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Electronic and optical properties of two-dimensional heterostructures based on Janus XSSe (X = Mo, W) and Mg(OH)₂: a first principles investigation

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Two-dimensional (2D) materials have attracted numerous investigations after the discovery of graphene. 2D van der Waals (vdW) heterostructures are a new generation of layered materials, which can provide more desirable applications. In this study, the first principles calculation was implemented to study the heterostructures based on Janus TMDs (MoSSe and WSSe) and Mg(OH)₂ monolayers, which were constructed by vdW interactions. Both MoSSe/Mg(OH)₂ and WSSe/Mg(OH)₂ vdW heterostructures have thermal and dynamic stability. Besides, XSSe/Mg(OH)₂ (X = Mo, W) possesses a direct bandgap with a type-I band alignment, which provides promising applications for light-emitting devices. The charge density difference was investigated, and 0.003 (or 0.0042) |e| were transferred from MoSSe (or WSSe) layer to Mg(OH)₂ layer, and the potential drops were calculated to be 11.59 and 11.44 eV across the interface of the MoSSe/Mg(OH)₂ and WSSe/Mg(OH)₂ vdW heterostructures, respectively. Furthermore, the MoSSe/Mg(OH)₂ and WSSe/Mg(OH)₂ vdW heterostructures have excellent optical absorption wave. Our studies exhibit an effective method to construct new heterostructures based on Janus TMDs and develop their applications for future light emitting devices.

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1. Introduction

Nowadays, two-dimensional (2D) materials have attracted numerous investigations since graphene was prepared by a mechanical stripping method.¹ Graphene was discovered to have novel thermal and electronic properties resulting from the linear band structure near the Dirac cone with zero bandgap.^{2–9} However, these characteristics of graphene also limit the applications in some nano-devices, which urged the studies on 2D semiconductors.^{10–17} Transition metal dichalcogenide (TMD) materials are one of the common layered semiconductor materials, which have excellent electronic,¹⁸ thermal,¹⁹ and optical properties.^{20,21} For example, the n-doping of WSe₂ was performed by the chemical vapor deposition (CVD) method, which can be used as an air-stable n-MOSFET possessing a mobility of about 70 cm² V⁻¹ s⁻¹.²² MoS₂ has high interfacial thermal conductance, about 2.0 × 10⁸ W K⁻¹ m⁻² with Au by

different interfacial angles, and the thermal ability of TMDs can also be decided by layers.²³ Similar to graphene nanoribbons, the mobility of the MoS₂ monolayer is 200 cm² V⁻¹ s⁻¹ at room temperature, indicating promising applications in tunnel FETs and transistors.²⁴ TMD materials are also reported to act as substrates to prepare 2D germanene²⁵ or nitrogen-doped graphene, which are efficient catalysts for redox reactions.²⁶ All these excellent properties of 2D materials show the promising applications for further nano-devices.^{27–31}

In order to expand the application of these layered materials, more interesting properties were developed by the prediction of 2D materials.^{32–36} For example, δ-phosphorene was proposed to be an auxetic material with a high negative Poisson's ratio (NPR) of about -0.267 along relative direction.³⁷ FeB₂ monolayer possesses a Dirac cone, which endows it with a Fermi velocity larger than that of graphene.³⁸ Using first principles calculations, 2D TiC₃ was reported by a remarkably novel storage capacity of about 1278 mA h g⁻¹ even with low barrier energy.³⁹ The new generation of 2D materials are promising candidates for the usages of photocatalytic, photovoltaic, and optical devices.⁴⁰ Besides, constructing a heterostructure by two different layered materials is also a decent method to create more applications for 2D materials.^{41–43} The novel electronic,⁴⁴ interfacial⁴⁵ and optical²⁹ properties of heterostructures formed by van der Waals (vdW) interactions have been exploited for

