Design of graphene-like gallium nitride and WS₂/WSe₂ nanocomposites for photocatalyst applications

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ABSTRACT The geometric, electronic and optical properties of the graphene-like gallium nitride (GaN) monolayer paired with WS₂ or WSe₂ were studied systematically using the first-principles calculations. GaN interacts with WS₂ or WSe₂ via van der Waals interaction and all the most stable configurations of these two nanocomposites exhibit direct band gap characteristics. Meanwhile, the type-II heterojunctions are formed because the conduction band minimums and valence band maximums are respectively contributed by WS₂ (or WSe₂) and GaN. The imaginary parts of the dielectric function and the absorption spectra of the heterostructures were also calculated and the relatively improved optical properties were observed because of the new interband transitions. In addition, the band offsets as well as the intrinsic electric fields resulting from the interlayer charge transfer indicate that the electron-hole pairs recombination can be effectively inhibited, which is conducive for the photocatalysis process. Moreover, the band gaps of the heterostructures can be modulated by applying biaxial strains and even shift away the conduction band edge potential from the H⁺/H₂ potential in a certain range, which further enhances the photocatalyst performance. The results indicate that GaN/WS₂ or GaN/WSe₂ nanocomposites are good candidate materials for photocatalyst or photoelectronic applications.

Keywords: first-principles calculation, graphene-like gallium nitride, transition-metal dichalcogenides, heterostructures, electronic structures, photocatalytic property

INTRODUCTION

The successful preparation of graphene [1] has inspired tremendous research interests into the two-dimensional (2D) materials with fascinating properties. Despite of the gapless drawback that hinders its practical applications

in the field effective transistors (FETs) [2], graphene still exhibits great potentials in various applications such as electrodes in supercapacitance and lithium-ion batteries [3–5], thermal conductive layers [6] in the electronic devices due to its ultra-high thermal conductivity, non-metal catalyst [7] owing to its chemical stability, etc. Foremost, graphene has triggered and boosted the prosperity and the progress of diverse 2D materials [8–13], which display distinctive and excellent properties in comparison to their bulk counterparts.

Monolayered transition metal dichalcogenides (TMDs), such as MoS₂, MoSe₂, WS₂ and WSe₂, etc. hold great promise in a variety of applications because of their outstanding electronic, optical, mechanical as well as electrochemical characteristics [14–16]. These single-layered TMDs have been utilized for FETs and manifest on-off ratios higher than 10⁶ at room temperature [17,18]. In addition, the direct band gaps favor their applications like photodiode [19], photovoltaic cell [20], photodetector [21] and photocatalyst [22,23], etc. However, in order to achieve tunable electronic properties and the basic p-n junction units as well as high-quality hole-hole separation for practical device application, a heterostructure containing different materials is crucial [24]. For 2D materials, they can form van der Waals heterostructures without dangling bonds on the interface when they come into contact with each other [25,26]. This is fundamentally different and more flexible than the conventional heterostructures formed by the covalently bonded materials. These van der Waals heterostructures make the p-n junction with ultimate thickness limit possible, for example, the gate-tunable

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diode-like current rectification and the photovoltaic response across the p-n interface are observed in MoS₂/WSe₂ heterobilayers [27].

The III-V compound semiconductors, especially gallium nitride (GaN) with hexagonal wurtzite or cubic zinc-blendes structure, are basic functional materials for optoelectronic devices [28,29]. Recently, theoretical predications have confirmed that the single-layered graphene-like GaN possesses high thermal stability comparable to that of AlN monolayer which has been experimentally synthesized [30–32]. Subsequently the GaN monolayer was studied as the co-catalyst for MoS₂ in consideration of the low catalytic efficiency of the pristine MoS₂ [32,33]. The existence of the co-catalyst can effectively prevent the recombination of the photoinduced electrons and holes and eventually facilitate the charge separation. Meanwhile, the wider absorption ranges of the heterostructures are also often found contrast to their corresponding constituent layers.

