Novel heterostructures by stacking layered molybdenum disulfides and nitrides for solar energy conversion†

Hui Zhang, Yan-Ning Zhang, Hao Liu and Li-Min Liu*

Two-dimensional graphene-like materials have attracted considerable attention for the further development of nanoscale devices. In this work, the structural, electronic and optical properties of freestanding graphene-like nitrides XN (X = B, Al and Ga) are studied by density functional calculations with the inclusion of the nonlocal van der Waals correction. The results show that all the studied nitrides are thermodynamically stable and their electronic structures can be easily tuned by forming the heterostructure with MoS2 monolayer. Although GaN and AlN monolayers retain the indirect band gap of bulk, MoS2–AlN and MoS2–GaN heterostructures have suitable direct gaps, complete electron–hole separation and fascinating visible light adsorption, which is promising for solar energy applications. Moreover, the MoS2–AlN heterostructure is a good candidate for enhanced photocatalytic activity of hydrogen generation from water.

1. Introduction

The discovery of graphene has intrigued tremendous studies on novel low-dimensional materials over the past few years due to its unique electronic structure and high charge carrier mobility. Nevertheless, the absence of intrinsic band gap hampers the direct applications of graphene in widespread devices such as field effect transistor (FET) and photocatalysis. Consequently, exploring new graphene-like 2D materials that exhibit unique and fascinating physical properties compared with their bulk counterparts is one of the most active fields to address this challenge. Abundant accomplishments make 2D materials prosperous beyond carbon-based materials, including elements and compounds.

There are two typical routes to fabricate 2D materials: one is to exfoliate free-standing, stable, low-dimensional materials from van der Waals solids, and the other is to fabricate 2D heterostructures from the covalent bonding materials. Taking the zinc-blende ZnSe as an example, the formation of large-area, freestanding ZnSe monolayer triggered a way to obtain 2D heterostructures from non-layered compounds. Moreover, the manipulation of electronic structures in heterostructures, by changing different materials and layer thickness, has been widely explored so as to meet distinct application requirements. Many promising features, such as tunable band gaps and visible light response, have been reported for graphene nanocomposites and their analogues such as h-BN, C3N4, and MoS2. Because of the advantages of 2D heterostructures, they offer great potential as functional materials with high performances. For example, MoS2–TiO2 heterostructures show enhanced photocatalytic efficiency and give the hydrogen production rate of 1.6 mmol h−1 g−1. Vertically stacked graphene-MoS2 metal heterostructures are fabricated as a new generation of field-effect-transistors with high on–off ratio >103 and current density of up to 5000 A cm−2.

The III–V compounds, especially nitrides XN (X = B, Al and Ga) with hexagonal wurtzite or cubic zinc-blende structures, are basic semiconductors for optoelectronics. Monolayer graphene-like BN, denoted as g-BN, has been fabricated experimentally but is not a good photocatalyst due to the large band gap (~6.07 eV). Thus, it is natural to wonder whether the other graphene-like monolayer nitrides, such as g-AlN and g-GaN, can be thermodynamically stable and also have extraordinary physical properties. On the other hand, the previous works have revealed that layered transition metal dichalcogenides (TMD) exhibit versatile electronic structures. For example, monolayer MoS2 transforms to a direct semiconductor of ~2.0 eV from an indirect bulk one, which is important for the applications in photocatalysis and FET. Therefore, we may expect some excellent properties in MoS2–XN heterostructures if they are stable.

The purpose of this study is to unveil a new group of graphene-like, single-layer 2D materials g-XN (X = B, Al and Ga). Particular attention will be focused on the following questions: (i) is it feasible to synthesize these single-layer materials? (ii)
What are the electronic properties of these monolayers? (iii) What fantastic properties can heterostructures possess by combining graphene-like g-XN (X = B, Al and Ga) with other single-layer materials such as MoS2? The calculated results exhibit the good stabilities of the free-standing 2D graphene-like AlN and MoS2–AlN monolayers beyond BN. The proposed MoS2–AlN and MoS2–AlN heterostructures possess many novel properties, such as moderate band gap, suitable band edge positions, electronic-hole separation, and fascinating visible light adsorption, which enable them to have great potential applications for solar energy conversion and photocatalysis. Our extensive investigation extends the scope of 2D structures and brings out novel properties for solar energy conversion applications.

