Photocatalytic Application of Two-dimensional Materials-based Heterostructure Based on Molybdenum and Tungsten Disulfides and Gallium Nitride: A Density-Functional Theory Study

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A R T I C L E    I N F O

Keywords
MoS 2/GaN
WS 2/GaN
Heterostructure system
Type II band alignment
Density Functional Theory
Photocatalytic

A B S T R A C T

Photocatalytic water splitting is one of the methods to produce hydrogen fuel by reducing the water into the oxygen and hydrogen provided that the bandgap of one catalyst is larger than +1.23 eV. In this paper, based on density functional theory, we investigated the structural, electronic and optical properties of heterostructure MoS 2 (WS 2 ) paired with GaN and we found out that MoS 2 /GaN/MoS 2 , WS 2 /GaN and WS 2 /GaN/WS 2 vdW heterostructures are potential photocatalysts for photocatalytic applications. From the band structure and electronic partial density of states (PDOS), we confirm that all simulated heterostructures are direct semiconductors of type II band alignment with valence band maximum and conduction band minimum localized at p orbital N atom of GaN and d 7 z orbital Mo (or W) atom of MoS 2 and WS 2 respectively. The band offset induced by efficient interlayer charge transfer form a staggered gap which aids in excition disassociation and charge separation. Our studied models are expected to harvest UV to visible light with absorption coefficient up to 3.38 × 10 5 cm -1 at wavelength of 102 nm. On top of that, our proposed heterosystem are also believed to be a promising device for various optoelectronic application specifically in from UV to near-infrared with high performance.

1. Introduction

Hydrogen has a great potential as an alternative fuel source for fossil fuels. Photocatalytic water splitting can be an effective mean to produce this fuel. Two critical mechanisms needed are solar energy in the presence of catalyst. Under the irradiation of sunlight, the water is reduced into oxygen and hydrogen [1] provided that the conduction band minimum (CBM) of the catalyst is more negative than the hydrogen reduction potential (0 eV) and the valence band maximum (VBM) is much greater than the water oxidation potential (≈1.23 eV) [2]. A direct bandgap semiconductor is able to split water under radiation due to the promoted electrons in the VBM to CBM. However, fast electron-hole pair recombination can occur [3] which reducing the number of free charge carrier available. The presence of cocatalyst in the form of heterostructure system with an appropriate band offset is said to be able to enhance the water splitting [4]. The offset can increase the charge migration across the VBM and CBM of each surface thus increases the free charge carriers while reducing the electron-hole recombination. A catalyst with longer semiconductor lifetime, efficient separation under visible irradiation and longer wavelength photons and stable material system is extensively being searched in order to improve the efficiency of the energy conversion in photocatalytic water splitting.

Recently, remarkable electrical and optical properties such as indirect-to-direct bandgap transition due to different number of layers,
strong light-matter interactions [5], high current on/off ratio [6] and huge exciton bind energy [7] exhibited by atomically thin 2D semiconductor has shown tremendous range of applications in both electronics and optoelectronics including transistor [6,9], photovoltaic [9], photodetector [10] and photocatalytic effect [11]. However, due to its relatively low catalytic efficiency, the recombination of electrons and holes are high. Hence the use of a co-catalyst which prevents such recombination is highly desired. In recent times, the III-N group was discovered to share the same hexagonal structure and in close lattice parameter with transition metal dichalcogenides (TMDCs) which make it easy to stack both types of material together without having to consider their lattice mismatch as well as aids in controlling stress between the TMDC substrate and nitride layer [12]. This provides a high crystal quality formation avoiding the recombination at the defects. The existing vertical intrinsic electric field both in 2D material and GaN enhance the photogenerated free charges carriers. The possibility of using III-N monolayer specifically GaN and AlN as the co-catalyst for TMDC layer have been studied by a few researchers. Jiaim Lio et al. reported the heterobilayers between MoS2 with GaN or AlN is an effective cocatalysis for more effective photocatalytic water splitting compared to MoS2 itself [13]. Hui Zang et al. reported in their studies that the heterobilayer MoS2/AlN and heterotriayer AlN/MoS2/AlN are most suitable for high solar energy conversion [14]. Apart from MoS2, Ruishen Meng et al. showed that the enhanced photocatalytic activity between WS2/GaN and WSe2 due to the presence of band offset and intrinsic electric field [15]. However, no detailed study has been made on the heterotriayers of MoS2 (or WS2) and GaN for its potential in photocatalytic activities.

