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# First-principles study on the structure and electronic properties of $M_2CS_x$ ( $M = Sc, Ti, Y, Zr$ and $Hf$ , $x = 1, 2$ )†

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Two-dimensional (2D) transition metal carbides/nitrides, known as MXenes, have attracted extensive attention due to their rich elemental composition and diverse surface chemistry. In this study, the crystal structure, electronic, mechanical, and electronic transport properties of  $M_2CS_x$  ( $M = Sc, Ti, Y, Zr$ , and  $Hf$ ,  $x = 1, 2$ ) were investigated by density functional theory (DFT). Our results showed that the studied  $M_2CS_x$  except  $Y_2CS_2$  are thermodynamically, dynamically, thermally, and mechanically stable. The p-d hybridization between the M-d state and the C/S-p state of  $M_2CS$  is stronger than that of the corresponding  $M_2CS_2$ . However, the antibonding state would appear near the Fermi level and thus reduce the thermal stability of the material due to the introduction of sulfur vacancies in the Y-free MXenes studied. In contrast, sulfur vacancies would significantly enhance the bonding states of Y–C and Y–S bonds and improve the stability of  $Y_2CS_x$ . This provides an explanation for the experimentally observed formation of non-stoichiometric  $Ti_2CS_{1.2}$ . The room-temperature electron mobilities of semiconductor  $Sc_2CS$  ( $Y_2CS$ ) along the x and y directions were determined to be 232.59 (818.51) and 628.22 (552.55)  $cm^2 V^{-1} s^{-1}$ , and the room-temperature hole mobilities are only 88.32 (1.64) and 61.75 (17.80)  $cm^2 V^{-1} s^{-1}$ . This work is expected to provide theoretical insights for the preparation and application of S-terminated MXenes.

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## 1. Introduction

MXenes are a large family of two-dimensional (2D) transition metal carbides, nitrides, and carbonitrides with diverse structures, compositions, and surface chemistries, and have been widely used in many fields such as energy storage,<sup>1,2</sup> electronic devices,<sup>3,4</sup> sensors,<sup>5,6</sup> catalysts,<sup>7,8</sup> the environment,<sup>9,10</sup> and biomedicine.<sup>11</sup> MXenes are prepared by a top-down synthesis approach, that is, selective etching of A-layer elements from MAX phase precursors. The general formula of MXenes is  $M_{n+1}X_nT_x$ , where M represents the transition metal element (such as Sc, Ti, V), X is the C or N element, n can vary from 1 to 4, and  $T_x$  (x is a variable) indicates the surface group. Since the first MXene ( $Ti_3C_2T_x$ ) was obtained by hydrofluoric acid etching

in 2011,<sup>12</sup> more than 30 stoichiometric MXenes have been prepared and more than 100 compositions of MXenes have been predicted.<sup>13</sup> In addition, the surface termination of MXenes is dependent on the synthesis approach and MXene composition.<sup>14–16</sup> For example, the surface terminations of MXenes produced by wet chemical etching techniques are generally F, O, and OH.<sup>15,17</sup> The halogen-terminated MXenes can be synthesized by etching in Lewis acid  $CuCl_2/CuBr_2/CuI_2$  molten salts.<sup>18,19</sup> These terminations can be substituted or eliminated by other functional groups such as S, Se, Te, NH groups through subsequent surface reactions, providing a new route to synthesize new MXenes that cannot be obtained by conventional Lewis acid etching.<sup>16,20</sup> The surface terminations of MXenes have a significant impact on the physical, chemical properties and structural stability of MXenes due to the overlapping of non-bonding valence electrons of transition metals through their low-energy electronic states.<sup>21–23</sup> Li *et al.* reported the I-terminated halogenated  $Ti_3C_2I_2$  MXene cathode can activate and stabilize reversible  $I^0/I^+$  redox couple in the  $I_2$ –Zn battery to achieve a high voltage plateau.<sup>24</sup> Superconductivity was first observed in  $Nb_2CT_x$  terminated with S, Se, or NH groups, while no superconducting transition was found for bare and O-terminated  $Nb_2C$ .<sup>16</sup> Some  $M_2CT_2$  ( $T = O, OH$  or S)-based multifunctional sulfur cathodes were found to effectively suppress the shuttling effect and exhibit excellent cycle performance and high specific capacity in lithium–sulfur

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batteries.<sup>25–27</sup> Zhu *et al.* showed the O, OH and F groups on  $\text{Zr}_2\text{CT}_x$  can be seemingly exchanged with S groups through the proposed reaction in  $\text{CS}_2$  solution.<sup>28</sup> A number of S-functionalized MXenes have been reported as electrode materials for potential metal ion batteries due to their lower diffusion barrier and higher storage capacity.<sup>29–37</sup> Luo *et al.* investigated the nitrogen reduction reaction (NRR) of Fe adsorbed on  $\text{Ti}_3\text{C}_2\text{O}_2$  or N/F/P/S/Cl-doped  $\text{Ti}_3\text{C}_2\text{O}_{2-x}$  MXene and found that F and S doping can reduce the energy barrier of the rate-determining step.<sup>38</sup> Bae *et al.* reported a new structural phase of  $\text{Sc}_2\text{CO}_2$  containing C3 trimers converted from the hexagonal carbon of the typical trigonal MXene phase, with two very active anion electrons located in the voids between C3 trimers.<sup>39</sup> Additionally, Wang *et al.* demonstrated that the stable  $\text{Sc}_2\text{CO}_2$  monolayer is an efficient  $\text{NH}_3$  gas sensor with high selectivity, high sensitivity and low recovery time through analytical methods based on optical and/or electronic response.<sup>40</sup> In comparison, without directly considering the material stability, Hu *et al.* reported that  $\text{Sc}_2\text{CS}_2$  could effectively capture the  $\text{NH}_3$  and nicotine, while the  $\text{Y}_2\text{CS}_2$  exhibits the extremely high sensitivity and selectivity towards  $\text{NO}$ .<sup>41</sup> Importantly, only non-stoichiometric chalcogen-terminated MXenes were observed in the experiment, *e.g.*  $x = 1.2$  and  $1.1$  for  $\text{Ti}_2\text{CS}_x$  and  $\text{Ti}_3\text{C}_2\text{S}_x$ , respectively,<sup>16</sup> despite the dynamical stability of stoichiometric  $\text{M}_2\text{CS}_2$  ( $\text{M} = \text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Fe}, \text{Y}, \text{Zr}, \text{Nb}, \text{Mo}, \text{Hf}, \text{Ta}$  and  $\text{W}$ ) and  $\text{Ti}_3\text{C}_2\text{S}_2$  have been theoretically confirmed by the calculated phonon dispersions and *ab initio* molecular dynamics (AIMD) simulations.<sup>27,29,42–49</sup> To the best of our knowledge, the non-stoichiometric structures, underlying stability mechanisms and associated physical properties of S-terminated MXenes remain unclear.

In this study, the structural stability, electronic structure, mechanical and electronic transport properties of  $\text{M}_2\text{CS}_x$  ( $\text{M} = \text{Sc}, \text{Ti}, \text{Y}, \text{Zr}$  and  $\text{Hf}$ ,  $x = 1, 2$ ) were investigated using density functional theory (DFT). Our results showed that the calculated cohesive energies and bond lengths of the M–C and M–S bonds of  $\text{M}_2\text{CS}$  are smaller than those of the counterpart  $\text{M}_2\text{CS}_2$  due to the more pronounced electron transfer and stronger p–d overlapping between M–d state and C/S–p state of  $\text{M}_2\text{CS}$ . In addition, due to the introduction of sulfur vacancy in the studied MXenes except  $\text{Y}_2\text{CS}_x$ , the antibonding state would appear near the Fermi level, reducing the thermal stability of the material. Furthermore, both  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  were found to be a thermodynamically stable and dynamically stable semiconductors with appropriate carrier mobility. This work is expected to provide clues for the design and preparation of novel MXenes.

