van der Waals trilayers and superlattices: modification of electronic structures of MoS$_2$ by intercalation†

Ning Lu,$^{ab}$ Hongyan Guo,$^{ab}$ Lu Wang,$^{cd}$ Xiaojun Wu$^c$ and Xiao Cheng Zeng$^{*be}$

We perform a comprehensive first-principles study of the electronic properties of van der Waals (vdW) trilayers via intercalating a two-dimensional (2D) monolayer (ML = BN, MoSe$_2$, WS$_2$, or WSe$_2$) between a MoS$_2$ bilayer to form various MoS$_2$/ML/MoS$_2$ sandwich trilayers. We find that the BN monolayer is the most effective sheet to decouple the interlayer vdW coupling of the MoS$_2$ bilayer, and the resulting sandwich trilayer can recover the electronic structures of the MoS$_2$ monolayer, particularly the direct-gap character. Further study of the MoS$_2$/BN superlattices confirms the effectiveness of the BN monolayer for the decoupling of the MoS$_2$–MoS$_2$ interaction. In addition, the intercalation of a transition-metal dichalcogenide (TMDC) MoSe$_2$ or WSe$_2$ sheet makes the sandwich trilayer undergo an indirect-gap to direct-gap transition due to the newly formed heterogeneous S/Se interfaces. In contrast, the MoS$_2$/WS$_2$/MoS$_2$ sandwich trilayer still retains the indirect-gap character of the MoS$_2$ bilayer due to the lack of the heterogeneous S/Se interfaces. Moreover, the 3D superlattice of the MoS$_2$/TMDC heterostructures also exhibits similar electronic band characters to the MoS$_2$/TMDC/MoS$_2$ trilayer heterostructures, albeit a slight decrease of the bandgap compared to the trilayers. Compared to the bulk MoS$_2$, the 3D MoS$_2$/TMDC superlattice can give rise to new and distinctive properties. Our study offers not only new insights into electronic properties of the vdW multilayer heterostructures but also guidance in designing new heterostructures to modify electronic structures of 2D TMDC crystals.

Introduction

Many experiments have demonstrated that two-dimensional (2D) transition-metal dichalcogenides (TMDCs) such as 2D MoS$_2$ and WS$_2$ crystals possess novel electronic,† optical,§ catalytic,‖ and mechanical properties.¶ Some examples of electronic properties of 2D MoS$_2$ crystals are sensitive to the number of layers, that is, the MoS$_2$ monolayer exhibits a direct bandgap with a value of $\sim$1.8 eV while a bilayer MoS$_2$ exhibits an indirect bandgap with a value of $\sim$1.5 eV.¶ As a result, significant enhancement of photoluminescence has been observed when MoS$_2$ is thinned to a single layer.¶ Previous study has also shown that when the MoS$_2$ bilayer is pulled apart into two separated monolayers, the direct transition ($K$–$K$) is insensitive to the separation while the indirect transition ($\Gamma$–$K$) increases dramatically.¶ It seems that the distance between the two monolayers or the interlayer vdW interaction can notably affect the electronic structures of two-dimensional (2D) layered TMDCs. Thus, one may ask two closely related questions: “can the MoS$_2$ bilayer be effectively decoupled via intercalation of a 2D sheet without being pulled far too apart?” or “To what extent, can the intercalation of a 2D sheet affect electronic properties of the MoS$_2$ bilayer?” The intercalation of a 2D sheet into the MoS$_2$ bilayer gives rise to a hybrid trilayer, coined as the vdW heterostructures by Geim and Grigorieva." Recently, successful fabrication of multilayer vdW heterostructures by stacking one layer on top of another in a precisely controlled sequence has been demonstrated experimentally.¶ The artificial vdW heterostructures can exhibit new and unusual properties that differ from their own constituent layers. For example, the vertical field-effect transistor and memory cell made of TMDC/graphene heterostructures‡§ as well as layered hybrids of MoS$_2$ and WS$_2$ have been realized in the laboratory.¶ Previous theoretical studies suggest that the direct-gap character of the MoS$_2$ monolayer can be retained in certain MoS$_2$ heterobilayer structures whose electronic properties can be further tuned by an in-plane strain or a vertical electric field.¶" In addition, the insulating BN monolayer is a good substrate for...
protecting high quality graphene electronics. A type-I band alignment for the BN monolayer and MoS2 monolayer is also reported. 3D heterostructures such as superlattices are predicted to possess new properties that differ from their corresponding bulk structures, thereby opening a new way of materials design.

