First principles study of structural, vibrational and electronic properties of graphene-like MX$_2$ (M=Mo, Nb, W, Ta; X=S, Se, Te) monolayers

Yi Ding$^{a, *}$, Yanli Wang$^b$,*, Jun Ni$^c$, Lin Shi$^d$, Siqi Shi$^b$, Weihua Tang$^b$

$^a$ Department of Physics, Hangzhou Normal University, Hangzhou, Zhejiang 310036, People’s Republic of China
$^b$ Department of Physics, Center for Optoelectronics Materials and Devices, Zhejiang Sci-Tech University, Xixia College Park, Hangzhou, Zhejiang 310018, People’s Republic of China
$^c$ Department of Physics, Key Laboratory of Atomic and Molecular Nanoscience (Ministry of Education), Tsinghua University, Beijing 100084, People’s Republic of China
$^d$ Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215125, People’s Republic of China

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Using first principles calculations, we investigate the structural, vibrational and electronic structures of the monolayer graphene-like transition-metal dichalcogenide (MX$_2$) sheets. We find the lattice parameters and stabilities of the MX$_2$ sheets are mainly determined by the chalcogen atoms, while the electronic properties depend on the metal atoms. The NbS$_2$ and TaS$_2$ sheets have comparable energetic stabilities to the synthesized MoS$_2$ and WS$_2$ ones. The molybdenum and tungsten dichalcogenide (MoX$_2$ and WX$_2$) sheets have similar lattice parameters, vibrational modes, and electronic structures. These analogies also exist between the niobium and tantalum dichalcogenide (NbX$_2$ and TaX$_2$) sheets. However, the NbX$_2$ and TaX$_2$ sheets are metals, while the MoX$_2$ and WX$_2$ ones are semiconductors with direct-band gaps. When the Nb and Ta atoms are doped into the MoS$_2$ and WS$_2$ sheets, a semiconductor-to-metal transition occurs. Comparing to the bulk compounds, these monolayer sheets have similar structural parameters and properties, but their vibrational and electronic properties are varied and have special characteristics. Our results suggest that the graphene-like MX$_2$ sheets have potential applications in nano-electronics and nano-devices.

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1. Introduction

Since the discovery of graphene [1,2], two-dimensional nanostructures have attracted lots of interests in nano-science and condensed matter physics [3–8]. Graphene is a monolayer carbon hexagonal sheet, which has a unique massless Dirac-like electronic excitation [3]. The two-dimensional graphene sheet is a semimetal, while for the graphene with finite width, it becomes a semiconductor or a half-metal depending on the edge shapes [4,5]. In the experiments, graphene sheets are initially obtained by micro-mechanical cleavage technique, using which the mono- and few-layer sheets are pulled from the layered graphite material [2]. Recently, several chemical methods, such as epitaxial growth on SiC surfaces, chemical vapor deposition on metal surfaces, reduction of graphite oxide, have been reported for the high-yield production of graphene [7–9]. Besides carbon-based nanostructures, other inorganic nanomaterials, especially whose structures are analogous to graphene, have also been synthesized and investigated [10]. For example, the two-dimensional BN sheet has been successfully synthesized by the micro-mechanical cleavage technique and chemical-solution-derived method [11]. Through high-resolution transmission electron microscopy, it has been observed that B and N atoms occupy one sublattice of the hexagonal sheet, respectively [12]. Different from graphene, due to the inequivalence of the two sublattices, the two-dimensional BN sheet is a wide band-gap semiconductor [13].