In present study, the electronic and optical properties of the GaN covered with WS₂ or WSe₂ monolayers were investigated via *ab initio* calculations. The lattice mismatches of the GaN and WS₂/WSe₂ are less than 1% and they both have the hexagonal lattice, which means that the high-quality heterostructures are achievable. Besides, the hybrid functional using Heyd-Scuseria-Ernzerhof (HSE06) was also utilized to obtain accurate electronic properties. We found that both the GaN/WS₂ and GaN/WSe₂ heterobilayers exhibited direct band gap characteristics and the optical spectrums of WS₂ and WSe₂ were relatively broader in the presence of GaN monolayer. The charges transfer from WS₂ or WSe₂ to GaN layer and form a polarized field in the interface region, which has a synergetic effect with the band offset and inhibits the electron-hole pair recombination. In addition, applying compressive and tensile strains can effectively tailor the band gaps of the heterostructures and may lead to the direct-indirect band gap transition. The results indicate that these materials can be used for photocatalysts and photoelectronics.

COMPUTATIONAL METHODS

In this work, all the calculations were performed using Cambridge Serial Total Energy Package (CASTEP) [13,34] based on the density functional theory (DFT). The ultrasoft pseudopotentials were employed to describe the electron-ion interaction. Since the van der Waals interaction is non-ignorable, the Perdew-Burke-Ernzerhof (PBE) of the generalized gradient approximation (GGA) with the van der Waals correction proposed by Tkatchenko and

Scheffler [35] (PBE-D) was adopted to describe the exchange correlation interaction. Many previous researches investigate 2D heterostructures with this dispersion correction method whose reliability has been verified [36–42]. In order to give a further confirmation about the accuracy of the PBE-D, we carried out the benchmark calculation of the bilayer graphene. The calculated interlayer distance and binding energy per C atom are 3.4 Å and 35.5 meV, respectively, which correspond well with the theoretical [43] and experimental [44] results. The energy cutoff was set to 550 eV. A Monkhorst-Pack k-point mesh of 8×8×1 and 16×16×1 were respectively used in the 2D Brillouin zone for the geometry optimization and static electronic structure calculations. The convergence criteria of the energy, maximum force and the maximum displacement for the geometry structures relaxations were less than 5×10^{−6} eV/atom, 0.01 eV/Å and 5×10^{−4} Å, respectively. Likewise, the phonon calculation was performed by using the finite displacement method on the basis of the convergence criteria. Considering the underestimation of the PBE functional on the band gap of semiconductor, the HSE06 hybrid functional [45] was also applied for more accurate electronic structure and optical properties calculations. The norm-conserving pseudopotentials together with the cutoff energy of 800 eV and 4×4×1 k-point grid were used in the HSE06 calculation.

Specifically, the vacuum spaces larger than 15 Å were adopted to prevent the neighboring layers interaction in the normal direction and the heterostructures were constructed by 1×1 unit cells of GaN, WS₂ or WSe₂. To evaluate the interlayer interaction intensity in a quantitative way, the binding energy (E_b) per unit cell was defined as, $E_b = E_{\text{GaN}/X} - E_{\text{GaN}} - E_X$, where $E_{\text{GaN}/X}$, E_{GaN} and E_X represent the total energy of the heterostructure, isolated GaN monolayer and isolated nanosheets ($X = \text{WS}_2$ or WSe_2), respectively.

RESULTS AND DISCUSSION

Based on the PBE-D method, the phonon dispersion spectrum of GaN monolayer is available in Fig. S1, and it shows all positive phonon frequency, indicating the dynamical stability of this layered structure. Likewise, the atomic configurations and the band structures of GaN, WS₂ and WSe₂ monolayers are provided in Fig. S2. Specifically, the optimized lattice parameters of the hexagonal GaN, WS₂ and WSe₂ monolayers are 3.221, 3.166 and 3.276 Å, and their bond lengths are 1.86, 2.41 and 2.52 Å, respectively, which agree well with previous studies [30,31,46,47]. Besides, the obtained electronic gaps of GaN, WS₂ and WSe₂ are 2.11, 1.875 and 1.688 eV, respectively in PBE level, while us-

ing HSE06, their corresponding band gaps are enlarged to 3.285, 2.345 and 2.209 eV [47,48].