The focus of this study is to investigate effects of intercalation of either an insulting BN monolayer or a semiconducting TMDC monolayer (MoSe2, WS2, or WSe2) into a MoS2 bilayer on the electronic properties of the vdW trilayer heterostructure and the corresponding vdW superlattice. Our computational results suggest that the BN monolayer is an ideal sheet to decouple the MoS2 bilayer while a MoSe2 or WSe2 sheet can turn the indirect-gap of the MoS2 bilayer into a direct-gap trilayer.

Computational methods

All calculations are performed within the framework of spin-polarized plane-wave density functional theory (PW-DFT), implemented in the Vienna ab initio simulation package (VASP). The Perdew–Burke–Ernzerhof (PBE) functional and projector augmented wave (PAW) potentials are used. The effect of vdW interaction is accounted for by using the dispersion corrected DFT (optB86-vdW functional). The vacuum length between two adjacent images in the supercell is longer than 15 Å. An energy cutoff of 500 eV is adopted for the plane-wave expansion of the electronic wave function. Geometric structures are relaxed until the force on each atom is less than 0.01 eV Å⁻¹ and the convergence criteria for energy is 1 × 10⁻⁵ eV.

Note that the optimized MoS2 monolayer exhibits a cell parameter of 3.18 Å, while the cell parameter of a h-BN monolayer is 2.52 Å, in good agreement with previous results. As such, the 5 × 5 BN supercell almost perfectly matches the 4 × 4 MoS2 supercell with the lattice mismatch less than 1%. For the MoS2/BN/MoS2 trilayer, the supercell is fixed while the atomic coordinates are relaxed. For other sandwich systems containing TMDC MoSe2, WS2, or WSe2, a 1 × 1 cell is used due to the fact that their lattice parameters are close to that of MoS2. In these cases, both the cell length and atomic coordinates are relaxed to obtain the lattice parameters at the lowest total energy. Bader’s atom in molecule (AIM) method based on charge density topological analysis is used for computing charge population.

Once the optimized structures are obtained, a hybrid functional in the Heyd–Scuseria–Ernzerhof (HSE06) form is used to give more accurate bandgaps. The spin–orbit (SO) interaction is included in all the band-structure calculations.

Results and discussion

Intercalation of a MoS2 bilayer with a BN monolayer

First, DFT/PBE calculations show that monolayer MoS2 is a semiconductor with a direct bandgap of 1.60 eV (see Table 1), in agreement with previous calculation. The MoS2 bilayer with the most stable C7 stacking, however, is a semiconductor with an indirect bandgap of 1.31 eV. HSE06 calculation enlarges the bandgaps of monolayer and bilayer MoS2 to 2.06 and 1.81 eV, respectively. For the BN monolayer, PBE calculation shows it is a semiconductor with a wide bandgap of 4.66 eV (Table 2).

Next, various MoS2/BN/MoS2 trilayer systems are built for which the lateral locations of the MoS2 monolayer and BN monolayer in different supercells are shown in Fig. 1. Specifically, we consider four different stacking orders: A1B1A1, A1B2A1, A1B1A2, and A1B1A3. PBE optimizations show that the total-energy differences among these configurations are typically less than 0.01 eV per formula cell, and the different stacking orders have little effect on the electronic structures. The binding energy of a trilayer, which measures the interlayer vdW interaction per supercell, is defined as: $E_{\text{BE}} = 2E_{\text{MoS2}} + E_{\text{BN}} - E_{\text{MoS2}/\text{BN}/\text{MoS2}}$, where $E_{\text{MoS2}}$ is the total energy of a MoS2 superlattice (SL) with different stacking orders. The SO effect is included in HSE06 calculation of the bandgap.