Binary metal-dichalcogenides also have similar layered structures as graphite. By chemical bath deposition method and the mechanochemical route, the molybdenum disulfide (MoS$_2$) films have been obtained in the experiments [14]. Besides, the two-dimensional MoS$_2$ sheet has been reported to be synthesized by high-resolution transmission electron microscopy, it has been observed that B and N atoms occupy one sublattice of the hexagonal sheet, respectively [12]. Different from graphene, due to the inequivalence of the two sublattices, the two-dimensional BN sheet is a wide band-gap semiconductor [13]. Binary metal-dichalcogenides also have similar layered structures as graphite. By chemical bath deposition method and the mechanochemical route, the molybdenum disulfide (MoS$_2$) films have been obtained in the experiments [14]. Besides, the two-dimensional MoS$_2$ sheet has been successfully synthesized by chemical methods in the experiment [15]. Previous theoretical studies show that bulk MoS$_2$ is an indirect-band-gap semiconductor [16,17], while the two-dimensional MoS$_2$ sheet is a direct-band-gap semiconductor [18]. The MoS$_2$ sheet could be rolled up into MoS$_2$ nanotubes, which are all semiconductors regardless of the chirality [19]. While for the MoS$_2$ sheets of finite width, the corresponding nanoribbons become ferromagnetic metals [20]. Similar to the MoS$_2$ sheet, the graphene-like WS$_2$ nanostructure has also been synthesized [15]. The corresponding WS$_2$ nanotubes are also semiconductors [21]. From Landolt-Börnstein database [22], we find that the
MoSe₂, MoTe₂, NbS₂, NbSe₂, WS₂, WSe₂, TaS₂, and TaSe₂ materials have the same layered structural type as that of MoS₂. However, among those materials, previous studies have only been performed on the two-dimensional sheets of the MoS₂, NbSe₂, and WS₂ systems [15,18]. Thus, it is promising to perform a systemic study on those graphene-like sheets, which is helpful for the fabrications and applications of those nanomaterials.

In this paper, we investigate the structural, vibrational and electronic properties of the two-dimensional MX₂ (M=Mo, Nb, W, Ta; X=S, Se, Te) sheets by first principles calculations. The lattice parameters, charge transfers, cohesive energies, Raman active and infrared active vibrational modes, and the band gaps of the MX₂ sheets are obtained and compared to the bulk ones in detail. We also discuss the metal doping effects and predict a semiconductor-to-metal transition in the MoS₂ and WS₂ sheets.

2. Methods

The first principle calculations are performed by VASP with a plane-wave set and projector augmented wave pseudopotentials [23]. Two types of exchange and correlation (XC) functionals, the Ceperly–Alder functional form of the local density approximation (LDA) and the Perdew–Burke–Ernzerhof (PBE) functional form of the generalized gradient approximation (GGA) are adopted in the calculations. The plane-wave cutoff energy is set to be 400 eV. The supercells are used to simulate the isolated sheets and in order to avoid interlayer interactions, the distance between sheets is set to larger than 12 Å. The supercells are used to simulate the isolated sheets and in order to avoid interlayer interactions, the distance between sheets is set to larger than 12 Å. The Monkhorst–Pack scheme is used to sample the Brillouin zone. The convergence of the force on each atom is less than 0.01 eV/Å. The Monkhorst–Pack scheme is used to sample the Brillouin zone. The structures are fully relaxed with a mesh of 12 × 12 × 1 and the mesh of k-space is increased to 15 × 15 × 1 and 24 × 24 × 1 in the static and density of state (DOS) calculations, respectively.

3. Results

3.1. Structural properties

The crystal structure of the monolayer MoS₂ sheet is shown in Fig. 1(a). Similar to BN, SiC, ZnO and other heterogeneous graphene-like sheets, Mo atoms occupy one sublattice of the hexagonal sheet and S atoms occupy the other. However, due to the chemical ratio of Mo:S=1:2, the Mo sublattice layer is sandwiched between two nearby S sublattice layers. We obtain the thickness of the MoS₂ sheet is 3.13 Å (3.12 Å) and the length of the Mo–S bond is 2.42 Å (2.39 Å) by the PBE (LDA) calculations. These calculated values agree well with the previous calculations by Li [20] and Ramakrishna Mathe [15]. The optimized lattice constant of the MoS₂ sheet is 3.19 Å (3.13 Å) with PBE (LDA), which is almost the same as the bulk value of 3.15 Å [20].

All the lattice parameters of the MX₂ sheets are listed in Table 1. It can be seen that the MoX₂ and WX₂ sheets, the NbX₂ and TaX₂ sheets have quite similar lattice parameters. For the same chalcogen, the difference of metals affects the lattice parameters slightly. For example, the in-sheet lattice constants of NbS₂ and TaS₂ sheets are only 0.15 Å longer than those of the MoS₂ and WS₂ ones. Four disulfide sheet, MoS₂, WS₂, NbS₂, and TaS₂ sheets, have a general thickness of 3.1 Å. However, different chalcogen atoms change the lattice parameters significantly. The diselenide and ditelluride sheets increase the thickness to 3.3 and 3.6 Å, respectively. Due to the increase of the chalcogen atomic radius, both the bond lengths d_M-X and the in-sheet lattice constants also increase in the sequence of MS₂ < MSe₂ < MTe₂ for the same metal atoms.

