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

Vasudeo Babar[¶], Hakkim Vovusha[¶], and Udo Schwingenschlög^{l*}

King Abdullah University of Science and Technology (KAUST),

Physical Science and Engineering Division (PSE), Thuwal 23955-6900, Saudi Arabia

Abstract

First principles calculations are performed to compare the adsorption of CO, NH₃, NO, and NO₂ molecules on monolayer, bilayer, and heterobilayer MoS₂ and WS₂, 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 NO₂ binds stronger to the sensor materials than the other gas molecules, resulting in enhanced charge transfer. Adsorption of paramagnetic NO and NO₂ has significant impact on the electronic states, in contrast to adsorption of non-magnetic CO and NH₃.

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

[¶] Equal contribution

* udo.schwingenschlogl@kaust.edu.sa

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_2O 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,

$$E_a = E[\text{sensor}] + E[\text{molecule}] - E[\text{sensor+molecule}], \quad (1)$$

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 MoS₂ and WS₂, 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 5×10^{-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 MoS₂ [24] and monolayer WS₂ [25]. The relaxed structures obtained after adding one CO, NH₃, NO, or NO₂ molecule to monolayer MoS₂ are shown in Figure 1(left). Qualitatively the same structures are found for adsorption on monolayer WS₂. We obtain for the CO, NH₃, NO, NO₂ molecules distances of 3.48, 3.28, 3.15, 3.25 Å from monolayer MoS₂ and distances of 3.43, 3.28, 3.14, 3.21 Å from monolayer WS₂, respectively. The computed

FIG. 1. Top and side views of relaxed monolayer (left) and bilayer (right) MoS₂ with different molecules adsorbed (white: H, black: C, blue: N, red: O, yellow: S, pink: Mo/W). Qualitatively the same structures are obtained for WS₂. Band structures are given for adsorption on both MoS₂ and WS₂. Corresponding results for the pristine materials are shown on top.

adsorption energies of the gas molecules on monolayer MoS₂ and WS₂ are summarized in Figure 2. It turns out that they are systematically higher on monolayer WS₂ than on monolayer MoS₂, in agreement with previous results [33]. We find that CO, NH₃, NO, and NO₂ donate 0.01 (0.04), 0.06 (0.05), 0.00 (−0.03), and −0.11 (−0.07) electrons to monolayer MoS₂ (WS₂), respectively. According to Figure 2, all gas molecules are physisorbed on monolayer MoS₂ and WS₂, where the slightly enhanced adsorption energy of NO₂ corresponds to the observation of higher charge transfer to the sensor material. The C atom of CO, N atoms of NH₃ and NO, and O atom of NO₂ point towards the sensor material. We find that the band gaps of monolayer MoS₂ and WS₂ amount to 1.66 and 1.79 eV, respectively, matching

FIG. 2. Comparison of the adsorption energies obtained for adsorption of CO, NH₃, NO, and NO₂ molecules on monolayer, bilayer, and heterobilayer MoS₂ and WS₂.

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 NH₃, while the adsorption of paramagnetic NO and NO₂ on monolayer MoS₂ (WS₂) 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 MoS₂. Qualitatively the same structures are found for adsorption on bilayer WS₂. 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, NH₃, NO, NO₂ molecules from bilayer MoS₂ (3.46, 3.29, 3.16, 3.26 Å) and bilayer WS₂ (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 WS₂ provides systematically stronger interaction than bilayer MoS₂. In addition, for each molecule the interaction is stronger on the bilayers than on the monolayers. For bilayer MoS₂ (WS₂) we find that CO, NH₃, NO, and NO₂ 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 MoS₂ and WS₂ amount to 1.22 (indirect) and 1.31 eV (indirect), respectively, in agreement

FIG. 3. Top and side views of relaxed MoS₂/WS₂ heterobilayers with different molecules adsorbed on the MoS₂ 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 WS₂ side of the heterobilayer. Band structures are given for adsorption on both the MoS₂ and WS₂ 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 NH₃ has no relevant influence on the conduction and valence bands, while the adsorption of paramagnetic NO and NO₂ on bilayer MoS₂ (WS₂) 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 MoS₂/WS₂ 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, NH₃, NO, and NO₂ on the sensor materials under consideration, compared to literature results for selected two-dimensional materials.

