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# Surface Modification of Titanium Carbide MXenes Monolayers (Ti<sub>2</sub>C and Ti<sub>3</sub>C<sub>2</sub>) via Chalcogenide and Halogenide Atoms

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Inspired by the recent successful growth of Ti<sub>2</sub>C and Ti<sub>3</sub>C<sub>2</sub> monolayers, here, we investigate structural, electronic, and mechanical properties of functionalized Ti<sub>2</sub>C and Ti<sub>3</sub>C<sub>2</sub> monolayers by means of density functional theory calculations. The results reveal that monolayers of Ti<sub>2</sub>C and Ti<sub>3</sub>C<sub>2</sub> are dynamically stable metals. Phonon band dispersion calculations demonstrate that two-surface functionalization of Ti<sub>2</sub>C and Ti<sub>3</sub>C<sub>2</sub> via chalcogenides (S, Se, and Te), halides (F, Cl, Br, and I), and oxygen atoms results in dynamically stable novel functionalized monolayer materials. Electronic band dispersions and the density of states calculations reveal that all functionalized monolayer structures preserve the metallic nature of both Ti<sub>2</sub>C and Ti<sub>3</sub>C<sub>2</sub> except the Ti<sub>2</sub>C-O<sub>2</sub>, which possesses behavior of an indirect semiconductor via full-surface oxygen passivation. In addition, it is shown that although, halide passivated Ti<sub>3</sub>C<sub>2</sub> structures are still metallic, there exist multiple Dirac-like cones around the Fermi energy level, which indicates that semi-metallic behavior can be obtained upon external effects by tuning the energy of the Dirac cones. In addition, the computed linear-elastic parameters prove the functionalization is a powerful tool in tuning the mechanical properties of stiff monolayers of bare Ti<sub>2</sub>C and Ti<sub>3</sub>C<sub>2</sub>. Our study discloses the electronic and structural properties of Ti<sub>2</sub>C and Ti<sub>3</sub>C<sub>2</sub> MXene monolayers are suitable for surface modification, which is highly desirable for materials properties engineering and device integration.

Inspired by the discovery of graphene<sup>1</sup> and due to its exceptional properties considerable research has been focused on two-dimensional materials (2DMs) including transition metal (TM) dicalcogenides<sup>5</sup>, phosphorene<sup>4</sup>, hexagonal boron nitrides<sup>2</sup>, silicene<sup>3</sup>, etc. 2DMs such as graphene<sup>6–8</sup>, MoS<sub>2</sub><sup>9</sup>, WS<sub>2</sub><sup>10</sup>, and boron nitride<sup>11,12</sup> are a type of nanomaterials that have attracted increasing attention in the last decade because of their fascinating

properties, which are different from their bulk counterparts<sup>13–16</sup>. Their inherent properties vary from those of their bulk structures due to their atomic thickness. Mechanical or chemical exfoliation and deposition methods are widely used to manufacture these materials<sup>17,18</sup>. Moreover, the quantum containment of electrons in the 2D plane imparts remarkable electrical and electronic characteristics<sup>19–21</sup>. The combination of proper mechanical and physical properties (thermal, electronic, optical) is also of large importance in development of new implementations, where mechanics is combined with condensed matter physics to construct a scalable theoretical structure<sup>22</sup>. In this regard, 2DMs are expected to have a large share in many applications, ranging from energy storage and conversion<sup>23,24</sup> to gas storage or separation<sup>25,26</sup>, photocatalysis<sup>27</sup>, high-performance sensors<sup>28,29</sup>, and membranes<sup>30</sup>.