The difference of chalcogens affects not only the lattice parameters, but also the cohesive energies. In our calculations, the cohesive energies are defined as $E_{c}(MX_{2}) = E_{MX_{2}} - E_{M}^{atom} - 2 \times E_{X}^{atom}$. Here, $E_{MX_{2}}$ is the total energy of the MX₂ sheet, $E_{M}^{atom}$ and $E_{X}^{atom}$ are the energies of the corresponding metal and chalcogen isolated atoms. When the cohesive energies are more negative, the MX₂ sheets are more favorable. For the MoS₂ sheet, our PBE calculations show the formation energy is −5.07 eV/atom, which is in accordance with the GGA result of −5.20 eV/atom and the pseudo-atomic numerical orbitals result of −5.00 eV/atom [20]. While the LDA calculations predict a larger value of −6.25 eV/atom. This phenomenon is common for the first principles calculations, since the LDA functional normally gets short lattices and high energies, while the GGA one has the contrary trends [24,25]. From Table 1, it can be seen that $E_{c}(MS_{2}) < E_{c}(MS_{2}) < E_{c}(MTe_{2})$. Using the Bader analysis [26], we obtain the charge transfers from the metal to the chalcogen atoms. As shown in Table 1, in the MoS₂ sheet, the Mo atom loses 0.90 e and each S atom gains 0.45 e. While in the MoSe₂ and MoTe₂ sheets, the charge transfers of Mo atoms decrease to 0.76 and 0.24 e, respectively. Due to the small charge transfers and elongated lattice constants, the cohesive energies of the MoSe₂ and MoTe₂ sheets decrease to −4.53 and −3.97 eV/atom, respectively. Since the W, Nb, and Ta atoms transfer more electrons to the chalcogen atoms than the Mo atoms, their corresponding sheets will have higher cohesive energies than the MoX₂ systems. We also calculate the formation energies of the MX₂ sheets as $E_{form} = E_{MX_{2}} - E_{M}^{bulk} - 2 \times E_{X}^{dimer}$. Here, $E_{M}^{bulk}$ and $E_{X}^{dimer}$ represent the atomic energies in their stable elemental structures. For the metals, the stable structure is a body-centered cubic (bcc) bulk with the Im-3m space group, while for the chalcogens, the stable structure is a molecular dimer. As shown in Table 1, all the MX₂ sheets have negative formation energies, which means the composing processes from the elemental forms are exothermic reactions and those MX₂ sheets are stable. The $E_{form}$ of MoS₂ and
WS₂ sheets are −1.42 and −1.37 (−1.71 and −1.65) eV/atom by the PBE (LDA) calculations. Comparing the $E_c$ and $E_{\text{form}}$ of the MX₂ sheets in Table 1, we find that the NbS₂ and TaS₂ sheets have higher cohesive and formation energies than the synthesized MoS₂ and WS₂ ones. It is possible to produce these sheets from their bulk structures by similar chemical methods for the MoS₂ and WS₂ materials [15].

### 3.2. Vibrational properties

For the low-dimensional nanostructures, Raman spectra is one important characterization tool in the experiments [27]. Recently, two groups have measured the Raman shift of the MoS₂ sheets [15,28], and Ramakrishna Matte et al. get a value of 404.7 cm⁻¹ [28], and Ramakrishna Matte et al. get a value of 404.7 cm⁻¹ [15]. Our calculated results agree well with these experimental values within 2% deviations. The $A_{1g}$ mode is an infrared active frequency of about 460 cm⁻¹, which needs further experimental verifications.

For other MX₂ sheets, the corresponding vibrational frequencies are listed in Table 1. Since the $E'$ and $A_{1g}$ modes are usually measured in the experiments [15,28], we focus on these two modes for different MX₂ sheets. The $E'$ and $A_{1g}$ modes of the MoSe₂ sheet are 344 (360) and 409 (423) cm⁻¹ by the PBE (LDA) calculations, which also agree well with the experimental results [15]. Since the movements of the chalcogen atoms contribute to the displacements mainly, the vibrational frequencies of the $E'$ and $A_{1g}$ modes are determined by the chalcogen atoms. Taking the MoX₂ sheets as an example, the $E'$ mode of the MoSe₂ sheet decreases by about 100 cm⁻¹ compared to the MoS₂ sheet. The out-sheet vibrational frequency of the MoSe₂ sheet also decreases fast as shown in Fig. 2. The $A_{1g}$ mode reduces to 233 cm⁻¹, which becomes less than the $E'$ mode. When the chalcogen atoms are the Te element, the MoTe₂ sheet has the $E'$ and $A_{1g}$ frequencies down to 230 and 167 cm⁻¹, respectively. For other WX₂, NbX₂, TaX₂ systems, we also obtain that the frequencies of $E'$ and $A_{1g}$ modes follow the order of MS₂ > MSe₂ > MTe₂.

