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# The Combined Effects of an External Field and Novel Functional Groups on the Structural and Electronic Properties of TMDs/Ti<sub>3</sub>C<sub>2</sub> Heterostructures: A First-Principles Study

Siyu Zheng <sup>1</sup>, Chenliang Li <sup>1,\*</sup>, Chaoying Wang <sup>1</sup>, Decai Ma <sup>2</sup> and Baolai Wang <sup>1</sup>

<sup>1</sup> College of Aerospace and Civil Engineering, Harbin Engineering University, Harbin 150001, China

<sup>2</sup> School of Physics and Engineering, Sun Yat-sen University, Guangzhou 510275, China

\* Correspondence: lichenliang@hrbeu.edu.cn

**Abstract:** The stacking of Ti<sub>3</sub>C<sub>2</sub> with transition metal dihalide (TMDs) materials is an effective strategy to improve the physical properties of a single material, and the tuning of the related properties of these TMDs/Ti<sub>3</sub>C<sub>2</sub> heterostructures is also an important scientific problem. In this work, we systematically investigated the effects of an external field and novel functional groups (S, Se, Cl, Br) on the structural and electronic properties of TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> heterostructures. The results revealed that the lattice parameters and interlayer distance of TMDs/Ti<sub>3</sub>C<sub>2</sub> increased with the addition of functional groups. Both tensile and compressive strain obviously increased the interlayer distance of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = S, Se, Cl, Br) and MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = Se, Br). In contrast, the interlayer distance of MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = S, Cl) decreased with increasing compressive strain. Furthermore, the conductivity of TMDs/Ti<sub>3</sub>C<sub>2</sub> increased due to the addition of functional groups (Cl, Br). Strain caused the bandgap of TMDs to narrow, and effectively adjusted the electronic properties of TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub>. At 9% compressive strain, the conductivity of MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub> increased significantly. Meanwhile, for TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub>, the conduction band edge (CBE) and valence band edge (VBE) at the M and K points changed linearly under an electric field. This study provides valuable insight into the combined effects of an external field and novel functional groups on the related properties of TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub>.

**Keywords:** TMDs/MXenes; electronic properties; density functional theory (DFT); functional groups; biaxial strain; electric field

**Citation:** Zheng, S.; Li, C.; Wang, C.; Ma, D.; Wang, B. The Combined Effects of an External Field and Novel Functional Groups on the Structural and Electronic Properties of TMDs/Ti<sub>3</sub>C<sub>2</sub> Heterostructures: A First-Principles Study. *Nanomaterials* **2023**, *13*, 1218. <https://doi.org/10.3390/nano13071218>

Academic Editor:

Lyubov G. Bulusheva

Received: 16 February 2023

Revised: 22 March 2023

Accepted: 28 March 2023

Published: 29 March 2023



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## 1. Introduction

Due to the inter-layer coupling effect, heterostructures formed by vertically stacking different two-dimensional (2D) materials can achieve ultra-high-performance improvements and possess unprecedentedly excellent physical properties [1–3]. The transition metal dihalides (TMDs) have excellent band gap widths in the range of 1.0 eV to 2.0 eV [4]. The monolayer MoS<sub>2</sub>, as a typical representative member of the most studied TMD family, is a semiconductor material with a direct band gap of 1.8 eV, and it is widely used in logic transistors and photodetector devices [5,6]. Similarly, the monolayer MoSe<sub>2</sub>, as another important member of TMDs, has many promising applications in electronics and optoelectronics due to its unique electronic, optical, mechanical, chemical, and thermal properties [7,8]. However, TMDs also have some negative properties that affect their application. For example, their carrier effective mass is relatively high, while the carrier mobility is very low [9,10], which hinders their application in high-performance nanodevices. Several studies have shown that the heterogeneous structures formed by stacking TMDs with other 2D materials can significantly modulate the structural, electronic, and mechanical properties of TMDs. For example, the studies of Biroju et al. [11] showed that MoS<sub>2</sub> stacked with a bilayer graphene heterostructure can improve

electronic conductivity, electrochemical properties, and photochemical properties. Li et al. [12] systematically investigated electron density differences and band gaps of  $\text{Cu}_3\text{N}/\text{MoS}_2$  heterostructures, and the results showed that the charge was mainly accumulated and consumed near the atoms, with only a small amount of charge accumulating between the layers, and the bandgap of  $\text{Cu}_3\text{N}/\text{MoS}_2$  heterostructures can be efficiently tuned with the variation of the interlayer distance. Moreover,  $\text{Cu}_3\text{N}/\text{MoS}_2$  heterostructures have a stable structure and excellent photoelectric properties. Celal et al. [13] investigated the structural and electronic properties of  $\text{GaN}/\text{MoSe}_2$  heterostructures with van der Waals (vdW) correction. An indirect band gap of 1.371 eV was obtained when the GaN monolayers were adsorbed on  $\text{MoSe}_2$  monolayers, while when GaN was stacked on  $\text{MoSe}_2$  monolayers, the indirect band gap in GaN monolayers was maintained at 0.341 eV. Based on these studies, we can conclude that combining TMDs with other two-dimensional layered materials to form heterogeneous structures may be an effective way to tune and improve the relevant properties of TMDs.

MXenes are a new and important member of the family of 2D materials discovered in recent years and are complex layered 2D material systems representing a large class of transition metal nitriles, carbides, and carbonitrides [14–16].  $\text{Ti}_3\text{C}_2$  is a typical transition metal carbide with multilayer metal ion adsorption behavior, with ultra-high electrical conductivity and extraordinary mechanical and electronic properties [17,18].  $\text{Ti}_3\text{C}_2$  is expected to be the most competitive material candidate in some fields, such as high-performance ultra-thin electronics and storage [19,20]. Mathis et al. [21] investigated the MXene nanosheets ( $\text{Al-Ti}_3\text{C}_2$ ), and found they have higher quality, increased oxidation resistance, and electronic conductivity increased to 20,000 S/cm.  $\text{Al-Ti}_3\text{C}_2$  is a promising electric nanodevice. Li et al. [22] systematically investigated the interfacial properties of monolayer  $\text{WS}_2$  in contact with a series of MXenes using first-principles calculations. The results showed that  $\text{Ti}_3\text{C}_2$  couples strongly with  $\text{WS}_2$ , leading to the metallization of monolayer  $\text{WS}_2$  and the formation of ideal Ohmic contacts in the vertical direction. Moreover, during the electrode fabrication process, the face-to-face stacking of 1 nm thickness MXene limits the accessibility to electrolyte ions [23,24], which hinders the electronic properties utilization of its surface. For  $\text{Ti}_3\text{C}_2$ , heterostructure stacking is also a valuable tool for improving the electronic properties since it can not only add the excellent properties of a single 2D material but also provide a stable gallery space [25–27], which could prevent face-to-face stacking of MXene. For example, Wu et al. [28] systematically investigated the energy storage and electronic properties of  $\text{N-Ti}_3\text{C}_2/\text{NiCo}_2\text{S}_4$  heterostructures. Owing to the unique heterostructure and friendly interfacial interaction, the  $\text{N-Ti}_3\text{C}_2/\text{NiCo}_2\text{S}_4$  heterostructure had a stable structure, low internal resistance, and excellent rate performance. Debow et al. [29] found that the strong electronic coupling between  $\text{Ti}_3\text{C}_2\text{O}_x$  and  $\text{TiO}_2$  is due to their proximity; the  $\text{Ti}_3\text{C}_2\text{O}_x$ -generated electrons are transferred into the conduction band of the  $\text{TiO}_2$  semiconductor over the Schottky barrier with a fast time constant of 180 fs, leading to an increase in conductivity.

Currently, there are a large number of studies on TMD and MXene heterostructures. Jing et al. [30] systematically investigated the structural and electronic properties of  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{T}_x$  ( $\text{T} = \text{OH}, \text{F}$  and  $\text{O}$ ) heterostructures, and the results showed that the  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{F}_2$  heterostructure is an *n*-type Schottky contact and the Schottky barrier height (SBH) is 0.73 eV, while the  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{O}_2$  heterostructure is a *p*-type Schottky contact with an SBH of 0.33 eV. Moreover, the tensile strain can effectively adjust the position of the conduction band edge (CBE) of  $\text{MoS}_2$ , which leads to an effective reduction of the Fermi energy level pinning and SBH, thus allowing for Ohmic contact. Guan et al. [31] studied heterostructures composed of  $\text{Ti}_3\text{C}_2\text{T}_2$  ( $\text{T} = \text{O}$  and  $\text{F}$  atoms) and metallic  $\text{MoS}_2$  (1T phase) for lithium-ion battery (LIB) applications. The different surface functional groups in MXenes were found to significantly alter the redox reaction of Li atoms in the  $\text{Ti}_3\text{C}_2\text{T}_2$  and 1T- $\text{MoS}_2$  interfaces. The diffusion curve became significantly flattened from the bared to O and F terminated  $\text{Ti}_3\text{C}_2$ , with the Schottky barrier height reducing dramatically from 0.80 eV to 0.22 eV and 0.29 eV, respectively. The surface functional group O or F can

remove the spatial site resistance of Li embedding by disrupting the strong interaction between the two layers while providing additional adsorption sites for Li diffusion. Li et al. [32] found that MoS<sub>2</sub>/Ti<sub>3</sub>C heterostructures have good thermoelectric and transport properties, and the applied electric field or strain can significantly improve their thermoelectric and transport properties. Xu et al. [33] found that MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> (T = OH, O, and F) heterostructures exhibit excellent electrochemical properties at very high currents and have a large potential for sodium ion storage, which can be applied to high-performance sodium-ion batteries. Ling et al. [34] demonstrated by a first-principles method that MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>-OH heterostructures can enhance the catalytic activity of MoS<sub>2</sub> at low sulfur vacancy concentrations. Combining the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>-OH heterostructure with strain engineering can realize the potential of efficient hydrogen production. Based on these previous studies, TMDs/MXenes heterostructures can improve the related properties of single TMDs or MXenes, and the surface functional groups of the monolayer MXenes are an effective way to tune the properties of the TMDs/MXenes heterostructures. However, these studies have mainly focused on the surface functional groups O, F, and OH.

Recently, Kamysbayev et al. [35] successfully synthesized MXenes with novel functional groups (S, Se, Cl, Br, Te) capped with Ti<sub>3</sub>C<sub>2</sub>, all of which showed in-plane tensile strain, especially Ti<sub>3</sub>C<sub>2</sub>Te<sub>2</sub>, which had the maximum in-plane tension, showing in-plane lattice expansion of more than 18%. Lattice expansion promoted the appearance of Ti<sub>3</sub>C<sub>2</sub> electron mobility over 10<sup>4</sup> cm<sup>2</sup>/V·s at room temperature, as well as superconductivity. Based on the studies of Kamysbayev et al. [35], it can be concluded that these novel functional groups (S, Se, Cl, Br) obviously induce a change in the related properties of Ti<sub>3</sub>C<sub>2</sub>. Moreover, as we know, the external field can induce fancy changes in the properties of 2D materials. However, it is still unclear about the effects of these novel functional groups (S, Se, Cl, Br) and external fields on the structural and electronic properties of the TMDs/Ti<sub>3</sub>C<sub>2</sub> heterostructures. In this paper, we first systematically investigated the structural and electronic properties of these TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = S, Se, Cl, Br) heterostructures using the density functional theory (DFT), and discussed in detail the effects of these novel surface functional groups on the related properties of these TMDs/Ti<sub>3</sub>C<sub>2</sub> heterostructures. In addition, we then further explored the effect of external biaxial strain and electric field on the structural and electronic properties of these TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> heterostructures.

## 2. Calculation Method

All calculations were performed within the framework of density functional theory using the CASTEP code [36]. The Perdew–Burke–Ernzerhof (PBE), based on the generalized gradient approximation (GGA), was used as the exchange–correlation function [37]. In order to accurately represent the van der Waals interactions between monolayer TMDs and 2D Ti<sub>3</sub>C<sub>2</sub>, a semi-empirical dispersion correction in Grimme format (DFT–D) was used [38]. The Ultrasoft pseudopotential [39] was used to describe the ion–electron interaction. The valence electrons performed as the [Ar]3p3d4s configuration for the Ti atom, the [Ne]3s3p configuration for the S and Cl atoms, the [Kr]4d5s configuration for the Mo atom, the [He]2s2p configuration for the C atom, and the [Ar]4p4s configuration for Br and Se atoms. The energy cutoff was set to 450 eV [40]. Structural optimization was performed using a 9 × 9 × 1 Monkhorst–Pack grid *K*-point sampling in the Brillouin zone in the unit cell, with the optimization energy convergence parameter set to 10<sup>−5</sup> eV/atom and the force convergence parameter on the atoms set to 0.03 eV/Å [41]. The *K*-point grid was increased to 11 × 11 × 1 for the calculation of energy bands and density of states [42]. A vertical vacuum layer thickness of more than 15 Å was set to prevent periodic boundary interactions between adjacent layers [43]. The binding energy of the TMDs/Ti<sub>3</sub>C<sub>2</sub> heterostructure was defined as:

$$E_b = (E_{TMDs/Ti_3C_2} - E_{Ti_3C_2} - E_{TMDs}) / A$$

where  $E_{TMDs/Ti_3C_2}$ ,  $E_{Ti_3C_2}$ , and  $E_{TMDs}$  are the total energies of the heterostructure, bare  $Ti_3C_2$ , and the TMD monolayer, respectively, and  $A$  is the interface area [44]. We not only investigated the structural and electronic properties of pristine TMDs/ $Ti_3C_2$  and TMDs/ $Ti_3C_2X_2$  ( $X = S, Se, Cl, Br$ ) but also explored the effect of biaxial strain on the structural and electronic properties of TMDs/ $Ti_3C_2$  and TMDs/ $Ti_3C_2X_2$  ( $X = S, Se, Cl, Br$ ) heterostructures. The biaxial strain was defined as:

$$\varepsilon_x = (a - a_0) / a_0 \times 100\%$$

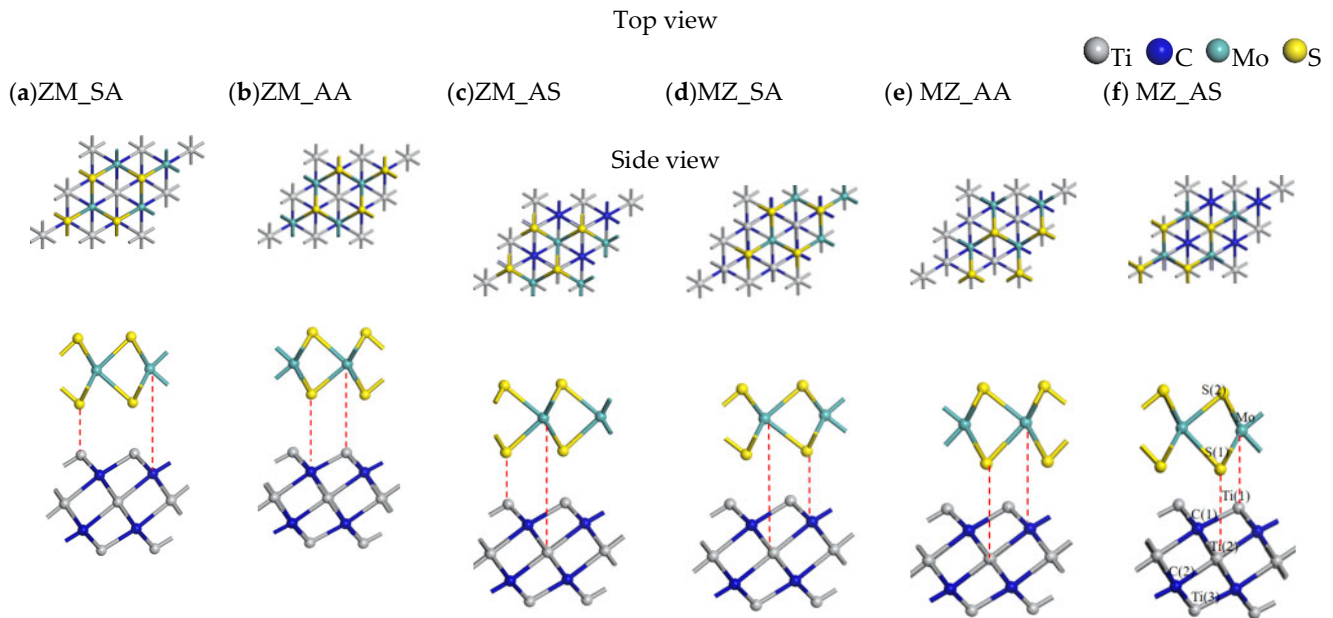
$$\varepsilon_y = (b - b_0) / b_0 \times 100\%$$

where  $a$  and  $a_0$  are the  $x$ -axis lattice constants in the presence and absence of strain, respectively; and  $b$  and  $b_0$  are the  $y$ -axis lattice constants in the presence and absence of strain, respectively [45]. In addition, positive (negative) values indicate tensile (compressive) strain. All heterostructure structures were relaxed.

### 3. Results and Discussions

#### 3.1. Structural Properties of the TMDs/ $Ti_3C_2$ Heterostructures

The lattice constants of our optimized  $MoS_2$ ,  $MoSe_2$ , and  $Ti_3C_2$  monolayers were 3.15 Å, 3.24 Å and 3.12 Å, respectively, which were in good agreement with the previous studies [46,47]. They all have a hexagonal crystal structure with a space group of  $P63/mmc$ , and they possess a lattice mismatch rate within a reasonable range of less than 4%, allowing the construction of heterostructures [48]. According to the high-symmetry stacking mode, there are six possible TMDs/ $Ti_3C_2$  configurations, taking  $MoS_2/Ti_3C_2$  heterostructures as an example, see Figure 1 (six high-symmetry  $MoSe_2/Ti_3C_2$  heterostructures, see Figure S1): (a) the ZM\_SA Configuration: S and Mo atoms of  $MoS_2$  are on top of Ti and C atoms of  $Ti_3C_2$ , respectively; (b) the ZM\_AA Configuration: S and Mo atoms of  $MoS_2$  are on top of C and Ti atoms of  $Ti_3C_2$ , respectively; (c) the ZM\_AS Configuration: S and Mo atoms of  $MoS_2$  are on top of Ti atoms and hollow sites of  $Ti_3C_2$ , respectively; (d) the MZ\_SA Configuration: S and Mo atoms of  $MoS_2$  are on top of C atoms and hollow sites of  $Ti_3C_2$ , respectively; (e) the MZ\_AA Configuration: Mo and S atoms of  $MoS_2$  are on top of C atoms and hollow sites of  $Ti_3C_2$ , respectively; (f) the MZ\_AS Configuration: Mo and S atoms of  $MoS_2$  are on top of Ti atoms and hollow sites of  $Ti_3C_2$ , respectively.



**Figure 1.** A schematic diagram of top and side views of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures for different stackings. (a) the ZM\_SA Configuration; (b) the ZM\_AA Configuration; (c) the ZM\_AS Configuration; (d) the MZ\_SA Configuration; (e) the MZ\_AA Configuration; (f) the MZ\_AS Configuration.

Table 1 lists our calculated binding energies, interlayer distance, and bond lengths for the six possible stacking configurations of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures. It can be seen that the binding energies of these MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures were all negative, indicating that the formation of all the heterostructures was exothermic. A lower binding energy represents a more stable heterostructure structure. The ZM\_SA configuration of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> had the lowest binding energy of  $-1.79 \text{ meV/\AA}$ , so it was energetically the most stable configuration among the six configurations. It is noted that the interlayer distance  $d$  of the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure was very small (in the range of  $1.68 \text{ \AA}$  to  $2.47 \text{ \AA}$ ), which indirectly indicated a strong interaction between the layers [49,50]. Table 2 presents the binding energy of  $-1.03 \text{ meV/\AA}$  for the most stable configuration SA\_ZM of the MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure, while the AS\_ZM configuration had the maximum binding energy of  $-0.39 \text{ meV/\AA}$ . The binding energies of all six configurations were negative, indicating the stability of the MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure. The interlayer distance  $d$  of the six configurations of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures ranged from  $1.89 \text{ \AA}$  to  $2.56 \text{ \AA}$ , which was similar to that of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures.

**Table 1.** Binding energy ( $E_b$ ), interlayer distance ( $d$ ), Mo–S(1) minus Mo–S(2) constant ( $d_{12}$ ), and bond lengths Ti–C ( $d_{\text{Ti-C}}$ ) for MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures, respectively.

Configurations	$E_b(\text{meV/\AA}^2)$	$d(\text{\AA})$	$d_{12}(\text{\AA})$	$d_{\text{Ti(3)-C(2)}}(\text{\AA})$	$d_{\text{Ti(1)-C(1)}}(\text{\AA})$
(a) ZM_SA	−1.79	1.68	0.069	2.059	2.125
(b) ZM_AA	−1.21	1.69	0.078	2.057	2.152
(c) ZM_AS	−1.42	2.47	0.031	2.058	2.069
(d) MZ_SA	−1.27	2.03	0.109	2.055	2.094
(e) MZ_AA	−1.48	1.92	0.134	2.057	2.081
(f) MZ_AS	−1.55	2.46	0.021	2.063	2.067

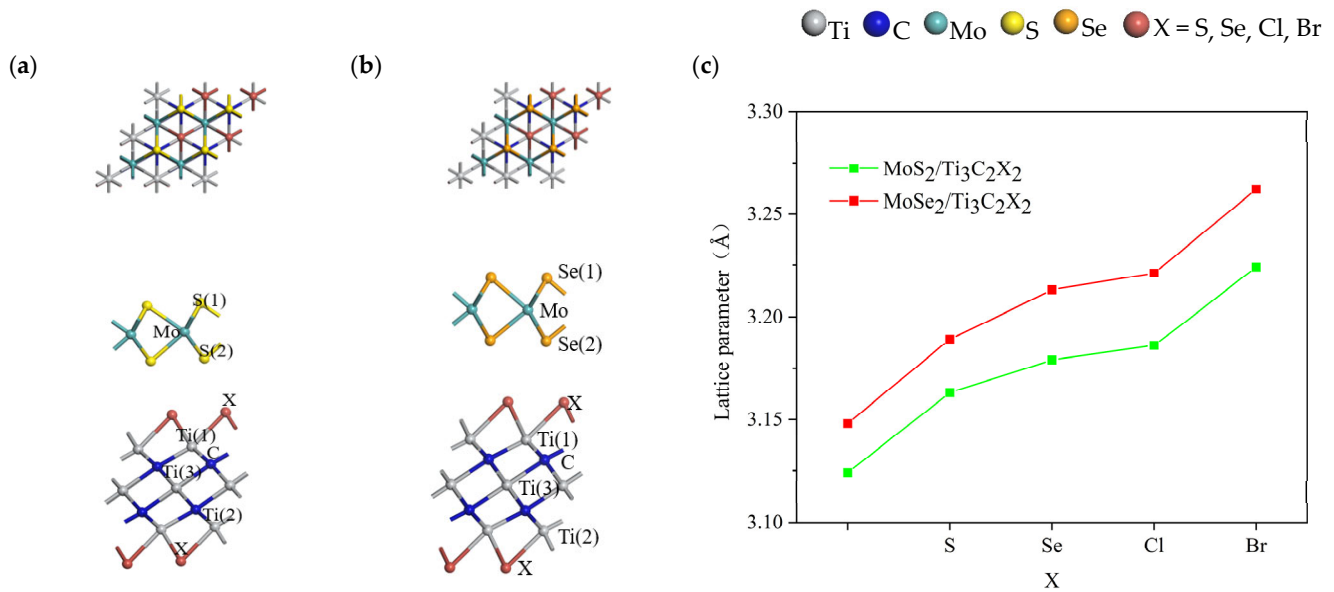
**Table 2.** Binding energy ( $E_b$ ), interlayer distance ( $d$ ), Mo–Se(1) minus Mo–Se(2) constant ( $d_{34}$ ), and bond lengths Ti–C ( $d_{\text{Ti-C}}$ ) for MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures, respectively.

Configurations	$E_b(\text{meV}\text{\AA}^2)$	$d(\text{\AA})$	$d_{34}(\text{\AA})$	$d_{\text{Ti(3)-C(2)}}(\text{\AA})$	$d_{\text{Ti(1)-C(1)}}(\text{\AA})$
(g) SA_ZM	−1.03	1.89	0.051	2.064	2.119
(h) AA_ZM	−1.01	2.56	0.013	2.071	2.073
(i) AS_ZM	−0.39	2.51	0.021	2.067	2.074
(j) SA_MZ	−0.76	2.12	0.101	2.061	2.096
(k) AA_MZ	−0.96	2.09	0.107	2.068	2.083
(m) AS_MZ	−0.59	2.01	0.063	2.069	2.122

A comparison of the data in Tables 1 and 2 showed that the binding energies of all these MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures were smaller than those of the corresponding MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures; meanwhile, MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> had a smaller interlayer distance than the MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures. These findings showed that the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures are more stable. We calculated the Ti–C bond length in the original monolayer Ti<sub>3</sub>C<sub>2</sub> as 2.057 Å. As shown in Tables 1 and 2, the Ti(3)–C(2) bond length  $d_{\text{Ti(3)-C(2)}}$  showed almost no change, but the Ti(1)–C(1) bond lengths of the upper layer of Ti<sub>3</sub>C<sub>2</sub> were stretched in the TMDs/Ti<sub>3</sub>C<sub>2</sub> heterostructures. The reason for this may be that the charge transfer from Ti<sub>3</sub>C<sub>2</sub> to TMDs leads to the stretching of the Ti(1)–C(1) bond. The Mo–S(1) minus Mo–S(2) value ( $d_{12}$ ) and Mo–Se(1) minus Mo–Se(2) value ( $d_{34}$ ) are also presented in Tables 1 and 2.  $d_{12}$  ranged from 0.021 Å to 0.134 Å, and  $d_{34}$  ranged from 0.013 Å to 0.107 Å, indicating that the TMDs/Ti<sub>3</sub>C<sub>2</sub> heterostructure slightly destabilizes the TMDs monolayer. Moreover, the  $d_{12}$  values in the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure were all greater than the  $d_{34}$  in the MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure, suggesting that the interlayer electron coupling effect of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> is greater than that of MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>. This conclusion was consistent with the results of our calculated interlayer distance and binding energy. We also noted that the binding energy and interlayer distance of the ZM\_SA configurations were the smallest, so the ZM\_SA configuration is the most stable configuration among the 12 configurations of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures and MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures considered here.

We also further investigated the effects of novel functional groups (S, Se, Cl, Br) on the structural properties of TMDs/Ti<sub>3</sub>C<sub>2</sub> heterostructures. Previous experimental studies [51] have shown that the Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = S, Se, Cl, Br) are the most stable when the surface functional groups of Ti<sub>3</sub>C<sub>2</sub> are located in the cavity centers of Ti atoms and aligned perpendicularly to the Ti atoms in the middle layer because of the site-blocked repulsion reaction between the C atoms and the surface functional groups. Therefore, in this work, when the surface of Ti<sub>3</sub>C<sub>2</sub> was terminated by functional groups (S, Se, Cl, Br) in MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> and MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> heterostructures, we focused on the case that the functional groups are located above the hole center of the Ti atom and perpendicular to the middle Ti atom, as shown in Figure 2a,b, respectively.

It can be clearly observed from Figure 2c that the lattice parameters of TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> heterostructures changed significantly due to the addition of surface functional groups. The lattice parameter of the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure was 3.124 Å. With the addition of each functional group, the lattice parameter obviously increased, and MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Br<sub>2</sub> had the maximum lattice parameter of 3.224 Å. The lattice parameter of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>S<sub>2</sub>, MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Se<sub>2</sub> and MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub> increased to 3.163 Å, 3.179 Å and 3.186 Å, respectively. Similarly, the lattice parameters of the MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure increased with the addition of functional groups. The lattice parameters of the MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure were 3.148 Å, while MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>S<sub>2</sub>, MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Se<sub>2</sub>, MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub>, and MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Br<sub>2</sub> were 3.189 Å, 3.213 Å, 3.221 Å, and 3.262 Å, respectively. Therefore, the surface functional groups had a significant effect on the structural properties of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> and MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub>.