Among the 2DMs MXenes with the chemical formula: M<sub>n+1</sub>X<sub>n</sub>T<sub>x</sub> (M = Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta; X = C, N; n = 1–3, T<sub>x</sub>=surface termination, e.g., -OH, -F, -O) are genuinely at the frontier of materials science and pledge new scientific and technical horizons<sup>31</sup>. MXenes, a rapidly growing class of 2D multi-layered transition metal carbides and nitrides introduced first by Naguib et al.<sup>32</sup> by discovery of the first two-dimensional (2D) titanium carbide (Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>). By a process known as inter-

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calation, MXenes accommodate different ions and molecules between monolayers, which is often a required step to exploit the material's unique properties and tailor them.<sup>33</sup> Since then, they are used in distinct applications which includes energy conversion and storage<sup>34</sup>, electromagnetic interference shielding<sup>35,36</sup>, adsorption<sup>37</sup>, anti-microbial activity<sup>38,39</sup>, membrane<sup>40</sup>, reinforcements<sup>41</sup>, and catalysis<sup>42</sup>. Besides the aforementioned properties, the MXenes surfaces can be functionalized with different chemical groups such as O, OH, and F, making them a good option for surface state engineering<sup>43</sup>.

Computationally, it has been shown that a change in surface termination can change electrical and optical properties. In this regard, several studies have been performed to consider the effect of surface functionalization on thermal transport<sup>44,45</sup>, electronic properties<sup>46–49</sup>, optical features<sup>50,51</sup>, and thermoelectric<sup>52,53</sup>, in different types of MXenes. H. Wang et al.<sup>56</sup> reported a hybrid electrode made of 2D NbN nanocrystals and self-assembled  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene. The good conductivity and porous nature of NbN monolayers have brought significant advantages for ion infiltration and electrolyte to facilitate, for utilizing in energy storage systems, at a high rate. As a result, NbN- $\text{Ti}_3\text{C}_2\text{T}_x$  electrodes have depicted a thickness independent rate performance, which is much better than the pristine MXene electrode. E. M. D. Siriwardane et al.<sup>57</sup> studied the structural, electronic, stability, ion kinetics, and electrochemical of  $\text{M}_2\text{CS}_2$  MXenes functionalized with sulfur (where M is referred to W, Mo, Cr, Ta, Nb, V, Hf, Zr, Ti, and Sc). The sulfur element preferred to seat at different sites, on pristine  $\text{M}_2\text{C}$  MXenes and constructed a dramatic stable compound. For  $\text{M}_2\text{CS}_2$  MXene structures with M= Nb, V, Hf, Zr, and Ti elements, full Li coverage attraction has been reported on both surfaces. R. Liu et al.<sup>58</sup> assembled a low-cost, efficient, and simple wearable and flexible pressure sensor using MXene and a piece of woven cotton fabric as the active material and substrate, respectively. The MXene-coated cotton can retain moisture and air permeability perfectly. The pressure sensor has been depicted excellent stability, a relaxation speed and rapid response, and high sensitivity. W. Y. Chen et al.<sup>59</sup> functionalized  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene with a superhydrophobic coating layer by utilizing fluoroalkylsilane (FAS) molecules. The analysis methods have demonstrated that the surface properties can be controlled by the functionalized groups.

Q. Zhao et al.<sup>60</sup> investigated  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene monolayer to remove uric acid and creatinine from simulated dialysate and aqueous solution. A high chemisorption rate has been reported with larger chemisorption capacity compared to other chemisorption materials like carbon, as a result of hydrophilic surface functionalizations and the open interlayer structure of  $\text{Ti}_3\text{C}_2\text{T}_x$ , which allow chemisorption between MXene monolayers. The properties of differently synthesized  $\text{Ti}_3\text{C}_2\text{T}_x$  MXenes strongly depend upon fluoride and hydroxy/oxy terminations, which has a higher creatinine chemisorption capacity. In addition to the mentioned research, the interest in 2D MXenes is dramatically increasing since modifying the properties of MXenes by variety of approaches has promoted their application in different fields<sup>61–65</sup>.