In this study, the electrical and optical properties of heterotriayer XSe2 (X = Mo, W) sandwiched between two GaN monolayers and monolayer GaN sandwiched between two XSe2 monolayers are investigated via density functional theory. We found out that not only that these two groups share the same hexagonal structure, the low lattice mismatch of about 1 to 2% indicates high quality heterostructure is possible. From the band structure and PDOS, we confirm that all simulated heterostructures are direct semiconductors of type II band alignment with VBmin localized at pz orbital N atom of GaN and CBM localized at dz2 orbital Mo (or W) atom of MoS2 and WS2. Our study indicates that the direct bandgap of XSe2/GaN/XSe2 is higher than the bilayer XSe2/GaN. We discover that, due to the high density of states contributed by MoS2 or WS2 layer, the addition of MoS2 WS2 layer widened the bandgap while addition of GaN layer narrows the bandgap. Furthermore, we found out that the VB location of MoS2/GaN/MoS2, WS2/GaN and WS2/GaN/WS2 are far greater than water oxidation potential of +1.23 eV and we could expect water splitting from the proposed heterotriayers.

2. Computational method

Using Cambridge Serial Total Energy Package (CASTEP) [16,17], this paper performs the calculations based on the first principle density functional theory (DFT). TMDCs have space group of P6/mmc and hexagonal lattice with honeycomb structure with X = Mo or W atoms sandwiched between the sulfides atoms [18]. The 2D wurtzite hexagonal GaN with P6/mmc space group is made into monolayer 2D graphene-like lattice. To describe the electron-ion interaction, the ultrasoft pseudopotentials was chosen with the functional of Perfer-Burke-Ernerzehof (PBE) of generalized gradient approximation (GGA). Due to the vdW interactions, the (PBE-D) dispersion exchange correction proposed by Tkachenko and Scheffler [19] with the approach of Grimme (DFT-D2) [20–22] was used throughout the calculation where the accurateness of this dispersion correction for 2D heterostructures has been proved in many previous studies [15,23,24]. In achieving the finest geometry electronic structures, the energy cutoff was set to 800 eV and a Monkhorst-Pack k-point mesh of $12 \times 12 \times 1$ was set in the 2D Brillouin zone for both heterostructures. All the structures were fully optimized with $5 \times 10^{-6}$ eV/atom convergence energy. The displacement and forces were set to be not more than $5 \times 10^{-3}$ A and 0.01 eV/A respectively. The compressibility was also set at medium taking into account the presence of TMDC. In order to investigate the optical properties, calculations were carried out using the norm-conserving pseudopotentials. Specifically, a large vacuum space of 35 A is applied to prevent the interaction between one layer and another along the c axis. All heterostructures were assembled by 3 x 3 x 1 unit cell to allow more degrees of freedom.

3. Results and discussion

3.1. Structural Parameter

In this work, we first perform the calculation on the most stable phase MoS2, WS2 and GaN. The structural and electronic properties are calculated and presented in Figure S1 for all structures of MoS2, WS2 and GaN using GGA-PBE functional which can be referred in supporting documents. Results are tabulated in Table 1 and compared with both previous experimental and theoretical studies. The obtained lattice parameters (a0) of MoS2, WS2 and GaN are 3.187 Å, 3.189 Å and 3.221 Å respectively and bond lengths of Mo–S, W–S, and Ga–N are 2.414 Å, 2.422 Å, and 1.861 Å respectively. Results show agreement with earlier theoretical studies [15,25,26]. When comparing the lattice constants of these isolated layers, it is noted that the lattice constants of both TMDCs are very close to the GaN presented suggesting that if these layers are to be stacked on top of each other, there should be no lattice mismatch issue where the lattice mismatch is about 1 to 2% only indicating a high quality heterostructure. Experimental work involving MoS2 and GaN has also been proven before [27]. At equilibrium state, MoS2 and WS2 is a direct bandgap semiconductor with a value of 1.632 eV and 1.804 eV respectively while monolayer GaN is an indirect bandgap of value 2.017 eV. The isolated layers are layered on top of each other according to the preferred heterostructure system. The heterostructures are built according to three systems which are XSe2/GaN heterobilayer, GaN/XSe2/ GaN and XSe2/GaN/ XSe2 heterotriayer where X = Mo or W (Ref Fig. 1).