**Figure 2.** Structural properties of TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> heterostructures. (a) Diagram of top and side views of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> heterostructures; (b) Diagram of top and side views of MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> heterostructures; (c) The lattice parameters of TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> heterostructures.

To further understand the stability of these TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> heterostructures, we calculated the binding energy, interlayer distance, and structural parameters of TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = S, Se, Cl, Br) as shown in Table 3. We provide the coordinates of the TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = S, Se, Cl, Br) optimized structure in the supplementary materials, see Table S1. The binding energies of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> and MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> were negative. The MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub> heterostructure possessed the highest binding energy (−3.12 meV/Å), while the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>S<sub>2</sub> heterostructure had the lowest binding energy (−8.44 meV/Å), indicating that the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>S<sub>2</sub> heterostructure was more stable. The interlayer distance of these heterostructures varied from 2.78 Å to 3.14 Å, which was significantly larger than that of the TMDs/Ti<sub>3</sub>C<sub>2</sub> heterostructure, and a larger interlayer distance indicated a weaker electronic coupling between the monolayer TMDs and Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub>. It can be concluded that MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> and MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> are typical van der Waals heterostructures.

**Table 3.** Binding energy ( $E_b$ ), interlayer distance ( $d$ ), Mo–S(1) minus Mo–S(2) or Mo–Se(1) minus Mo–Se(2) constant ( $d_{56}$ ), and bond lengths Ti–X  $d_{Ti-X}$  and Ti–C  $d_{Ti-C}$  for TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = S, Se, Br, Cl) heterostructures, respectively.

Configurations	$E_b(\text{meV}\text{\AA}^2)$	$d(\text{\AA})$	$d_{56}(\text{\AA})$	$d_{Ti(1)-C}(\text{\AA})$	$d_{Ti(2)-X}(\text{\AA})$	$d_{Ti(1)-X}(\text{\AA})$
MoS <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> S <sub>2</sub>	−8.44	2.83	0.009	2.182	2.397	2.389
MoS <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> Se <sub>2</sub>	−3.95	2.78	0.007	2.146	2.520	2.496
MoS <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> Cl <sub>2</sub>	−3.17	3.02	0.003	2.104	2.503	2.492
MoS <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> Br <sub>2</sub>	−8.42	3.07	0.004	2.117	2.626	2.621
MoSe <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> S <sub>2</sub>	−3.55	3.03	0.003	2.193	2.501	2.403
MoSe <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> Se <sub>2</sub>	−4.82	3.00	0.000	2.170	2.628	2.542
MoSe <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> Cl <sub>2</sub>	−3.12	3.14	0.003	2.120	2.509	2.506
MoSe <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> Br <sub>2</sub>	−8.41	2.99	0.001	2.127	2.638	2.617

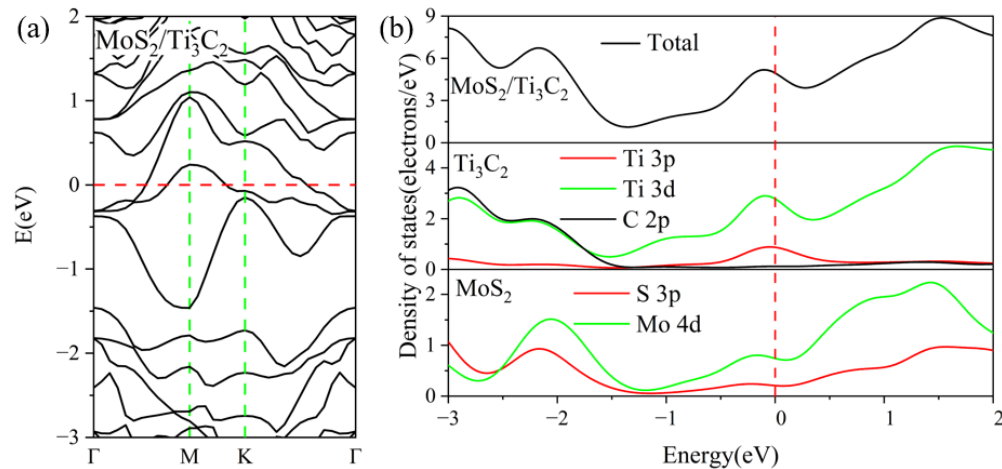
It can also be seen from Table 3 that in MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> and MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub>, the surface functional group of monolayer Ti<sub>3</sub>C<sub>2</sub> caused an increase in the Ti–C bond length ( $d_{Ti-C}$ ). Among them, the  $d_{Ti-C}$  of the MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>S<sub>2</sub> heterostructure reached 2.193 Å, an increase of 0.136 Å from the original 2.057 Å. The Ti–C bond length  $d_{Ti-C}$  of the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub>

heterostructure increased by 0.047 Å. The bond lengths between Ti(1) and X in the top layer of  $\text{Ti}_3\text{C}_2\text{X}_2$  were almost the same as those between Ti(2) and X in the bottom layer of  $\text{Ti}_3\text{C}_2\text{X}_2$ , which means that the stacking of  $\text{MoS}_2$  and  $\text{MoSe}_2$  in these heterostructures hardly changes the spatial structure of  $\text{Ti}_3\text{C}_2\text{X}_2$ . The strong coupling between the  $\text{Ti}_3\text{C}_2$  and TMD interface was weakened by the functional group (S, Se, Cl, Br). The value of  $d_{56}$  was defined as Mo–Se(1) minus Mo–Se(2) or Mo–S(1) minus Mo–S(2) in TMDs/ $\text{Ti}_3\text{C}_2\text{X}_2$  (X = S, Se, Cl, Br). The  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{S}_2$  heterostructure possessed the maximum  $d_{56}$  (0.009 Å), while  $d_{56}$  was zero in the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Se}_2$  heterostructure, indicating that the spatial structure and two-dimensional properties of the original  $\text{MoSe}_2$  were well preserved. The above results show that the addition of surface functional groups can seriously weaken the electronic coupling between the monolayer TMDs and  $\text{Ti}_3\text{C}_2$ .

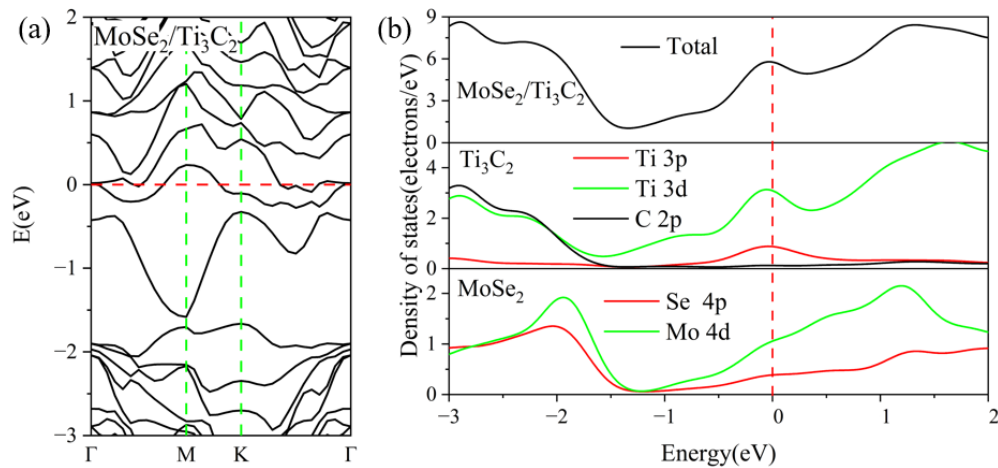
### 3.2. Electronic Properties of the TMDs/ $\text{Ti}_3\text{C}_2\text{X}_2$ Heterostructures

To investigate the electronic properties of the TMDs/ $\text{Ti}_3\text{C}_2$  heterostructures, we choose the most stable configurations of ZM\_SA and SA\_ZM to further study the electronic properties of  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{X}_2$  and  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{X}_2$ , respectively. The energy band structures and density of states of the  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  heterostructure are presented in Figure 3. The Fermi energy level is set at zero energy. From Figure 3a, it can be seen that some energy bands cross the Fermi energy level, indicating the metallic nature of the  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  heterostructure. Because of a strongly coupled interaction between the  $\text{MoS}_2$  and  $\text{Ti}_3\text{C}_2$  monolayer, the energy bands have been hybridized severely. The total and partial density of states of the  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  heterostructure is shown in Figure 3b; it can be seen that the energy band near the Fermi level is mainly dominated by the 3d orbit of the Ti atom and the 4d orbit of the Mo atom. Remarkably, the electrons of the S 3p orbit in the conduction band are unusually more than that of the Ti 3p orbit. Therefore, the conduction band is mainly contributed by the Mo 4d, S 3p, and Ti 3d orbitals. The energy band structures and density of states of the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure are presented in Figure 4. We note that the energy band of the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure (see Figure 4a) has no obvious hybridization around the Fermi level, which is different from the  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  heterostructure. Compared with  $\text{MoS}_2/\text{Ti}_3\text{C}_2$ ,  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  has more concentrated energy bands, leading to a decrease in conductivity. The total and partial density of states of the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure is shown in Figure 4b; we know that the energy bands near the Fermi energy level are dominated by Ti 3d and Mo 4d orbitals. The Ti 3p orbital and C 2p orbital make a slight contribution near the Fermi energy level. The conduction band is mainly formed by Ti 3d and Mo 4d orbitals, while the valence band is formed by C 2p, Ti 3d, and Mo 4d orbitals, and the C 2p orbital plays a dominant role in the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure. Finally, by comparing the density of states of  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  with that of the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure, we find that the peak of Ti 3d and Mo 4d in the  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  heterostructure moves towards a higher energy level.





**Figure 3.** (a) the band structure, and (b) the total and partial density of states of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>. The Fermi level is set to 0 eV.



**Figure 4.** (a) the band structure, and (b) the total and partial density of states of MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>. The Fermi level is set to 0 eV.

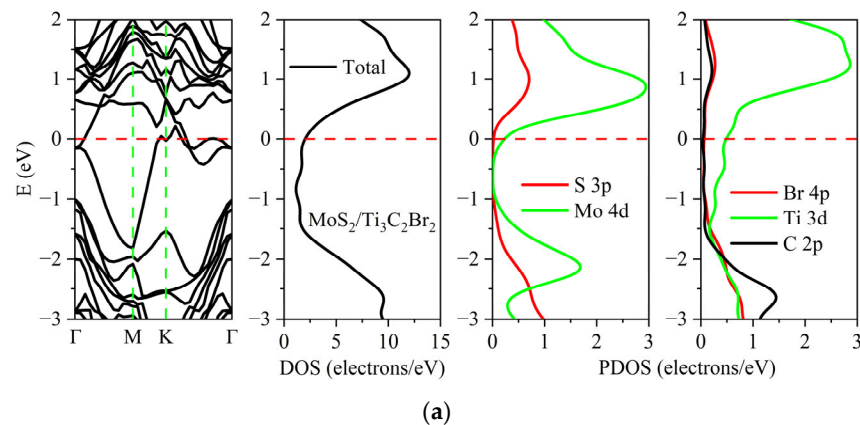
It is well known that both MoS<sub>2</sub> and MoSe<sub>2</sub> are semiconductors in nature and exhibit a direct band gap at the K point in the Brillouin zone [52]. However, our calculations show that the S 3p orbitals, the Se 4p orbitals, and the Mo 4d orbitals in the TMDs/Ti<sub>3</sub>C<sub>2</sub> heterostructure have a large number of electrons crossing the Fermi energy level, which is sufficient to indicate that Ti<sub>3</sub>C<sub>2</sub> induces a significant change in the electronic properties of the TMDs monolayer.

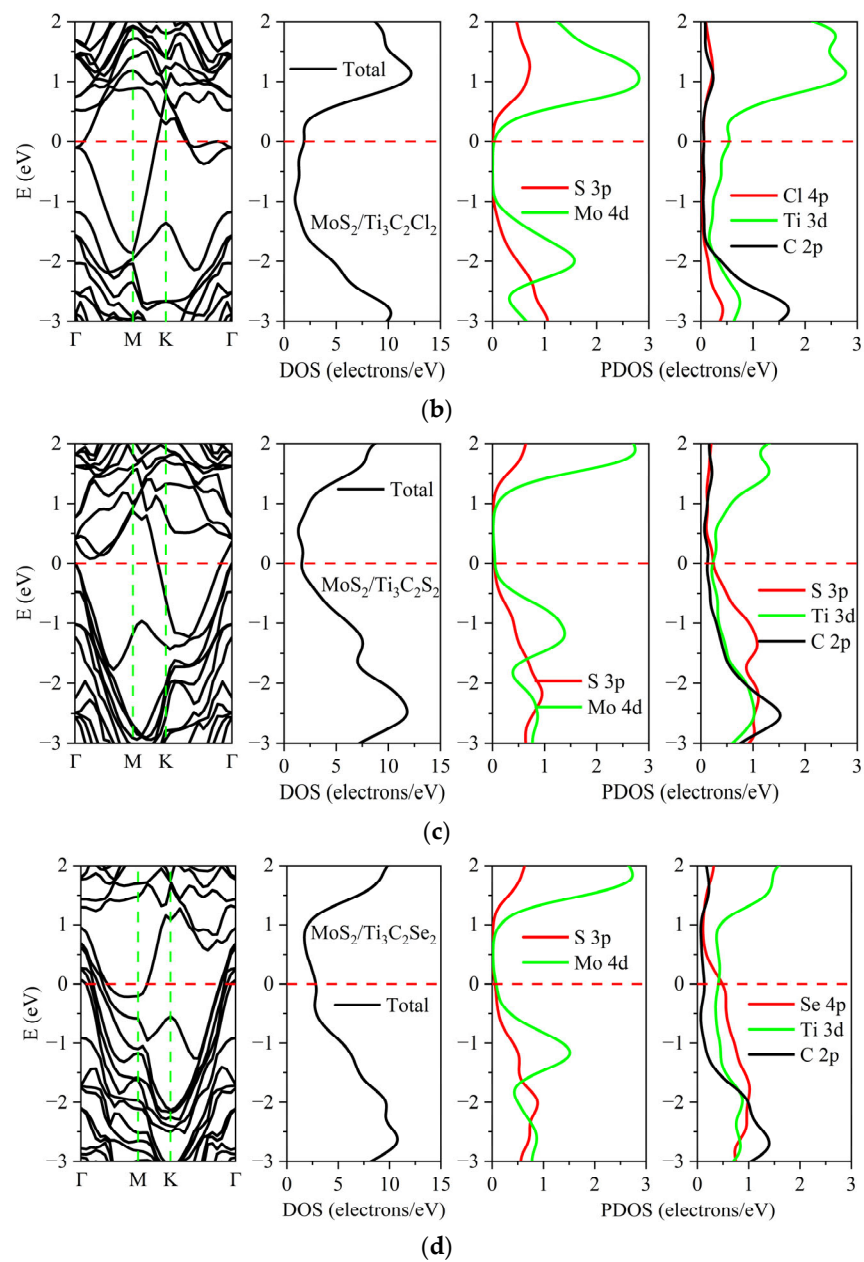
To further understand the electronic properties, the Mulliken charge and bond populations of TMDs/Ti<sub>3</sub>C<sub>2</sub> were calculated; see Tables S2 and S3. The interlayer electron coupling of the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure is strong due to the overlap of electron clouds between MoS<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub> (the bond population of the S–Ti bond is 0.48 Å). The Ti<sub>3</sub>C<sub>2</sub> in the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure obtains 0.06 *e* from the upper MoS<sub>2</sub> layer, and the Ti atom in Ti<sub>3</sub>C<sub>2</sub> loses 1.55 *e*, and 1.50 *e* of Ti is transferred to the C atom. The bonding behavior of the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure is covalent in nature, as indicated by the bond populations. For MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>, the bond population of the Se–Ti bond has a large negative value (−0.83 Å), suggesting a weak van der Waals interaction between MoSe<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub>. According to the positive and negative values of the bond population, we can conclude that the bonding behavior in the MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure is a combination of covalent and ionic bonds.