Stimulated by the approaches described above, we have explored the structural and electronic properties of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$

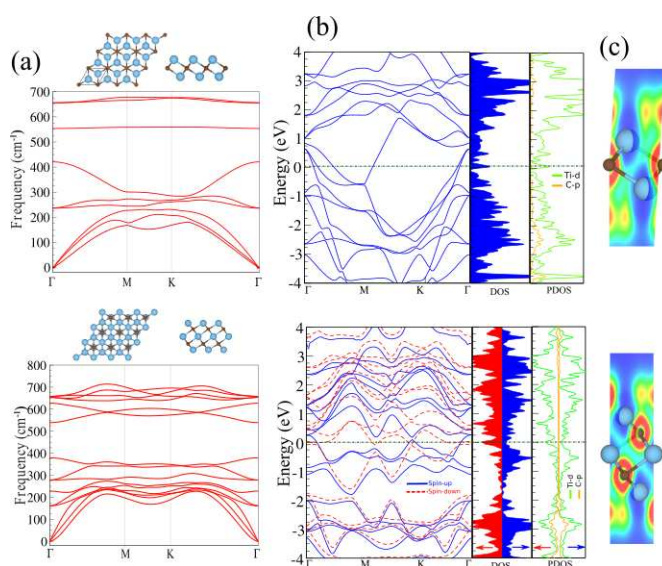
monolayers and have investigated the effect of functionalization on them by first-principle calculations. We have found out that 2D  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  MXenes are promising materials with metallic characteristics, while oxygen passivated  $\text{Ti}_2\text{C}$  monolayer has been shown to possess semiconducting behavior.

## 1 Method

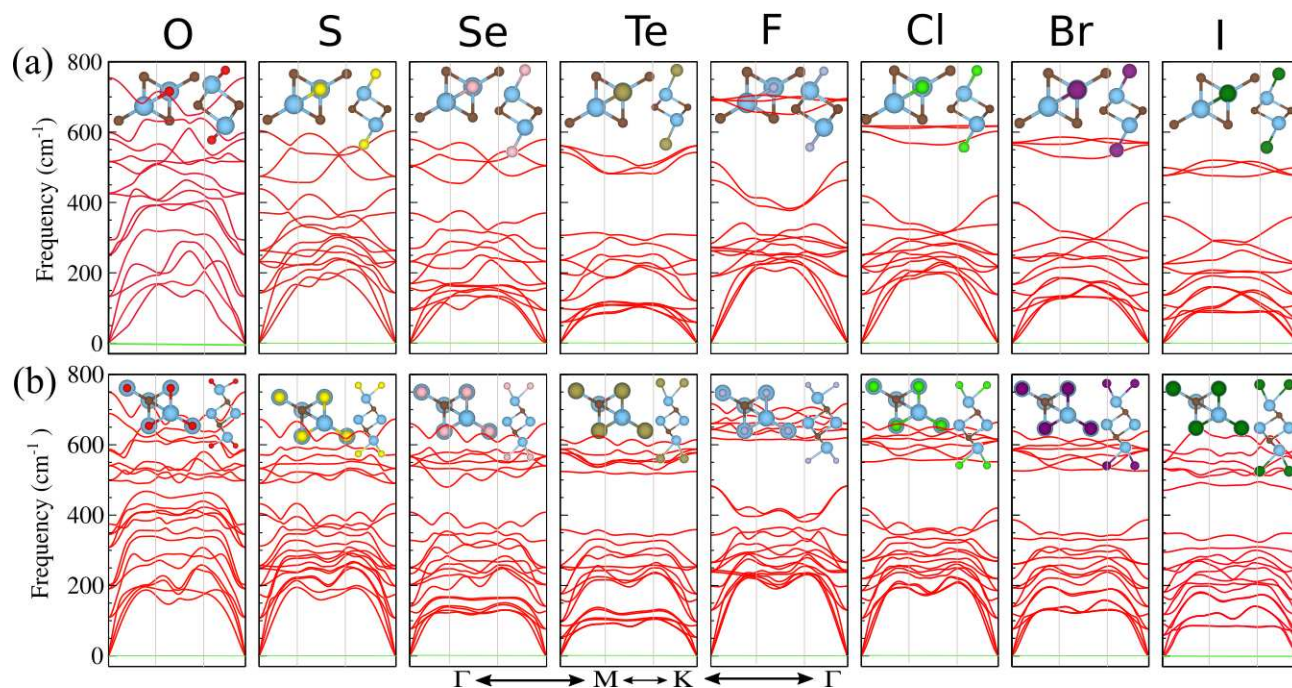
The density-functional theory (DFT)-based calculations were performed employing the plane-wave basis projector augmented wave (PAW) method along with the generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE)<sup>66,67</sup> functional as implemented in the Vienna *ab-initio* Simulation Package (VASP)<sup>68,69</sup>. Van der Waals (vdW) correction proposed by Grimme was used to describe the long-range vdW interactions<sup>70</sup>. In addition, charge transfers analysis was accomplished using the Bader technique<sup>71</sup>. The kinetic energy cut-off of 500 eV was set for plane-wave expansion and the energy was minimized between each electronic steps below  $10^{-8}$  eV. In order to get fully-optimized structures, total Hellmann-Feynman forces were reduced to  $10^{-7}$  eV/Å. The integration over the  $\mathbf{k}$ -point mesh was performed using  $21 \times 21 \times 1$  Monkhorst-Pack scheme for the primitive unit cell<sup>72</sup>. The PHONOPY code<sup>73</sup> was employed in order to obtain phonon band dispersions based on the small-displacement methodology.

