

First-Principles Study of the Optical Properties of TMDC/Graphene Heterostructures

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Abstract: The transition-metal dichalcogenide (TMDC) in the family of MX_2 ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{S}, \text{Se}$) and the graphene (Gr) monolayer are an atomically thin semiconductor and a semimetal, respectively. The monolayer MX_2 has been discovered as a new class of semiconductors for electronics and optoelectronics applications. Because of the hexagonal lattice structure of both materials, MX_2 and Gr are often combined with each other to generate van der Waals heterostructures. Here, the MX_2/Gr heterostructures are investigated theoretically based on density functional theory (DFT). The electronic structure and the optical properties of four different MX_2/Gr heterostructures are computed. We systematically compare these MX_2/Gr heterostructures for their complex permittivity, absorption coefficient, reflectivity and refractive index.

Keywords: TMDC; graphene; heterostructure; MoS_2 ; WS_2 ; MoSe_2 ; WSe_2 ; permittivity; absorption coefficient; reflectivity; refractive index

1. Introduction

Materials in confined geometries are hosts to novel phenomena. For example, in one dimension (1D), the fractional charge excitation or the soliton is found in the electronic properties of the organic polyacetylene [1], and the Haldane conjecture [2], which corresponds to the symmetry-protected topological phase, is experimentally found in the spin-1 magnetic chain, e.g., CsNiCl_3 , $[\text{Ni}(\text{HF}_2)(3\text{-Clpyridine})_4]\text{BF}_4$, $\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NO}_2(\text{ClO}_4)$ and Y_2BaNiO_5 [3–8]. Quantum states conversion through entanglement manipulations [9] as well as new types of quantum phase transitions with a negative central charge [10] are among the recently investigated 1D systems.

Examples of novel physical phenomena in two dimension (2D) include quantum Hall systems in semiconductors [11], the supersolid phase of atomic systems in the optical lattice [12,13] and Dirac electrons in graphene [14]. Graphene (Gr) is one of the most widely investigated 2D materials; it possesses a high mobility [15–19] and is driven by Dirac cone dispersions near the Fermi level at the K-point and the K'-point in the hexagonal Brillouin zone [20]. However, the gapless nature of Gr limits its applications in the semiconductor industry. Therefore, finding new 2D materials with a large band gap is an interesting topic. Note that a new allotropy of carbon, the 2D biphenylene monolayer, was discovered very recently [21–24].

In addition to the carbon, a number of 2D materials with an energy band gap have been synthesized, including the quantum spin Hall insulator HgTe [25,26], free-standing silicene [27] and the transition-metal dichalcogenide (TMDC) family. Monolayer TMDCs [28–39], such as molybdenum disulfide (MoS_2) [40,41], molybdenum diselenide (MoSe_2) [42], tungsten disulfide (WS_2) [43] and tungsten diselenide (WSe_2) [44,45], have been found to be direct gap semiconductors [46] and have emerged as new optically active materials for novel device applications. The TMDCs in the family of MX_2 , where $\text{M} = \text{Mo}, \text{W}$ and $\text{X} = \text{S}, \text{Se}$, have a rather large energy band gap compared to HgTe and silicene; thus, these materials are more versatile as candidates for thin, flexible device applications and useful for a variety



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of applications including transistors [47], lubrication [48], lithium-ion batteries [49] and thermoelectric devices [50]. Other TMDCs, e.g., PbTaSe_2 , $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ and NiTe_2 , can exhibit more unusual physical properties such as topological superconductivity and Dirac and Weyl semimetal physics [51–56]. Two-dimensional hydrogenated NiTe_2 , PdS_2 , PdSe_2 , and PtSe_2 monolayers also exhibit a quantum anomalous Hall effect [57].

One of the approaches used to broaden the application of 2D materials is to form a heterostructure in which similar lattice structures for different monolayers are usually required, e.g., the hexagonal lattices of TMDC, Gr, boron nitride [58], and boron phosphide (BP) [59]. It has been suggested that MX_2/BP heterostructures have a good ability for optical absorption [59]. On the other hand, the MX_2/Gr of the type-I van der Waals heterostructures have attracted much attention for their electronic properties. Research on MoS_2/Gr [60–62], MoSe_2/Gr [63–65], WS_2/Gr [66] and WSe_2/Gr [67,68] has revealed that MX_2/Gr is favorable for electronics applications and field-effect transistors. However, there are relatively few studies on its optical properties [69–71]; therefore, comprehensive research on the optical properties of MX_2/Gr is desired.