2. Methodology

In this work, all density functional theory (DFT) calculations were performed with Vienna ab initio Simulation Package (VASP).29,30 Projector-augmented-wave (PAW) potentials31 were used to account for electron–ion interactions. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional32 was used to treat the electron exchange correlation interactions. The more accurate Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional is used to determine the bond gaps and optical properties. The vdW interaction is corrected by the DFT-D2 approach.33

To remove spurious interactions between neighboring structures due to periodic calculations, a vacuum layer thickness larger than 10 Å was employed between the slabs. We used the energy cutoff of 600 eV, and a (16 × 16 × 1) Monkhorst-Pack k-point grid to sample the 2D Brillouin zone (BZ).34 The equilibrium geometries were fully optimized with both the lattice vectors and atom coordinates relaxed with the tolerance of less than 0.01 eV Å⁻¹ on each atom. The phonon calculations were performed by using the direct approach implemented in Phonopy package.35 The Real-space force constants were calculated from the Hellmann–Feynman forces by introducing displacements to supercells based on the finite displacement method.36 Then, the dynamical matrices and phonon frequencies were obtained via the force constants.

3. Results and discussion

3.1 G-XN (X = B, Al and Ga) monolayers

The atomic configurations of g-XN monolayers are shown in Fig. 1(a). The g-XN monolayer has a 2D honeycomb-like hexagonal lattice with two atoms in the unit cell, X atom at (0, 0, 0) and N atom at (1/3, 2/3, 0). When X = B, Al and Ga, the optimized lattice constants a of g-XN are 2.51 Å, 3.15 Å, and 3.26 Å, and the bond lengths of XN are 1.45 Å, 1.81 Å, and 1.88 Å, respectively.

The phonon dispersion spectrum is a reliable tool to check whether the virtual structure is stable.37 A stable structure has all positive phonon frequencies for all modes over the Brillouin zone, whereas imaginary frequencies appear when the structure is dynamically unstable. In phonon calculations, 6 × 6 supercells were employed, and the first BZ was sampled by 4 × 4 K-meshes. The full phonon dispersion spectra for the three monolayers along the high-symmetry directions in Brillouin zone are shown in Fig. 1(b). No imaginary vibration frequency appears for each structure, indicating that they have high phonon stability. As the g-BN monolayer has been successfully fabricated by experiments,4 we may expect the fabrication of the other two monolayers in the future. The electronic band structures shown in Fig. 1(c) suggest that monolayers g-BN, AlN and GaN are all indirect band gaps. The monolayer g-BN has a large band gap of 4.69 eV, in good agreement with the previous GGA value of 4.56 eV,48 but is underestimated than experimental 6.07 eV, which often happens in GGA calculations.49 In contrast, g-AlN exhibits a decreased band gap of 2.75 eV, and g-GaN has the smallest band gap of 2.00 eV. Compared with the bulk nitrides, the band gaps of 2D monolayers are decreased, e.g. by 33% for AlN (4.1 eV for wurtzite structures with GGA-PBE).

3.2 MoS2–XN heterostructures

As shown in Fig. 2(a), the bilayer heterostructures are constructed by stacking MoS2 and g-XN monolayers, denoted as MoS2–XN for simplicity in this paper. The calculated lattice constant of the MoS2 monolayer is 3.18 Å. We used the unit cells for MoS2–AlN and MoS2–GaN and obtained the optimized lattice constants of 3.16 Å and 3.23 Å, respectively. Thus, the lattice mismatch between MoS2 and g-AlN/GaN is quite small, only 0.9% and 1.8% for X = Al and Ga, respectively. The lattice mismatch between the unit cell of BN and MoS2 is around 20%. To minimize the lattice mismatch between the two stacking sheets, a supercell that contains 4 × 4 MoS2 and 5 × 5 g BN unit cells of monolayer was employed. The optimized lattice constant of MoS2–BN is 12.67 Å with MoS2 lattice being 0.4% compressed and g-BN lattice being 1.0% stretched.

The ground state geometries of MoS2–XN heterostructures are determined by the weak vdW interactions between neighboring layers. The equilibrium interlayer distance, dMoS2/XN, is defined as the distance between the S atoms in MoS2 layers and the neighboring XN planes. In addition, the interlayer adhesion energy is calculated by the definition: $E_{\text{ad}} = (E_{\text{MoS}_2} + E_{\text{XN}} - E_{\text{MoS}_2/XN})/S$, where $E_{\text{MoS}_2/XN}$, $E_{\text{MoS}_2}$, and $E_{\text{XN}}$ represent the total energies of optimized MoS2–XN heterostructures, the pure MoS2 and g-XN monolayer, and S is the interface area, respectively.