## 2 $\text{Ti}_2\text{C}$ and $\text{Ti}_3\text{C}_2$ monolayers

The geometric atomic structure, phonon dispersion, electronic band structure with the corresponding density of states (DOS) and partial density of states (PDOS) of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers, are depicted in Figs. 1(a-c) top and bottom, respectively. After optimization, the lattice parameters of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  are calcu-



**Fig. 1** (a) Phonon spectrum of pristine  $\text{Ti}_2\text{C}$  (top panel) and  $\text{Ti}_3\text{C}_2$  (bottom panel). Atomic structure of  $\text{Ti}_2\text{C}/\text{Ti}_3\text{C}_2$  monolayer indicated in the top panel. Azure and brown balls represent the Ti and C atoms, respectively. (b) Electronic structure (b) and PDOS (c) of  $\text{Ti}_2\text{C}$  (top of panel) and  $\text{Ti}_3\text{C}_2$  (bottom of panel) monolayers. (c) refers to contour plot of the electron localization function (ELF). Red (blue) region denotes high (low) electron density.



**Fig. 2** Phonon spectrum of the functionalized  $\text{Ti}_2\text{C}$  (a) and  $\text{Ti}_3\text{C}_2$  (b) monolayers. Insets are top and side views of atomic structures of monolayers.

lated to be 3.04 and 3.09 Å, respectively. Notice that, each C atom in the studied structures is covalently bonded with its neighboring Ti atoms, and the bond length of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$ , are found to be 2.10 and 2.21 Å, respectively. The thicknesses of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  are calculated to be 2.31 and 4.66 Å, respectively. The calculated lattice parameters, bond lengths and thicknesses of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  are in good agreement with the corresponding experimental and theoretical values<sup>74,76–80</sup>.

The contour plot of the electron localization function (ELF) are illustrated in Figs. 1(c) top and bottom, respectively. Based on the charge analysis, each Ti atom gains approximately 1.86e from the adjacent C atoms in  $\text{Ti}_2\text{C}$ , while in  $\text{Ti}_3\text{C}_2$ , each Ti atom gains 1.75e from the adjacent C atoms. The charge redistribution within the two monolayers is due to the different electro-negativity of Ti and C atoms -1.54 and 2.54, respectively. The cohesive energy per atom was calculated using the following equation<sup>74</sup>:

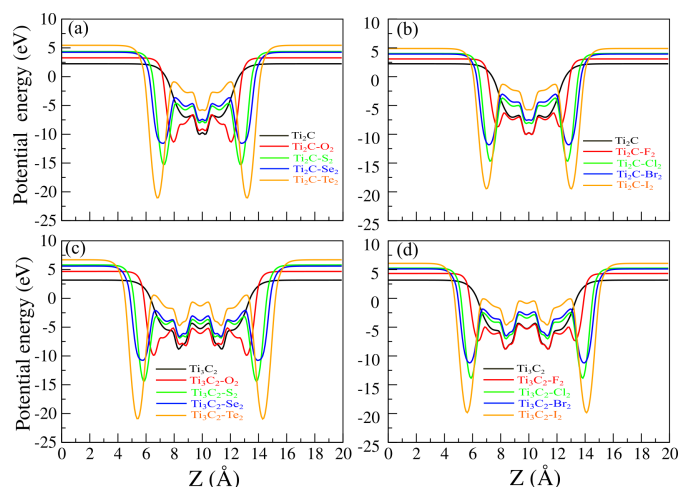
$$E_{\text{coh}} = (nE_{\text{Ti}} + mE_{\text{C}} - E_{\text{MXenes}})/N, \quad (1)$$