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catalysis,^{46,47} electronics and optoelectronics.⁴⁸ C₂N/WS₂ vdW possesses a high carrier mobility of 2406.50 cm² V⁻¹ s⁻¹ for holes along some transportation directions.⁴⁹ BCN/C₂N vdW can be used as a direct Z-Scheme photocatalyst for water splitting with the e–h recombination time of about 2 ps.⁵⁰ Recently, black/red phosphorus was investigated to possess type-I band alignment and also could switch to a Z-scheme photocatalyst.⁵¹ A type-I heterostructure, MoTe₂/WSe₂, showed a novel photoluminescence performance from the MoTe₂ layer (about 1.1 eV).⁵² The PbI₂/WS₂ heterostructure also possessed an intrinsic type-I band structure with a decent narrower bandgap; interestingly, the diffusion coefficients of PbI₂ for electrons and holes were similar to about 0.039 and 0.032 cm² s⁻¹, respectively.⁵³ All these studies demonstrate the promising applications for future light emitting devices⁵⁴ and optoelectronic applications.^{55–57} Recently, among tremendous 2D material family, TMDs with the Janus structure have attracted wide attention, which destroy the symmetry of the original crystal structure inducing more novel properties^{10,58} after the preparation of MoSse.^{59,60} The Janus TMD materials have pronounced carrier mobility ranging from 28 to 606 cm² V⁻¹ s⁻¹.^{61,62} Besides, a Janus chromium dichalcogenide was proved to have the ability to separate the photogenerated electrons and holes, and the excited carriers had a lifetime of about 2 ns calculated by the time domain density functional theory.⁶³ Interestingly, the electronic property of the MoSse monolayer can be tuned by a tensile strain from direct to indirect bandgap, and the excellent visible-light absorption performance promises its use as a photocatalyst.⁶⁴ The WSe monolayer can be used as a promising HER catalyst because the basal plane can be easily activated and such Janus asymmetry can enhance the HER activity.⁶⁵ The dipole moment, vibrational frequency, and Rashba parameters of WSe were also induced by its asymmetric Janus structure,⁶⁶ which have potential usage for efficient photocatalysts. More recently, monolayered Mg(OH)₂ sheets were reported to be obtained by the hydrothermal crystal growth technique with stable and classy chemical and vibrational properties, which are potential candidates as flexible optoelectronics.⁶⁷ 2D Mg(OH)₂ also showed unique structural and electronic characteristics in the heterostructure.^{68,69} Moreover, some MoSse- and WSe-based heterostructures have been reported, such as MoSse/WSe,⁷⁰ Hf₂NT₂/MSse (T = F, O, OH; M = Mo, W),⁷¹ MoSse/WSe₂,⁷² graphene/MoSse,⁷³ while reports on MoSse/Mg(OH)₂ and WSe/Mg(OH)₂ heterostructures are still rare. Therefore, considering such novel electronic and optical properties of such synthesized MoSse, WSe and Mg(OH)₂, it is worth constructing the heterostructures by XSse (X = Mo, W) and Mg(OH)₂ to develop the charming characteristics and the potential applications.

Therefore, in this study, we performed the first principles calculation, to investigate the heterostructures formed by Janus TMDs (MoSse and WSe) and Mg(OH)₂. After deciding the structure of the heterostructures, the thermal and dynamic stabilities were addressed. Then, the band alignment of those layered materials was checked, and the interfacial characteristics, charge density difference and potential drop were studied.

The optical properties were also calculated from the optical absorption spectrum.

2. Methods

Based on the density functional theory (DFT), in this simulation work, the first principles calculation was employed, which was implemented by the Vienna *ab initio* simulation package (VASP).⁷⁴ We used the projector augmented wave potentials (PAW) and generalized gradient approximation (GGA) to explain the core electron and exchange correlation functional, respectively,^{75–77} using the Perdew–Burke–Ernzerhof (PBE) functional. To achieve more accurate results of the bandgap, the Heyd–Scuseria–Ernzerhof (HSE06; screening parameter 0.2 Å⁻¹, mixing parameter 0.25) exchange–correlation functionals were used.⁷⁸ The cut-off energy was set as 550 eV, and the *k*-point grids of the Monkhorste–Pack in the first Brillouin zone was 15 × 15 × 1. Besides, the DFT-D3 method of Grimme was also conducted for the corrections of the vdW and dipole.⁷⁹ A thickness of 25 Å was employed for the vacuum layer to prevent the interactions of the layers. The energy of the calculated system and Hellmanne–Feynman force were controlled with a convergence within 1 × 10⁻⁵ eV and 0.01 eV · Å⁻¹, respectively. For the calculation of the phonon spectra, the density functional perturbation theory (DFPT) within the PHONOPY code was used.^{80,81}