After the geometry optimization of these monolayers, the heterobilayers are constructed by respectively stacking the monolayers together. To search for one energetically reasonable structure, six different stacking configurations for GaN/WS₂ (WSe₂) are proposed, as illustrated in Fig. S3. The optimizations were carried out for all the configurations with the same convergence criteria. Consequently, both the most energetically favorable stacking configurations for GaN/WS₂ and GaN/WSe₂ are patterns I, as shown in Fig. 1a, where the Ga atoms of GaN are directly above the S (Se) atoms of WS₂ (WSe₂), the N atoms of GaN are directly on top of the W atoms of WS₂ (WSe₂) and the hexagonal rings of the two layers coincide on the top view of the lattice. The lattice constant of GaN/WS₂ (WSe₂) was optimized to be 3.193 Å (3.249 Å), meaning that the lattice mismatches between GaN and WS₂ or WSe₂ are less than 1%. The detailed structure (E_b , interlayer distance) and

electronic parameters (Hirshfeld charge transfer, band gap) of all the stacking configurations are listed in Table 1, from which we can see that the most stable stackings have the most negative E_b , smallest interlayer distance (except for the pattern V for GaN/WSe₂) as well as the largest charge transfer. The calculated E_b for GaN/WS₂ and GaN/WSe₂ heterobilayers are in the range of 40 to 62.4 meV/atom (21 to 30.6 meV Å⁻²), more negative than that of the bilayer graphene and close to the typical van der Waals binding energy of ~20 meV Å⁻² [49]. Meanwhile, the separation between GaN and WS₂ (WSe₂) is larger than 2.9 Å. Therefore, we can deduce that the GaN/WS₂ (WSe₂) heterostructures are dominated by the van der Waals interaction. Since the pattern I possesses the lowest total energies together with the binding energy for GaN/WS₂ and GaN/WSe₂, we only consider this configuration in the following relative calculations. For simplicity, GaN/WS₂ and GaN/WSe₂ are used to refer to their structures in pattern I.

The electronic band structures and local density of

Figure 1 (a, d) Atomic structure; (b, e) electronic band structure calculated by both of PBE (red lines) and HSE 06 level (black lines); and (c, f) LDOS and PDOS obtained by HSE 06 level of the GaN/WS₂ and GaN/WSe₂ nanocomposites, respectively. The N atoms and Ga atoms are presented in dark blue and brown color; while the origin, deep yellow, and light blue balls correspondingly denote S, Se and Mo atoms. The smearing values of the LDOSs and PDOSs are set to be 0.1 eV.

Table 1 Calculated binding energy (E_b), interlayer distance (d), Hirshfeld charge transfer (ΔQ), energy band gaps (E_g) calculated by PBE-D method for all the configurations of the GaN/WS₂ and GaN/WSe₂ heterostructures. The negative signs of the ΔQ represent the charges transfer from the other layers to GaN layer

	Configuration	E_b (meV)	d (Å)	ΔQ	E_g (eV)
GaN/WS ₂	I	−312	2.984	−0.05	1.088/1.948(HSE06)
	II	−217	3.562	−0.02	1.472
	III	−274	3.227	−0.03	1.481
	IV	−215	3.574	−0.02	1.451
	V	−306	3.013	−0.05	1.133
	VI	−273	3.242	−0.03	1.461
GaN/WSe ₂	I	−309	3.008	−0.05	1.617/2.097(HSE06)
	II	−224	3.623	−0.02	1.668
	III	−223	3.626	−0.02	1.670
	IV	−268	−0.268	−0.03	1.671
	V	−294	−0.294	−0.05	1.582
	VI	−272	−0.272	−0.04	1.715

states (LDOSs, acquired by projecting DOS onto two different layers in the heterobilayers) of the GaN/WS₂ and GaN/WSe₂ are displayed in Fig. 1, and both the two heterobilayers are direct-bandgap semiconductors with the valence band maximum (VBM) and conduction band minimum (CBM) located in the K point of the Brillouin zone (BZ). Clearly, the overall profiles of the band structures calculated by these two kinds of methods are consistent, apart from the increase in the band gap values by the hybrid functional. Besides, the VBM and CBM are separately dominated by the GaN and WS₂ or WSe₂ (see in the LDOS profiles), forming the typical type-II semiconductors. The band gaps of GaN/WS₂ and GaN/WSe₂ calculated by HSE06 are 1.948 and 2.097 eV, respectively, which are smaller than that of their monolayers ascribed to the interlayer interactions and the band offset. To gain deeper insight into the electronic structures and further describe the GaN/WS₂ (WSe₂) interaction, the atom projected density of

states (PDOSs) are given in Fig. 1. The electronic states of GaN/WS₂ (WSe₂) around the Fermi level are mainly constituted by the N p, Ga p, S p (Se p) and Mo d orbitals. Their VBMs are primarily contributed by the N p orbitals, while the CBMs are predominantly contributed by the W d orbitals.