### 3.3. Electronic properties

Although the difference of chalcogen atoms affects the structural and vibrational properties, it has little influence on the electronic properties. Figs. 1(c) and (d) show the electronic structure of the MoS₂ sheet. The MoS₂ sheet is a semiconductor with a direct-band gap at the K point. The PBE (LDA) gap value

### Table 1

<table>
<thead>
<tr>
<th>$a$ (Å)</th>
<th>$d_{a-x}$ (Å)</th>
<th>$h$ (Å)</th>
<th>$E_c$ (eV/atom)</th>
<th>$E_{\text{form}}$ (eV/atom)</th>
<th>$\Delta Q$ (eV)</th>
<th>$E'$ (cm⁻¹)</th>
<th>$E$ (cm⁻¹)</th>
<th>$A_{1g}$ (cm⁻¹)</th>
<th>$A_{2g}$ (cm⁻¹)</th>
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<td>374</td>
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<td>290</td>
<td>392</td>
<td>411</td>
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<td>174</td>
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<td>−1.37</td>
<td>1.00</td>
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<td>0.98</td>
<td>300</td>
<td>360</td>
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<td>238</td>
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<td>−1.38</td>
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<td>174</td>
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<td>131</td>
<td>242</td>
<td>228</td>
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<td>91</td>
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<td>TaSe₂</td>
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<td>0.34</td>
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is 1.67 (1.86) eV, which agrees well with the latest MoS$_2$ photoluminescence experiment [29] and previous theoretical studies [18,20]. Similar to the MoS$_2$ sheet, both the MoSe$_2$ and MoTe$_2$ ones are also direct-band-gap semiconductors as shown in Figs. 3(a) and (b). Fig. 3(c) displays the typical band structure of the WTe$_2$ sheet. For the three WX$_2$ sheets, we find they have analogous semiconducting properties. However, both the NbX$_2$ and TaX$_2$ sheets become metals. As shown in Fig. 3(d), the NbS$_2$ sheet exhibits metallic behavior with one band crossing the Fermi level. The partial DOS analysis indicates this band is mainly attributed to the d orbitals of Nb atoms. Since the Nb (Ta) atom is one d electron less than the Mo (W) atom, the top d-character valence bands are not fully occupied and the metallicity appears in the NbX$_2$ (TaX$_2$) sheets. This result is consistent with the
experimental observation that the TaS$_2$ films present robust metallic behaviors [30]. Thus, these metallic NbX$_2$ and TaX$_2$ sheets would be one type of conducting materials for nano-devices.

For the semiconducting MoX$_2$ and WX$_2$ sheets, the calculated PBE and LDA band gaps are listed in Table 2. It is well-known that the traditional DFT calculations perform well for the properties of the ground state, but generally underestimate the band gaps of materials [24]. In order to predict accurate band gaps, extra calculations are carried out by two ways. One way is utilizing the Heyd–Scuseria–Ernzerhof (HSE) hybrid XC functional. Comparing with the PBE results, the HSE calculations increase the band gaps by about 0.5 eV. The band gaps of the MoS$_2$ and WS$_2$ sheets are up to 2.25 and 2.32 eV, respectively. The other way is doing the GW correction. The GW correction greatly increases the band gaps. As shown in Table 2, the MoX$_2$ and WX$_2$ sheets have the GW gaps ranging from 1.8 to 3 eV. However, no matter whether the traditional XC functional, hybrid XC functional, or GW correction is used, the band gaps of the MoX$_2$ and WX$_2$ sheets follow the same order of disulfide $>$ diselenide $>$ ditelluride. Considering that those direct-gaps are around 2–3 eV, the semiconducting MoX$_2$ and WX$_2$ sheets can be used as solar energy materials, luminescent materials, and so on.