The binding energy (*E*) of the layered materials in this work was calculated by the following equation:

$$E = E_{\text{H}} - E_{\text{XSse}} - E_{\text{Mg(OH)}_2}, \quad (1)$$

where *E*_H, *E*_{XSse} and *E*_{Mg(OH)₂} represent the total energy of the XSse/Mg(OH)₂ heterostructure, XSse and Mg(OH)₂ monolayers, respectively. The charge-density difference ($\Delta\rho$) of the XSse/Mg(OH)₂ heterostructure was obtained from the following equation:

$$\Delta\rho = \rho_{\text{H}} - \rho_{\text{XSse}} - \rho_{\text{Mg(OH)}_2}, \quad (2)$$

where ρ_{H} , ρ_{XSse} and $\rho_{\text{Mg(OH)}_2}$ are used to explain the charge density of the isolated XSse/Mg(OH)₂ heterostructure, XSse and Mg(OH)₂ monolayers, respectively. The optical absorption of the materials was obtained using the following formula:

$$\alpha(\omega) = \frac{\sqrt{2}\omega}{c} \left\{ [\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)]^{1/2} - \varepsilon_1(\omega) \right\}^{1/2} \quad (3)$$

where ω , α and *c* are utilized to express angular frequency, absorption coefficient and the speed of light, respectively, and $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the dielectric constant for real and imaginary parts.

3. Results and discussion

The structures of the monolayered MoSse, WSe and Mg(OH)₂ were optimized first, as shown in Fig. 1. The calculated lattice parameters of MoSse, WSe and Mg(OH)₂ were 3.228, 3.269 and 3.140 Å, respectively, showing the very small lattice mismatch



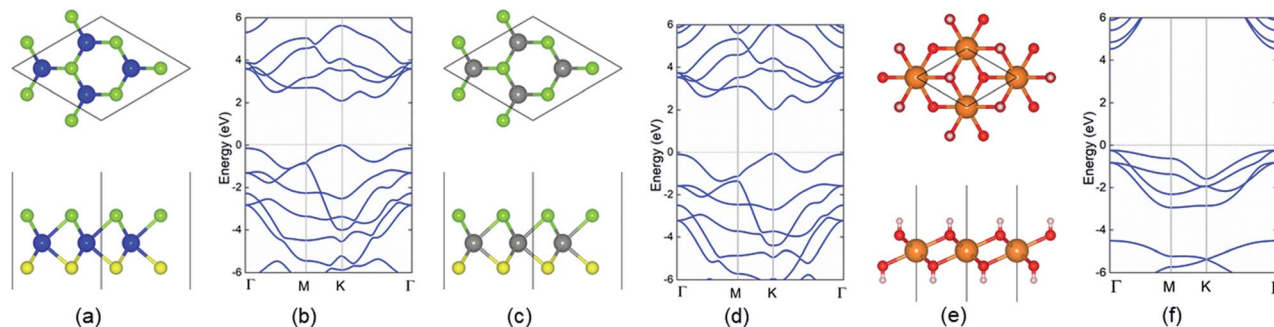


Fig. 1 Schematic of the structures of pristine (a) MoSe, (c) WSe and (e) Mg(OH)₂ monolayers; the blue, cyan, yellow, grey, orange, red and white spheres represent Mo, Se, S, W, Mg, O and H atoms, respectively. The band structure of pristine (b) MoSe, (d) WSe and (f) Mg(OH)₂ monolayers obtained by the HSE06 method; the Fermi level is set as 0 shown by dash line.