To confirm we are obtaining the most energetically stable structure, for each proposed heterostructure system, we consider four different configurations, each of them are optimized upon similar convergence criteria. The most stable structure is evaluated based upon the lowest energy difference, $\Delta E$ which defined as

$$\Delta E = E - E_0$$

where $E$ and $E_0$ is the total energy of each configuration and the most stable configuration (configuration with the lowest total energy) respectively. All various stacking configurations are shown in Figure S3, Figure S4 and Figure S5 and the details are tabulated in Table S2, S3 and S4 respectively which details are described in supporting document. Hence our further discussion is based on the most stable configurations obtained for each type of heterostructure. Table 1 present the lattice constant a0, formation energy Ef, interlayer spacing db, bandgap value Eg and bandgap characteristics for all assembled heterostructure. The MoS2/GaN and WS2/GaN heterobilayers are fully relaxed to 3.209 Å and 3.207 Å respectively. As seen in Table 1 and Table 2, the a0 value of these heterostructures is close to the a0 value of unit cell Mo (or W) S2 and

<table>
<thead>
<tr>
<th>Materials</th>
<th>Layer</th>
<th>$a_0$ (Å)</th>
<th>$L_E = \frac{E_f}{E_{\text{GGA PRE}}} - \frac{E_{\text{GGA PRE EXP}}}{E_{\text{GGA PRE EXP}}} + \frac{E_{\text{GGA PRE EXP}}}{E_{\text{GGA PRE EXP}}}$</th>
<th>$E_f$ (eV)</th>
<th>$E_{\text{GGA PRE EXP}}$ (eV)</th>
<th>$E_{\text{GGA PRE EXP}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS2</td>
<td>1H</td>
<td>3.187</td>
<td>2.414</td>
<td>1.632</td>
<td>1.59 [28]</td>
<td>1.90 [29]</td>
</tr>
<tr>
<td>WS2</td>
<td>1H</td>
<td>3.189</td>
<td>2.422</td>
<td>1.804</td>
<td>1.75 [28]</td>
<td>2.00 [30]</td>
</tr>
<tr>
<td>GaN</td>
<td>1H</td>
<td>3.221</td>
<td>1.861</td>
<td>2.017</td>
<td>2.11 [13]</td>
<td></td>
</tr>
</tbody>
</table>
GaN. Thus, the lattice mismatch between X$_2$ – GaN is proven less than 1% as predicted earlier of about 0.7% and 0.6% for X = Mo and W respectively. The close lattice match relation between assembled heterostructures and isolated layers can be noted too in-plane bond lengths. From the result, the in-plane lattice parameter $a_0$ of MoS$_2$ (or WS$_2$)/GaN heterolayer is 0.202 Å (0.018 Å) larger than the MoS$_2$ and WS$_2$ single layer value and 0.012 Å (0.014 Å) lower than the single layer GaN. This is said to be caused by the small percent adjustments in order to balance the strain energy induced by the few percent lattice mismatch (<1.0%). To further verify the stability of this bilayer system, the formation energy $E_f$ of heterostructure and interlayer distance $d_i$ between the layers are also calculated and analyzed. The formation energy $E_f$ is defined as:

$$ E_f = E_{\text{heterostructure}} - xE_{\text{GaN}} - yE_{\text{GaN}} $$

(2)

where $E_{\text{heterostructure}}$ is the ground state total energy of the stacked layers, $E_{\text{GaN}}$ is the total energy of monolayer GaN where $x$ referring to the number of GaN layer and $E_{\text{GaN}}$ is the total energy of monolayer MoS$_2$ or WS$_2$ with $y$ referring to the number of MoS$_2$ or WS$_2$ layer. A positive and negative $E_f$ value signifies that the assembled heterostructure is either weakly or strongly held together respectively. The calculated formation energy for MoS$_2$/GaN, WS$_2$/GaN, GaN/MoS$_2$/GaN, GaN/WS$_2$/GaN, MoS$_2$/GaS/MoS$_2$ and WS$_2$/GaS/WS$_2$/GaS are –172 meV, –306 meV, –341 meV, –403 meV, –475 meV, and –511 meV respectively. For both heterostructures, we obtained a negative formation energy signifying that the heterostructures are stable and are held together strongly. On top of that, the MoS$_2$ (or WS$_2$)/GaN stacked bilayer heterostructures has $d_i$ value larger than 2.9 Å. Thus, we can infer that both heterobilayers are controlled by the weak van der Waals interaction [19]. We then proposed the novel heterotrilayers consisting of GaN/MoS$_2$/GaN and GaN/WS$_2$/GaS where MoS$_2$ or WS$_2$ is sandwiched between two GaN monolayers.