## 2. Computational details

All the first-principles calculations were carried out by using Vienna *Ab initio* Simulation Package (VASP). Projector augmented wave (PAW) method<sup>50</sup> was employed to describe the electron–core interactions and the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) was used to treat the exchange–correlation potential of valence electrons.<sup>51</sup> And the DFT–D3 method with Becke–Johnson damping were included in all calculations to account for the van

der Waals (vdW) interaction.<sup>52</sup> The cutoff energy of plane waves was set to 500 eV. The Monkhorst–Pack meshes with  $12 \times 12 \times 1$  and  $9 \times 9 \times 1$  *k*-points were used to sample the Brillouin zone for the calculations of  $\text{M}_2\text{CS}_2$  and  $\text{M}_2\text{CS}$  cells, respectively. A large vacuum thickness of 20 Å was used to avoid the spurious interaction between adjacent monolayers. The structures studied were fully optimized using conjugate gradient algorithm, and the energy and force convergences of  $10^{-8}$  eV and  $10^{-6}$  eV Å<sup>−1</sup> were used for the calculations. In addition, density functional perturbation theory implemented in PHONOPY software was used to calculate phonon spectra to check the dynamical stability of the structures investigated.<sup>53,54</sup> And the  $4 \times 4 \times 1$  supercell of  $\text{M}_2\text{CS}_2$ ,  $2 \times 2 \times 1$  supercell of  $\text{M}_2\text{CS}$ , plane wave with a cut-off energy of 650 eV and  $4 \times 4 \times 1$  *k*-point meshes were used for force constant calculations. AIMD simulations were performed for 4 ps in NVT ensemble with a time step of 1.0 fs to assess thermal stability of  $\text{M}_2\text{CS}_x$ . The Nosé–Hoover thermostat was applied to control the temperature. In order to predict the electronic transport properties, band gap center  $E_{\text{BGC}}$  was calculated by using GGA–PBE functional and calibrated against vacuum level.<sup>55</sup> The band edge of MXene could be accurately evaluated as follows.<sup>56–58</sup>

$$E_{\text{VBM}} = E_{\text{BGC}} - \frac{1}{2}E_{\text{g}} \quad (1)$$

$$E_{\text{CBM}} = E_{\text{BGC}} + \frac{1}{2}E_{\text{g}} \quad (2)$$

Here  $E_{\text{g}}$  is the calculated band gap of MXene. Carrier mobility of 2D MXenes was studied based on the deformation potential theory according to eqn (3) because the carrier mobility of a 2D intrinsic inorganic semiconductor is mainly dominated by the phonon scattering.<sup>59,60</sup>

$$\mu_{2\text{D}} = \frac{2e\hbar^3 C_{2\text{D}}}{3k_{\text{B}} T E_i^2 |m^*|^2} \quad (3)$$

Here,  $\hbar$  is the reduced Planck constant,  $T$  is the temperature,  $k_{\text{B}}$  is the Boltzmann's constant,  $e$  is the elementary charge.  $m^* = \hbar^2/(\partial^2 E/\partial k^2)$  is the effective mass of charge,  $C_{2\text{D}}$  is the elastic modulus under the strain  $\Delta a/a_0$  along the transport direction, determined by  $C_{2\text{D}} = [\partial^2 E/\partial(\Delta a/a_0)^2]/S_0$ , where  $E$  and  $S_0$  is the total energy and the area of optimized supercell. And  $E_i$  represents the deformation potential constant of valence-band maximum for holes and conduction-band minimum for electrons, calculated by  $E_i = \partial E_{\text{edge}}/\partial(\Delta a/a_0)$ , where  $E_{\text{edge}}$  is the energy of *i*th energy band under a small compressive or tensile strain  $\Delta a/a_0$  along the transport direction. All the structures were visualized by Materials Studio or VESTA3 software.<sup>61</sup>

## 3. Results and discussion

### 3.1. Crystal structure and stability of $\text{M}_2\text{CS}_x$

Four possible configurations for sulfur terminations of a  $\text{M}_2\text{CS}_2$  crystal were considered in Fig. S1.† In order to assess the relative thermodynamic stabilities of the configurations studied, cohesive energy  $E_{\text{coh}}$  was calculated by

$$E_{\text{coh}} = [E_{\text{tot}}(\text{M}_2\text{CS}_x) - 2E(\text{M}) - E(\text{C}) - xE(\text{S})]/(3 + x) \quad (4)$$



where  $E_{\text{tot}}(\text{M}_2\text{CS}_x)$  is the total energy of  $\text{M}_2\text{CS}_x$ ,  $E(\text{M})$ ,  $E(\text{C})$ , and  $E(\text{S})$  are the energies of isolated M, C, and S atoms, respectively. From the calculated total energies of  $\text{M}_2\text{CS}_2$  configurations in Table S1,<sup>†</sup> it is found that the sulfur layers on both sides of the most stable configuration of  $\text{M}_2\text{CS}_2$  ( $\text{M} = \text{Ti}$ ,  $\text{Zr}$  and  $\text{Hf}$ ) (as shown in Fig. 1 and S1B<sup>†</sup>) are directly projected to the bottom metal layer, while in the most stable configuration of  $\text{Sc}_2\text{CS}_2$  and  $\text{Y}_2\text{CS}_2$ , the sulfur atoms on one side are projected directly to the bottom metal atoms, while the sulfur atoms on the opposite side are projected directly to the carbon atoms in the middle layer (as shown in Fig. 1 and S1C<sup>†</sup>). Apparently, stable  $\text{Ti}_2\text{CS}_2$ ,  $\text{Zr}_2\text{CS}_2$ ,  $\text{Hf}_2\text{CS}_2$  are symmetric type-A structures, while energetically preferred asymmetric type-B structures do exist in  $\text{Sc}_2\text{CS}_2$  and  $\text{Y}_2\text{CS}_2$ . Interestingly, the stable configuration of the studied  $\text{M}_2\text{CS}_2$  resembles the counterpart  $\text{M}_2\text{CO}_2$ .<sup>40,62</sup> However, Zhang *et al.*<sup>42</sup> reported that  $\text{Sc}_2\text{CS}_2$  and  $\text{Y}_2\text{CS}_2$  are actually stabilized in distortion variants of the asymmetric type-B phase depicted in Fig. 1 type-B. Therefore, the relative stability of the type-B phase and the distorted type-B phase of  $\text{Sc}_2\text{CS}_2$  and  $\text{Y}_2\text{CS}_2$  was compared, and the results are displayed in Table S2 and Fig. S2.<sup>†</sup> Noteworthy, the dipole-corrected total energies of type-B  $\text{Sc}_2\text{CS}_2$  and  $\text{Y}_2\text{CS}_2$  calculated in this study are larger than those reported by Zhang *et al.*<sup>42</sup> probably due to the higher convergence criteria used in this study. And the distorted structures of type-B  $\text{Sc}_2\text{CS}_2$  and  $\text{Y}_2\text{CS}_2$  were optimized back to the type-B phase with the structural symmetry switched off, resulting in their almost identical total energies. This is probably due to the fact that the imaginary phonon modes around the high symmetry point  $K$  that lead to the distortion disappear in our calculated phonon spectra (Fig. S6<sup>†</sup>). This similar distorted structure was also found in transition metal dichalcogenides, but it was determined as a transient state between the 2H phase and the  $T_d$  phase.<sup>63</sup> Therefore, further exploration of this possible distorted phase of type-B  $\text{Sc}_2\text{CS}_2$  and  $\text{Y}_2\text{CS}_2$  is beyond the scope of this study.