where  $E_{\text{Ti}}$  and  $E_{\text{C}}$  and  $E_{\text{O}}$  represent the energies of isolated single Ti and C atoms, respectively,  $E_{\text{MXenes}}$  represents the total energy of the MXene. While the  $n$ ,  $m$  and  $N$  are the number of Ti, C and total atoms, correspondingly. The cohesive energies of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers are found to be: -0.173 and -0.6 eV/atom, respectively, which indicates that  $\text{Ti}_3\text{C}_2$  is more favorable than the pristine  $\text{Ti}_2\text{C}$ , which coincides well with previous calculations<sup>74</sup>.

The results obtained for the phonon spectra of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers are depicted in Fig. 1(a) which agree with some published spectra<sup>81,82</sup>. For the  $\text{Ti}_2\text{C}$  monolayer, there are nine vibrational modes, including three acoustic modes and six optical modes because its primitive cell contains three atoms. Two of the six optical phonon modes are nondegenerate and two doubly

degenerate at the  $\Gamma$ -point. Three acoustic modes are the out-of-plane acoustic (ZA), transverse acoustic (TA), and in-plane longitudinal acoustic (LA) modes. Near the  $\Gamma$ -point, the ZA mode has a quadratic dispersion, while both TA and LA modes possess a linear dispersion. In the case of  $\text{Ti}_3\text{C}_2$  monolayer, the phonon spectrum has 15 vibrational modes. Only four of 12 optical phonon modes of the  $\text{Ti}_3\text{C}_2$  are nondegenerate, the rest are degenerate at the  $\Gamma$  point.

In the phonon spectra of both  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers, there is a frequency range where both acoustic and optical vibrational modes coexist. The lack of gap between the acoustic and optical modes can cause a strong acoustic-optical scattering, which greatly affects the thermal conductivity of the  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers. More importantly, there are no imaginary frequencies in the phonon spectra of both  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers. It implies that  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers are dynamically stable, so they can be experimentally synthesized as freestanding monolayers. The electronic band structure with the corresponding density of states (DOS) and projected DOS (PDOS) of pristine  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers are presented in Fig. 1(b). Our computational results demonstrate that  $\text{Ti}_2\text{C}$  is a metal, while  $\text{Ti}_3\text{C}_2$  exhibits a ferromagnetic-metal behavior with 1.9  $\mu_B$  in the ground state. In both monolayers, the contribution of the orbitals of Ti atoms to the electronic bands, especially above the Fermi level, is dominant. From Fig. 1(b) it can be seen that the contribution of the C atoms orbitals is evident below the Fermi level, in the energy range from -2.5 eV to -4.0 eV for both monolayers. The calculated band structures and DOS/PDOS of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers are in good agreement with previous reports<sup>74,83–85</sup>. The contour plot of the electron localization function (ELF) is shown in Fig. 1(c). The red and blue regions denote high and low electron density, respectively. The electron density is enriched around



**Fig. 3** Potential average of functionalized  $\text{Ti}_2\text{C}$  monolayer with (a) chalcogen and (b) halogen atoms as well as functionalized  $\text{Ti}_3\text{C}_2$  monolayer with (c) chalcogen and (d) halogen atoms.

the carbon atoms, while there is an electron depletion around the Ti atoms as it is manifested in the inset of Fig. 1(c).