The Mulliken charge analysis shows that more electrons are transferring from Ti<sub>3</sub>C<sub>2</sub> to MoS<sub>2</sub> in the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure. We also noted that the Mo atom in MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>

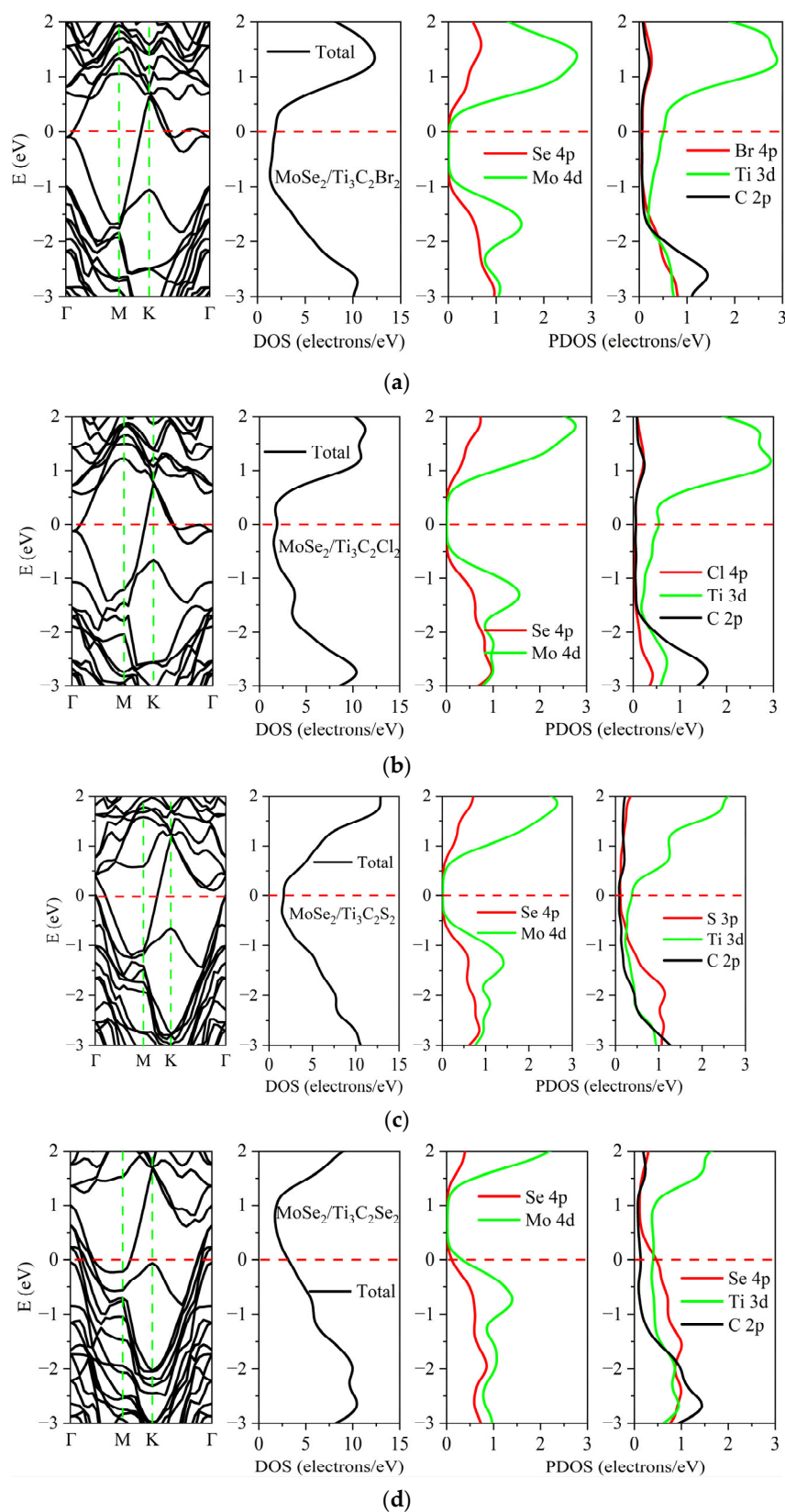
and  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  obtains  $0.35e$  and  $0.01e$ , respectively. Moreover, the partial density of states in Figures 3b and 4b shows that the density of the electrons of the Mo  $4d$  orbital in the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure at the Fermi energy level is much higher than that in the  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  heterostructure. As a result, the Mo  $4d$  orbital in  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  obtains more electrons from other atoms than that in  $\text{MoS}_2/\text{Ti}_3\text{C}_2$ .

The electronic properties of these heterostructures were affected by the surface termination atoms of  $\text{Ti}_3\text{C}_2$ , as illustrated in Figures 5 and 6. Compared with  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  and  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$ , the electronic properties of  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{X}_2$  and  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{X}_2$  were obviously different. Although TMDs/ $\text{Ti}_3\text{C}_2\text{X}_2$  heterostructures still exhibited metallic behavior, the peak values of density of states (DOS) at the Fermi level were lower than those of TMDs/ $\text{Ti}_3\text{C}_2$  heterostructures. Based on our calculated DOS, it is worth noting that  $\text{MoS}_2$  and  $\text{MoSe}_2$  retained the semiconductor nature in the TMDs/ $\text{Ti}_3\text{C}_2\text{X}_2$  heterostructures. This means that the presence of surface functional groups (Cl, Br, S, Se) weakened the interaction strength between TMDs and  $\text{Ti}_3\text{C}_2$ . Compared with the DOS of the original monolayer  $\text{MoS}_2$  and  $\text{MoSe}_2$ , see Figures S2 and S3, that of  $\text{MoS}_2$  and  $\text{MoSe}_2$  in  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{Br}_2$  and  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{Cl}_2$  showed an upward shift of the Fermi energy level. From the partial density of states (PDOS) of  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{Br}_2$  and  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{Cl}_2$ , it can be seen that the energy band near the Fermi level was mainly contributed to by the Ti  $3d$  orbit. The Mo atom  $4d$  orbital in  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{Br}_2$  made a small charge contribution, while the Mo atom  $4d$  orbital in  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{Cl}_2$  made almost no charge contribution to the Fermi level. In addition, the atoms of the functional groups Cl and Br made almost no contribution near the Fermi level, as shown in Figure 5a,b. When the  $\text{Ti}_3\text{C}_2$  surface was terminated by S and Se functional groups, the DOS of  $\text{MoS}_2$  and  $\text{MoSe}_2$  showed a downward shift of the Fermi level, while the S  $3p$  and Se  $4p$  orbitals made an obvious charge contribution near the Fermi level. The energy band near the Fermi level became flatter, and the effective mass of the electron was larger, so the conductivity decreased. It can be seen from the density of states of  $\text{Ti}_3\text{C}_2\text{X}_2$  ( $X = \text{S}, \text{Se}$ ) that the S  $3p$  and Se  $4p$  orbital charges and Ti  $3d$  orbital generated strong hybridization, respectively, as shown in Figure 5c,d. The metal behavior of the  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{X}_2$  ( $X = \text{Br}, \text{Cl}, \text{S}, \text{Se}$ ) heterostructure was mainly dominated by the Ti  $3d$  orbital charge.





**Figure 5.** Band structures and densities of states of the  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  heterostructure with different terminated groups: (a) -Br, (b) -Cl, (c) -S and (d) -Se. The Fermi level is set to 0 eV. The vertical dashed line gives the location of the Fermi level. The red line represents the Fermi level. The green line represents the high symmetry point of the Brillouin zone.

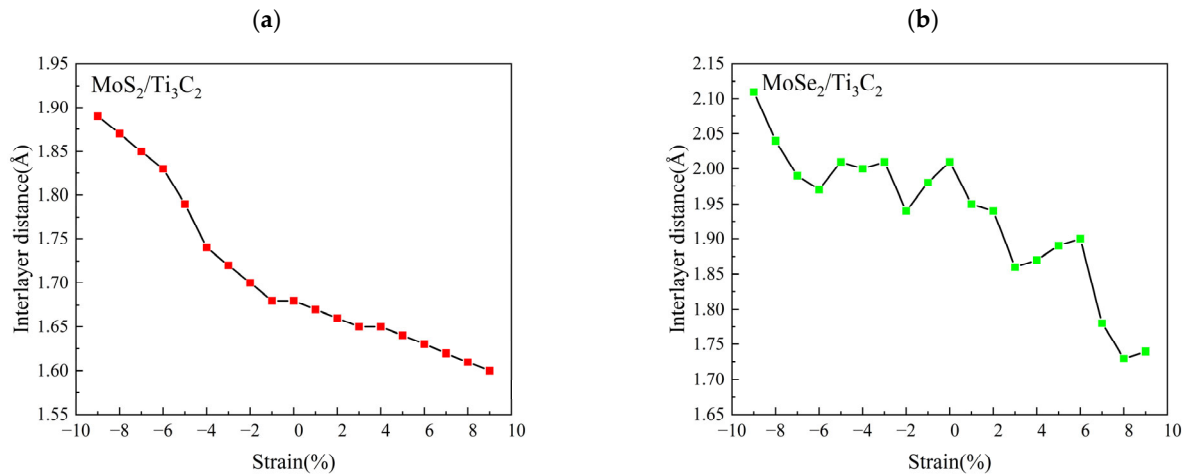


**Figure 6.** Band structures and densities of states of the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure with different terminated groups: (a) -Br, (b) -Cl, (c) -S and (d) -Se. The Fermi level is set to 0 eV. The vertical dashed line gives the location of the Fermi level.

Figure 6a shows the energy band and density of states of the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Br}_2$  heterostructure. The bottom of the conduction band of  $\text{MoSe}_2$  moved downward and coincides with the Fermi level. At the Fermi energy level, only the Ti 3d orbital charge contributed. For  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Cl}_2$  and  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{S}_2$ , as shown in Figure 6b,c, the Fermi energy level was located between the top of the valence band and the bottom of the conduction band. The Ti 3d orbital dominated the metal properties of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Cl}_2$  and  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{S}_2$ . For  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Se}_2$ , as shown in Figure 6d, the energy band structure of  $\text{MoSe}_2$  remained unchanged, and the Fermi level was located at the top of the valence band. The Se 4p and Ti 3d orbitals in  $\text{Ti}_3\text{C}_2\text{Se}_2$  generate strong hybridization, which dominated the conductivity of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Se}_2$ . Moreover, the PDOS of  $\text{MoSe}_2$  and  $\text{MoS}_2$  showed that both S 3p orbitals in  $\text{MoS}_2$  and Se 4p orbitals in  $\text{MoSe}_2$  made no charge contribution at the Fermi energy level. When S and Se were used as the functional group terminal in  $\text{Ti}_3\text{C}_2$ , the S 3p and Se 4p orbital charges played a leading role in the Fermi energy level.