To further investigate the interlayer interaction on the electronic properties, the effective mass of GaN, WS₂ and WSe₂ monolayer and the heterostructures are calculated and listed in Table 2. It is obvious that the overall effective masses of isolated GaN, WS₂ and WSe₂ are in good consistency with the previous researches [50,51]. The electron effective masses (m_e^*) of the single-layered GaN are $0.269m_0$ in the direction of Γ to K and $0.162m_0$ in the direction of Γ to M, which are much smaller than the corresponding hole effective masses (m_h^*). After the contact of GaN and WS₂ or WSe₂, almost all the carrier effective masses of the heterostructures become heavier because of the interlayer

Table 2 Predicted effective masses of the GaN monolayer and GaN/WS₂ (WSe₂) heterostructure. Carrier type 'e' and 'h' denote 'electron' and 'hole', thus the m_e^*/m_0 and m_h^*/m_0 respectively represent the electron effective mass and hole effective mass. $\Gamma \rightarrow K$, $K \rightarrow M$, $M \rightarrow \Gamma$ and $\Gamma \rightarrow M$ refers to the direction of the effective mass.

	$\Gamma \rightarrow K$		$K \rightarrow M$	
	m_e^*/m_0	m_h^*/m_0	m_e^*/m_0	m_h^*/m_0
GaN	0.269 ($\Gamma \rightarrow M$)	1.256	0.162 ($M \rightarrow \Gamma$)	1.582
WS ₂	0.353	0.456	0.340	0.479
WSe ₂	0.391	0.486	0.418	0.566
GaN/WS ₂	0.345	1.465	0.366	1.748
GaN/WSe ₂	0.437	1.929	0.439	1.858

coupling. Owing to the formation of the type-II semiconductor, the m_e^* and m_h^* of the heterostructures inherit from WS_2 (or WSe_2) and GaN, respectively. The effective mass increase in the GaN/ WS_2 nanocomposite is not apparent, with the increments of m_e^* and m_h^* less than $0.1m_0$, indicating that most of the electronic properties of the constituent layers are well preserved. However, the increments of m_e^* and m_h^* of GaN/ WSe_2 are relatively larger, as reflected by the flatter slope of the highest valence band and the lowest conduction band. This is attributed to the orbital hybridization, which is supported by the PDOS (Figs 1c and f) that there are evident electronic states overlaps between N p and Mo d orbitals in the valence band region near the Fermi level (from -3 to 0.7 eV).

The optical properties of the heterostructures are discussed on the basis of the imaginary part of the dielectric function and absorption spectra under parallel polarization compared to those of pristine GaN and WS_2 (or WSe_2) monolayer. These optical properties were obtained by the HSE06 functional considering the inaccurate description of

the DFT method on the electronic characteristics. Nevertheless, the calculations using PBE-D functional were also carried out for comparison. As clearly shown in Fig. 2, the overall profiles of the dielectric functions or the absorption spectra of the GaN monolayer acquired from HSE06 are very similar to the ones obtained by PBE-D method except for the slight weakening of the peaks and the blue shift of the absorption edges attributed to the more precise band gap characterization. The optical absorptions for the pristine GaN monolayer appear at about 3.3 eV, which is the consequence of the intrinsic transition from N p in the VBM to the conduction band. In regard to the GaN/ WS_2 (WSe_2) nanocomposites, the absorption edge occurs at around 2 eV, which is due to the transition from the VBM (N p) to the CBM (W d). The absorption edge of the heterostructures has slight red shift compared to that of the insolated WS_2 or WSe_2 because of the small difference in the band gap values. Apart from the weakening in the peaks at around 4 eV (~ 300 nm), the GaN/ WS_2 manifests more enhanced optical response in the UV light region (100 – 240

Figure 2 The calculated imaginary part (ϵ_2) of dielectric function (a, c) and the absorption spectra (b, d) for GaN/ WS_2 and GaN/ WSe_2 , respectively. The smearing values of the PDOSs were set to be 0.1 eV.

nm). Nevertheless, it is remarkable to find a overall enhancement of the absorption intensity in the GaN/WS₂ composites. As have been demonstrated in many pervious researches, the interlayer coupling can induce new interband transitions that lead to the evolution of the optical properties [52–54].