### 3 Surface functionalization

In the next step, we gain insight into the chemical functionalization of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers with chalcogen (O, S, Se, and Te) and halogen (F, Cl, Br, and I) atoms. Upon chemical modification, the structure of the systems is significantly altered which may affect even their stability. Table I shows the lattice parameters, bond lengths and thicknesses of functionalized  $\text{Ti}_2\text{C-X}_2$  and  $\text{Ti}_3\text{C}_2\text{-X}_2$  are larger than the corresponding values of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$ , except for  $\text{X}=\text{O}$ , which is in line with some reported results<sup>74,86</sup>. Moreover, the binding energies of functional atoms on both monolayers are calculated using the equation below:

$$E_{\text{bind}} = (E_{\text{MXenes}} + 2 * E_{\text{X}} - E_{\text{func-MXenes}}) / 2, \quad (2)$$

where  $E_{\text{MXenes}}$  and  $E_{\text{func-MXenes}}$  stand for the total energies of bare and functionalized monolayers, while  $E_{\text{X}}$  denotes the energies of the isolated atoms.

In Table 1 the computed results for the binding energies of atoms on the surfaces of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers are provided. The calculated  $E_{\text{bind}}$  of  $\text{Ti}_2\text{C-X}_2$  and  $\text{Ti}_3\text{C}_2\text{-X}_2$  follow an order of X functionalization  $\text{O} > \text{S} > \text{Se} > \text{Te}$  and  $\text{O} > \text{F} > \text{Cl} > \text{Br} > \text{I}$  due to the decrease in  $d_2$  (the bond length at the surface). Note, the O atom has the highest binding energy per atom (9.98 and 9.88 eV/atom for  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers, respectively). Apparently, except for the F atom, there is a decreasing trend from  $\text{Ti}_2\text{C}$  to  $\text{Ti}_3\text{C}_2$  indicating the better chemical suitability of the  $\text{Ti}_2\text{C}$  monolayer. As the number of Ti and C atoms increases in the formula of the bare MXene, the occupied orbitals increase and thus, the unoccupied orbitals number decreases and this leads to a slightly lower binding energy of the adatoms.

In Fig. 2, we illustrate the results obtained for the phonon spectra of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  after complete chemical modification via the chalcogen and halogen atoms. From Fig. 2, it is obvious that all configurations of the chemically functionalized  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$

with the chalcogen and halogen atoms are dynamically stable because there are no negative frequencies in their phonon spectra. The value of the phonon frequency, especially the frequency of the optical modes, depends strongly on the size of the chalcogen and halogen atoms. The maximum frequency of the optical modes decreases as the chalcogen (halogen) atom changes from O to Te (F to I). In the case of O-termination, the Ti-O bond stretching gives rise to higher optical phonon frequencies at the  $\Gamma$  point. The same holds true in the case of the F-termination, while for the other atoms the highest phonon frequency at the  $\Gamma$  decreases as the atomic radius and mass increases. The phonon bands of  $\text{Ti}_2\text{CO}_2$ ,  $\text{Ti}_2\text{CF}_2$  and  $\text{Ti}_3\text{C}_2\text{O}_2$  are similar to some previous studies<sup>87,88</sup>.