On the basis of the most stable structure of  $\text{M}_2\text{CS}_2$ , all possible configurations of  $\text{M}_2\text{CS}$  were constructed by  $2 \times 2 \times 1$

cell expansion and removal of half of the S terminations, which were done by disorder code.<sup>64</sup> There are six possible configurations for  $\text{Ti}_2\text{CS}$ ,  $\text{Zr}_2\text{CS}$ ,  $\text{Hf}_2\text{CS}$  as depicted in Fig. S3,<sup>†</sup> and nine possible configurations for  $\text{Sc}_2\text{CS}$ ,  $\text{Y}_2\text{CS}$  as shown in Fig. S4.<sup>†</sup> Interestingly, it can be seen from Tables S3 and S4<sup>†</sup> that the S groups on both sides of all studied  $\text{M}_2\text{CS}$  are preferentially arranged in stripes, as shown in Fig. S3 DEF and S4 DEF.<sup>†</sup> That is, the strip-like S groups on both sides of  $\text{M}_2\text{CS}_2$  are removed in turn, so that the number of S atoms removed on both sides is identical. More importantly, among all the arrangements of stripe-like S terminations, the stripe-like S terminations on both sides of  $\text{M}_2\text{CS}$  are preferentially parallel and the distance between the two stripe-like S groups is the shortest in the  $xy$  plane as displayed in Fig. 1 type-C or S3D and S4F.<sup>†</sup> This can maintain the crystalline structure of  $\text{M}_2\text{CS}_2$  to the greatest extent. Furthermore, it is evident from Table S3<sup>†</sup> that it is most energetically unfavorable to completely remove the S atoms on one side of the symmetric type-A  $\text{M}_2\text{CS}_2$  to expose the MXene, but this is not necessarily the case for the asymmetric type-B  $\text{M}_2\text{CS}_2$ . As with the symmetric type-A phase, it is most energetically unfavorable to remove all the S atoms projected to the bottom M atoms of the asymmetric type-B  $\text{M}_2\text{CS}_2$  (Fig. S4A<sup>†</sup>). But it can be seen from Table S4<sup>†</sup> that removing all S atoms projected to C atoms (Fig. S4I<sup>†</sup>) is easier than removing 1 S atom projected to the bottom M atom and 3 S atoms projected to the C atoms (Fig. S4G and H<sup>†</sup>). Importantly, considering the small energy differences among the three configurations A, B, and C of the stoichiometric  $\text{M}_2\text{CS}_2$  in Table S1,<sup>†</sup> the most stable non-stoichiometric  $\text{M}_2\text{CS}$  configurations derived from these three configurations were also investigated and presented in Fig. S5,<sup>†</sup> and their corresponding calculated energies are listed in Table S5.<sup>†</sup> It is evident from Table S5<sup>†</sup> that the total energy of the most stable configuration of  $\text{M}_2\text{CS}$  ( $\text{M} = \text{Sc}$ ,  $\text{Ti}$ ,  $\text{Y}$ ,  $\text{Zr}$ , and  $\text{Hf}$ ) with stripe-like S terminations derived from symmetric type-A  $\text{M}_2\text{CS}_2$  (Fig. 1 and S1B<sup>†</sup>) is the smallest, indicating that regardless of the stable configuration of  $\text{M}_2\text{CS}_2$ , the stripe-like S terminations

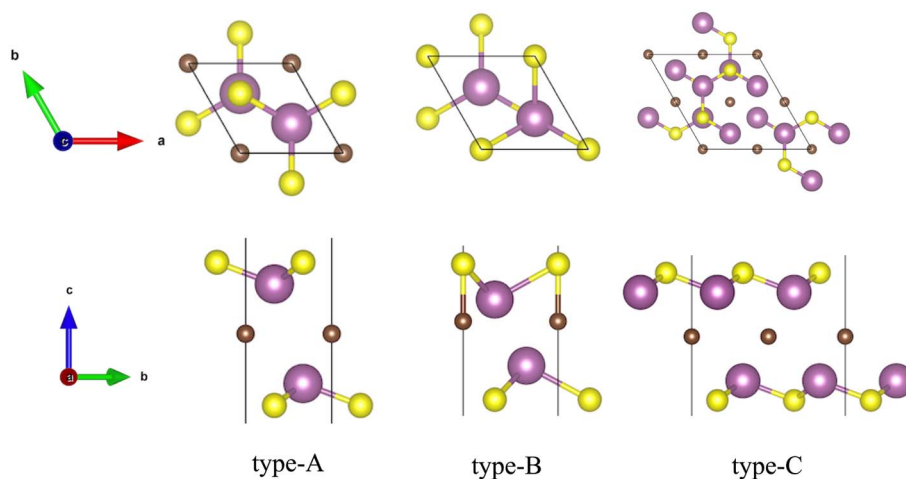


Fig. 1 The optimized most stable configurations of  $\text{M}_2\text{CS}_x$  ( $\text{M} = \text{Sc}$ ,  $\text{Ti}$ ,  $\text{Y}$ ,  $\text{Zr}$  and  $\text{Hf}$ ,  $x = 1, 2$ ). Type-A: the top and side views of the most stable configurations of  $\text{M}_2\text{CS}_2$  ( $\text{M} = \text{Ti}$ ,  $\text{Zr}$  and  $\text{Hf}$ ), type-B: the top and side views of the most stable configurations of  $\text{Sc}_2\text{CS}_2$  and  $\text{Y}_2\text{CS}_2$ , type-C: the top and side views of the most stable configurations of  $\text{M}_2\text{CS}$  ( $\text{M} = \text{Sc}$ ,  $\text{Ti}$ ,  $\text{Y}$ ,  $\text{Zr}$  and  $\text{Hf}$ ).



**Table 1** The calculated Lattice constant (Å), space group, cohesive energy  $E_{\text{coh}}$  (eV per atom) and bond lengths (Å) of M–S and M–C bonds of  $\text{M}_2\text{CS}_x$  (M = Sc, Ti, Y, Zr and Hf,  $x = 1, 2$ )

Material	Lattice constant		Bond length		Space group	$E_{\text{coh}}$	Material	Lattice constant		Bond length		Space group	$E_{\text{coh}}$
	$a$		M–S	M–C				$a$		M–S	M–C		
$\text{Sc}_2\text{CS}_2$	3.76		2.484/2.459	2.293/2.650	$P3m1$	−6.03	$\text{Sc}_2\text{CS}$	6.82		2.474	2.253	$P2_1/m$	−6.30
$\text{Ti}_2\text{CS}_2$	3.16		2.395	2.189	$P3m1$	−6.70	$\text{Ti}_2\text{CS}$	6.17		2.358	2.093	$P2_1/m$	−7.00
$\text{Y}_2\text{CS}_2$	4.17		2.628/2.605	2.485/2.877	$P3m1$	−6.52	$\text{Y}_2\text{CS}$	7.37		2.656	2.429	$P2_1/m$	−6.62
$\text{Zr}_2\text{CS}_2$	3.44		2.531	2.394	$P3m1$	−8.13	$\text{Zr}_2\text{CS}$	6.64		2.508	2.278	$P2_1/m$	−8.15
$\text{Hf}_2\text{CS}_2$	3.40		2.508	2.366	$P3m1$	−7.92	$\text{Hf}_2\text{CS}$	6.54		2.477	2.260	$P2_1/m$	−8.14

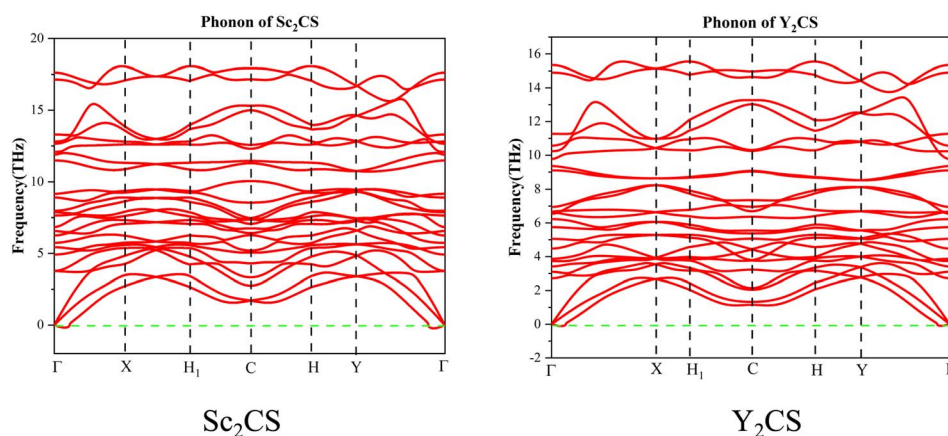
**Table 2** Loewdin atomic charge of  $\text{M}_2\text{CS}_x$  (M = Sc, Ti, Y, Zr and Hf,  $x = 1, 2$ )