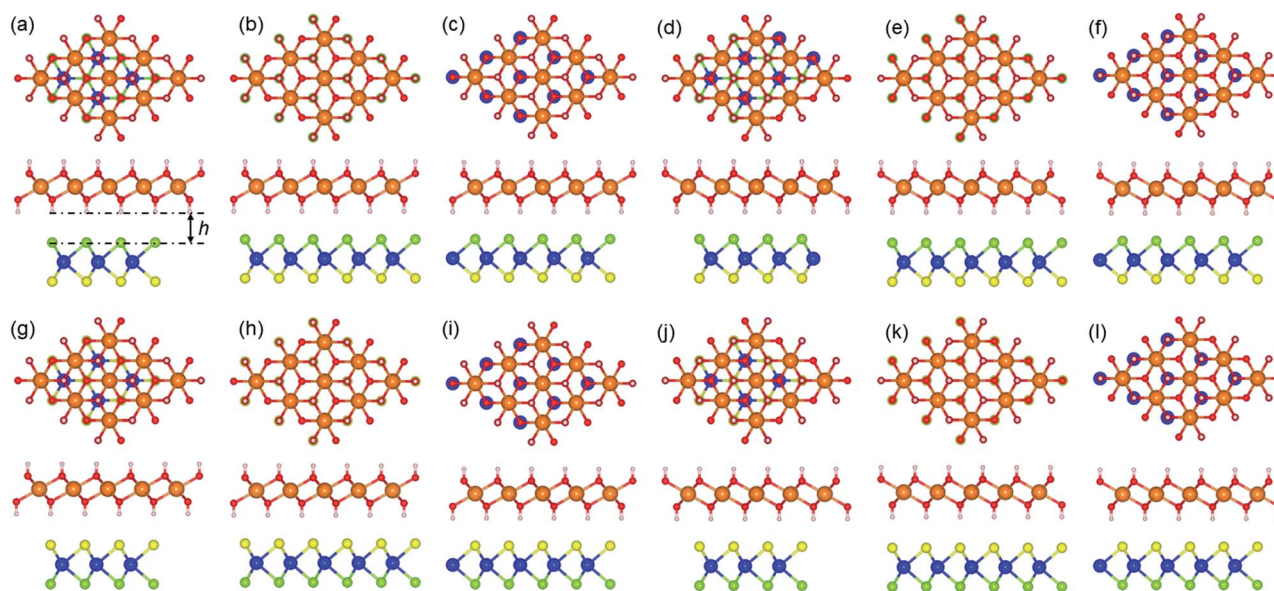


Fig. 2 Top and side views of the XSe/Mg(OH)₂ heterostructures (X = Mo, W) constructed as different stacking styles: (a) S-1, (b) S-2, (c) S-3, (d) S-4, (e) S-5, (f) S-6, (g) S-7, (h) S-8, (i) S-9, (j) S-10, (k) S-11 and (l) S-12.

Table 1 The binding energy (E , meV Å⁻²), the distance of the interface (h , Å), and bond length (L , Å) of the XSe/Mg(OH)₂ heterostructures constructed by different stacking styles

	MoSe/Mg(OH) ₂					WSe/Mg(OH) ₂				
	E	h	$L_{\text{Mo-S}}$	$L_{\text{Mo-Se}}$	$L_{\text{Mg-O}}$	E	h	$L_{\text{W-S}}$	$L_{\text{W-Se}}$	$L_{\text{Mg-O}}$
S-1	-76.610	2.54	2.41	2.53	2.12	-78.157	2.55	2.42	2.53	2.13
S-2	-79.617	2.21	2.41	2.53	2.12	-81.506	2.19	2.42	2.54	2.12
S-3	-79.719	2.22	2.41	2.53	2.12	-81.640	2.19	2.42	2.53	2.13
S-4	-79.628	2.22	2.41	2.53	2.13	-81.494	2.19	2.42	2.53	2.12
S-5	-76.588	2.55	2.41	2.53	2.12	-78.124	2.56	2.42	2.53	2.13
S-6	-79.752	2.20	2.41	2.53	2.12	-81.652	2.19	2.42	2.54	2.12
S-7	-75.259	2.47	2.41	2.53	2.12	-57.472	2.15	2.63	2.62	2.07
S-8	-77.134	2.25	2.41	2.53	2.12	-79.157	2.17	2.42	2.54	2.13
S-9	-77.635	2.21	2.41	2.53	2.13	-79.517	2.20	2.42	2.54	2.13
S-10	-77.500	2.18	2.41	2.53	2.13	-79.393	2.17	2.42	2.54	2.13
S-11	-75.248	2.49	2.41	2.53	2.13	-76.910	2.48	2.42	2.54	2.13
S-12	-77.410	2.21	2.41	2.53	2.12	-79.281	2.24	2.42	2.54	2.13



(about 2.76% and 4.02%) for the MoS₂/Mg(OH)₂ and WS₂/Mg(OH)₂ heterostructures. Besides, the bond length of Mo–S, Mo–Se, W–S, W–Se in the optimized monolayered MoS₂ and WS₂ were obtained as 2.414, 2.529, 2.428 and 2.542 Å, respectively. Furthermore, the band structures of those layered materials are also demonstrated in Fig. 1. It can be found that MoS₂, WS₂ and Mg(OH)₂ had direct bandgaps of 2.100, 2.077 and 4.690 eV, respectively, which were in good agreement with other reports.^{69,82}