### 3.3. Effect of Biaxial Strain on the Structural and Electronic Properties of the TMDs/ $\text{Ti}_3\text{C}_2$ Heterostructures

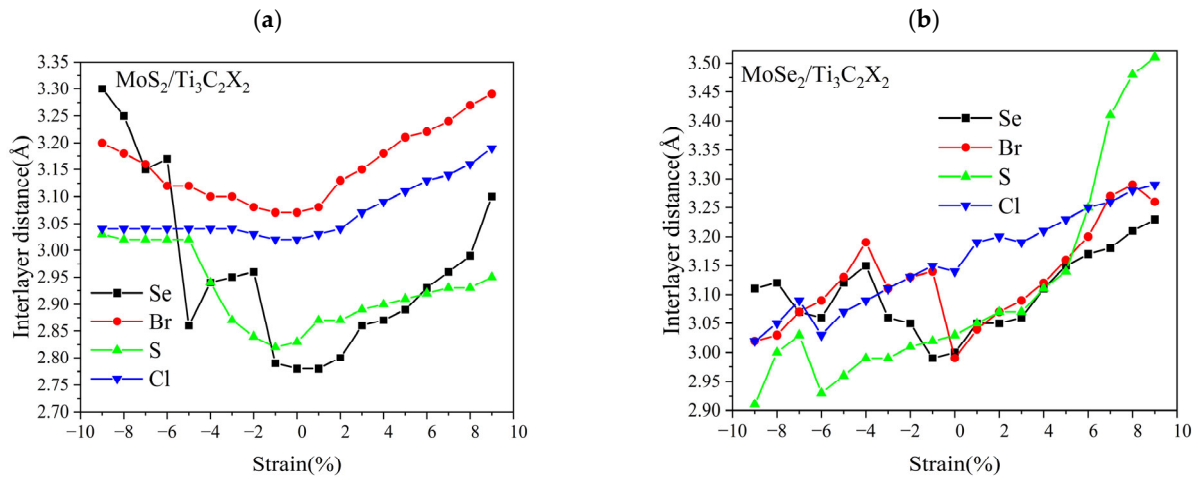
Strain can be used to tune the electronic properties of two-dimensional materials [53,54]. Here, we systematically investigated the effect of biaxial strain on the structural and electronic properties of TMDs/ $\text{Ti}_3\text{C}_2$  and TMDs/ $\text{Ti}_3\text{C}_2\text{X}_2$ . Considering a series of biaxial tensile or compressive strains  $\varepsilon$  in 0.01 steps from  $-9\%$  to  $+9\%$ ,  $\varepsilon > 0$  and  $\varepsilon < 0$  represented the tensile and compressive strains, respectively. Figure 7a shows the variation curve of the  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  interlayer distance with biaxial tensile (compressive) strain. It can be seen that the interlayer distance  $d$  of the  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  heterostructure varies linearly with an increasing biaxial tensile or compressive strain. The interlayer distance of  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  decreases to  $1.56 \text{ \AA}$  when the biaxial tensile strain reaches  $9\%$ . Therefore, the biaxial tensile strain can enhance the electronic coupling strength between the monolayer  $\text{MoS}_2$  and  $\text{Ti}_3\text{C}_2$ . However, its interlayer distance gradually increases when subjected to biaxial compressive strain, and the interlayer distance increased to  $1.89 \text{ \AA}$  at  $9\%$  compressive strain, indicating that the electron coupling strength between the monolayer  $\text{MoS}_2$  and  $\text{Ti}_3\text{C}_2$  is severely weakened by the biaxial compressive strain. Figure 7b presents the variation curve of the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  interlayer distance with the biaxial tensile (compressive) strain. The result is completely different to that of the  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  heterostructure. The interlayer distance of the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure shows a fluctuating change with an increasing biaxial tensile or compressive strain. Based on the above Mulliken charge and bond populations analysis of  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  and  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$ , it can be seen that the bond population of S–Ti in  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  is positive, while that of Se–Ti in  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  is negative. Therefore, the reason may be that the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure has van der Waals interactions rather than strong electron coupling interactions.



**Figure 7.** (a) Relationship curve between MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> interlayer distance and biaxial strain, (b) Relationship curve between MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> interlayer distance and biaxial strain.

We further investigated the effect of the biaxial tensile and compressive strain on the interlayer distance  $d$  of TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> heterostructures; see Figure 8. It can be seen that under the condition of the applied strain, the interlayer distance of TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> heterostructures presents a completely different behavior to that of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>. The reason is the different electronic coupling strength between the monolayer TMDs and Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> due to the surface functional groups. The interlayer distance between MoS<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub> remains almost unchanged under the compressive strain, while it increases slightly with the increase in the tensile strain, as shown in Figure 8a. The interlayer distance of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Se<sub>2</sub> heterostructures presents a steady increase under tensile strain. When the compressive strain is in the range from 0 to 5%, its interlayer distance rapidly increases; when the compressive strain is above 5%, its interlayer distance is almost unchanged. For the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Br<sub>2</sub> heterostructure, under the condition of compressive or tensile strain, the coupling strength between valence electrons of Br atoms and the 4*d* orbital of Mo atoms is weakened. As a result, the interlayer distance between MoS<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub>Br<sub>2</sub> increases slightly with the increase in the applied strain. Compared with MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = S, Br, Cl), the interlayer distance of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Se<sub>2</sub> presents a significantly fluctuating change in the case of compressive strain. The reason may be that the Se atom induces the aberration of a crystal lattice due to its larger atomic radii [35]. When the compressive strain is applied, the lattice distortion becomes more pronounced, resulting in the fluctuation of the interlayer distance. For MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = S, Se, Cl, Br), we also observed a similar trend under the condition of compressive strain; see Figure 8b. Therefore, we concluded that the fluctuation in the interlayer distance in MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = Se) and MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> is mainly attributed to the existence of the Se atom, and the displacement of the Se atom affects the structural stability of these heterostructures.





**Figure 8.** (a) Relationship curve between  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{X}_2$  (X = Se, Br, S, Cl) interlayer distance and biaxial strain, (b) Relationship curve between  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{X}_2$  (X = Se, Br, S, Cl) interlayer distance and biaxial strain.

Figure 8b shows that the interlayer distance of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{X}_2$  dramatically increases with the increase in the tensile strain, and the interlayer distances of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Se}_2$  and  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Br}_2$  at 9% tensile strain increase to 3.23 Å and 3.26 Å, respectively. Under the compressive strain, their interlayer distance increases nonlinearly. Therefore, the applied strain weakened the interlayer interaction between  $\text{MoSe}_2$  and  $\text{Ti}_3\text{C}_2\text{X}_2$  (X = Se, Br). For  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{S}_2$  and  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Cl}_2$ , their interlayer distance presents the same trend under the applied strain. Under the tensile strain, the interlayer distance increases, while under the compressive strain, the interlayer distance becomes increasingly smaller. Moreover, the interlayer distance of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{S}_2$  is more sensitive to the applied strain than that of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Cl}_2$ . It is noted that the interlayer distance of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{S}_2$  increased to 3.52 Å at 9% tensile strain, in contrast; its interlayer distance decreased to 2.91 Å at 9% compressive strain.

To explore the effect of biaxial strain on the electronic properties of TMDs/ $\text{Ti}_3\text{C}_2$  heterostructures, we first investigated the Mulliken charge of TMD/ $\text{Ti}_3\text{C}_2$  heterostructure under tensile and compressive strain. Table 4 shows the Mulliken charge population of  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  heterostructures, at free strain,  $\text{Ti}_3\text{C}_2$  loses  $0.07e$ , which is transferred to the monolayer  $\text{MoS}_2$ . At a tensile strain of 9%,  $\text{Ti}_3\text{C}_2$  loses more electrons ( $0.11e$ ). Moreover, Mo atoms also lose 0.05 electrons when subjected to tensile strain. At a compressive strain of 9%,  $\text{Ti}_3\text{C}_2$  loses fewer electrons ( $0.03e$ ). Table 5 shows the Mulliken charge population of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructures. At a compressive strain of 9%,  $\text{MoSe}_2$  loses more electrons ( $0.08e$ ), which are transferred to  $\text{Ti}_3\text{C}_2$ . These results showed that the interlayer electron transfer in both  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  and  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  can be well regulated by biaxial strain. The difference is that in the  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  heterostructure the electrons are transferred from  $\text{Ti}_3\text{C}_2$  to  $\text{MoS}_2$ , while in the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure, the electrons are transferred from  $\text{MoSe}_2$  to  $\text{Ti}_3\text{C}_2$ . Moreover, in the  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  heterostructure the transferring electrons increase with increasing tensile strain, while in the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure, they increase with increasing compressive strain.

**Table 4.** Mulliken charge (electron) of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>.

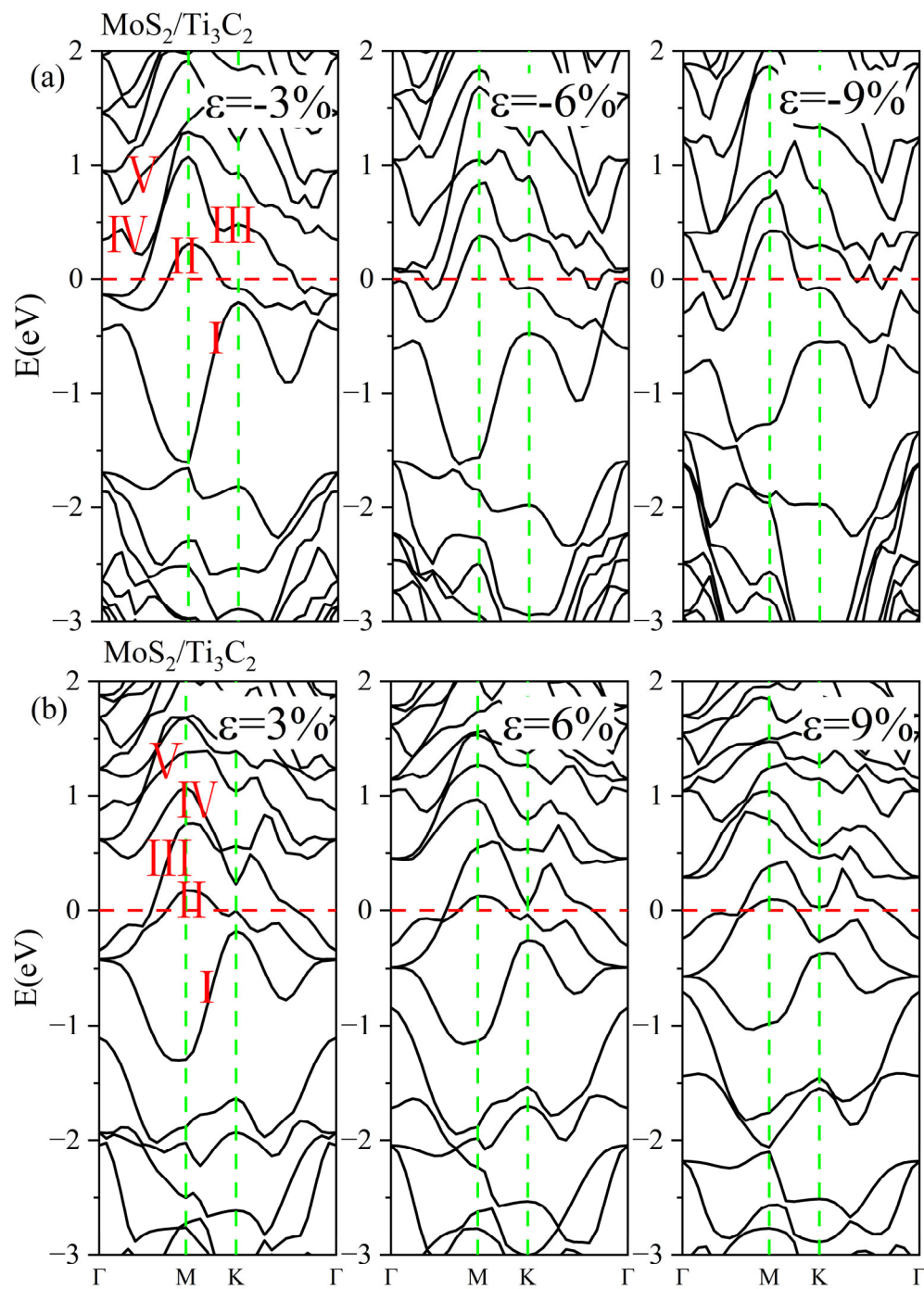
Species	Ion	Total	Charge	Total	Charge	Total	Charge
		Compressive 9%		Strain Free		Tensile 9%	
C	1	4.70	−0.70	4.75	−0.75	4.78	−0.78
C	2	4.69	−0.69	4.71	−0.71	4.71	−0.71
S	1	5.94	0.06	5.98	0.02	6.05	−0.05
S	2	6.01	−0.01	6.06	−0.06	6.11	−0.11
Ti	1	11.24	0.76	11.25	0.75	11.34	0.66
Ti	2	11.62	0.38	11.59	0.41	11.57	0.43
Ti	3	11.72	0.28	11.63	0.37	11.49	0.51
Mo	1	14.08	−0.08	14.03	−0.03	13.95	0.05

**Table 5.** Mulliken charge (electron) of MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>.

Species	Ion	Total	Charge	Total	Charge	Total	Charge
		Compressive 9%		Strain Free		Tensile 9%	
C	1	4.69	−0.69	4.71	−0.71	4.71	−0.71
C	2	4.70	−0.70	4.75	−0.75	4.78	−0.78
Se	1	5.87	0.13	5.86	0.14	5.90	0.10
Se	2	5.68	0.32	5.77	0.23	5.74	0.26
Ti	1	11.27	0.73	11.27	0.73	11.36	0.64
Ti	2	11.71	0.29	11.62	0.38	11.49	0.51
Ti	3	11.71	0.29	11.67	0.33	11.69	0.31
Mo	1	14.37	−0.37	14.35	−0.35	14.33	−0.33

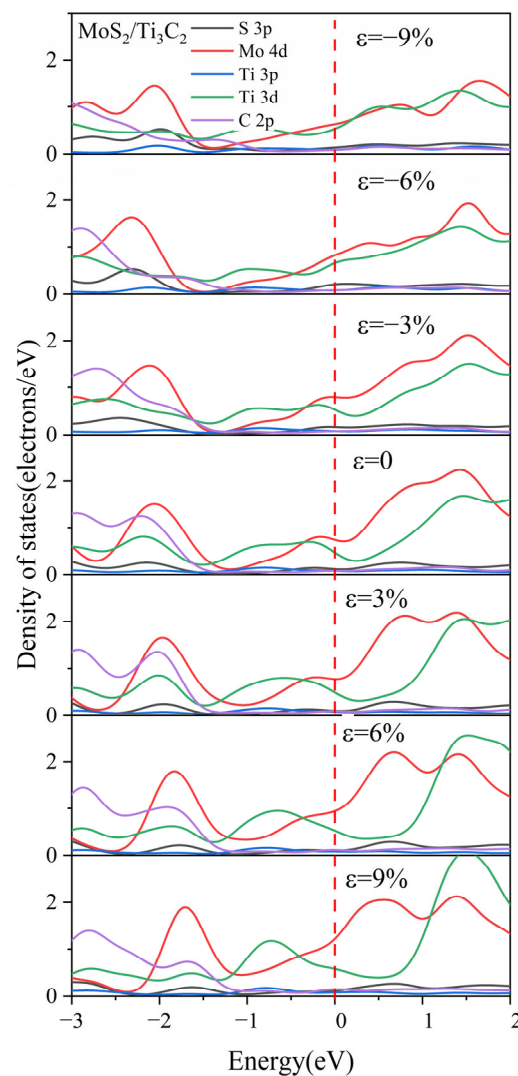
To further investigate the effect of biaxial strain on the electronic properties of TMDs/Ti<sub>3</sub>C<sub>2</sub> heterostructures, we calculated their energy band structures and density of states under different strains. Figure 9a presents the energy band structures of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures under compressive strain. As the compressive strain increased, the valence band I moved down and away from the Fermi energy level, and it became flatter and flatter. The energy bands II and III at the  $\Gamma$  point were split, and the energy band II became more dispersed. Moreover, the energy bands III and IV were combined, and then they moved away from the Fermi energy level with increasing compressive strain. Figure 9b shows the energy band structures of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures under tensile strain. It can be seen that the increase in the tensile strain caused the valence bands I, II, and III to move away from the Fermi energy level and become flatter. Moreover, the conduction bands IV and V moved toward the Fermi energy level, and they showed more hybridization, resulting in an increase in the conductivity of the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure [55].