Material	C	S	M	Material	C	S	M
$\text{Sc}_2\text{CS}_2$	−1.53	−0.31/−0.85	1.32/1.46	$\text{Sc}_2\text{CS}$	−1.95	−0.94	1.45/1.48
$\text{Ti}_2\text{CS}_2$	−1.73	−0.56	1.42	$\text{Ti}_2\text{CS}$	−1.90	−0.78	1.30/1.38
$\text{Y}_2\text{CS}_2$	−0.85	−0.43/−0.10	0.75/0.63	$\text{Y}_2\text{CS}$	−0.91	−0.46	0.67/0.70
$\text{Zr}_2\text{CS}_2$	−1.59	−0.54	1.36	$\text{Zr}_2\text{CS}$	−1.63	−0.69	1.28/1.30
$\text{Hf}_2\text{CS}_2$	−1.08	−0.31	0.85	$\text{Hf}_2\text{CS}$	−1.02	−0.42	0.70/0.73

of  $\text{M}_2\text{CS}$  tend to be located on top of the underlying metal layer as shown in Fig. 1 type-C.

The calculated lattice constants, cohesive energies, space groups and bond lengths of M–S and M–C bonds of the most stable configurations of  $\text{M}_2\text{CS}_2$  and  $\text{M}_2\text{CS}$  studied are shown in Table 1. For all  $\text{M}_2\text{CS}_x$  ( $x = 1$  or  $2$ ) studied, the cohesive energy of  $\text{M}_2\text{CS}_x$  is negative, compared to the respective  $E_{\text{coh}}$  values of −6.38 and −5.06 eV per atom for  $\text{Sc}_2\text{CO}_2$  (ref. 65) and  $\text{Ti}_2\text{CO}_2$ ,<sup>66</sup> which indicates that they are thermodynamically stable to the isolated constituent atoms. The space group of the  $\text{M}_2\text{CS}_2$  studied is  $P3m1$ , consistent with the experimental observations of traditional stoichiometric MXenes,<sup>16</sup> while the space group of  $\text{M}_2\text{CS}$  (M = Sc, Ti, Y, Zr, and Hf) is  $P2_1/m$ . The lattice parameter  $a = 3.16$  Å of  $\text{Ti}_2\text{CS}_2$  and the lattice constant  $a = 6.17$  Å of  $\text{Ti}_2\text{CS}$  are close to the experimentally observed  $a$  value of 3.21 Å for  $\text{Ti}_2\text{CS}$ .<sup>16</sup> And the lattice constants of  $\text{M}_2\text{CS}_2$  (M = Sc, Ti, Zr and Hf) are slightly larger than those of the corresponding  $\text{M}_2\text{CO}_2$  (i.e. 3.41, 3.04, 3.31 and 3.27 Å for  $\text{Sc}_2\text{CO}_2$ ,  $\text{Ti}_2\text{CO}_2$ ,  $\text{Zr}_2\text{CO}_2$  and  $\text{Hf}_2\text{CO}_2$ )<sup>67</sup> due to the weaker M–S bond relative to the M–O bond.

Clearly, it can be seen that the lattice constant of  $\text{Y}_2\text{CS}_x$  is the largest among the studied  $\text{M}_2\text{CS}_x$  with the same formula due to the weak interatomic bonding of Y–C and Y–S, which will be explained in detail in Section 3.2. The calculated Ti–C bond length of 2.09 Å and Ti–S bond length of 2.36 Å for the  $\text{Ti}_2\text{CS}$  are in good agreement with the experimentally observed Ti–C and Ti–S bond lengths of 2.14 Å and 2.41 Å.<sup>16</sup> Importantly, the M–C and M–S bond lengths of the  $\text{M}_2\text{CS}_2$  studied are longer than those of the counterpart  $\text{M}_2\text{CS}$ . And the calculated  $E_{\text{coh}}$  of the  $\text{M}_2\text{CS}_2$  studied are greater than those of the counterpart  $\text{M}_2\text{CS}$ . In addition, it can be found from Table 2 that the net negative charge of S and C atoms of the  $\text{M}_2\text{CS}_2$  studied are smaller than those of the corresponding  $\text{M}_2\text{CS}$ , which indicates that more electrons are transferred from the M atom to the C and S atoms of the  $\text{M}_2\text{CS}$  than the corresponding  $\text{M}_2\text{CS}_2$ . The significant charge transfer can also be visually observed from the charge density difference in Fig. S6.† This confirms that the M–C and M–S bonds of  $\text{M}_2\text{CS}$  are stronger than the corresponding  $\text{M}_2\text{CS}_2$ .

**Fig. 2** The calculated phonon dispersions of the  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$ .



In order to further check the dynamical stability of MXenes, the phonon dispersion curves of  $M_2CS_x$  were calculated. It is worth mentioning that small imaginary frequencies near the  $\Gamma$  point are often observed in the calculated phonon spectra of 2D systems, which could be caused by numerical noise owing to the vacuum region.<sup>68–70</sup> As shown in Fig. 2 and S6,<sup>†</sup> almost no imaginary frequency is observed in the phonon dispersions of  $M_2CS$  ( $M = Sc, Ti, Zr$ , and  $Y$ ), and some small negative frequencies near the  $\Gamma$  point appear in the phonon dispersion curves of  $M_2CS_2$  ( $M = Sc, Ti, Zr$ , and  $Hf$ ) and  $Hf_2CS$ . This is an indication of dynamic stabilities of  $M_2CS_x$  studied except  $Y_2CS_2$ , consistent with the fact that  $Ti_2CS$  was found in experiments.<sup>16</sup> As a comparison, the exception  $Y_2CS_2$  shows significant imaginary frequencies in the phonon dispersion, consistent with previously reported results by Zhang *et al.*<sup>42</sup> and Li *et al.*,<sup>68</sup> which is a sign that the formation of the  $Y_2CS_2$  MXene probably needs more inspection from experiments. Then, AIMD simulations were performed to further evaluate the dynamical and thermal stabilities of the  $M_2CS_x$  studied as displayed in Fig. 3. There is no broken M–C and M–S bonds or obvious structural reconstruction within a simulation of 4 ps at 300 K for the  $M_2CS$  ( $M = Sc, Y$ , and  $Zr$ ) and even at 900 K for the  $M_2CS_2$  ( $M = Sc, Ti, Zr$ , and  $Hf$ ) and  $Hf_2CS$ , manifesting the good thermal stability of these S-terminated MXenes. While for  $Ti_2CS$ , at 300 K, a structural reconstruction of part of the S-terminations moving from the top of bottom metal to the top of the carbon layer is observed, indicating that the strip-like S-terminations of  $Ti_2CS$  are temperature-sensitive. In contrast,  $Y_2CS_2$  exhibits a pronounced destruction within 4 ps simulations at 300 K,