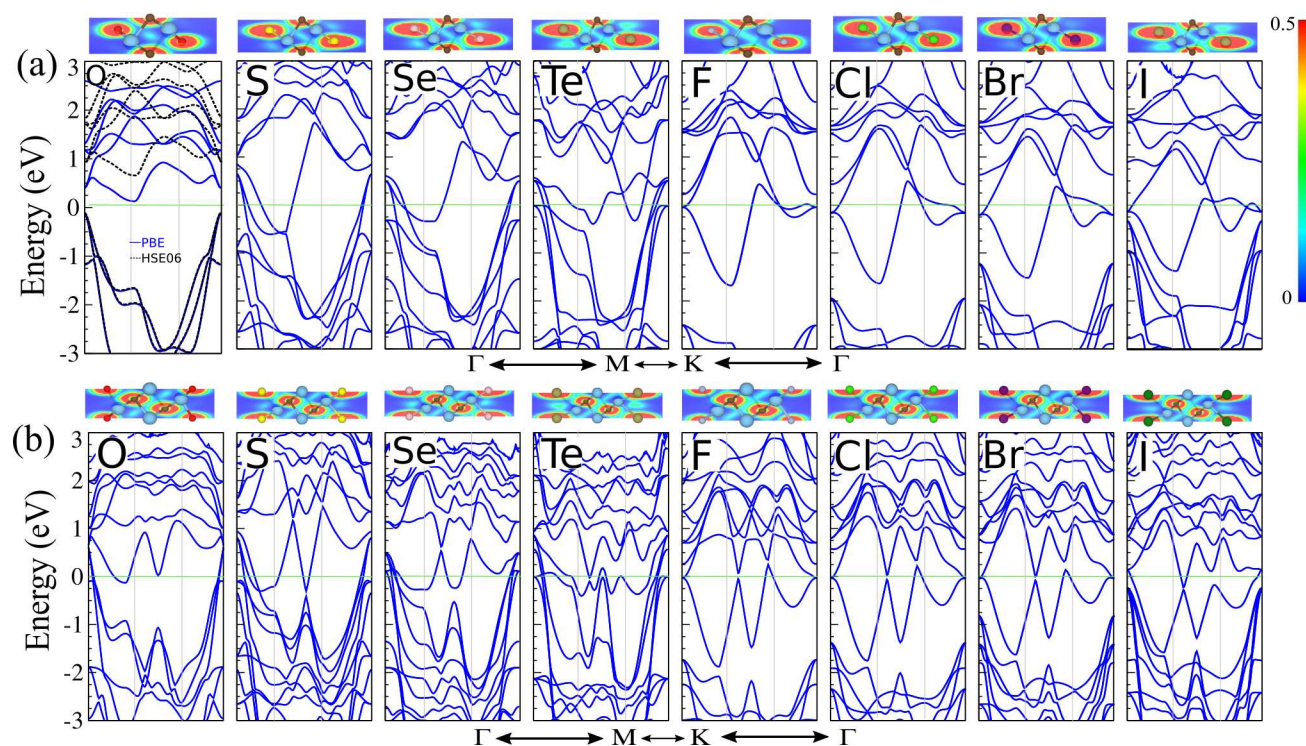
Fig. 3 presents the results of calculations for the plane-average electrostatic potential of chemically functionalized  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  with chalcogen and halogen atoms. Due to the symmetrical structure, there is no difference in the potential between the two sides of these monolayers. The electrostatic potential of all monolayers, including pristine and functionalized  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  ones, are flat in the vacuum region. Compared to the pristine  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers, the potential of functionalized  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers are deeper, in which, the potential of functionalized by Te(I) monolayers are the deepest one compared to that of the other chalcogen (halogen) atoms. Also, the depth and the height of the planar part of the potential increases as the electronegativity decreases - see Figs. 3(a-d). The height of the planar electrostatic potential for  $\text{Ti}_3\text{C}_2\text{-X}_2$  is larger than that for the corresponding one of  $\text{Ti}_2\text{C-X}_2$ . We have also calculated the work function  $\Phi$  of all investigated monolayers and the values obtained are listed in Tab. 1. Note that the  $\Phi$  refers to the electron's ability to escape from the material surface and can be estimated by the minimum energy for an electron to move from the Fermi and vacuum level. The work function of materials depends strongly on their electron affinity, ionization energy and electronegativity (see table I). The results obtained demonstrate the work function of  $\text{Ti}_2\text{C-X}_2$  is larger than the corresponding one of  $\text{Ti}_3\text{C}_2\text{-X}_2$ . It implies that electrons can more easily escape from the  $\text{Ti}_3\text{C}_2\text{-X}_2$  surface than from the  $\text{Ti}_2\text{C-X}_2$  ones (see Tab. 1).