Next, we consider the metal-doped effects on the MX$_2$ sheets. Since the MoS$_2$ and WS$_2$ sheets have been successfully fabricated [15] and the Nb atom can substitute Mo atom in the MoS$_2$ bulk material [31], we investigate four situations as the Nb-, W-doped MoS$_2$ sheet and the Ta-, Mo-doped WS$_2$ sheet. A 3x3 supercell is used, in which the distance between the doped atoms is larger than 9.5 Å. For the Nb-doped MoS$_2$ sheet, the formation energy is denoted as $E_{\text{form}} = E_{\text{Nb-MoS}_2} - E_{\text{pure MoS}_2} - E_{\text{Nb atom}} + E_{\text{Mo atom}}$. Here, $E_{\text{Nb-MoS}_2}$ and $E_{\text{pure MoS}_2}$ correspond to the total energies of Nb-doped and pure MoS$_2$ sheets, respectively. The $E_{\text{form}}($Nb–MoS$_2)$ is calculated to be $-0.84$ eV/unit. Similarly, we obtain $E_{\text{form}}$ ($W$–MoS$_2$) = $-1.93$ eV/unit, $E_{\text{form}}($Ta–WS$_2)$ = $-0.38$ eV/unit, and $E_{\text{form}}($Mo–WS$_2)$ = $1.90$ eV/unit. The negative formation energies indicate the corresponding substitutional reactions could happen.

Table 2
The calculated band gaps at the K-point of the semiconducting MoX$_2$ and WX$_2$ sheets within different XC functionals of PBE, LDA, HSE, and GW correction.

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<th>PBE (eV)</th>
<th>LDA (eV)</th>
<th>HSE (eV)</th>
<th>GW (eV)</th>
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<td>2.66</td>
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<td>1.74</td>
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<td>WTe$_2$</td>
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<td>1.14</td>
<td>1.55</td>
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</tbody>
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Fig. 4. (a and c) The total and partial DOSs of the Nb-doped and W-doped MoS$_2$ sheets. (b and d) The corresponding charge differences of the doping systems. (e and f) The total and partial DOSs of the Ta-doped and Mo-doped WS$_2$ sheets.
Thus, the Nb-doped MoS2, W-doped MoS2 and Ta-doped WS2 sheets are possible to be formed in the experiments. Fig. 4 shows the electronic properties of those doping systems. The Nb-doped MoS2 sheet becomes a metal. From the charge difference in Fig. 4(b), we can see the Nb atoms lose more electrons than the Mo atoms. Considering the Nb atom is one d-electron less than the Mo atom, the Nb atoms act as holes doped in the MoS2 sheet. It causes the downshift of the Fermi level and induces a semiconductor-to-metal transition in the MoS2 sheet. While the W atoms behave quite similarly to the Mo atoms, little is changed after W doping in the MoS2 sheet. The W-doped MoS2 sheet is a semiconductor with a PBE band gap of 1.65 eV, which is almost identical to that of the pure MoS2 sheet. In the WS2 sheet, like the Nb-doped MoS2 system, the Ta doping induces a semiconductor-to-metal transition shown in Fig. 4(e). While for the Mo doping, Fig. 4(f) displays the Mo-doped WS2 sheet is still a semiconductor with a PBE band gap of 1.75 eV.

### 4. Discussions

Finally, we compare the structures and properties of the monolayer sheets to the bulk 2 H-like structures [16,20,31]. Table 3 shows the calculated results of bulk disulfide compounds. Since the PBE XC functional is hard to describe the van der Waals interactions between the layers, which give much longer lattice constants along the c-axis than the experimental values [22], we just compare the LDA results and find the similarities and differences of monolayer sheets to the bulks as following: (1) The sheets and bulks have similar structural properties. From Tables 1 and 3, it can been seen that the lattice parameters within the layered structure such as in-sheeth constant \(a\), bond length \(d_{M-X}\), sheet thickness \(h\) are almost the same for the sheets and bulks. However, the metals transfer less charges to the S atoms in the sheets than in the bulks, which induces a little weaker cohesive energies for the monolayers. For the MoS2 sheet, its \(E_c\) is 0.04 eV/atom lower than the bulk one. Similarly, the WS2, NbS2, and TaS2 sheets also have a little smaller cohesive energies than the bulks. These energy differences between the bulks and monolayers are about 0.04–0.05 eV/atom. Comparing with the normal room temperature (0.025 eV), it indicates that producing the disulfide sheets from their bulk structures is energetically feasible. (2) The vibrational properties of sheets are different from the bulks. The \(E_0\) frequencies of the bulks are all smaller than those in the sheets. While for the \(A_0\) mode, the frequencies are nearly the same for the MoS2 and WS2 sheets and bulks, but for the NbS2 and TaS2 compounds, the frequencies of the monolayers are smaller than those of the bulks. In the experiments, those \(E\) and \(A_0\) modes have been used to distinguish the components and thickness of MoS2 samples [28,32], and Lee et al. have reported that the \(E\) mode softens, while the \(A_0\) mode stiffens with the increase of the MoS2 sample thickness [28]. Our calculated results are in accordance with this phenomenon, and predict the \(E\) and \(A_0\) modes for the NbS2 and TaS2 compounds will have stronger thickness dependence. (3) The electronic properties of sheets are also varied. Fig. 5 depicts the