which can be regarded as evidence of poor thermal stability, consistent with the observation of significant imaginary frequency. From the above analysis, it can be seen that the studied  $M_2CS_x$  except  $Y_2CS_2$  has good dynamical and thermal stability, and it is particularly noted that the strip-shaped S functional groups of  $Ti_2CS$  are temperature sensitive and easily disturbed. Chen *et al.*<sup>71</sup> demonstrated that the stabilization of a certain surface configuration of MXene was the statistical average of the adsorption and desorption of surface functional groups. Thus, the total energy of a certain surface configuration is a function of the chemical potential of the functional group. When the chemical potential of the S functional group is high, close to its upper limit (*i.e.*, the chemical potential of elemental  $S_8$ ), the stoichiometric  $M_2CS_2$  is the thermodynamically most favorable configuration under such condition. As a comparison, when the chemical potential of the S functional group is small, the non-stoichiometric  $M_2CS_x$  may be the thermodynamically preferred configuration, and even  $M_2CS_x$  would decompose into bare  $M_2C$  and elemental sulfur or sulfide. In the experimental preparation,<sup>16,20</sup> sulfur-functionalized MXene was obtained by functional group substitution of halogen-functionalized MXene by  $Li_2S$  or intercalation of bare MXene by  $FeS$  or  $CuS$ . Under such preparation conditions, the chemical potential of the S functional group is generally lower, which is more conducive to the formation of non-stoichiometric S-functionalized MXenes, which may be the reason why no stoichiometric S-functionalized MXenes were observed experimentally. Zhu *et al.*<sup>28</sup> theoretically clarified the feasibility of interconversion of  $Zr_2CO_2$  and excess  $CS_2$  to  $Zr_2CS_2$  under the release of  $COS$ .

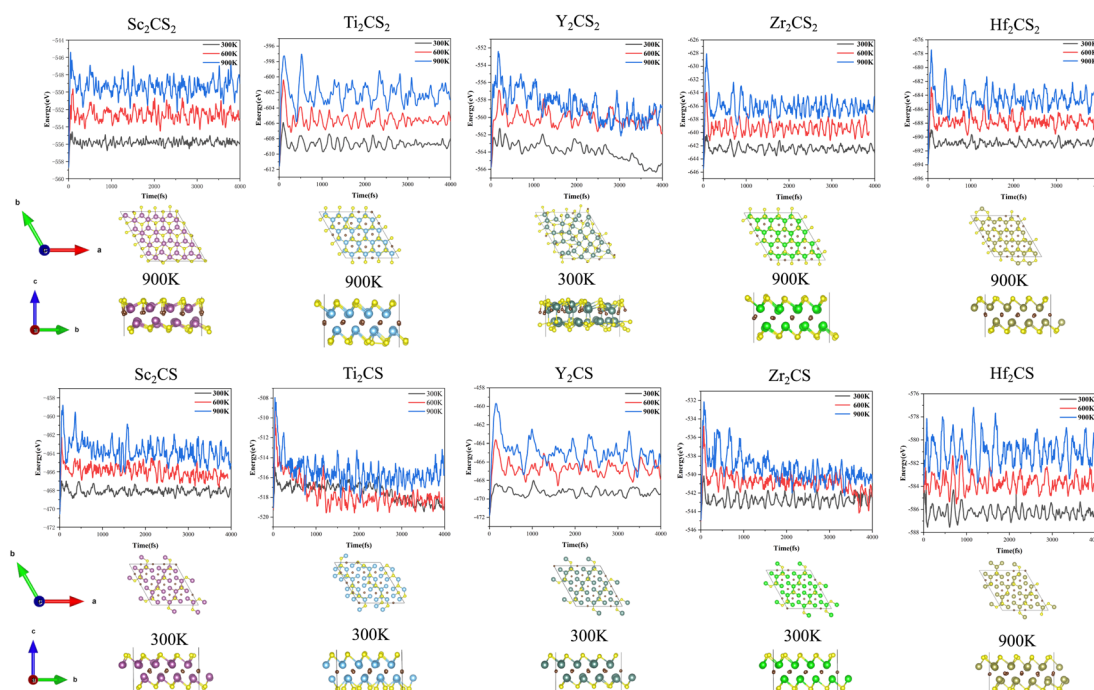
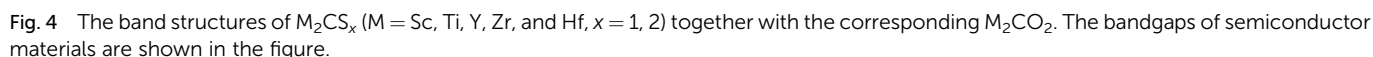


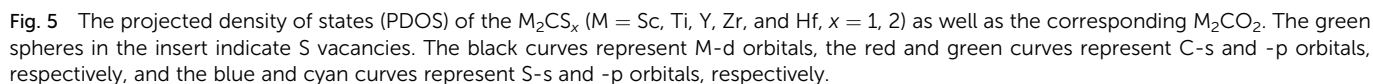
Fig. 3 Free energy fluctuations with respect to time at 300 K, 600 K and 900 K in AIMD simulations for  $M_2CS_x$  ( $M = Sc, Ti, Y, Zr$ , and  $Hf$ ,  $x = 1, 2$ ), and the obtained structures of  $M_2CS_x$  after AIMD simulations at specific temperature. The specified temperature in the figure is the highest temperature at which the structure can be kept stable among the three temperatures studied. Noteworthy, the reconstruction of the surface functional groups of  $Ti_2CS$  and the pronounced destruction of  $Y_2CS_2$  were observed at the lowest temperature studied, 300 K.





### 3.2. Electronic structure and bonding mechanism of $M_2CS_x$

previous reported results.<sup>40,67</sup> Interestingly, four sulfur-terminated MXenes  $\text{Sc}_2\text{CS}_2$ ,  $\text{Y}_2\text{CS}_2$ ,  $\text{Sc}_2\text{CS}$ , and  $\text{Y}_2\text{CS}$  were identified as indirect bandgap semiconductors with bandgaps of 1.56, 1.85, 0.68, and 0.92 eV, respectively, which are larger than the bandgaps of 1.56 and 1.37 eV for the counterparts  $\text{Sc}_2\text{CO}_2$  and  $\text{Y}_2\text{CO}_2$ . In contrast, the energy bands of the studied  $\text{M}_2\text{CS}_x$  ( $\text{M} = \text{Ti, Zr, and Hf}$ ,  $x = 1, 2$ ) crossing Fermi level exhibit the metallic-like features due to the presence of nonbonding M-d states at the Fermi level in Fig. 5. Since the traditional PBE functional generally underestimates the band gap of the material, the band gap of the sulfur-terminated MXene was corrected



by the HSE06 functional.<sup>72</sup> After HSE06 correction, the band gaps of  $\text{Sc}_2\text{CS}_2$ ,  $\text{Y}_2\text{CS}_2$ ,  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  were increased to 2.54, 2.75, 1.43 and 1.69 eV, respectively. Their suitable bandgap endows them with great potential as electronic devices. Cautious inspection from the calculated band gaps of  $\text{M}_2\text{CS}_x$  ( $\text{M} = \text{Sc}$  and  $\text{Y}$ ,  $x = 1, 2$ ) reveals that sulfur vacancy defects increase the unbonded electrons near the Fermi level of metal atoms on the MXene surface leading to the attenuation of the band gap.

In order to study the underlying bonding mechanism of the studied  $\text{M}_2\text{CS}_x$ , the projected density of states (PDOS) of  $\text{M}_2\text{CS}_x$  together with the corresponding  $\text{M}_2\text{CO}_2$  for comparison were investigated as depicted in Fig. 5. For all MXenes studied, the electronic states above the Fermi level are dominated by nonbonding  $t_{2g}$  states and antibonding  $e_g^*$  states of the M-d orbital. Noteworthily, the S-p state of  $\text{M}_2\text{CS}_x$  overlaps with the M-d state in the energy range from  $-4.5$  eV to  $0$  eV, while the O-p state of  $\text{M}_2\text{CO}_2$  hybridizes with the M-d state around  $-6$  to  $-2$  eV, which is an implication of the stronger M-O bond than M-S bond. Resembling the corresponding  $\text{M}_2\text{CO}_2$ , due to the splitting of the 5-fold degenerate M-d orbitals of  $\text{M}_2\text{CS}_2$  in the octahedral crystal field of  $\text{MX}_6$ , 5 hybridization peaks of the S-p state are observed, which are more conspicuous in  $\text{Y}_2\text{CS}_2$  and  $\text{Sc}_2\text{CS}_2$ , but this phenomenon disappears in  $\text{M}_2\text{CS}$  due to the presence of S vacancies. In particular, the p-d hybridization peaks between S and Y of  $\text{Y}_2\text{CS}_2$  are very localized, reflecting the weak nature of the Y-S bond, which are significantly improved in  $\text{Y}_2\text{CS}$ . More importantly, the hybridization peaks between the M-d orbital and the C-p or S-p orbital of  $\text{M}_2\text{CS}$  are remarkably higher than those of the corresponding  $\text{M}_2\text{CS}_2$ , which can be

regarded as evidence that the M-C and M-S bonds in  $\text{M}_2\text{CS}$  are stronger than those in  $\text{M}_2\text{CS}_2$ .