When the heterostructure is formed by XS₂ and Mg(OH)₂, 12 representative stacking configurations of XS₂/Mg(OH)₂ should be taken into consideration. Fig. 2 shows these 12 different stacking configurations of XS₂/Mg(OH)₂. The most stable stacking style of the XS₂/Mg(OH)₂ heterostructure was decided using the binding energy (*E*), and the *E* of the XS₂/Mg(OH)₂ heterostructure is explained in Table 1, which shows that S-6 is the most stable configuration with the *E* values of –79.752 and –81.652 meV Å^{–2}, respectively. The calculated binding energy of XS₂/Mg(OH)₂ demonstrated the vdW forces between the interface of the MoS₂ (or WS₂) and Mg(OH)₂ monolayers.^{83,84} The obtained bond length of Mo–S, Mo–Se, W–S and W–Se of MoS₂ and WS₂ in their heterostructures, displayed in Table 1, suggested a slight change compared to the pristine MoS₂ and WS₂ monolayers, which can further prove the weak vdW forces in the XS₂/Mg(OH)₂ heterostructure. Besides, the distance of the interface of the MoS₂/Mg(OH)₂ and WS₂/Mg(OH)₂ vdW heterostructures were obtained to be 2.20 and 2.19 Å, respectively, which were also smaller than that of graphite (3.336 Å).⁸³ Furthermore, the following investigations of the XS₂/Mg(OH)₂ vdW heterostructures are all based on the S-6 stacking configuration.

Then, we also used the AIMD method to further investigate the thermal stability of the XS₂/Mg(OH)₂ vdW heterostructures

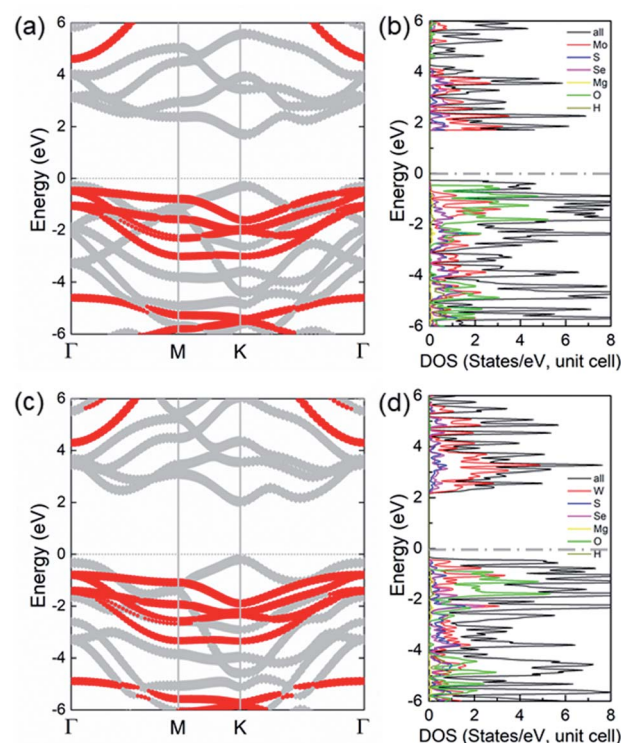


Fig. 4 Projected band structures of the (a) MoS₂/Mg(OH)₂ and (c) WS₂/Mg(OH)₂ vdW heterostructures; the red and grey marks represent the contributions of the XS₂ and Mg(OH)₂ layers, the Fermi level is set as 0 shown by dash line. The partial charge densities of the (b) MoS₂/Mg(OH)₂ and (d) WS₂/Mg(OH)₂ vdW heterostructures.

with a Nosé–Hoover heat bath scheme.⁸⁵ To consider the constraints of lattice translational, we constructed a 6 × 6 × 1 supercell for the MoS₂/Mg(OH)₂ and WS₂/Mg(OH)₂ vdW