### Table 1

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### Table 2

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monolayer, $E_{\text{BN}}$ is the total energy of a BN monolayer, and $E_{\text{MoS}_2/\text{BN}/\text{MoS}_2}$ is the total energy of a MoS$_2$/BN/MoS$_2$ trilayer. As listed in Table 1, the computed binding energies of the MoS$_2$/BN/MoS$_2$ heterostructure with A1B1A1, A1B2A1, A1B1A2, and A1B1A3 stacking orders are 0.36 eV, 0.36 eV, 0.37 eV, and 0.36 eV, respectively, reflecting the weak vdW interaction between the MoS$_2$ layer and BN layer. Taking the A1B1A1 stacking as an example, its electronic structure is shown in Fig. 2c. Clearly, the trilayer retains the direct-gap character of the MoS$_2$ monolayer. The computed bandgap is 1.58 eV, and both the conduction band minimum (CBM) and valence band maximum (VBM) are located at the K point, both contributed by the MoS$_2$ layers. Like the PBE calculation, the HSE06 calculation also suggests a direct-gap character but the bandgap increases to 2.00 eV (ESI Fig. S1†). The electronic structure is more or less the same with different stacking orders (A1B1 and A1B2) of MoS$_2$ and BN layers is considered and our calculations show that the two stacking orders give nearly the same results. For both stacking orders, the optimized cell parameters are $a = b = 12.62$ Å and $c = 9.86$ Å. As shown in Fig. 2d, the superlattice exhibits a direct gap of 1.69 eV, and both the VBM and CBM are located at the K point and both are contributed by MoS$_2$ layers as in the case of the MoS$_2$/BN/MoS$_2$ trilayer system. The slightly enhanced bandgap compared to the trilayer system is largely due to a slight reduction of the cell parameters $a$ and $b$. In summary, results of both the vdW trilayer and superlattice show that the alternatively stacked BN and MoS$_2$ monolayers can retain the direct-gap character of the MoS$_2$ monolayer. In other words, the BN monolayer is an effective divider to decouple the interlayer coupling for MoS$_2$.

**Intercalation of a MoS$_2$ bilayer by MoSe$_2$, WS$_2$ or WSe$_2$ monolayer**

Previous experimental and theoretical studies demonstrate that the MoS$_2$ bilayer is a semiconductor with an indirect bandgap. Recent theoretical studies of TMDC heterobilayers also show that the interlayer interaction due to heterointerfaces (e.g., S/Se) can notably affect the electronic properties. Thus, it is interesting to study the extent to which the intercalation of a heterogeneous TMDC monolayer between two MoS$_2$ bilayers affects the electronic properties.

Previous theoretical studies show that the C7 and T stacking patterns give the lowest energy for many heterobilayers and the electronic structure is more or less the same with different stacking orders. Here, we adopt two different stacking orders for the trilayers (see Fig. 3), namely, the ABA and ACA. For the ABA trilayer, the interface AB is in C7 stacking, while for the ACA trilayer, the interface AC is in T stacking. Again, we find that the two stacking orders give rise to nearly the same electronic properties.

The polarization within the S/Se interfaces is responsible for the direct-gap character of heterobilayers in previous studies. The MoS$_2$/MoSe$_2$/MoS$_2$ trilayer entails two S/Se interfaces. In view of the MoS$_2$ bilayer possessing an indirect bandgap, the intercalation of the MoSe$_2$ monolayer induces an indirect to direct transition. As shown in Fig. 4a, the MoS$_2$/MoSe$_2$
MoSe₂/MoS₂ trilayer exhibits a direct bandgap of 0.69 eV. The VBM is located at the K point and is mainly contributed by the MoSe₂ layer, while the CBM is also located at the K point and is mainly contributed by MoS₂ layers. It is desirable that CBM and VBM are contributed from two different TMDC monolayers, particularly for the electron–hole separation. ESI (Fig. S2†) shows a more accurate HSE06 computation of band structures of the trilayers. The computed bandgap is 0.97 eV, wider than that from PBE computation. However, the electronic structures and the VBM and CBM are similar to those based on PBE computation.

Because of the lack of the S/Se interfaces, as shown in Fig. 4b, the MoS₂/WS₂/MoS₂ trilayer still exhibits an indirect gap of 1.05 eV. The VBM is located at the Γ point and is mainly contributed by the WS₂ monolayer, while the CBM is located at the K point and is mainly contributed by the two MoS₂ layers. Computed band structures based on the HSE06 functional is shown in ESI Fig. S2†. Again, the trilayer still exhibits the indirect-gap character but the bandgap increases to 1.47 eV.