The calculated dMoS2/XN for MoS2–XN are 3.4 Å, 2.7 Å, and 2.9 Å for X = B, Al and Ga, respectively. The corresponding $E_{\text{ad}}$ for MoS2–XN (X = B, Al and Ga) are 15 meV Å⁻², 26 meV Å⁻², and 20 meV Å⁻², respectively. Both the interlayer distance and adhesion energy of MoS2–XN are comparable with the values of bilayer MoS2, i.e., d_{bilayer-MoS2} = 3.1 Å and $E_{\text{ad}}$ = 17 meV Å⁻². The smaller interlayer distance suggests the higher adhesion energy. Therefore, the MoS2–AlN and MoS2–GaN heterostructures should be more stable than bilayer MoS2.

To further understand the binding of the heterostructures, the three-dimensional charge density differences are calculated by subtracting the calculated electronic charge of MoS2–XN from that of the independent MoS2 and g-XN monolayers. As shown in Fig. 2(a), the charge transfer at the interface of MoS2–
BN is negligible, which agrees with the relatively large interfacial distance and small adhesion energy between MoS$_2$ and BN. Interestingly, charge densities of MoS$_2$–AlN and MoS$_2$–GaN exhibit large redistributions, especially at the interfacial region. The electron accumulation occurs at the interface and depletion is within the monolayers. Such a result suggests the MoS$_2$–AlN and MoS$_2$–GaN form the relatively strong adhesive interface.

The calculated band structures of the heterostructures are shown in Fig. 2(b). Interestingly, indirect band gaps of g-XN monolayers transform to direct ones in all MoS$_2$–XN heterostructures. For solar energy conversion applications, light with a photon energy close to the band gap can produce an electron–hole pair. This process occurs quite easily in a direct band gap semiconductor because the electron does not need a large momentum. From this aspect, the direct-band-gap MoS$_2$–XN heterostructures are expected to have high solar energy conversion efficiency compared to indirect-band-gap g-XN monolayers.

The calculated band gaps change among 0.50–1.78 eV for heterostructures with PBE functional. It has been well recognized that the typical DFT with GGA level is inadequate to describe the electronic structures of some semiconductors and usually underestimates the band gap due to the spurious electronic self-interaction present within this theory. The Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional can usually predict more reasonable band gaps than GGA. For example, the band gap of monolayer g-BN monolayer is 4.69 eV with GGA calculation but is 5.69 eV with HSE06 calculation, much closer to the experimental value (~6.07 eV (ref. 20)). Therefore, the band gaps are further examined with the HSE06 functional. As shown in Fig. S1,† HSE functional only enlarges band gaps compared with the PBE but does not change the trend of electronic structures. More interestingly, both the heterostructures of MoS$_2$/GaN and MoS$_2$/AlN exhibit modest band gaps. For example, the band gap of MoS$_2$/AlN is about 2.00 eV, which is greatly favorable for the adsorption of the visible light.

As shown in Fig. 2(c), the projected density of states (PDOS) clearly depicts the valence band maximum (VBM) and the conduction band minimum (CBM) of heterostructures. In single-layer MoS$_2$, VBM and CBM are contributed by Mo-3d$_{x^2-y^2}$ and Mo-3d$_{z^2}$, whereas in single-layer g-XN, they are contributed by N-2p$_z$ and N-2p$_x$ + p$_y$, respectively. The detailed band alignments of MoS$_2$–XN heterostructures are shown in Fig. 3(a), in which the band edge positions are calculated with HSE06. The formation of type-II heterostructures is an effective approach to enhance charge separation efficiency for improved photocatalytic activity and water splitting efficiency. In a type-II band alignment, the position of VBM and CBM of a semiconductor, i.e. g-XN, is higher than that of another, i.e. MoS$_2$. Fig. 3(a) indicates that MoS$_2$–AlN and MoS$_2$–GaN belong to type-II band alignments, whereas MoS$_2$–BN does not. Thus, the VBM and CBM of the MoS$_2$–BN heterostructure preserve the same feature of MoS$_2$ monolayer, and both the VBM and CBM charges concentrate on the MoS$_2$ side for MoS$_2$–BN, as shown in Fig. 1.

Fig. 1 The (a) atomic structures, (b) phonon dispersions and (c) electronic band structures of g-XN (X = B, Al and Ga), calculated with PBE functional. Green and gray balls represent N and X atoms, respectively.
However, the VBM of MoS$_2$–AlN and MoS$_2$–GaN comes from N-2p\_z. This indicates a complete separation of VBM and CBM on g-XN and MoS$_2$ monolayers, respectively, in MoS$_2$–AlN and MoS$_2$–GaN, as depicted more clearly in Fig. 3(c) and (d). It is well known that one of the most effective ways to enhance photocatalytic activity is to avoid electron–hole pair recombination.\textsuperscript{40,41} The photo-generated electrons and holes will be spontaneously separated for MoS$_2$–AlN and MoS$_2$–GaN heterostructures, which suppresses charge recombination and enhances the photocatalytic efficiency.