In consideration of the direct band gap larger than 1.23 eV, the type-II semiconductor characteristics together with the relatively enhanced absorption spectra of the GaN/WS₂ and GaN/WSe₂ heterobilayers, it is worthwhile to evaluate their photocatalytic performance. From the PDOS presented in Figs 1c and f, we can see that, the band gap of GaN in the GaN/WS₂ (GaN/WSe₂) spans from 0.2 to 3.4 eV (0.2 to 3.5 eV), while WS₂ (WSe₂) has the band gap spanning from 0 to 2.3 eV (0.1 to 2.3 eV), forming the type-II heterojunction. The top part of the highest valence band is mainly composed of the GaN states, while the WS₂ or WSe₂ contributes to the bottom part of the lowest conduction band. Consequently, the valence band offset (VBO) between the GaN and WS₂ (WSe₂) is about 0.2 eV (0.1 eV for GaN/WSe₂), whereas the conduction band offset (CBO) between them is about 1.1 eV (1.2 eV for GaN/WSe₂). Based on the analysis and the DOSs presented

above, the band edge potentials of the nanocomposites *versus* the normal hydrogen electrode (NHE) are depicted in Figs 3a and b [33,55,56]. The VBM energies of these two heterostructures are more positive than the oxidation potential (1.23 eV) of H₂O/O₂ for water splitting, and their CBM energies are more negative than the reduction potential for the reduction of H⁺ to produce H₂. In the photocatalysis process, the electrons can be photo-generated from the conduction bands of the GaN monolayers when the nanocomposites are illuminated with incident lights. Because of the existence of CBO, these photo-excited electrons will be easily injected to the conduction band of the WS₂ or WSe₂. It should be noted that these electrons can be effectively utilized since the WS₂ and WSe₂ layers have adequate chemical potentials to react with the hydrogen ions to produce hydrogen [57]. Simultaneously, the photogenerated holes in the WS₂ or WSe₂ layers will drift to the VB of the GaN layers due to the VBO. Therefore, the excited electron-hole can be gathered separately on the WS₂ (or WSe₂) and GaN, on which the reduction and oxidation reaction can occur, respectively.

To explore the charge transfer process as well as the interlayer interaction in the heterostructures, their charge

Figure 3 Calculated VBM and CBM potential and plane-integrated electron density difference of the GaN/WS₂ and GaN/WSe₂ nanocomposites.

density differences plots were calculated by subtracting the electronic charge of the isolated GaN and WS₂ (or WSe₂) monolayers from that of the hybrid nanocomposites, which are shown in Figs 3c and d. Herein, the cyan and purple respectively represent charge accumulation and depletion. Obviously, there are large charge redistributions in the interlayer regions. Combined with Hirshfeld charge transfer we can find that the charges transfer from WS₂ or WSe₂ to the GaN layer, leading to a weak donor-acceptor coupling. A polarized field that points from the WS₂ (or WSe₂) to GaN is formed because the holes and electrons respectively accumulate on the WS₂ (or WSe₂) and GaN layers. It should be pointed out that the spontaneous electron-hole recombination could be detrimental for the photocatalytic performance. Nevertheless, this polarized field has the synergistic effect with the band offset for the separation of the electron-hole pairs and hinders them from recombination. Eventually, the carrier lifetime is prolonged, which is good for the photocatalysis.

It has been demonstrated that applying strain is an effective method to modulate the electronic properties of the heterostructures [39,38,40,58,59]. Thus, the biaxial homogenous strains are implemented to the GaN/WS₂ and GaN/WSe₂ nanocomposites to investigate the specific influence. The band gap variation trend calculated by the PBE-D functional as a function of applied compressive (negative) and tensile (positive) strains is plotted in Fig. 4. Clearly, the GaN monolayer possesses the largest slope and the best linearity of the band gap variation, which shows the susceptibility of its electronic structure to strains. Similarly, the GaN/WS₂ (WSe₂) also displays its sensitive response to strain, the band gaps decrease monotonically