In this communication, we theoretically investigate the optical properties of MX_2/Gr heterostructures. By means of a density functional theory simulation, we systematically compare the energy band structures, the density of states, complex permittivity, absorption coefficients, reflectivity, and refraction indexes.

2. Materials and Methods

The first-principles calculations are based on the local-density approximation (LDA) proposed by Kohn and Sham [72], which approximates the total energy of the multielectron system. The simulations were implemented using the software package NANODCAL and its accompanying software packages DEVICESTUDIO and OPTICCAL [73,74]. A plane wave basis was set with a cutoff energy of 80 Hartree and a $5 \times 5 \times 1$ Γ -centered k -points grid. The atomic structures were relaxed until the force was smaller than $0.03 \text{ eV}/\text{\AA}$ and the total energy convergence criterion was set as 10^{-4} eV . In order to avoid interactions in the vertical direction between neighboring slabs, a vacuum layer of $24 \text{ \AA}$ was added between different slabs.

The lattice constants of the MoS_2 , MoSe_2 , WS_2 , WSe_2 and Gr monolayers were $3.166 \text{ \AA}$, $3.288 \text{ \AA}$, $3.153 \text{ \AA}$, $3.282 \text{ \AA}$ and $2.47 \text{ \AA}$, respectively [32,63]. For all the MX_2/Gr heterostructures, lattice mismatch ratios less than 5% were achieved by choosing a 3×3 MX_2 supercell and a 4×4 Gr supercell, as shown in Figure 1. The details of the lattice mismatch ratios are listed in Table 1. After the structure optimization, the lattice contents were $9.668 \text{ \AA}$, $9.854 \text{ \AA}$, $9.648 \text{ \AA}$ and $9.845 \text{ \AA}$ for MoS_2/Gr , MoSe_2/Gr , WS_2/Gr and WSe_2/Gr , respectively. The details of the atom–atom distances as well as the MX_2 layer–Gr layer distances are listed in Table 2. The total number of atoms in the simulations was 59 for MX_2/Gr , 27 for the 3×3 monolayer of MX_2 , and 32 for the 4×4 monolayer of Gr.

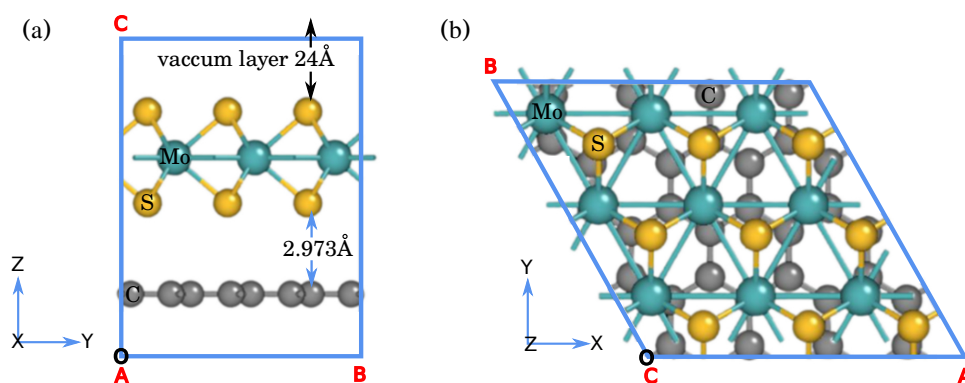


Figure 1. The stacking of the 3×3 MoS_2 supercell and the 4×4 Gr supercell. (a) The side view. (b) The top view. For the other MX_2/Gr , the atom–atom distances are listed in Table 2.

Table 1. The lattice mismatch ratios and the binding energies of TMDCs/graphene with 3×3 supercell of MX_2 and 4×4 supercell of graphene.