To explore bonding/antibonding states of bonds of the studied  $\text{M}_2\text{CS}_x$  ( $\text{M} = \text{Sc}, \text{Ti}, \text{Y}, \text{Zr}$ , and  $\text{Hf}$ ,  $x = 1, 2$ ), the projected crystal orbital Hamilton population ( $p\text{COHP}$ ) was calculated using the LOBSTER program,<sup>73</sup> as shown in Fig. 6. A positive value of  $-p\text{COHP}$  indicates a bonding state, and a negative value indicates an antibonding state. The hybridization between M and C and between M and S of the investigated  $\text{M}_2\text{CS}$  is stronger than that of the corresponding  $\text{M}_2\text{CS}_2$  (seen in Fig. 5) leading to greater splitting of bonding and antibonding states in Fig. 6, *i.e.* farther away from the Fermi energy level, consistent with the reported results of  $\text{Ti}_2\text{CO}_2$ .<sup>74</sup> However, the introduction of sulfur vacancies will increase the non-bonding  $e_g$  states of the metal d orbitals, thereby making the antibonding states appear near the Fermi level and significantly reducing the thermal stability of the material, consistent with the AIMD simulation results. Especially, both the bonding and antibonding states of the Y-S bond of  $\text{Y}_2\text{CS}_2$  are very small, again manifesting a weak Y-S bond, leading to the largest lattice constant of  $\text{Y}_2\text{CS}_2$  among all studied MXenes. On the contrary, the bonding states of the Y-C and Y-S bonds of  $\text{Y}_2\text{CS}$  are very obviously enhanced, significantly improving the stability of  $\text{Y}_2\text{CS}_x$ . Consequently, the d-p hybridization between the metal and C/S atoms of  $\text{M}_2\text{CS}$  is significantly higher than that of the corresponding  $\text{M}_2\text{CS}_2$ , resulting in stronger M-C and M-S bonds in  $\text{M}_2\text{CS}$  than in  $\text{M}_2\text{CS}_2$ . However, due to the introduction of sulfur vacancies in other studied MXenes except  $\text{Y}_2\text{CS}_x$ , the antibonding state would appear near the Fermi level, reducing the thermal stability of the material. On the contrary, sulfur

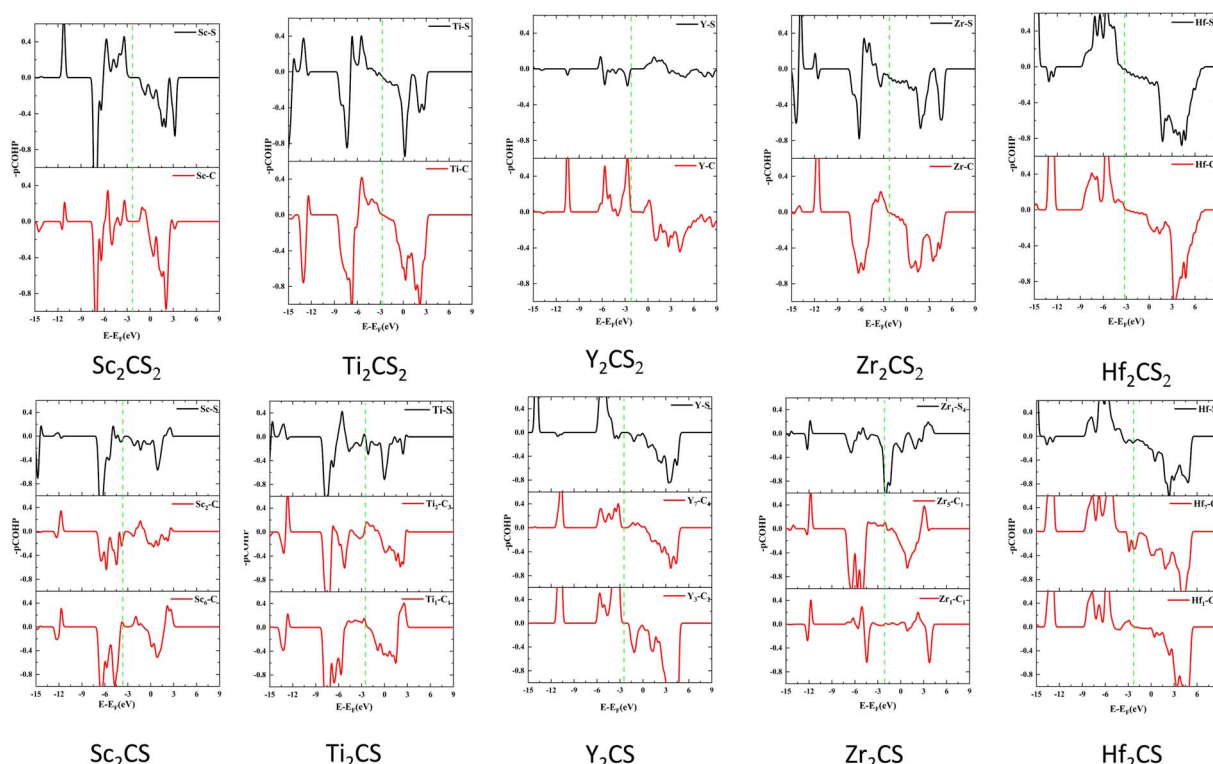


Fig. 6 The calculated COHP curves of  $\text{M}_2\text{CS}_x$  ( $\text{M} = \text{Sc}, \text{Ti}, \text{Y}, \text{Zr}$ , and  $\text{Hf}$ ,  $x = 1, 2$ ). The vertical green dotted line represents the Fermi level.





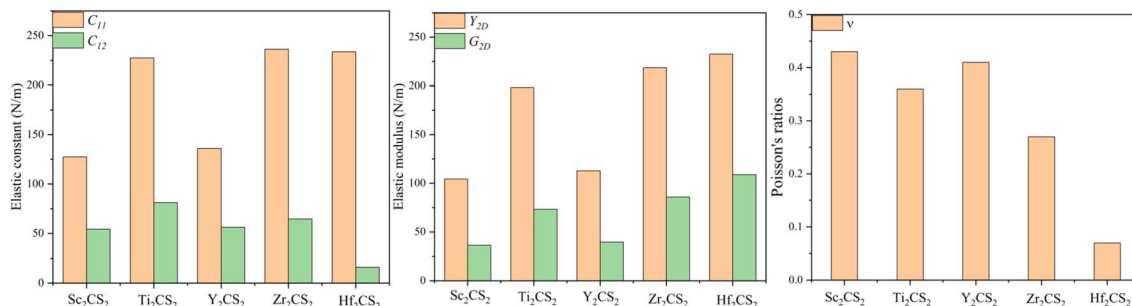


Fig. 7 The elastic constants  $C_{11}$ ,  $C_{12}$ , in-plane Young's moduli  $Y_{2D}$ , in-plane shear moduli  $G_{2D}$  (in  $\text{N m}^{-1}$ ), and Poisson's ratios  $\nu$  of the  $\text{M}_2\text{CS}_x$  MXenes studied.

vacancies would significantly enhance the bonding states of Y–C and Y–S bonds and improve the stability of  $\text{Y}_2\text{CS}_x$ .