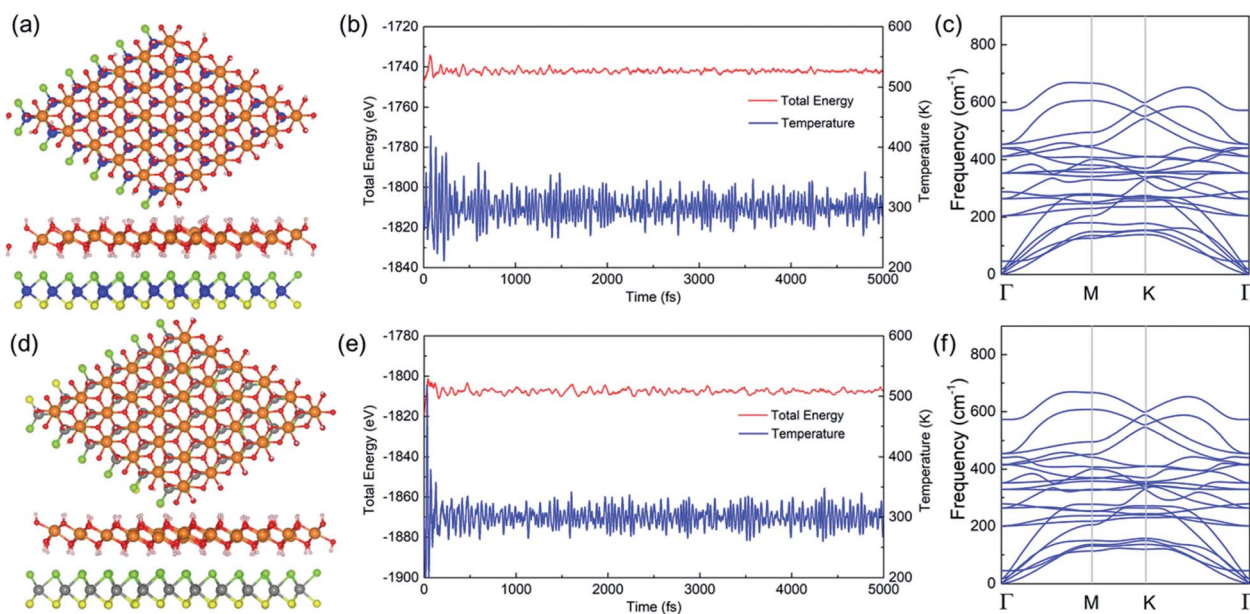


Fig. 3 The snapshot of the (a) MoS₂/Mg(OH)₂ and (d) WS₂/Mg(OH)₂ vdW heterostructures under the temperature of 300 K after 5 ps; the fluctuations of the temperature and total energy of the (b) MoS₂/Mg(OH)₂ and (e) WS₂/Mg(OH)₂ system during the AIMD simulation; the phonon dispersions of (c) the MoS₂/Mg(OH)₂ and (f) WS₂/Mg(OH)₂ vdW heterostructures.



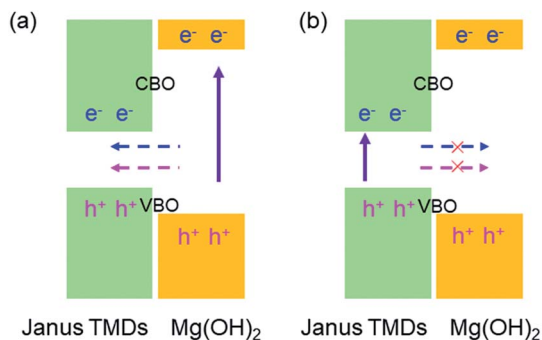


Fig. 5 The band alignment schematic for the migration of free electrons and holes at the interface of the XSSE/Mg(OH)₂ vdW heterostructure.

heterostructures in the AIMD simulation, which contained 288 atoms totally. The ambient temperature of the simulation was set as 300 K, and the structures of the MoSSe/Mg(OH)₂ and WSSE/Mg(OH)₂ vdW heterostructures after relaxation for 5 ps are shown in Fig. 3(a) and (d), respectively. It can be found that the structures of the MoSSe/Mg(OH)₂ and WSSE/Mg(OH)₂ vdW heterostructures still remained intact after 5 ps under 300 K, revealing the robust thermal stability of the heterostructures. In addition, the change of temperature and total energy during the AIMD calculation of both layered systems are shown in Fig. 3(b) and (e), respectively. The temperature and total energy

exhibited a convergence with the simulation step, guaranteeing the reliability of the results. The phonon dispersions were calculated (Fig. 3(c) and (d)) to further evaluate the stability of the MoSSe/Mg(OH)₂ and WSSE/Mg(OH)₂ vdW heterostructures. It is worth noting that no imaginary frequency existed in their phonon spectra, suggesting a dynamic stability.

The projected band structure of the XSSE/Mg(OH)₂ vdW heterostructures shown in Fig. 4 obtained by the HSE06 method. Both MoSSe/Mg(OH)₂ and WSSE/Mg(OH)₂ vdW heterostructures possess direct bandgaps of 1.996 and 2.233 eV, respectively. The grey and red marks represent the donation of the band from MoSSe (or WSSE) and Mg(OH)₂ layers, respectively; thus, the CBM and VBM of the XSSE/Mg(OH)₂ vdW heterostructures were contributed by the MoSSe (or WSSE) layer, showing a type-I band structure for the heterostructures. The calculated partial density of states of the XSSE/Mg(OH)₂ vdW heterostructures is also shown in Fig. 4(b) and (d), which further explains the type-I band alignment that the CBM and VBM of the MoSSe/Mg(OH)₂ and WSSE/Mg(OH)₂ vdW heterostructures resulted from Mo and W atoms, respectively.