with the increase of the tensile strain and when the compressive strain is larger than 2%, while they increase when the compressive strain is less than 2%. Specifically, the band structures of the heterostructures may suffer from the direct-indirect band gap transition when the tensile strain reaches to 8% for GaN/WS₂ or reaches to 10% for GaN/WSe₂ (see Figs S4 and S5 in the Supplementary information). A close examination of the PDOSs (displayed in Fig. 4b) of GaN/WS₂ under strains of -6%, -2%, 0%, 2% and 6% is performed to gain insight into the origin of band gap variation [60]. The locations of the N p orbitals that contribute to the VBMs of the heterostructures stay almost the same and the position of the W d orbitals in the valence band exhibit only tiny changes. However, the W d orbitals in the conduction band regions that contribute to the CBM shift toward/away from the Fermi level, which directly results in the band gap reduction/increase. Correspondingly, when the applied compressive strain is less than 4%, the conduction band potential of the WS₂ will shift to a more negative region which is farther away from the reduction potential (H⁺/H₂) while the valence band potential of the GaN stays unchanged. Thus, the CBOs of the nanocomposites shrink compared to the ones without strains. Therefore, applying compressive strain less than 4% may enhance the photocatalyst performance of the nanocomposites.

CONCLUSIONS

In summary, we carried out the density functional calculations to study the electronic and optical properties of the GaN/WS₂ and GaN/WSe₂ heterostructures with van der Waals corrections. The calculation results show that both

Figure 4 (a) Computational band gap variation (PBE-D) of the GaN monolayer and GaN/WS₂ (WSe₂) as a function of strain, ranging from -10 to 10. (b) The PDOS (PBE-D) of GaN/WS₂ under the strains of -6%, -4%, 0%, 4% and 6%.

two nanocomposites are type-II semiconductors with direct band gap about 2 eV, in which the CBMs and VBMs are respectively contributed by WS₂ (or WSe₂) and GaN, respectively. Meantime, the effects of the interlayer coupling on the effective mass and the optical properties were also investigated. The increases in the effective mass compared to the constituent layers are not apparent because of the weak interaction. Nevertheless, the imaginary parts of the dielectric function and the absorption spectra of the heterostructures were calculated and new optical performance was observed because of the new interband transitions. The studies on the band alignment indicate that these two heterostructures are suitable for photocatalysis. In addition, the intrinsic electric fields induced by the charge transfer can further prevent the electron-hole pairs from recombination, which facilitates the photocatalyst performance. What's more, the applications of the biaxial strain can effectively tune the electronic properties of the nanocomposites. In particular, when a compressive strain less than 4% is imposed to the GaN/WS₂, the band gap will increase and the conduction band edge potential will shift away from the H⁺/H₂ potential, which will be beneficial for the photocatalyst performance.

Received 26 August 2016; accepted 22 September 2016;
published online 9 November 2016

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Acknowledgments This research was supported by the National Natural Science Foundation of China (51303033), Guangxi Natural Science Foundation (2014GXNSFCB118004), Guangxi Key Laboratory Foundation of Manufacturing Systems and Advanced Manufacturing Technology (15-140-30-002Z), and Guilin Science and Technology Development Foundation (20140103-3). Jiang J is supported by the Innovation Project of Guangxi Graduate Education (YCSZ2015142).

Author contributions These authors contributed equally to this work., and Chen X conceived the study. Meng R and Jiang J performed the DFT calculations. Meng R wrote the manuscript. All authors read and approved the final manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supplementary data are available in the online version of the paper.

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应用于光催化的类石墨烯氮化镓和二硫化钨/二硒化钨纳米复合材料的设计

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摘要 本文利用第一性原理对类石墨烯GaN和WS₂/WSe₂构成的复合材料的结构, 电学及光学性质进行了系统的研究. 氮化镓和WS₂/WSe₂之间通过范德华力进行相互作用, 且这两种纳米复合结构中最稳定的构型都显示出直接带隙的特征. 同时, 由于导带底和价带顶分别由WS₂ (或WSe₂) 和GaN贡献, 这两种复合结构形成了第二类异质结. 我们对这两种异质结构的介电函数虚部和吸收光谱进行了计算并观察到由带间跃迁所引起的光学性质的增强. 此外, 能带偏移以及由电荷转移所产生的内建电场能够有效地抑制电荷-空穴对的复合, 这对于光催化过程十分有利. 通过施加双轴应变能有效地调节这两个异质结的带隙, 甚至能在一定程度上使导带边远离H⁺/H₂势能, 从而进一步地提升异质结构的光催化性能. 研究结果表明GaN/WS₂和GaN/WSe₂是优异的光催化和光电应用的候选材料.