MX_2/Gr	MoS_2/Gr	MoSe_2/Gr	WS_2/Gr	WSe_2/Gr
mismatch ratio	1.83%	0.10%	2.04%	0.01%
E_b	−194 meV	−146 meV	−178 meV	−246 meV

The binding energies E_b are calculated by the energy difference between the heterostructures and the monolayers:

$$E_b = E_{\text{MX}_2/\text{Gr}} - E_{\text{MX}_2} - E_{\text{Gr}}, \quad (1)$$

where $E_{\text{MX}_2/\text{Gr}}$, E_{MX_2} and E_{Gr} are the total energies of the heterostructures, isolated MX_2 and Gr, respectively. It is interesting to compare other heterostructures, such as MX_2/BP [59], as regards binding energies. The interface binding energies of the most stable configurations of MoS_2/BP , MoSe_2/BP , WS_2/BP and WSe_2/BP are −196 meV, −130 meV, −201 meV and −141 meV, respectively [59]. As listed in Table 1, all the binding energies for the MX_2/Gr heterostructures in this study are negative, and the values are close to MX_2/BP , demonstrating that the structural stability of MX_2/Gr is similar to that of MX_2/BP .

Table 2. The optimized atom–atom distances as well as the MX_2 layer–Gr layer distances.

MoS_2/Gr	Mo-S	Mo-C	S-C	C-C	$\text{MoS}_2\text{-Gr}$
	2.404 Å	4.826 Å	3.089 Å	1.600 Å	2.973 Å
MoSe_2/Gr	Mo-Se	Mo-C	Se-C	C-C	$\text{MoSe}_2\text{-Gr}$
	2.349 Å	4.920 Å	3.270 Å	1.626 Å	3.161 Å
WS_2/Gr	W-S	W-C	S-C	C-C	$\text{WS}_2\text{-Gr}$
	2.379 Å	4.774 Å	3.078 Å	1.596 Å	2.954 Å
WSe_2/Gr	W-Se	W-C	Se-C	C-C	$\text{WSe}_2\text{-Gr}$
	2.354 Å	4.940 Å	3.286 Å	1.625 Å	3.178 Å

3. Results

3.1. Band Structures

The direct band gaps of the MoS_2 , MoSe_2 , WS_2 and WSe_2 monolayers were 1.82 eV, 1.56 eV, 1.95 eV and 1.64 eV, respectively, [36], where both the conduction band minimum (CBM) and the valence band maximum (VBM) were at the K-point in the Brillouin zone. The Dirac point of the Gr was located at the K-point and pinned to the Fermi level. All the results of the energy band structures for the MX_2 monolayers are consistent with the existing literature [17,35]. Now we report the energy band structures and the electronic density of states (DOS) for the four MX_2/Gr , as shown in Figure 2. We found that the band structure of MX_2/Gr could basically be regarded as the overlap of the band structures of the MX_2 and Gr monolayers. Due to van der Waals interactions, the Dirac point opens a small gap of 8.3 meV, 7.9 meV, 8.86 meV and 3.53 meV for MoS_2/Gr , MoSe_2/Gr , WS_2/Gr and WSe_2/Gr , respectively. The total and partial DOS values of MX_2/Gr are also shown in Figure 2. The partial DOS is the relative contribution of a particular orbital to the total DOS. The d-orbital contributions mainly come from the W or Mo atoms, and the p-orbital contributions come from S or Se, and C atoms. Contributions from the s-orbital are minimal. These results reflect a fairly weak interfacial coupling at the interface between MX_2 and Gr.