In the XSSE/Mg(OH)₂ vdW heterostructure, the CBM and VBM were both fixed in the layered materials with a narrower bandgap, MoSSe (or WSSE), as shown in Fig. 5. When the electrons in the wide-gap layer, Mg(OH)₂, were excited to the CBM, the holes were also induced at the VBM. By the assistance of the conduction band offset (CBO) and valence band offset (VBO), the excited electrons and holes of the Mg(OH)₂ layer both

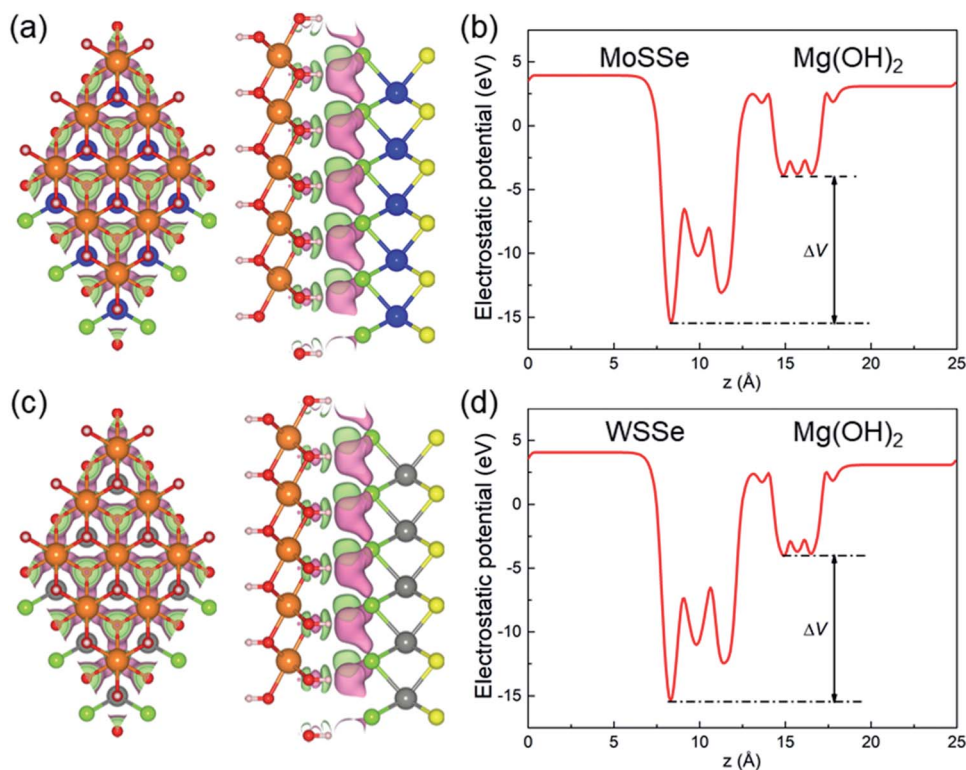


Fig. 6 The isosurfaces of charge density difference of the (a) MoSSe/Mg(OH)₂ and (c) WSSE/Mg(OH)₂ vdW heterostructures, the obtaining and the losing of electrons are demonstrated by cyan and violet marks, respectively; the isosurface level of charge difference is set as 0.015 |e|; the calculated potential drop across interface of the (b) MoSSe/Mg(OH)₂ and (d) WSSE/Mg(OH)₂ vdW heterostructures.



migrated to the CBM and VBM of the XSe layer, respectively, as shown in Fig. 5(a). The CBO and VBO of the MoS₂/Mg(OH)₂ (or MoS₂/Mg(OH)₂) vdW heterostructure were obtained as 2.937 eV (or 2.260) eV and 0.199 eV (or 0.597 eV), respectively. Besides, the radiative recombination of the electrons and holes was promoted by the quantum confinement in the XSe layer, suggesting the potential candidate as light-emitting device.⁸⁶ Furthermore, the electron-hole pairs excited in the narrow-gap XSe layer were prevented to transfer to the Mg(OH)₂ layer because of the lower energies.⁵⁴

Fig. 6(a) and (c) demonstrate the charge density difference between the interface of the XSe and Mg(OH)₂ layers, which shows that the MoS₂ (or WSe₂) layer acts as an electron-donor, while Mg(OH)₂ layer receives the electrons. Furthermore, the Bader-charge analysis method⁸⁷ was employed to quantitatively calculate the electron transfer, and the Mg(OH)₂ layer obtained 0.003 (or 0.0042) |e| from the MoS₂ (or WSe₂) layer in their heterostructure. Such small electron transfers also explain the weak vdW forces between the interface of the XSe/Mg(OH)₂ vdW heterostructures. Besides, after the Janus TMDs contact with the Mg(OH)₂ layer and reach an equilibrium, the potential differences between the interface of the heterostructure are addressed, as shown in Fig. 6(b) and (d). There is a potential drop between the interface calculated to be 11.59 and 11.44 eV for MoS₂/Mg(OH)₂ and WSe₂/Mg(OH)₂ vdW heterostructures, respectively, which can also act as an effective driving force to promote the carrier in Fig. 5(a).