### 3.2. Electronic Properties

The electronic structure of the heterostructure is evaluated in terms of band gap (BG), electronic partial density of states (PDOS), and charge transfer using the GGA functional with DFT-D2 adoption which further explanation can be found in Supporting Information. The MoS$_2$/GaN and WS$_2$/GaS heterobilayers show a direct bandgap of value 0.789 eV and 1.039 eV using PBE vdW and increased to 1.387 eV and 1.667 eV using HSE06 respectively (refer Figure S6 in supporting documents) where the $k$-vectors in the Brillouin zone are located at the same position for CBM and VBM. It was observed that HSE functional retain the electronic structure and only widens the bandgap of the PBE. In order to acknowledge the precise bandgap value given by HSE06, we consider employing the GGA-PBE result with 0.6 scissors. When increasing the layer number, the bandgap is expected to decrease due to the influence of quantum confinement in z direction, thus explaining the bandgap of these bilayers heterostructure are lower than their respective single layer MoS$_2$, WS$_2$ and GaN (refer Table 1 and Table 2). Same case was found in MoS$_2$/WS$_2$ heterostructure due to the band offset attribution [31]. From our calculation, we obtain a smaller bandgap value of MoS$_2$/GaN than WS$_2$/GaN (refer inset Fig. 2a and 2b) signifying that the dipole-dipole interaction between Mo and S atom is much more favorable than W and S atom. For GaN/MoS$_2$/GaS and GaN/WS$_2$/GaS, we discovered that the bandgap of these heterotrilayers closes more than in heterobilayers due to the quantum confinement effect resulting in a much lower bandgap value. This heterotrilayers create a greater dipole-dipole force between the GaN and MoS$_2$ (or WS$_2$) layers. The GaN/MoS$_2$/GaS is noticed to have a smaller direct bandgap opening between p-bonding and π*-antibonding states at high symmetry Dirac K point of 1.150 eV than GaN/WS$_2$/GaS of 1.380 eV due to stronger dipole-dipole interaction created by molybdenum and sulphur than tungsten and sulphur.

Comparing the PDOS contributed by each atom of these

<table>
<thead>
<tr>
<th>Heterostructure</th>
<th>Stable Stacking</th>
<th>$a_0$ (Å)</th>
<th>$L_{\text{SS}}/L_{\text{Ga}-\text{N}}$ (Å)</th>
<th>$L_{\text{SS}}/L_{\text{Ga} \rightarrow \text{N}}/L_{\text{SS}}$ (Å)</th>
<th>$L_{\text{Ga}-\text{N}}/L_{\text{SS}}/L_{\text{Ga} \rightarrow \text{N}}$ (Å)</th>
<th>$d_i$ (Å)</th>
<th>$E_f$ (meV)</th>
</tr>
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<tbody>
<tr>
<td>MoS$_2$/GaN</td>
<td>III</td>
<td>3.209</td>
<td>2.413/1.853</td>
<td>-</td>
<td>-</td>
<td>3.080</td>
<td>1.389</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
<td>-172</td>
</tr>
<tr>
<td>WS$_2$/GaN</td>
<td>I</td>
<td>3.207</td>
<td>2.415/1.852</td>
<td>-</td>
<td>-</td>
<td>3.093</td>
<td>1.507</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
<td>-341</td>
</tr>
<tr>
<td>MoS$_2$/MoS$_2$</td>
<td>A</td>
<td>3.204</td>
<td>2.413/1.850/2.411</td>
<td>-</td>
<td>-</td>
<td>3.133</td>
<td>1.744</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
<td>-403</td>
</tr>
<tr>
<td>WS$_2$/WS$_2$</td>
<td>A</td>
<td>3.203</td>
<td>2.415/1.848/2.417</td>
<td>-</td>
<td>-</td>
<td>3.062/2.006</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>1.744</td>
<td>-403</td>
</tr>
<tr>
<td>GaN/ MoS$_2$/GaS</td>
<td>a</td>
<td>3.210</td>
<td>-</td>
<td>-</td>
<td>1.854/2.413/1.854</td>
<td>3.130</td>
<td>1.150</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
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<td>-475</td>
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<tr>
<td>GaN/ WS$_2$/GaS</td>
<td>a</td>
<td>3.210</td>
<td>-</td>
<td>-</td>
<td>1.853/2.416/1.853</td>
<td>3.051/3.061</td>
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<td></td>
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<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>1.380</td>
<td>-511</td>
</tr>
</tbody>
</table>
in Fig. 2c and 2d, the same reason was found that lead to the high bandgap value of GaN/MoS$_2$/GaN than GaN/WS$_2$/GaN where GaN/MoS$_2$/GaN has X atom with considerably higher amount of d orbital. MoS$_2$/GaN/MoS$_2$ and WS$_2$/GaN/WS$_2$ trilayers also shows a direct bandgap of value 1.507 eV and 1.744 e V respectively. Clearly, the monolayer MoS$_2$ band character is preserved in these types of trilayers.