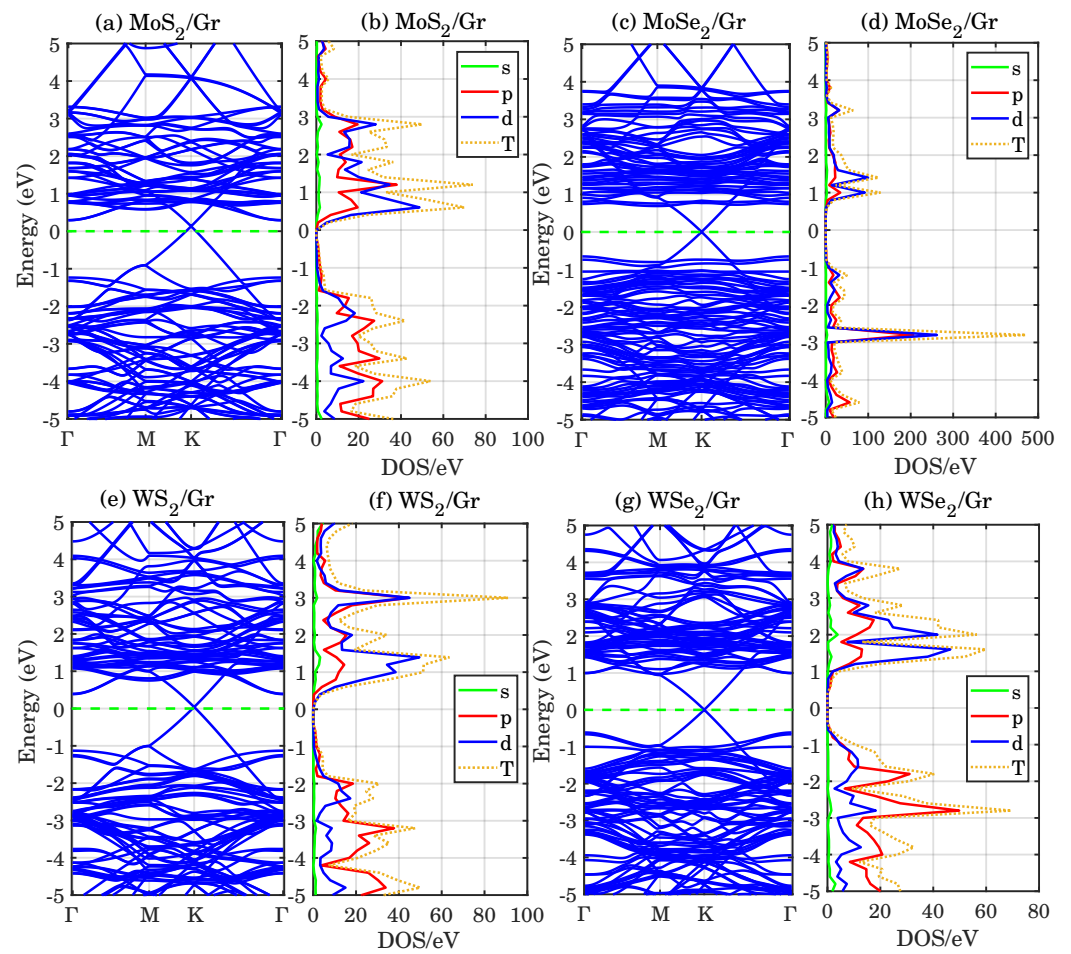


Figure 2. The energy band structures and the DOS for the MX₂/Gr van der Waals heterostructures. The partial DOS values are labeled with s, p, or d, corresponding to the orbital contributions, and the total DOS is labeled with T. (a,b) MoS₂, (c,d) MoSe₂, (e,f) WS₂, (g,h) WSe₂.

The Schottky contacts are formed between the semiconducting MX₂ and the metallic Gr. The Schottky barrier is one of the most important characteristics of a semiconductor–metal junction and dominates the transport properties. Based on the Schottky–Mott model [75–77], at the interface of the metal and semiconductor, an n-type Schottky barrier height (SBH) Φ_{Bn} is defined as the energy difference between the Fermi level E_F and the conduction band minimum E_C , i.e., $\Phi_{Bn} = E_C - E_F$. Similarly, the p-type SBH Φ_{Bp} is defined as the energy difference between E_F and the valence band maximum E_V , i.e., $\Phi_{Bp} = E_F - E_V$. The n/p-type Schottky contacts are classified by the smaller SBH. The SBH are $\Phi_{Bn} = 0.29$ eV and $\Phi_{Bp} = 1.23$ eV for MoS₂/Gr, $\Phi_{Bn} = 0.75$ eV and $\Phi_{Bp} = 0.65$ eV for MoSe₂/Gr, $\Phi_{Bn} = 0.39$ eV and $\Phi_{Bp} = 1.13$ eV for WS₂/Gr, and $\Phi_{Bn} = 1.00$ eV and $\Phi_{Bp} = 0.61$ eV for WSe₂/Gr, respectively. Therefore, MoS₂/Gr, MoSe₂/Gr, WS₂/Gr and WSe₂/Gr are the n-type, p-type, n-type and p-type Schottky contacts, respectively [64,66,67].