	CO	NH ₃	NO	NO ₂	Method	Reference
monolayer MoS ₂	88	160	114	169	DFT-D2	This work
monolayer WS ₂	110	180	132	206	DFT-D2	This work
bilayer MoS ₂	92	166	118	175	DFT-D2	This work
bilayer WS ₂	117	187	138	217	DFT-D2	This work
MoS ₂ /WS ₂ heterobilayer, MoS ₂ side	93	166	116	177	DFT-D2	This work
MoS ₂ /WS ₂ heterobilayer, WS ₂ side	114	186	135	213	DFT-D2	This work
monolayer MoS ₂	128	250	211	276	LDA	[24]
monolayer MoS ₂	13	44	14	43	GGA	[24]
monolayer WS ₂	127	216	215	412	GGA	[25]
Graphene	14	31	29	67	GGA	[35]
h-BN	97	100	117	125	LDA	[36]
MoS ₂ /WS ₂ in-plane heterojunction	120	186	216	550	LDA	[26]
MoS ₂ /WS ₂ in-plane heterojunction	1	28	21	28	GGA	[26]
MoS ₂ /WS ₂ in-plane heterojunction	90	158	122	161	DFT-D2	[26]

Ref. [34]. Figure 3 shows the structures obtained for adsorption of the molecules on the MoS₂ side of the heterobilayer. Adsorption on the WS₂ side of the heterobilayer results in qualitatively the same structures. Again the C atom of CO, N atoms of NH₃ and NO, and O atom of NO₂ 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, NH₃, NO, and NO₂ adsorbed on the MoS₂ (WS₂) side of the heterobilayer, respectively. The corresponding adsorption energies, see Figure 2, are higher for adsorption on the WS₂ than on the MoS₂ side. We find that CO, NH₃, NO, and NO₂ donate 0.01 (−0.01), 0.09 (0.03), −0.00 (−0.05), and −0.04 (−0.13) electrons to the MoS₂ (WS₂) side of the heterobilayer, respectively. According to Figure 3, the pristine MoS₂/WS₂ 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

FIG. 4. Transport setup and current-voltage characteristics obtained for monolayer and bilayer MoS₂ without and with adsorbed NO₂ molecule.

structures given in Figure 3 for adsorption of the different molecules on the MoS₂ and WS₂ sides of the heterobilayer again indicate that the valence and conduction bands are not significantly affected by the adsorption of non-magnetic CO and NH₃, while the adsorption of paramagnetic NO and NO₂ 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 MoS₂.

The adsorption energies of Figure 2 follow the orders NO₂ > NH₃ > 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 MoS₂ and WS₂ 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 MoS₂, 260 meV for bilayer WS₂, and 200 meV for the MoS₂/WS₂ heterobilayer. We observe that it correlates with the adsorption energy for all gas molecules. For example, NO₂ is adsorbed stronger on

bilayer WS_2 (217 meV) than on the MoS_2/WS_2 heterobilayer (213 meV) than on monolayer WS_2 (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 MoS_2 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 MoS_2 without and with adsorbed NO_2 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, NH_3 , NO, and NO_2 molecules on monolayer, bilayer, and heterobilayer MoS_2 and WS_2 . The calculated adsorption energies show that in each case the gas molecule is physisorbed, with NO_2 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 WS_2 than on monolayer and bilayer MoS_2 , respectively, while the charge transfers are similar. On both sides of the MoS_2/WS_2 heterobilayer it is intermediate between bilayer MoS_2 and bilayer WS_2 . Adsorption of non-magnetic CO and NH_3 has little impact on the band structure, whereas the paramagnetic molecules NO and NO_2 induce flat in-gap bands. Bilayer and heterobilayer MoS_2 and WS_2 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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