**Figure 9.** (a) Energy band structures of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure under different compress strains. (b) Energy band structures of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure under different tensile strains. The Fermi level is set to 0 eV. The red line represents the Fermi level. The green line represents the high symmetry point of the Brillouin zone. I/II/III/IV/V represents different energy bands.

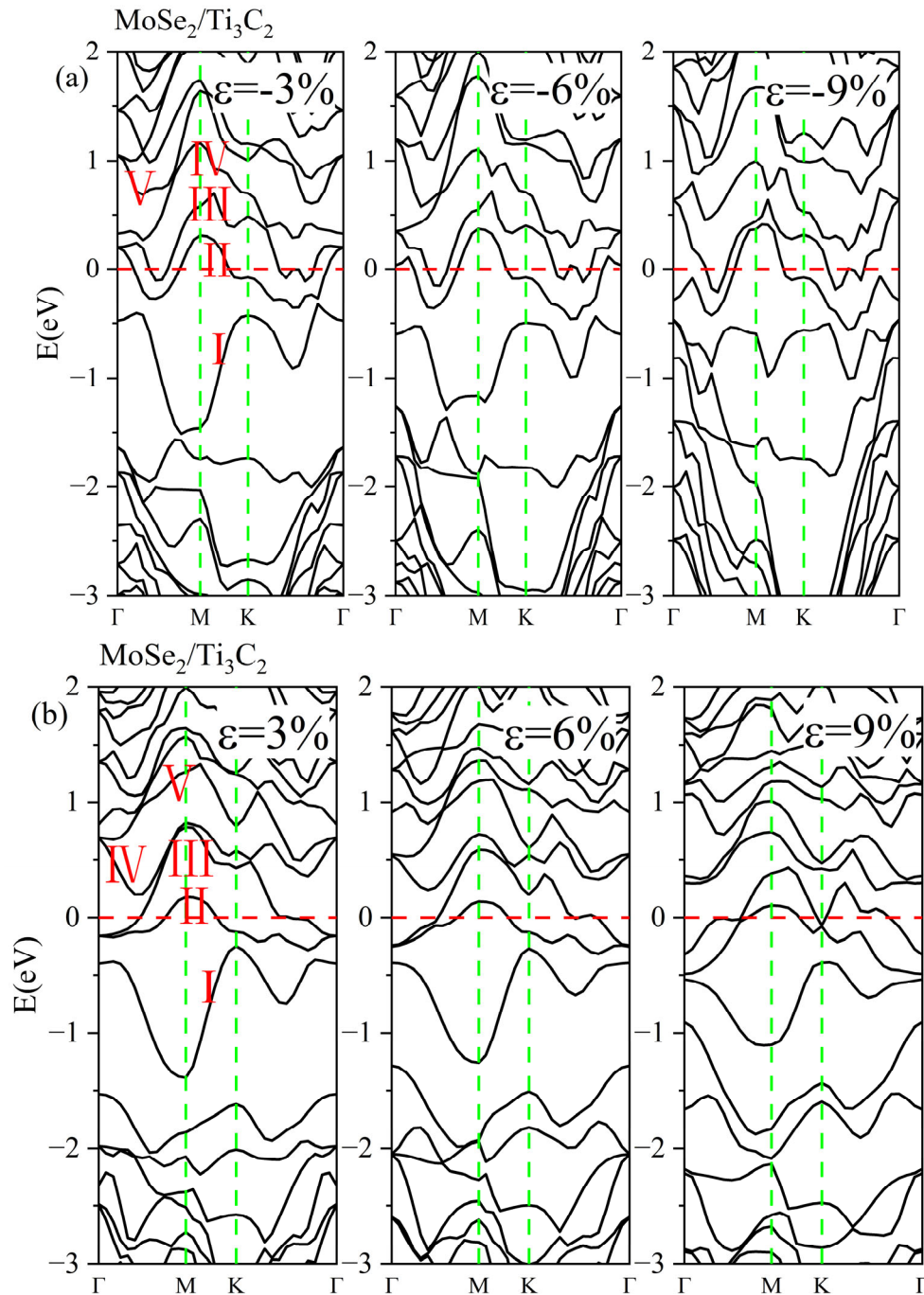
Figure 10 shows the DOS of the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure under different biaxial strains. It was obvious that the Fermi energy level was dominated by Mo 4*d* and Ti 3*d* orbitals. Moreover, the contribution of the Mo 4*d* orbital to the conduction band lessened with increasing compressive strain, while the contribution of Mo 4*d* and Ti 3*d* orbitals to the valence band increased with the increasing tensile strain. It can also be seen that the peak value of Ti atoms in the range of the conduction band increased with increasing tensile strain, while the peak value of Mo atoms remained almost unchanged with increasing tensile strain. The peak value of Mo atoms in the range of the valence band increased with the tensile strain and moved toward the Fermi energy level. Based on our calculated DOS of the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure, the interlayer interaction between the monolayer MoS<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub> presented different behavior under tensile and compressive strain, and the interaction strength was strengthened under tensile strain, but weakened under compressive strain.



**Figure 10.** The partial density of states (PDOS) of MoS<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub> for the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure with different biaxial strains. The Fermi level is set to 0 eV.

Figure 11a gives the energy band structures of the MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure under different compressive strains. With increasing compressive strain, the conduction bands III and IV gradually merged at the  $\Gamma$  point and moved away from the Fermi level. The valence band I become flatter, while the valence band II crossing the Fermi level became

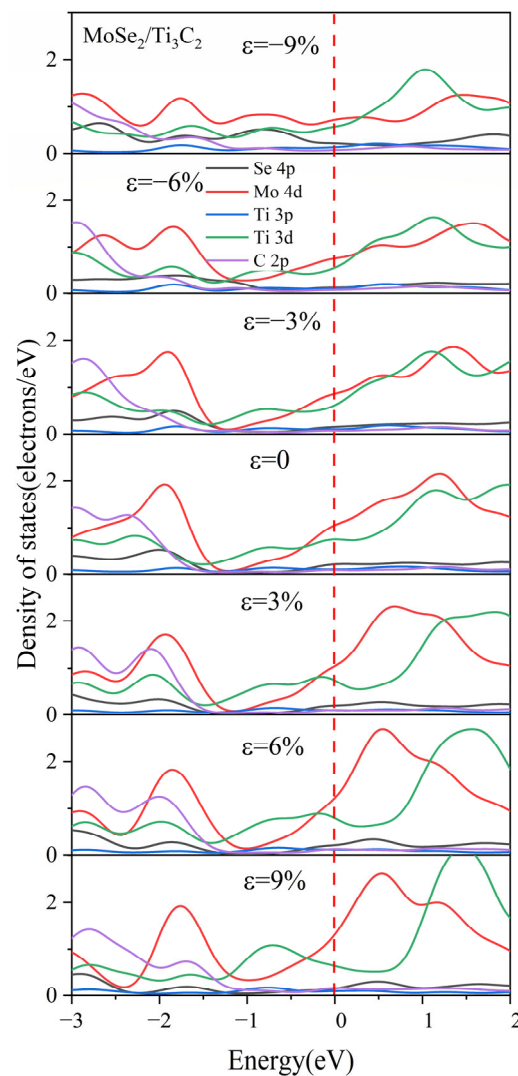
more tortuous, indicating a decrease in conductivity. Figure 11b displays the energy band structures of the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure under different tensile strains. As the tensile strain increased, the energy bands II and III were split at the  $\Gamma$  point, and the energy bands IV and V showed more hybridization. Moreover, the energy bands crossing the Fermi energy level became more dispersed under tensile strain, inducing an increase in conductivity. We also noted that the pseudogap of the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure disappeared with increasing compressive or tensile strain. Therefore, the applied strain can effectively tune the electronic properties of the TMDs/ $\text{Ti}_3\text{C}_2$  heterostructures.



**Figure 11.** (a) Energy band structures of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure under different compressive strains. (b) Energy band structures of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure under different tensile strains.

The Fermi level is set to 0 eV. The red line represents the Fermi level. The green line represents the high symmetry point of the Brillouin zone. I/II/III/IV/V represents different energy bands.

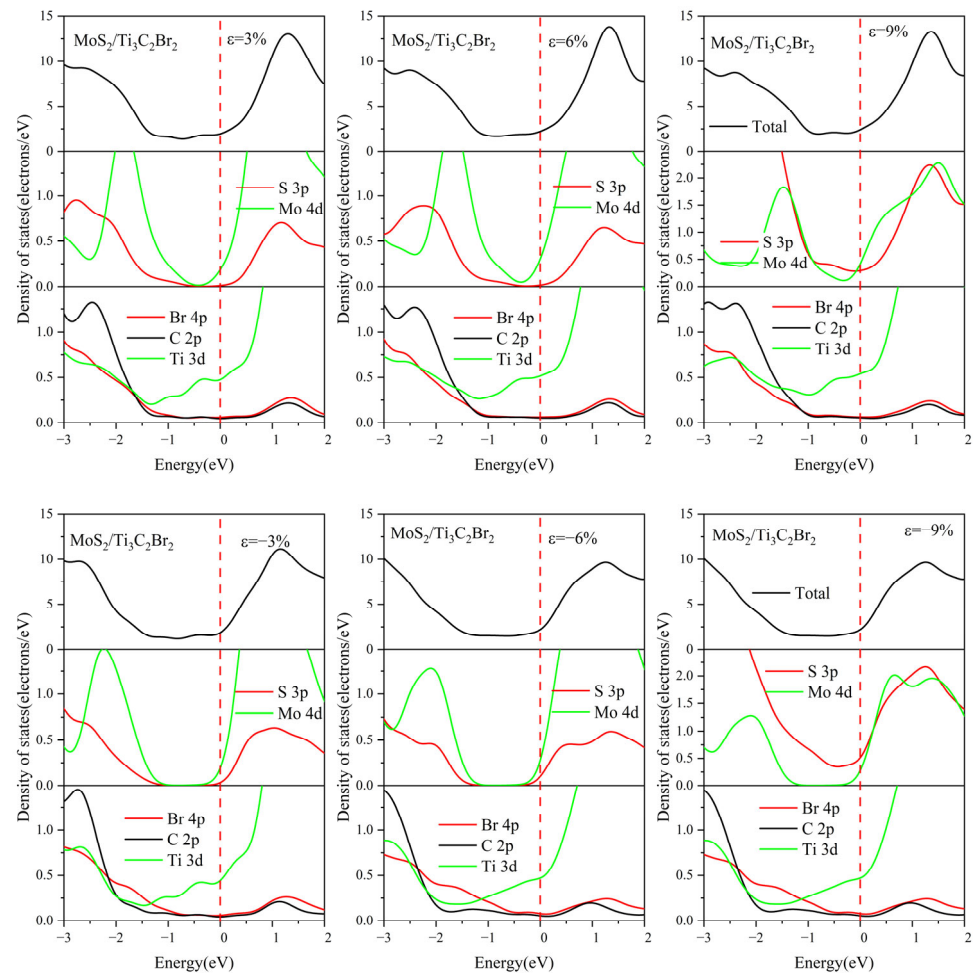
Figure 12 illustrates the DOS of the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure with different biaxial strains. The peak value of Mo 4d orbitals at  $-1.8$  eV gradually decreased under compressive strain, while the peak value of Ti 3d orbitals at  $0.9$  eV increased with increasing compressive strain. Under tensile strain, the peak value of both the Ti 3d orbital at  $0.9$  eV and the Mo 4d orbital at  $1.2$  eV increased with increasing tensile strain. Moreover, the peak value of Ti 3d orbitals moved away from the Fermi level, while in contrast, the peak value of the Mo 4d orbitals moved toward the Fermi energy level. It can be inferred from the variation of the DOS of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure with the strain that tensile strain increases the interlayer interaction, while compressive strain weakens the interlayer interaction. This result was consistent with the  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  heterostructure.



**Figure 12.** The partial density of states (PDOS) of  $\text{MoSe}_2$  and  $\text{Ti}_3\text{C}_2$  for the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure with different biaxial strains. The Fermi level is set to 0 eV. The red line represents the Fermi level.