3.2. Optical Properties

In order to understand the optical properties, the complex permittivity or the so-called dielectric function was computed under the long-wave approximation, i.e., $\vec{q} = 0$. The complex permittivity $\epsilon(\omega) = \epsilon_{\text{real}}(\omega) + i\epsilon_{\text{imag}}(\omega)$ as a function of incident photon energy is [78]

$$\epsilon(\omega) = 1 + \frac{2e^2}{\epsilon_0 m^2} \frac{1}{V} \sum_{\alpha\beta} \frac{|\langle \psi_\beta | \hat{e} \cdot \vec{p} | \psi_\alpha \rangle|^2}{(E_\beta - E_\alpha)^2 / \hbar^2} \frac{f(E_\alpha) - f(E_\beta)}{E_\beta - E_\alpha - \hbar\omega - i\eta} \quad (2)$$

where e is the electron charge, ϵ_0 is the vacuum permittivity, m is the electron mass, $\hat{e}$ is the direction of the vector potential, $\vec{p}$ is the momentum operator, $\hbar\omega$ is the photon energy, and $f(E_\alpha)$ and $f(E_\beta)$ are the Fermi–Dirac distribution functions. Since $\epsilon = n_c^2$, i.e., $\epsilon_{\text{real}} + i\epsilon_{\text{imag}} = (n + i\kappa)^2$, the refraction index n and the extinction coefficient κ are obtained:

$$n^2 = \frac{|\epsilon| + \epsilon_{\text{real}}}{2}, \quad (3)$$

$$\kappa^2 = \frac{|\epsilon| - \epsilon_{\text{real}}}{2}. \quad (4)$$

The real part ϵ_{real} is caused by various kinds of displacement polarization inside the material and represents the energy storage term of the material. The imaginary part ϵ_{imag} is related to the absorption of the material, including gain and loss. Therefore, the permittivity must be real in the absence of the incident photon energy, i.e., $\epsilon(\omega = 0) = \epsilon_{\text{real}}$. It is expected that the smaller the energy gap of a material, the larger its $\epsilon(0)$. On the other hand, since the DOS only appears in a finite range of energy in the numerical simulation, electron transitions by the absorption of photons do not occur if the photon energy is too large. Therefore, without photon absorption the computed ϵ_{imag} is close to zero in the large limit of the incident photon energy, and the permittivity approaches a constant real value.

In Figure 3, we show the real part and the imaginary part of the complex permittivity for MX_2/Gr heterostructures and MX_2 and Gr monolayers. Since the energies corresponding to the peak positions of the DOS in the conduction and valence bands of the MX_2/Gr were smaller than those of MX_2 , the peak positions of the real part $\epsilon_{\text{real}}(\omega)$ of MX_2/Gr in Figure 3c had a red shift compared with the MX_2 in Figure 3a. The highest peak corresponding energy of the imaginary part $\epsilon_{\text{imag}}(\omega)$ of the MX_2/Gr in Figure 3d was about 0.8 eV to 0.9 eV, which corresponds to the position where the real part decreases the fastest.