The light absorption capacity of the XSe, Mg(OH)₂ and the XSe/Mg(OH)₂ vdW heterostructure were investigated, as shown in Fig. 7. It is obvious that near the wavelength range of visible light (about 380–700 nm) the MoS₂, WSe₂ and XSe/Mg(OH)₂ vdW heterostructures exhibited an excellent optical absorption spectrum. In detail, the MoS₂/Mg(OH)₂ and WSe₂/Mg(OH)₂ vdW heterostructures possessed pronounced absorption peaks of $5.496 \times 10^5 \text{ cm}^{-1}$ and $4.295 \times 10^5 \text{ cm}^{-1}$ at 352 nm and 367 nm, respectively. The XSe/Mg(OH)₂ vdW heterostructures displayed the ability to absorb sunlight absorption over a wide

range in the visible and NIR regions, which considerably overlap the wavelength range of the solar spectrum. Besides, high absorption peaks appeared in the visible region approximately at the wavelengths of 562 and 495 nm for the MoS₂/Mg(OH)₂ and WSe₂/Mg(OH)₂ vdW heterostructures by $1.432 \times 10^5 \text{ cm}^{-1}$ and $1.656 \times 10^5 \text{ cm}^{-1}$, respectively, which were higher than those of other TMD-based heterostructures, such as WS₂/BSe ($14.09 \times 10^4 \text{ cm}^{-1}$),⁸⁸ g-GaN/BSe ($1.470 \times 10^5 \text{ cm}^{-1}$)⁸⁹ and g-GaN/BlueP ($0.48 \times 10^5 \text{ cm}^{-1}$).⁴⁵ The novel optical absorption characteristic of the XSe/Mg(OH)₂ vdW heterostructures also revealed their potential uses as optoelectronic devices.

4. Conclusions

DFT calculations were explored systematically to study 2D heterostructures based on Janus TMDs and Mg(OH)₂. The heterostructures of MoS₂/Mg(OH)₂ and WSe₂/Mg(OH)₂ were formed by vdW forces with thermal and dynamic stability. Importantly, both XSe/Mg(OH)₂ vdW heterostructures possessed a semiconductor performance with direct bandgap values of 1.996 and 2.233 eV, respectively. The band alignment of the XSe/Mg(OH)₂ vdW heterostructure showed a type-I band structure for both heterostructures, which indicates that they are desirable candidates for light-emitting devices. Besides, the charge density difference analysis demonstrated that the MoS₂ and WSe₂ layers donated 0.003 and 0.0042 |e| to the Mg(OH)₂ layer in their heterostructures, respectively. Furthermore, both heterostructure had fantastic visible light absorptivity. The work provides a theoretical guidance to design new heterostructures based on Janus TMD materials for future nano-devices.

Conflicts of interest

There are no conflicts to declare.

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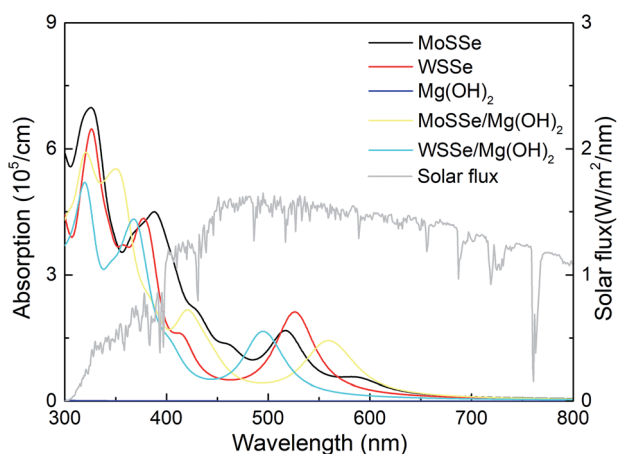


Fig. 7 The optical absorption spectrum of the monolayered XSe, Mg(OH)₂ and XSe/Mg(OH)₂ vdW heterostructures calculated by the HSE06 functional.



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