Ning Lu et al. in their study proved that the MoS$_2$/vacuum layer/MoS$_2$ retain a direct bandgap [32]. We analyzed that the bandgap produced by this trilayers is quite high compared to MoS$_2$/GaN and WS$_2$/GaN heterobilayer. Moreover, the larger bandgap of this type of trilayer compared to GaN/MoS$_2$/GaN and GaN/WS$_2$/GaN trilayers are largely due to very high percentage of Mo atom d-orbital electrons and S atom
p-orbital electron. Because of this large quantity of Mo and S atoms, the N atom with the highest electronegativity in GaN is outnumbered hence the dipole-dipole interaction does not take place much in this heterostructure. From the band structure and PDOS, we confirm that all simulated heterostructures are direct semiconductors with VBM localized at pz orbital N atom of GaN and CBM localized at dz² orbital Mo (or W) atom of MoS₂ and WS₂ claiming that they are of type II band alignment.

To further realize the electronic behavior of interfaces between these two 2D materials, it is important that we understand their band alignment on top of to discover the potential activity in the applications of water splitting. Fig. 3 depicts the band alignment with respect to water reduction and oxidation potential levels using these two 2D materials. The CBM and VBM position of MoS₂/GaN and WS₂/GaN does not differ much since the bandgap value of nanosheet MoS₂ and WS₂ itself are quite near to each other. For all our proposed heterostructures, the CBM are only slightly more negative than the hydrogen reduction potential indicating low reduction power for the reduction of H₂ to produce H₂O provided that the MoS₂ and WS₂ have sufficient chemical potential [33] and can be further enhanced with the help of cocatalyst for a complete water splitting. The VBM of MoS₂/GaN, GaN/MoS₂/GaN and GaN/WS₂/GaN are slightly more negative than the water oxidation potential which tells that these heterostructure cannot be able to oxidize the water well. An example of excellent water splitting feature can be seen monopolarized by MoS₂/GaN/MoS₂, WS₂/GaN and WS₂/GaN/WS₂ since the VBM are more positive than the water oxidation potential (1.23 eV), therefore we could expect complete water splitting by these three types of heterostructure.

Additionally, in order to understand the electron flow of the integral layers, we ran out VBM-CBM calculation on the subsurface orbital as shown in Fig. 4. The VBM and CBM of all simulated vdW heterostructures are mainly attributed by dz² orbital Mo (or W) and pz orbital N atom respectively implying that the oxygen reduction and production takes place at the MoS₂ (or WS₂) and GaN monolayer respectively. Subsequently, when light corresponding or greater than the bandgap of respective heterostructures strikes them, photogenerated electron is transferred from the VBM of GaN to CBM of Mo (or W) S₂ separating the hydrogen and oxygen at the respective monolayers.

To study the interlayer charge transfer in the heterostructure, we calculate and plot their charge density difference as shown in Fig. 5 based on the equation

$$\Delta \rho = \rho_{\text{total}} - \rho_{\text{GaN}} - \rho_{\text{WS₂}}$$

where $\rho_{\text{total}}$, $\rho_{\text{GaN}}$, and $\rho_{\text{WS₂}}$ are the total charge density of the stacked layers, monolayer GaN, monolayer MoS₂ or WS₂, number of GaN layer and number of MoS₂ or WS₂ layer respectively [34]. The electron rich region and depletion region are illustrated by blue and red region respectively. Remarkably, all heterostructure display large charge distributions at the interfacial region. On top of that, a multilayer charge transfer in MoS₂ (WS₂)/GaN shows that GaN layer loses 0.04 e (0.01 e) whereas MoS₂ (WS₂) accepts 0.04 e (0.01 e) leading to a weak donor-acceptor coupling [15].

