterobilayer minus total energies of the two component layers) per unit cell turns out to be 150 meV for bilayer MoS$_2$, 260 meV for bilayer WS$_2$, and 200 meV for the MoS$_2$/WS$_2$ heterobilayer. We observe that it correlates with the adsorption energy for all gas molecules. For example, NO$_2$ is adsorbed stronger on
bilayer WS₂ (217 meV) than on the MoS₂/WS₂ heterobilayer (213 meV) than on monolayer WS₂ (206 meV). Therefore, the bilayers and heterobilayers are more effective as gas sensing materials than the monolayers. This observation agrees with the fact that a field effect transistor device based on mechanically exfoliated MoS₂ provides a stronger response to NO gas in the multilayer than in the monolayer case [12]. To confirm our conclusions we study the transport properties of monolayer and bilayer MoS₂ without and with adsorbed NO₂ molecule using the Smeagol code [37, 38]. The current-voltage characteristics in Figure 4 shows higher current for the bilayer than the monolayer, in agreement with the trends observed for the adsorption energy.

IV. CONCLUSION

We have studied the adsorption of CO, NH₃, NO, and NO₂ molecules on monolayer, bilayer, and heterobilayer MoS₂ and WS₂. The calculated adsorption energies show that in each case the gas molecule is physisorbed, with NO₂ binding stronger to the sensor materials than the other molecules (which is reflected by enhanced charge transfer). It turns out that the adsorption strength is higher on monolayer and bilayer WS₂ than on monolayer and bilayer MoS₂, respectively, while the charge transfers are similar. On both sides of the MoS₂/WS₂ heterobilayer it is intermediate between bilayer MoS₂ and bilayer WS₂. Adsorption of non-magnetic CO and NH₃ has little impact on the band structure, whereas the paramagnetic molecules NO and NO₂ induce flat in-gap bands. Bilayer and heterobilayer MoS₂ and WS₂ not only inherit excellent gas sensing properties from the monolayers but even improve the performance. The same is expected to apply to few layer films (which share the indirect band gap nature).

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REFERENCES