### 3.3. Mechanical properties

The fabrication of 2D crystal-based electronics generally requires high in-plane stiffness to avoid curling and obtain free-standing membranes. Therefore, the mechanical properties of  $\text{M}_2\text{CS}_x$  ( $\text{M} = \text{Sc}, \text{Ti}, \text{Y}, \text{Zr}, \text{and Hf}$ ,  $x = 1, 2$ ) were investigated by examining their elastic constants. Elastic constants  $C_{ij}$  of 2D crystal can be obtained by the first-principles energy-strain method, which is based on the energy variant by applying a small strain  $\varepsilon$  onto the equilibrium structure. Subsequently, the in-plane Young's modulus  $Y_{2D}$ , in-plane shear modulus  $G_{2D}$  (in  $\text{N m}^{-1}$ ), and Poisson's ratios  $\nu$  can be obtained by eqn (5)–(7)<sup>70</sup>

$$Y_{2D} = (C_{11}^2 - C_{12}^2/C_{11}) \quad (5)$$

$$G_{2D} = 1/2(C_{11} - C_{12}) \quad (6)$$

$$\nu = C_{12}/C_{11} \quad (7)$$

The 2D crystal structure is determined to be mechanically stable when all elastic constants satisfy the well-known Born–Huang criteria:<sup>75</sup> For a trigonal  $\text{M}_2\text{CS}_2$  structure:  $C_{11} > 0$ ,  $C_{11} > |C_{12}|$ ,  $C_{66} > 0$ , and for a monoclinic  $\text{M}_2\text{CS}$  structure:  $C_{11} > 0$ ,  $C_{11}C_{12} > C_{12}C_{12}$ ,  $C_{ij} > 0$ . The calculated elastic constants of  $\text{M}_2\text{CS}_x$  ( $\text{M} = \text{Sc}, \text{Ti}, \text{Y}, \text{Zr}, \text{and Hf}$ ,  $x = 1, 2$ ) in Fig. 7 and Table 3 meet the mechanical stability criteria, indicating they are mechanically stable under ambient conditions. It is evident that all the in-plane stiffnesses of  $\text{Sc}_2\text{CS}_x$  and  $\text{Y}_2\text{CS}_x$  are much smaller than those of the  $\text{M}_2\text{CS}_x$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{and Hf}$ ) probably

due to the smaller cohesive energies of  $\text{Sc}_2\text{CS}_x$  and  $\text{Y}_2\text{CS}_x$  relative to  $\text{M}_2\text{CS}_x$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{and Hf}$ ). And the maximum  $Y_{2D}$  and  $G_{2D}$  values of  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  are larger than those of  $\text{Sc}_2\text{CS}_2$  and  $\text{Y}_2\text{CS}_2$ , respectively, due to the stronger M–C and M–S bonds of  $\text{M}_2\text{CS}$  compared with  $\text{M}_2\text{CS}_2$ , while  $\text{M}_2\text{CS}_x$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{and Hf}$ ) show the opposite trend, which may be caused by the anti-bonding states of M–C bond occurring at the Fermi level of  $\text{M}_2\text{CS}$  (Fig. 6). The in-plane Young's modulus and in-plane shear modulus of 104.39 and 36.61  $\text{N m}^{-1}$  for  $\text{Sc}_2\text{CS}_2$  is the smallest among all the studied  $\text{M}_2\text{CS}_2$ , which are smaller than those of  $\text{Sc}_2\text{CO}_2$ .<sup>67</sup> Noteworthy, the calculated in-plane Young's moduli of the semiconductors  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  are 125.06–140.35 and 82.77–125.34  $\text{N m}^{-1}$ , respectively, which are comparable to those of  $\text{MoSe}_2$  (125  $\text{N m}^{-1}$ ) and  $\text{MoS}_2$  (168  $\text{N m}^{-1}$ ),<sup>76</sup> indicating that  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  monolayer have good mechanical properties. And it is further found that their Poisson's ratios  $\nu$  are all within 0.3. Since the low Poisson's ratio is favorable for the application of MXenes in flexible device materials,<sup>66</sup>  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  MXenes have the potential to be used as flexible electronic devices.

### 3.4. Carrier mobility of nonstoichiometric $\text{Sc}_2\text{CS}$ and $\text{Y}_2\text{CS}$ MXenes

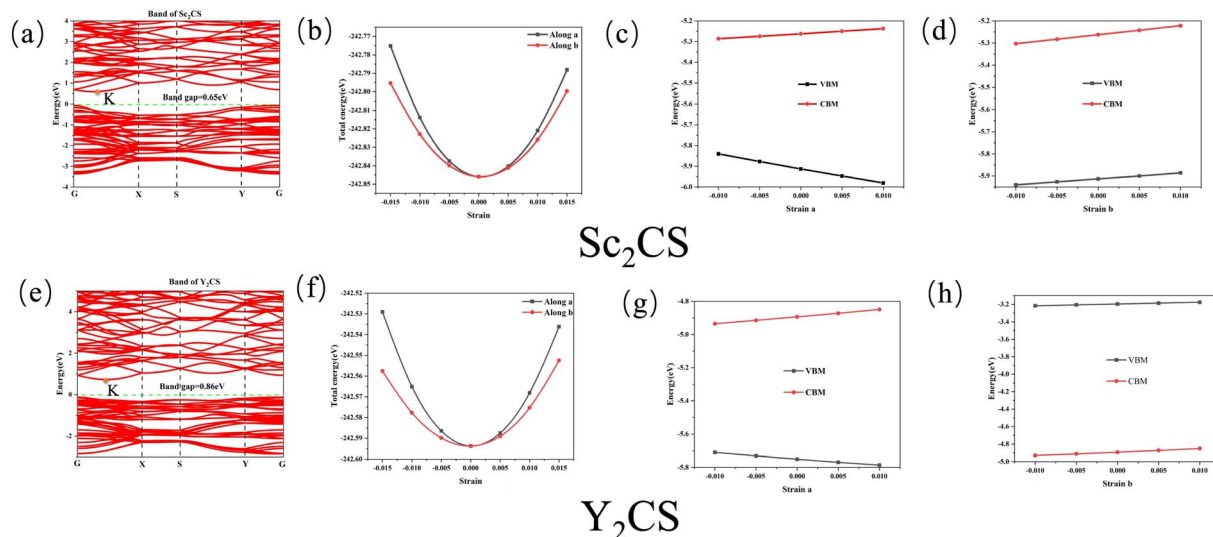
Carrier mobility is an important physical quantity to measure the performance of electronic devices. The orthorhombic  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  supercell was adopted to calculate the carrier mobility according to deformation potential theory. As shown in Fig. 8a and e, the valence band maximum (VBM) of  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  at  $\Gamma$  point is observed while the conduction band minimum (CBM) appears at the  $K$  point along  $\Gamma$ –X direction in the electronic band structure of nonstoichiometric  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$ . As an important band structure-derived property, effective masses of

Table 3 The elastic constants  $C_{11}$ ,  $C_{12}$ , in-plane Young's moduli  $Y_{2D}$ , in-plane shear moduli  $G_{2D}$  (in  $\text{N m}^{-1}$ ), and Poisson's ratios  $\nu$  of the  $\text{M}_2\text{CS}_x$  MXenes studied

	$C_{11}$	$C_{12}$	$Y_{2D}$ (min)	$Y_{2D}$ (max)	$G_{2D}$ (min)	$G_{2D}$ (max)	$\nu$ (min)	$\nu$ (max)
$\text{Sc}_2\text{CS}$	138.95	42.61	125.06	140.35	50.16	50.99	0.27	0.31
$\text{Ti}_2\text{CS}$	194.49	55.80	175.98	196.30	70.03	75.02	0.23	0.30
$\text{Y}_2\text{CS}$	120.15	38.14	82.77	125.34	36.05	43.62	0.25	0.49
$\text{Zr}_2\text{CS}$	196.50	56.84	176.01	194.32	69.85	74.81	0.24	0.31
$\text{Hf}_2\text{CS}$	217.28	58.13	197.22	210.13	79.22	82.62	0.24	0.28







**Fig. 8** (a) and (e) The calculated band structure of  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  monolayer in the orthogonal supercell, (b) and (f) energy–strain relationship along  $x$  ( $\Gamma$ – $X$ ) and  $y$  ( $\Gamma$ – $Y$ ) directions of  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  supercell, and (c), (d), (g) and (h) band edges as a function of strain along  $x$  and  $y$  directions of  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  supercell, respectively.