To comprehend the above analysis, Fig. 6 (a) and (b) displays the conduction band offset (CBO) and valence band offset (VBO) between the MoS₂/GaN and WS₂/GaN respectively. The CBO and VBO between the MoS₂ (or WS₂) and GaN layers are approximately 0.69 (or 0.31) and 0.58 (or 0.58) eV respectively. The presence of CBO causes the photo-generated electrons in GaN to move to the CB of the MoS₂ (or WS₂) layer, while the presence of VBO drive the photogenerated holes in the MoS₂ (or WS₂) layer migrate to the VB of the GaN layer therefore overcoming the fast electron-hole recombination. Hence this type of band offset is said to overcome the electron-hole recombination problem.

The optical properties for this heterostructure is analyzed through absorption coefficient. This graph evaluates the photon energies which are most likely to be absorbed by the heterostructures and benefit in the design of a suitable device application. From the graph in Fig. 7, our heterostructure shows a good coverage from ultraviolet to visible light spectrum. The highest peak absorbed is in the region of UV light at around 103 nm for all six heterostructures constructed. Furthermore, although MoS₂ and WS₂ have a close value of lattice constant, the layering between WS₂ and GaN is seen to displays more enhanced and optical response in the UV light region than MoS₂ and GaN heterostructure. As such, the absorption spectrum is wider when going from the heterobilayer WS₂/GaN to heterotrilayer WS₂/GaN/WS₂ and GaN/WS₂/GaN. Same pattern is noticeable for the layering between MoS₂ and GaN too. Our studied models are believed to harvest UV to visible light with absorption coefficient up to $3.3\times10^5$ cm$^{-1}$ at the respective 102 nm wavelength. So far, few theoretical studies have been carried out involving MoS₂/GaN and WS₂/GaN heterobilayer for photo electrolysis application, but none has been carried out for the vdW trilayers involving these materials. Hence our result could be widely applied in not only photo electrolysis application but also other optoelectronic application involving solar, laser and light emitter for a greater device performance.

4. Conclusion

In summary, using the first-principle study, the structural, electronic properties and the optical properties of three pairs of heterostructures have been appropriately discussed. The proposed design can be synthesized experimentally without having too much difficulties due to the close lattice match alongside weak van der Waals attraction between respective monolayers. From the negative formation energy that we gained, our suggested heterostructures are all stable and attached well with each other. However, since MoS₂ gives a lower binding energy with GaN than WS₂, the MoS₂ is expected to detach easily from gallium nitride than WS₂. The direct and type II band alignment and built-in electric field across the interface showed by all heterostructures simulated not only make them as suitable candidates for electron – hole.

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**Fig. 3.** Band edge positions calculated by DFT-D2. The dashed lines are standard water redox potential. The reference potential is the vacuum level.

**Fig. 4.** Schematic illustration of the electron transfer and charge density variations in the respective monolayers.

**Fig. 5.** Potential versus NHE (eV) for all systems under study. The reference potential is the vacuum level.
separation, but also promising novel devices for various optoelectronic and nanoelectronics applications covering from ultraviolet to near-infrared with high performance. We found out that MoS$_2$/GaN/MoS$_2$, WS$_2$/GaN and WS$_2$/GaN/WS$_2$ vdW heterostructures are the most appropriate for photocatalytic applications. Integrating a monolayer GaN in the 2D TMDC heterostructures create a new unexplored synthetic and benefit in many potential optoelectronic applications. Future work can be further carried on by using the hybrid DFT-HSE06 functional to best investigate the electronic structure.
Fig. 7. Absorption spectra of the heterostructure between (a) MoS₂ – GaN and (b) WS₂ – GaN. Smearing value is set at 0 eV.

Associated Content

Supporting Information
Electronic Structure of MoS₂, WS₂, and GaN and Stacking Order of Heterostructures

Declaration of Competing Interest
The authors report no declarations of interest.

Acknowledgments
The author would like to acknowledge financial support from FRGS Grant FP034-2017A and IIRG013C-2019 and Ionics Materials & Devices (IMADE) Research Laboratory, Institute of Science, UTM Malaysia for the facilities provided during completion of this project.

Appendix A. Supplementary data
Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1101/j.mtccomm.2020.10.1646.

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