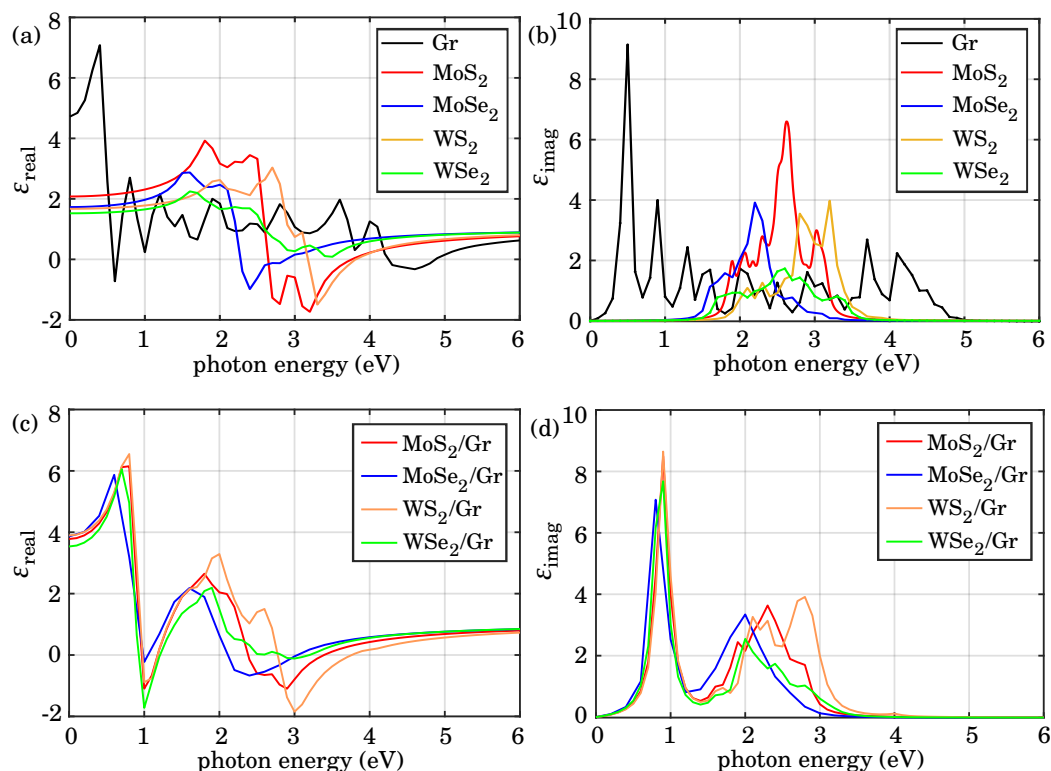


Figure 3. The complex permittivities for MX_2/Gr heterostructures and MX_2 and Gr monolayers as functions of incident photon energy. (a,c) The real part of the permittivity ϵ_{real} . (b,d) The imaginary part of the permittivity ϵ_{imag} .

After obtaining the dielectric function, the absorption coefficient α is computed by

$$\alpha = \frac{2\omega\kappa}{c}, \quad (5)$$

and the reflectivity R is

$$R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2}. \quad (6)$$

Figure 4 compares MX_2/Gr , MX_2 and Gr for their absorption coefficient α , reflectivity R and refractive index n . Since MX_2/Gr has a smaller optical band gap compared with the MX_2 monolayer, MX_2/Gr has a wider range of light absorption, from 0.6 eV to 4 eV. As shown in Figure 4b,e, MX_2/Gr had a higher reflectivity than MX_2 in the infrared area ($\hbar\omega < 1.2$ eV), and had a higher reflectivity than Gr in the visible light area. We compare the real part of the permittivity of monolayer MX_2 in Figure 3a with the refractive index of monolayer MX_2 in Figure 4c, and compare the real part of the permittivity of the MX_2/Gr heterostructure in Figure 3c with that of MX_2/Gr in Figure 4f. It was found that the changing trends from Figure 3a to Figure 4c are similar to those from Figure 3c to Figure 4f. This means that the real part of the dielectric constant dominates the effect of the refractive index. The above simulation results suggest that MX_2/Gr heterostructures are good candidate materials for optical applications.