The MoS₂/WSe₂/MoS₂ trilayer still exhibits a direct gap of 0.39 eV due to the presence of the two Se/S interfaces (see Fig. 4c). The VBM at the K point is mainly contributed by the WSe₂ layer, while the CBM at the K point is mainly contributed by MoS₂ layers. Again, as shown in ESI Fig. S2†, HSE06 calculation confirms the main character of electronic properties. To further analyze the effect of the polarization within the Se/S interfaces, charge transfer between neighboring layers is computed (see ESI Table S1†). For MoS₂/MoSe₂/MoS₂ and MoS₂/WSe₂/MoS₂ trilayers, a 0.02 e per unit cell is transferred from the MoSe₂ (or WSe₂) layer to the MoS₂ layer. In contrast, for the MoS₂/WS₂/MoS₂ trilayer with S/S interfaces, the charge transfer between two neighboring layers is nearly zero. This result further demonstrates that the interfacial polarization has an important effect on the electronic properties of the trilayer heterostructures.

Lastly, we consider a 3D superlattice made of hybrid MoS₂ monolayers and other monolayers. As shown in Fig. 4, for each superlattice, two stacking orders including AB with a C7 interface and AC with a T interface are investigated. The binding energies and cell parameters for the AB and AC stacking are close to one another in all the configurations (see ESI Table S1†). For the MoS₂/MoSe₂ superlattice, PBE calculations suggest that its bandgap is still indirect, with a value of 0.62 and 0.59 eV respectively, for the AB and AC stacking. The bandgap is about 0.1 eV less than that of the corresponding trilayer. The CBM is still located at the K point and contributed mainly by the MoS₂ layers (Fig. 4d), while the VBM energy at the Γ and K point differs only by 10 meV, and is mainly contributed by the MoSe₂ layers. On the other hand, the HSE06 calculations suggest that the MoS₂/MoSe₂ superlattice is a direct-gap semiconductor with a value of 0.88 and 0.92 eV, respectively, for the AB and AC stacking. The bandgap is about 0.1 eV lower than that of the corresponding trilayer. The CBM is still located at the K point and contributed mainly by the MoS₂ layers (Fig. 4d), while the VBM energy at the Γ and K point differs only by 10 meV, and is mainly contributed by the MoSe₂ layers. The VBM energy in the K point is 77 meV lower than the Γ point (ESI Fig. S2†). For the MoS₂/WS₂ superlattice, both PBE and HSE06 calculations suggest that it is an indirect-gap semiconductor with a bandgap value 0.95 and 1.35 eV, respectively, for the AB stacking. Finally, both PBE and HSE06 calculations suggest that the MoS₂/WSe₂ superlattice is a direct-gap semiconductor with a value of 0.3 and 0.5 eV for the
AB stacking, and 0.35 and 0.54 eV for the AC stacking. Both bandgaps are smaller than those of the corresponding trilayers. Again, the bandgap reduction is mainly due to a slightly enlarged cell parameter (see ESI Table S1†).

Conclusions

In conclusion, our first-principles calculations show that the BN monolayer is a highly effective single sheet to decouple the interlayer vdW interaction of the MoS2 bilayer. The resulting vdW trilayer heterostructure can recover the electronic structures of a single MoS2 monolayer, particularly its direct-gap character. Further study of the 3D MoS2/BN superlattices confirms the effectiveness of the BN monolayer for decoupling the interlayer interaction. Expectedly, this conclusion has implications to MoS2 based heterostructures as well as to other TMDC-based vdW heterostructures. We have also investigated intercalation of a TMDC MoSe2 or WSe2 sheet between two MoS2 sheets and found that the resulting vdW trilayer undergoes an indirect-gap to direct-gap transition due to the newly formed heterogeneous S/Se interfaces. In contrast, the MoS2/WS2/MoS2 vdW trilayer still retains the indirect-gap character of the MoS2 bilayer due to the lack of the heterogeneous S/Se interfaces. Further study together with their novel properties may be tested in the laboratory in the near future.

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References

28 (a) Y. Ma, Y. Dai, M. Guo, C. Niu and B. Huang, Nanoscale, 2011, 3, 3883–3887; (b) J. Kang, J. Li, S-S. Li, J.-B. Xia and