### Table 3

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<thead>
<tr>
<th></th>
<th>(a) ((\text{Å}))</th>
<th>(d_{M-X}) ((\text{Å}))</th>
<th>(h) ((\text{Å}))</th>
<th>(E_c) (eV/atom)</th>
<th>(E_{form}) (eV/atom)</th>
<th>(\Delta Q) (e)</th>
<th>(E) (eV/atom)</th>
<th>(A_0) (cm(^{-1}))</th>
</tr>
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<tbody>
<tr>
<td>MoS2</td>
<td>PBE 3.19 2.42 3.13 14.22</td>
<td>-5.07 -1.42 1.06 374 396</td>
<td>LDA 3.13 2.39 3.12 12.09</td>
<td>-6.29 -1.75 1.03 389 411</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>WS2</td>
<td>PBE 3.19 2.42 3.15 13.64</td>
<td>-5.71 -1.37 0.88 344 405</td>
<td>LDA 3.13 2.39 3.13 12.13</td>
<td>-6.93 -1.69 1.00 357 423</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>NbS2</td>
<td>PBE 3.36 2.49 3.14 13.38</td>
<td>-5.44 -1.57 1.31 280 372</td>
<td>LDA 3.29 2.46 3.12 11.88</td>
<td>-6.50 -1.86 1.20 307 388</td>
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<tr>
<td>TaS2</td>
<td>PBE 3.34 2.48 3.13 13.38</td>
<td>-5.92 -1.60 1.14 280 388</td>
<td>LDA 3.27 2.45 3.11 11.98</td>
<td>-6.92 -1.89 1.13 293 400</td>
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Fig. 5. The DOSs of bulk and monolayer MS2 (M=Mo, W, Nb, Ta) compounds. (a) MoS2, (b) WS2, (c) NbS2 and (d) TaS2.
5. Conclusions

In summary, we have investigated the structural, vibrational, and electronic properties of the graphene-like MX$_2$ monolayers by first principles calculations. We find that:

1. The NbS$_2$ and TaS$_2$ sheets are even more stable than the synthesized MoS$_2$ and WS$_2$ ones, which suggests it is possible to produce these sheets from their bulk structures by similar chemical methods for the MoS$_2$ and WS$_2$ materials.

2. The MoX$_2$ and WX$_2$ sheets have similar lattice parameters, vibrational modes, as well as electronic structures. Analogous relationships also exist between the NbX$_2$ and TaX$_2$ sheets. However, the MoX$_2$ and WX$_2$ sheets are semiconductors, while the NbX$_2$ and TaX$_2$ ones are metals.

3. The hybrid HSE functional and GW calculations show the semiconducting sheets have the band gaps of about 1.5–3 eV, which follow the order of MS$_2 >$ MSE$_2 >$ MTe$_2$. When doping the Nb and Ta atoms into the sheets, a semiconductor-to-metal transition occurs in the MoS$_2$ and WS$_2$ systems.

4. Comparing to the bulk compounds, these monolayer sheets have similar structural parameters and properties, but their vibrational and electronic properties are varied. The semiconducting sheets have larger band gaps than the bulk compounds, and the metallic sheets have much smaller DOSs at the Fermi level than the bulk ones.

Our studies demonstrate that transition-metal dichalcogenide sheets, the inorganic analogs of graphene, have rich electronic structures for potential applications in nano-electronics, molecular sensing, and optical devices.

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References


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