In addition to bilayer heterostructures as discussed above, we also study the trilayer sandwiched heterostructures: one MoS$_2$ (g-XN) monolayer is sandwiched by two g-XN (MoS$_2$) monolayers, denoted as trilayer-I (-II). The calculated atomic configurations and band structures with the HSE06 functional of MoS$_2$–AlN and MoS$_2$–GaN trilayer heterostructures are shown.
in Fig. 4. The trilayer structure shows similar electronic structure profiles as the bilayer heterostructure. For example, the direct band gap of trilayer-I MoS$_2$/AlN heterostructure is 1.90 eV, very close to the corresponding value of 2.00 eV in the bilayer structure. Therefore, both the bilayer and trilayer-I MoS$_2$/AlN heterostructures are favorable for the solar energy conversion. Nevertheless, we note that the trilayer-II heterostructure, which contains two MoS$_2$ monolayers, only has a smaller indirect band gap, exactly as the case of bilayer MoS$_2$ becoming an indirect one (as shown in Fig. S2†).

### 3.3 Photocatalytic ability

The photocatalyst process in water splitting includes two reactions:

\[
2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{O}_2 + 4\text{H}^+
\]

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2
\]

Therefore, in addition to an appropriate band gap of the semiconductor, a good photocatalyst material generally needs suitable VBM and CBM energy levels: a VBM energy lower than the oxidation potential (−5.67 eV) of H$_2$O/O$_2$ to first split water, and a CBM energy higher than the reduction potential (−4.44 eV) of H$^+$/H$_2$ to further produce H$_2$. The CBM and VBM energy levels for all materials calculated with HSE06 with respect to the vacuum energy level are shown in Fig. 5. Except for the trilayer-II MoS$_2$–AlN and MoS$_2$–GaN, the VBM positions of other materials vary from −5.97 eV to −5.92 eV, which are obviously lower than the oxidation potential. On the other hand, the CBM energy of MoS$_2$–GaN bilayer and trilayer-I structures are a little lower than the reduction potential. Fig. 5 clearly depicts that the MoS$_2$–AlN bilayer and trilayer-I heterostructures are suitable for solar energy conversion applications among these 2D materials.

In order to fully utilize the solar energy, another vital requirement for a high-performance photocatalytic material is that it should have a wide adsorption range of solar energy. The optical absorption coefficients directly reflect the absorption range of the spectrum and are critical in the solar energy conversion realm. The optical adsorption spectrum of bilayer heterostructures are obtained by calculating the imaginary part of the complex dielectric function with HSE06. The solar energy is distributed mainly in visible (50%) and infrared light (43%). However, traditional photocatalysts such as TiO$_2$ are mostly active only under ultraviolet irradiation. Fig. 6 shows the calculated optical absorption spectra of MoS$_2$ and the bilayer heterostructures by using HSE06 functional.
that the present heterostructures possess a relatively stronger adsorption index in the visible light range (390–760 nm, 1.64–3.19 eV) than MoS$_2$. In particular, although the MoS$_2$ does not have an obvious adsorption index in infrared light (1.64 eV), the MoS$_2$–GaN heterostructure exhibits considerable adsorption index in the infrared light zone. Such results indicate that the efficiency of solar energy utilization of MoS$_2$ could be largely improved by heterostructures with AlN and GaN.

4. Conclusions

In summary, the phase stability and electronic properties of graphene-like 2D g-XN (X = B, Al, and Ga) monolayers and heterostructures with MoS$_2$ are carefully investigated through self-consistent vdW-DF calculations. We found that the g-AlN and g-GaN monolayers have thermodynamic stabilities exactly as g-BN through phonon calculations, exploring new graphene-like 2D structures that might be synthesized experimentally. The indirect band gaps in g-XN monolayers become direct gaps when stacking g-XN on a MoS$_2$ monolayer. In particular for X = Al and Ga, the MoS$_2$–AlN and MoS$_2$–GaN heterostructures show suitable band gaps (2.00 eV and 1.44 eV, respectively), complete electron–hole separation and a strong optical adsorption index, making them promising candidates for solar energy conversion. Furthermore, the MoS$_2$–AlN heterostructure is expected to be a good photocatalyst due to its suitable VBM and CBM alignments with the oxidation and reduction potentials of hydrogen generation from water. Our extensive investigations give insights for the development of novel 2D structures with high performance for applications.

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