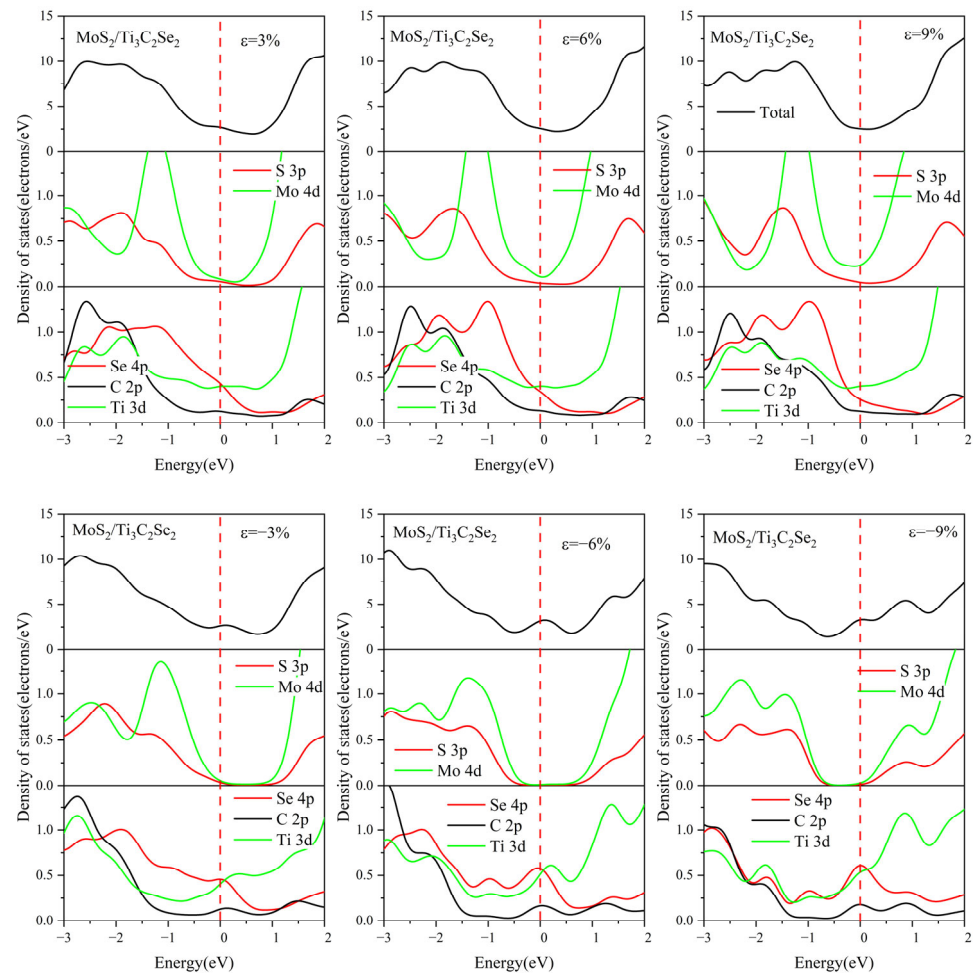
We also investigated the DOS of  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{X}_2$  under different biaxial strains, as shown in Figures 13, 14, S5 and S6. Compared with  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{Se}_2$  and  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{Br}_2$ , the external strain had a slight effect on the DOS of  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{Cl}_2$  and  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{S}_2$ , see

Figures S5 and S6. The monolayer MoS<sub>2</sub> remained in its band gap when a compressive strain was applied, while its band gap gradually disappeared with increasing tensile strain. This indicated that the tensile strain can improve the interaction strength between the monolayer MoS<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub> (or Ti<sub>3</sub>C<sub>2</sub>S<sub>2</sub>). For MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Se<sub>2</sub> and MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Br<sub>2</sub>, the tensile strain induced the Mo 4d orbital to cross the Fermi level, indicating that the semiconductor nature of the monolayer MoS<sub>2</sub> was completely destroyed. This means more electrons were transferred from the monolayer Ti<sub>3</sub>C<sub>2</sub>Br<sub>2</sub> (or Ti<sub>3</sub>C<sub>2</sub>Se<sub>2</sub>) to MoS<sub>2</sub>. We also noted that the S 3p orbital in MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Br<sub>2</sub> obviously crossed the Fermi level when the compressive strain reached 9%. In contrast, compressive strain cannot result in the S 3p and Mo 4d orbitals crossing the Fermi level in MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Se<sub>2</sub>, suggesting that MoS<sub>2</sub> can preserve its band gap under compressive strain, while the position of its conduction band minimum (CBM) and valence band maximum (VBM) will be obviously shifted.



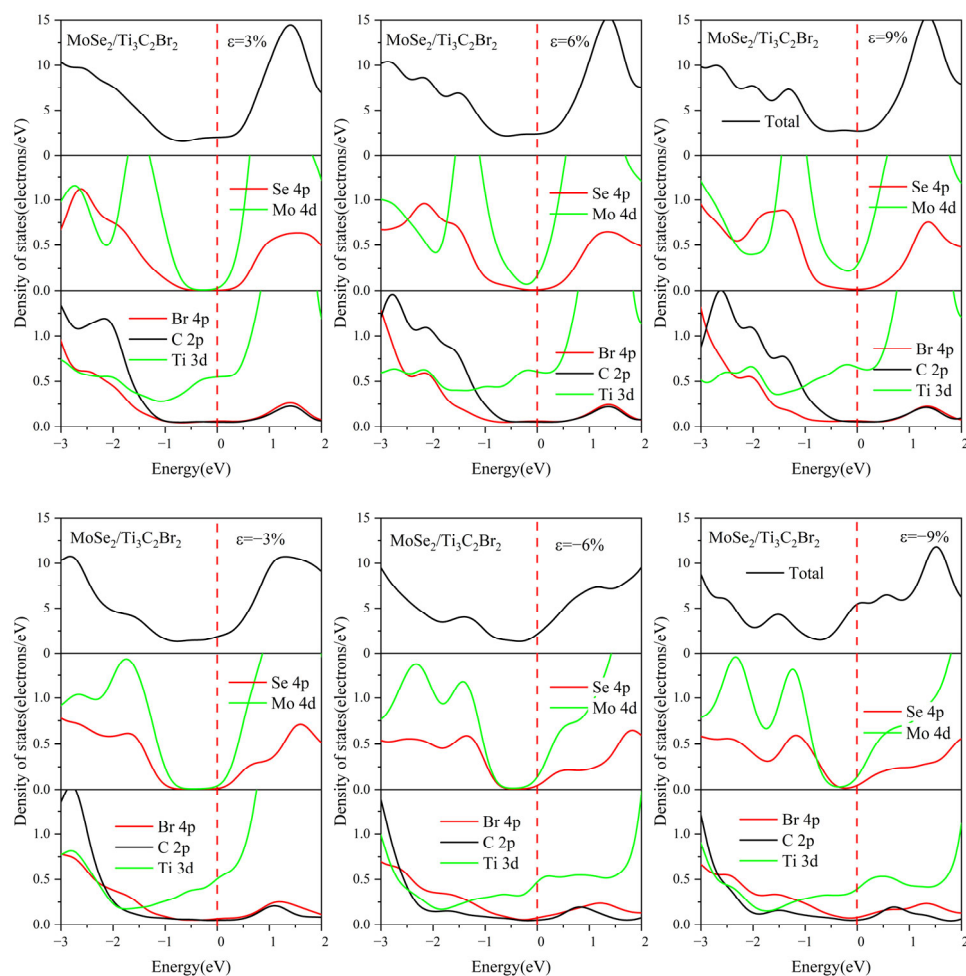
**Figure 13.** Density of states of the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Br<sub>2</sub> heterostructure with different biaxial strains. The Fermi level is set to 0 eV.



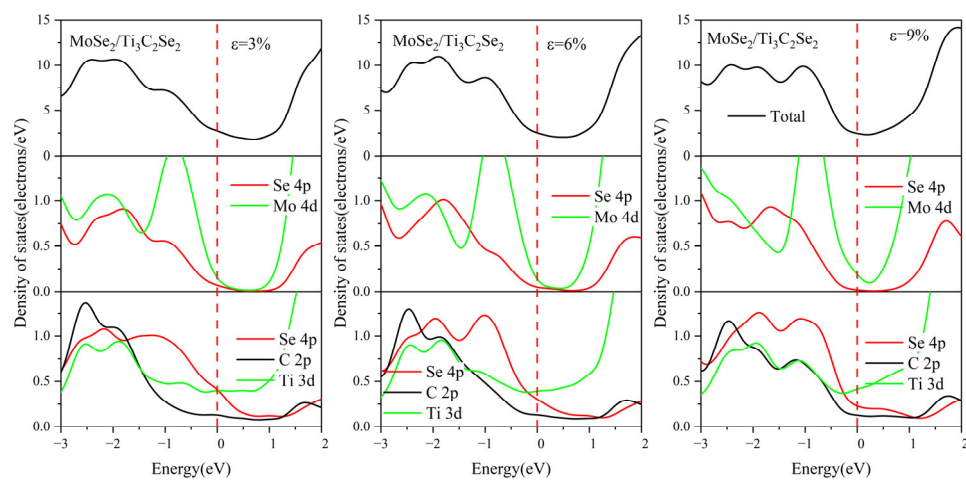


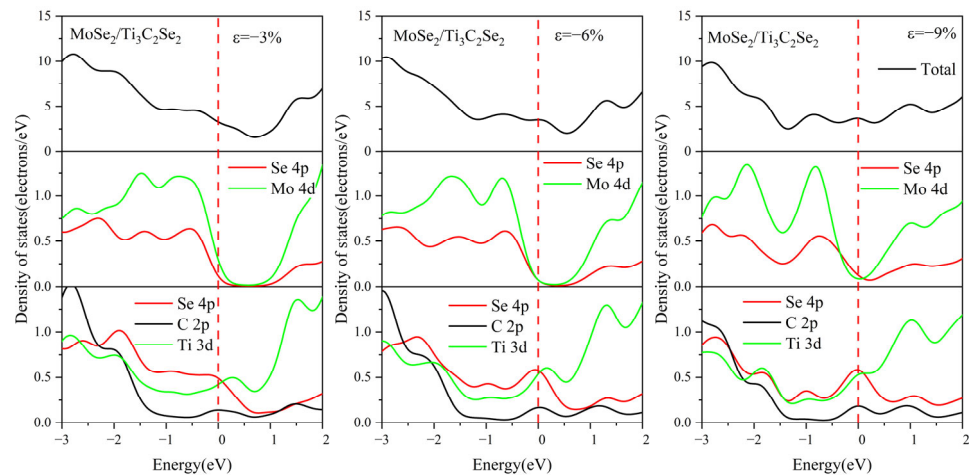
**Figure 14.** Density of states of the  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{Se}_2$  heterostructure with different biaxial strains. The Fermi level is set to 0 eV.

For comparison, the DOS of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{X}_2$  under different biaxial strains was also investigated, see Figures 15, 16, S7 and S8. For these four kinds of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{X}_2$  heterostructures, the band gap of monolayer  $\text{MoSe}_2$  disappeared with increasing compressive or tensile strain, and the Mo 4d orbitals and Se 4p orbitals passed through the Fermi energy levels. Therefore, the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{X}_2$  heterostructure is more sensitive to external strain than the  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{X}_2$  heterostructure. Moreover, these  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{X}_2$  heterostructures had a similar response to external strain. When there was no strain, the single-layer  $\text{MoSe}_2$  maintained its original semiconductor properties (see Figure 6), and the Fermi energy level was at the VBM of the  $\text{MoSe}_2$ . When the tensile or compressive strain was above 6%,  $\text{MoSe}_2$  was transformed into a conductor. The tensile and compressive strain can obviously increase the charge contribution of Mo 4d orbitals and Se 4p orbitals at the Fermi energy level. Moreover, under compressive strain, the PDOS peak value of these  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{X}_2$  heterostructures becomes sharper, indicating that the electron localization is strong.



**Figure 15.** Density of states of the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Br}_2$  heterostructure with different biaxial strains. The Fermi level is set to 0 eV.





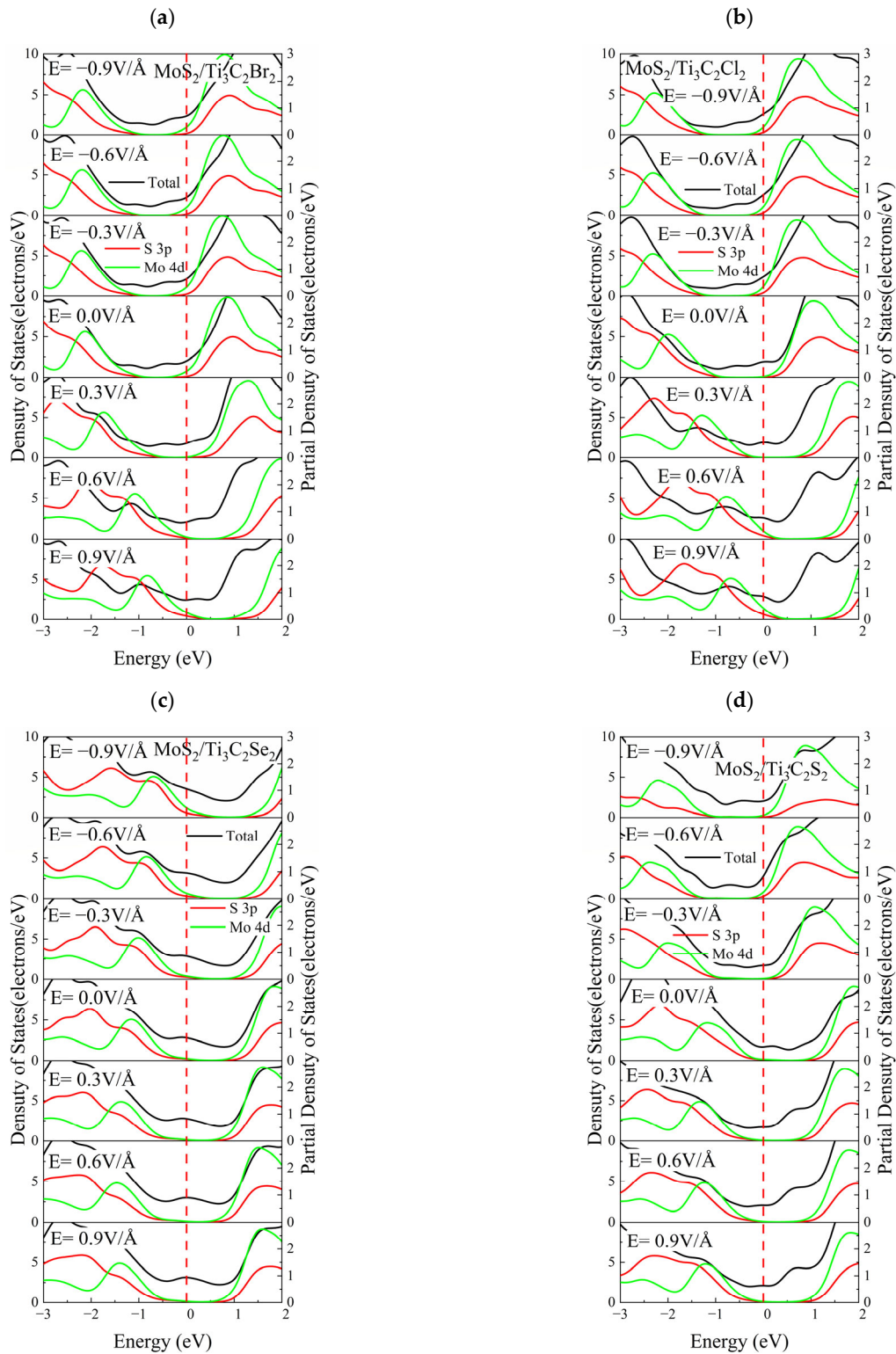
**Figure 16.** Density of states of the MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Se<sub>2</sub> heterostructure with different biaxial strains. The Fermi level is set to 0 eV.