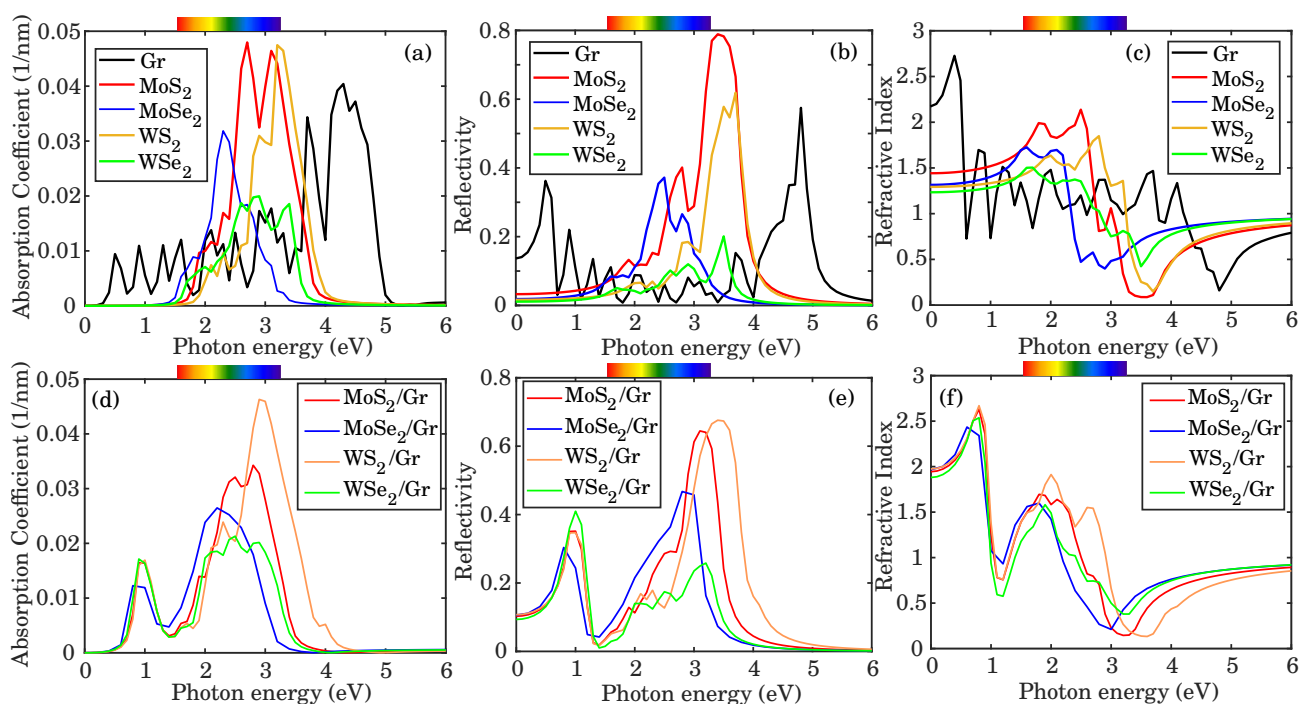


Figure 4. The comparison of MX_2/Gr heterostructures and MX_2 and Gr monolayers according to their (a,d) absorption coefficient α , (b,e) reflectivity R and (c,f) refractive index n . The rainbow bars represent the energy range of visible light, from 1.59 eV to 3.26 eV.

4. Discussion

Two-dimensional heterostructures based on TMDCs exhibit the enhancement of electrical and optoelectrical properties, which are promising for next-generation optoelectronics devices. We systematically computed the complex permittivity $\epsilon(\omega)$, absorption coefficient $\alpha(\omega)$, reflectivity $R(\omega)$ and refractive index $n(\omega)$ for MX_2/Gr heterostructures, where $M = \text{Mo}, \text{W}$; and $X = \text{S}, \text{Se}$. Our results qualitatively agree with those from previous studies on MoS_2/Gr [69] and WSe_2/Gr [70], where red shifts in the $\alpha(\omega)$, $R(\omega)$ and $n(\omega)$ were found compared with MoS_2 and WSe_2 monolayers. We extended the investigations to

other MX₂/Gr heterostructures, and found qualitatively similar behavior in their optical properties.

It is worth comparing our MX₂/Gr results with the recent simulation results on the MX₂/BP in terms of absorption abilities [59]. Although different types of van der Waals heterostructures were found in MX₂/BP (type-I for MoS₂/BP and WS₂/BP; type-II for MoSe₂/BP and WSe₂/BP), all the materials of MX₂/BP have excellent absorption abilities in the infrared and visible light range, i.e., $\alpha(\omega) \approx 0.01 \text{ nm}^{-1}$ to 0.05 nm^{-1} for the wavelength $400 \text{ nm} \leq \lambda \leq 1200 \text{ nm}$ [59]. In our study, all the MX₂/Gr were type-I heterostructures, and the values of the absorption coefficients were in the same range compared with MX₂/BP in the infrared and visible light range. Therefore, MX₂/Gr can be utilized as alternative materials for the applications of solar optoelectronics devices.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

TMDC	Transition metal dichalcogenide
Gr	Graphene
SBH	Schottky barrier height
DFT	Density functional theory
DOS	Density of states
CBM	Conduction band minimum
VBM	Valence band maximum

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