**Table 4** The calculated carrier mobilities of nonstoichiometric  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$

	Carrier type	Direction	$C_{2D}$ ( $\text{J m}^{-2}$ )	$E_1$ (eV)	$m^*$ ( $m_e$ )	$\mu$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )	$\tau$ (fs)
$\text{Sc}_2\text{CS}$	Electron	$x$	111.98	7.03	0.70	232.59	92.58
		$y$	84.33	4.06	0.64	628.22	228.62
	Hole	$x$	111.98	2.42	3.30	88.32	165.72
		$y$	84.33	4.06	2.04	61.75	71.72
$\text{Y}_2\text{CS}$	Electron	$x$	91.02	4.30	0.55	818.51	255.98
		$y$	57.66	3.95	0.58	552.55	182.23
	Hole	$x$	91.02	3.76	14.04	1.64	13.11
		$y$	57.66	2.01	6.35	17.80	64.28

electrons at  $K$  point and holes at  $\Gamma$  point of  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  were calculated and shown in Table 4. For both  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$ , it can be readily found that the effective hole mass is much larger than the effective electron mass, suggesting that electrons can have higher mobility than holes under an external electric field due to the much smaller effective mass. Interestingly, the effective electron mass and effective hole mass of  $\text{Sc}_2\text{CS}$  along  $x$  direction are larger than those along  $y$  direction, respectively, and the effective hole mass of  $\text{Y}_2\text{CS}$  material also shows the same trend, showing effective mass anisotropy. In detail, the effective mass of electrons of  $\text{Sc}_2\text{CS}$  along  $x$  direction is  $0.70m_e$ , which is 9.4% larger than that along  $y$  direction, while the effective mass of holes along  $x$  direction ( $3.30m_e$ ) is 61.8% larger than that along  $y$  direction. In comparison, for  $\text{Y}_2\text{CS}$ , the effective electron masses along the  $x$  and  $y$  directions are almost equal, but the effective hole mass along the  $x$  direction is 1.21 times larger than along the  $y$  direction. Besides the effective mass, the deformation potential constant  $E_1$  and elastic modulus  $C_{2D}$  of  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  MXene were also calculated. The  $C_{2D}$  value of electrons and holes of  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  along  $x$  direction is 111.98 and 91.02  $\text{J m}^{-2}$ , which is 32.8% and 57.9%

larger than those along the  $y$  direction, respectively. Additionally, the  $E_1$  values (7.03 eV) of holes at  $\Gamma$  point of  $\text{Sc}_2\text{CS}$  along  $x$  direction is 1.73 times that along  $y$  direction, while the  $E_1$  of electrons at  $K$  point along the  $x$  direction is only 0.60 times that along the  $y$  direction. And the deformation potential constants of holes at  $\Gamma$  point of  $\text{Y}_2\text{CS}$  along  $x$  and  $y$  directions are 4.30 and 3.76 eV, which are 0.35 and 1.75 eV larger than those of electrons at  $K$  point along  $x$  and  $y$  directions, respectively.

Therefore, according to eqn (3), the electron mobilities and hole mobilities of  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  are predicted and summarized in Table 4. The room-temperature electron mobilities of  $\text{Sc}_2\text{CS}$  along the  $x$  and  $y$  directions were determined to be 232.59 and 628.22  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ , respectively, compared with the room-temperature hole mobilities of only 88.32 and 61.75  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  along the  $x$  and  $y$  directions. That is, the electron mobilities along the  $x$  and  $y$  directions are about 2.63 and 10.17 times that of the holes, respectively, due to the large difference in effective mass, which exhibits pronounced anisotropy. Resembling the charge transport of  $\text{Sc}_2\text{CS}$ , the electron mobilities of  $\text{Y}_2\text{CS}$  along the  $x$  and  $y$  directions (818.51 and 552.55  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ , respectively) are 498 and 30 times higher than the hole mobilities



along the  $x$  and  $y$  directions. Therefore, it can be said that the charge transport of  $\text{Sc}_2\text{CS}$  is predominated by electron, which is different from our recently reported  $\text{Sc}_2\text{CO}_2$  with similar electron and hole mobilities.<sup>40</sup> In addition, the predicted carrier mobility of non-stoichiometric  $\text{Sc}_2\text{CS}$  is much higher than that of  $\text{MoS}_2$  monolayer,<sup>77</sup> but much smaller than that of  $\text{Sc}_2\text{CO}_2$  (ref. 40) due to defect scattering caused by sulfur vacancies. Therefore, the structurally stable  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  with suitable carrier mobility and mechanical properties may serve as an excellent nanoelectronic material.

## 4. Conclusion

In this study, the structural stability, electronic structure, elastic and charge transport properties of  $\text{M}_2\text{CS}_x$  ( $\text{M} = \text{Sc}, \text{Ti}, \text{Y}, \text{Zr}$ , and  $\text{Hf}$ ,  $x = 1, 2$ ) were studied by using first-principles density functional theory. The studied  $\text{M}_2\text{CS}_x$  except  $\text{Y}_2\text{CS}_2$  were determined to be thermodynamically, dynamically, thermally, and mechanically stable, suggesting that these S-functionalized MXenes can be successfully prepared. In contrast to all studied  $\text{M}_2\text{CO}_2$  being indirect bandgap semiconductors, only four S-terminated MXenes ( $\text{Sc}_2\text{CS}_2$ ,  $\text{Y}_2\text{CS}_2$ ,  $\text{Sc}_2\text{CS}$ , and  $\text{Y}_2\text{CS}$ ) were identified as indirect bandgap semiconductors. The p-d hybridization between the M-d state and the S/C-p state of  $\text{M}_2\text{CS}$  is stronger than that of  $\text{M}_2\text{CS}_2$ , indicating that the bonding strength of the M-C/S bond in  $\text{M}_2\text{CS}$  is stronger. However, due to the introduction of sulfur vacancies in the Y-free MXene, an antibonding state would occur near the Fermi level, thereby reducing the thermal stability of the material. On the contrary, the sulfur vacancies would significantly enhance the bonding state of Y-C and Y-S bonds and improve the stability of  $\text{Y}_2\text{CS}_x$ . These provides an explanation for the experimentally observed formation of non-stoichiometric  $\text{M}_2\text{CS}_x$ . And the room-temperature electron mobilities of  $\text{Sc}_2\text{CS}$  ( $\text{Y}_2\text{CS}$ ) along the  $x$  and  $y$  directions were determined to be 232.59 (818.51) and 628.22 (552.55)  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ , compared with the room-temperature hole mobilities of only 88.32 (1.64) and 61.75 (17.80)  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ , which are much higher than that of  $\text{MoS}_2$  monolayer, but much smaller than that of  $\text{Sc}_2\text{CO}_2$  due to defect scattering caused by sulfur vacancies. Therefore,  $\text{Sc}_2\text{CS}$  and  $\text{Y}_2\text{CS}$  with suitable carrier mobility and mechanical properties are promising as an excellent nanoelectronic materials. This work is expected to provide theoretical insights for the preparation and application of S-terminated MXenes and the discovery of novel MXene materials.

## Conflicts of interest

The authors declare no competing financial interest.

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