### 3.4. Effect of Electric Field on the Electronic Properties of the TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> Heterostructures

Some studies [56,57] have shown that the electric field is a useful way to tune the electronic properties of heterostructures. In this section, we focus on the effects of the vertical electric field on the electronic properties of TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> heterostructures. To determine the effect of different directions of the applied electric field on the electronic properties of these heterostructures, we defined that the direction of the TMDs pointing to Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> was the positive direction of the applied vertical electric field, and the reverse direction was negative. The gradient from  $-0.9 \text{ V/\AA}$  to  $+0.9 \text{ V/\AA}$  for the applied electric field was taken in steps of  $0.3 \text{ V/\AA}$ .

Figure 17 shows the DOS of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> and PDOS of MoS<sub>2</sub> in MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = S, Se, Cl, Br) under different electric fields. The monolayer MoS<sub>2</sub> maintained its band gap under the positive and negative electric fields. The position of the valence band maximum (VBM) and conduction band minimum (CBM) of MoS<sub>2</sub> in MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Br<sub>2</sub> and MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub> remained almost unchanged under the negative electric field. In contrast, the VBM and CBM of MoS<sub>2</sub> in MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Br<sub>2</sub> and MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub> underwent a significant shift under the positive electric field, and the peak of the Mo 4d orbital moved toward a higher energy level, as shown in Figure 17a,b. Compared with MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Br<sub>2</sub> and MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub>, the effect of the electric field on the VBM and CBM of MoS<sub>2</sub> in MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Se<sub>2</sub> and MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>S<sub>2</sub> presented a completely reverse case. The position of VBM and CBM of MoS<sub>2</sub> in MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Se<sub>2</sub> and MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>S<sub>2</sub> remained almost unchanged under the positive electric field, while obviously moving under the negative electric field. Moreover, the peak position of the Mo 4d orbital remained almost constant, see Figure 17c,d. The DOS values of MoSe<sub>2</sub> in MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = S, Se, Cl, Br) under different electric fields were investigated, and the results were very similar to the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub>, see Figure S4. Compared with MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Br<sub>2</sub> and MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Se<sub>2</sub>, the total DOS of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>S<sub>2</sub> and MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub> obviously moved near the Fermi Level, suggesting the shift of VBE and CBE of MoS<sub>2</sub>. Moreover, under the condition of a positive electric field, the total DOS of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub> presented a sharp peak around 1 eV.

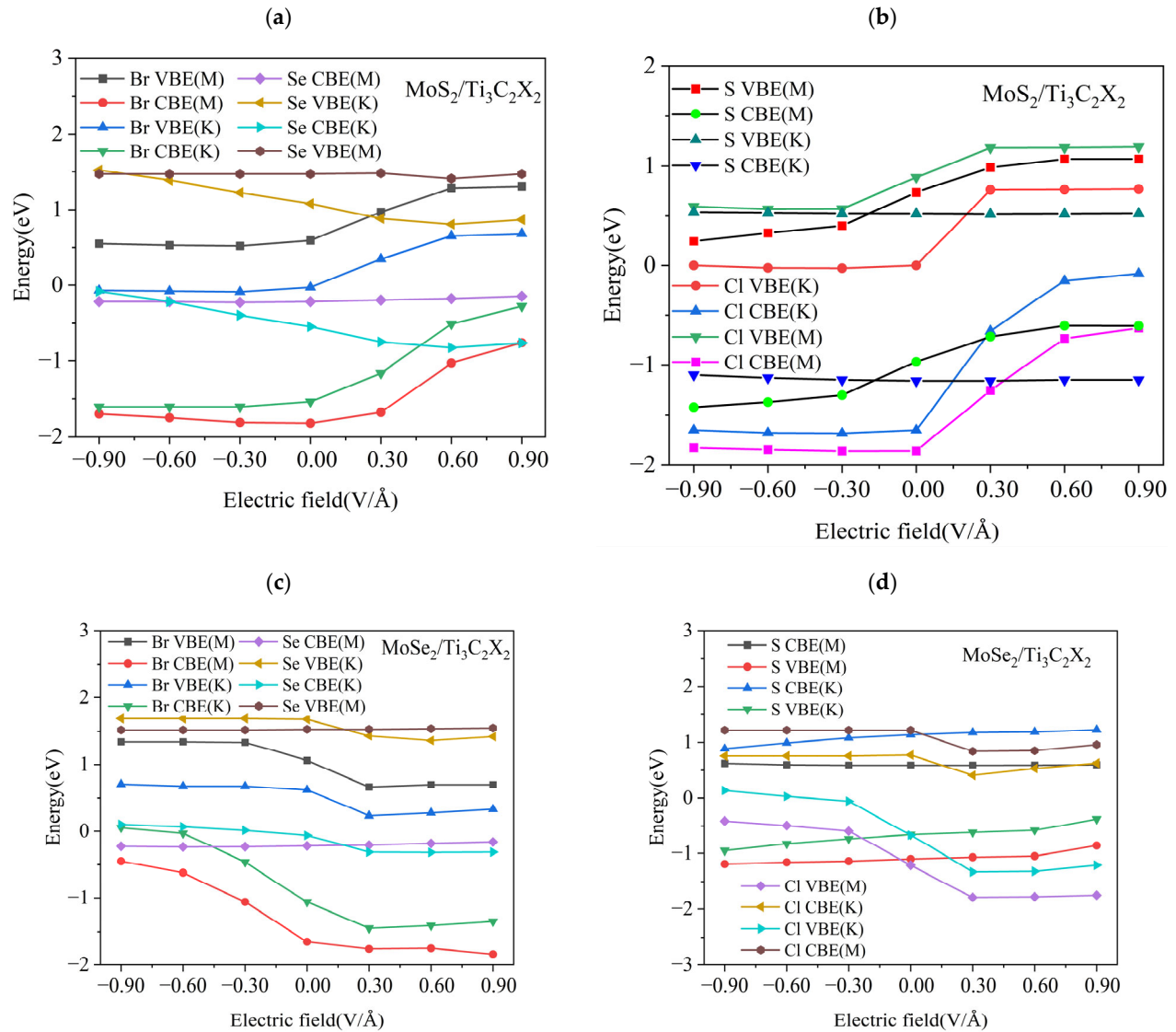




**Figure 17.** The DOS of  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{X}_2$  and PDOS of  $\text{MoS}_2$  in  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{X}_2$  heterostructures under different electric fields. (a) X-Br, (b) X-Cl, (c) X-Se and (d) X-S.

We further analyzed the energy band structure of TMDs/ $\text{Ti}_3\text{C}_2\text{X}_2$  ( $\text{X} = \text{S}, \text{Se}, \text{Cl}, \text{Br}$ ) heterostructures near the Fermi energy level in the electric field range from  $-0.9 \text{ V/\AA}$  to

0.9 V/Å, as shown in Figure 18. Figure 18a gives the variation patterns of the energy band edges at the M and K points near the Fermi energy level for MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = Se, Br) heterostructures under different electric fields. For MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Br<sub>2</sub>, the conduction band edge (CBE) and valence band edge (VBE) at both the M and K points moved towards a higher energy level with increasing electric field strength in the positive direction, while they were almost pinned under the negative electric field. In contrast, both the CBE and the VBE of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Se<sub>2</sub> at the K point moved towards a higher energy level with increasing negative electric field strength, while the CBE at the K point under the positive electric field moved towards a lower energy level. Under the positive electric field, both the CBE and VBE of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Se<sub>2</sub> at the M point remained unchanged. For MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = S, Cl), see Figure 18b, the VBE and CBE of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub> at the M point and K point near the Fermi level were similar to those of the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Br<sub>2</sub> heterostructure. The energy level of both the CBE and VBE of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>S<sub>2</sub> at the M point increased linearly with increasing positive electric field strength, while it decreased slightly with the negative electric field. It is worth noting that the CBE and VBE of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>S<sub>2</sub> at the K point were almost pinned under the positive and negative electric fields. For MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Br<sub>2</sub>, the energy level of the CBE and VBE at the M and K points decreased linearly with an increasing positive electric field, while it increased with an increasing negative electric field, see Figure 18c. The energy band edge of MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Se<sub>2</sub> was almost independent of the positive and negative electric fields. From Figure 18d, we know that for MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>S<sub>2</sub> the energy level of the CBE and VBE at the K point and M point were insensitive to the external electric field. For MoSe<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub>, the energy level of the CBE at the K point and M point showed a slight change under the condition of the positive electric field, while it could be pinned when the negative electric field was applied. The energy level of the VBE at the K point and M point remained unchanged when the electric field strength was increased to 0.3 V/Å. The energy band edges of TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = S, Se, Cl, Br) heterostructures showed a significant change near the Fermi energy level under different directional electric fields, indicating that the combined functional group with the electric field can effectively tune the related properties of TMDs/Ti<sub>3</sub>C<sub>2</sub>X<sub>2</sub> (X = S, Se, Cl, Br) heterostructures.



**Figure 18.** (a) The VBE and CBE at M and K points of  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{Br}_2$  and  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{Se}_2$  under different electric fields. (b) The VBE and CBE at M and K points of  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{S}_2$  and  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{Cl}_2$  under different electric fields. (c) The VBE and CBE at M and K points of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Se}_2$  and  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Br}_2$  under different electric fields. (d) The VBE and CBE at M and K points of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{S}_2$  and  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Cl}_2$  under different electric fields.

#### 4. Conclusions

The effects of biaxial strain and functional groups as well as electric fields on the structural and electronic properties of TMDs/ $\text{Ti}_3\text{C}_2$  heterostructures were systematically investigated based on the density functional theory method. The six possible configurations of  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  and  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructure stacks were first designed, and then geometrically optimized. ZM\_SA were identified as the most energetically stable structural types of  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  heterostructures with a binding energy of  $-1.79 \text{ meV}/\text{\AA}^2$ . The most energetically stable structure type of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructures was SA\_ZM, its binding energy of  $-1.03 \text{ meV}/\text{\AA}^2$ . The surface functional groups (S, Se, Cl, Br) of the monolayer  $\text{Ti}_3\text{C}_2$  resulted in the lattice expansion of TMDs/ $\text{Ti}_3\text{C}_2\text{X}_2$  heterostructures, and

the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Br}_2$  heterostructure possessed the maximum lattice parameters (3.262 Å). The conductivity of  $\text{MoS}_2/\text{Ti}_3\text{C}_2$  and  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  can be enhanced by increasing the biaxial tensile strain. When the surface of the monolayer  $\text{Ti}_3\text{C}_2$  was occupied by S, Se, Cl, or Br, the coupling strength between the monolayer TMDs and  $\text{Ti}_3\text{C}_2$  was obviously weakened, while the biaxial strain effectively improved their interaction strength. The different surface functional groups induced a different response of the electronic properties of TMDs/ $\text{Ti}_3\text{C}_2\text{X}_2$  heterostructures to the external electric field. The energy bands around the Fermi energy level of TMDs/ $\text{Ti}_3\text{C}_2\text{X}_2$  heterostructures obviously changed under the combined effect of surface functional groups with an electric field. These results demonstrated that TMDs/ $\text{Ti}_3\text{C}_2\text{X}_2$  (X = S, Se, Cl, Br) heterostructures possess rich electronic properties. Moreover, both  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{X}_2$  (X = Se, Br) and  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{X}_2$  (X = S, Se, Cl, Br) are rather sensitive to an external strain field, while only TMDs/ $\text{Ti}_3\text{C}_2\text{X}_2$  (X = Cl, Br) strongly depends on an external positive electric field. We hope that these studies can provide a theoretical foundation for the application of TMDs/MXenes heterostructures in the field of high-performance nanoelectronic devices.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano13071218/s1>, Figure S1: A schematic diagram of top and side views of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$  heterostructures for different stackings; Figure S2: Band structures and densities of states of the  $\text{MoS}_2$ ; Figure S3: Band structures and densities of states of the  $\text{MoSe}_2$ ; Figure S4: The DOS of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{X}_2$  and PDOS of  $\text{MoSe}_2$  in  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{X}_2$  heterostructures under different electric fields. (a) X-Br, (b) X-Cl, (c) X-Se and (d) X-S; Figure S5: Density of states of the  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{Cl}_2$  heterostructure with different biaxial strains; Figure S6: Density of states of the  $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{S}_2$  heterostructure with different biaxial strains; Figure S7: Density of states of the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{Cl}_2$  heterostructure with different biaxial strains; Figure S8: Density of states of the  $\text{MoSe}_2/\text{Ti}_3\text{C}_2\text{S}_2$  heterostructure with different biaxial strains; Table S1: Optimized structural parameters for the TMDs/ $\text{Ti}_3\text{C}_2\text{X}_2$  (X = S, Se, Br, Cl) heterostructure; Table S2: Mulliken charge (electron), bond length (Å) and bond populations of  $\text{MoS}_2/\text{Ti}_3\text{C}_2$ ; Table S3: Mulliken charge (electron), bond length (Å) and bond populations of  $\text{MoSe}_2/\text{Ti}_3\text{C}_2$ .

**Author Contributions:** S.Z.: Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Validation, Visualization, Roles/Writing—original draft, Writing-review & editing. C.L.: Conceptualization, Investigation, Methodology, Funding acquisition, Project administration, Supervision, Validation, Writing—review & editing. C.W.: Investigation, Visualization. D.M.: Investigation, Visualization. B.W.: Investigation, Visualization. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the National Natural Science Foundation of China (12172097) and the Natural Science Foundation of Heilongjiang Province, China (LH2021A006). And The APC was funded by the National Natural Science Foundation of China (12172097).

**Data Availability Statement:** Data are available on request from the corresponding author.

**Conflicts of Interest:** The authors declare that there is no conflict of interest regarding publication of this manuscript.

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