#### 3.1 Electronic properties

It is well-known that almost all MXene monolayers are metals and one can turn their electronic properties by surface functionalization. In Fig. 4, we present our computational results for the band structures of the functionalized MXene monolayers with chalcogen and halogen atoms  $\text{Ti}_2\text{C-X}_2$  and  $\text{Ti}_3\text{C}_2\text{-X}_2$ . As expected,  $\text{Ti}_2\text{C}$  became a semiconductor with an energy gap of 0.25 (1.01) eV at the PBE (HSE06) level after being fully functionalized with oxygen atoms. The band gap value agrees well with previous calculations<sup>82,87</sup>.  $\text{Ti}_2\text{C-O}_2$  possesses characteristics of an indirect semiconductor with the valence band maximum (VBM) located at the  $\Gamma$ -point and the conduction band minimum (CBM) lying on the MK-path. However, with exception of  $\text{Ti}_2\text{C-O}_2$ , the functionalized  $\text{Ti}_2\text{C-X}_2$  and  $\text{Ti}_3\text{C}_2\text{-X}_2$  still preserve metallic characteristics after surface functionalization. It is worth mentioning that the Dirac cones are created in  $\text{Ti}_3\text{C}_2\text{-X}$  ( $\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$ ) at the M and

**Table 1** The structural and electronic parameters including lattice constant  $a$ ; Ti-C ( $d_1$ ) and Ti-X ( $d_2$ ) bond lengths; Ti-C-Ti [in  $\text{Ti}_2\text{C}$ ] and C-Ti-C [in  $\text{Ti}_3\text{C}_2$ ] ( $\theta_1$ ) and X-Ti-X ( $\theta_2$ ) bond angles; the thickness layer defined by the difference between the largest and smallest  $z$  coordinates of atoms ( $t$ ) the binding energy per atom, ( $E_b$ ); the charge transfer from Ti to X atoms ( $\Delta Q$ ); the work function ( $\Phi$ ); the band gap ( $E_g$ ), and electron affinity ( $E_a$ ), ionization energy ( $E_I$ ) and electronegativity ( $\chi$ ) for X atom<sup>75</sup>.

	$a$ (Å)	$d_1$ (Å)	$d_2$ (Å)	$t$ (Å)	$\theta_1$ (°)	$\theta_2$ (°)	$E_b$ (eV/atom)	$\Phi$ (eV)	$\Delta Q$ (eV)	$E_g$ (eV)	$E_a$ (eV)	$E_I$ (eV)	$\chi$
$\text{Ti}_2\text{C-O}_2$	3.03	2.18	1.97	4.45	92.18	100.16	9.98	5.80	0.97	0.25(1.01)	1.46	13.62	3.44
$\text{Ti}_2\text{C-S}_2$	3.18	2.20	2.40	5.52	87.55	83.17	6.83	6.03	0.68	M	2.08	10.36	2.58
$\text{Ti}_2\text{C-Se}_2$	3.22	2.20	2.54	5.82	85.93	78.65	6.03	5.39	0.56	M	2.02	9.75	2.55
$\text{Ti}_2\text{C-Te}_2$	3.29	2.18	2.82	6.36	82.53	71.18	5.09	4.40	0.43	M	1.97	9.01	2.10
$\text{Ti}_2\text{C-F}_2$	3.05	2.10	2.15	4.77	86.91	90.27	7.33	4.93	0.69	M	3.40	17.42	3.98
$\text{Ti}_2\text{C-Cl}_2$	3.22	2.15	2.49	5.52	83.32	80.31	5.38	4.64	0.56	M	3.61	12.97	3.16
$\text{Ti}_2\text{C-Br}_2$	3.31	2.18	2.63	5.75	81.68	77.83	4.56	4.32	0.51	M	3.36	11.8	2.96
$\text{Ti}_2\text{C-I}_2$	3.45	2.23	2.82	6.02	79.12	75.49	3.46	3.81	0.56	M	3.05	10.45	2.66
$\text{Ti}_3\text{C}_2\text{-O}_2$	3.03	2.15 (2.19)	1.97	6.98	90.46	100.18	9.88	6.12	0.97	M	1.46	13.62	3.44
$\text{Ti}_3\text{C}_2\text{-S}_2$	3.14	2.20 (2.17)	2.39	8.04	89.04	81.79	6.76	6.15	0.65	M	2.08	10.36	2.58
$\text{Ti}_3\text{C}_2\text{-Se}_2$	3.14	2.21 (2.14)	2.56	8.37	89.05	76.22	5.96	5.29	0.53	M	2.02	9.75	2.55
$\text{Ti}_3\text{C}_2\text{-Te}_2$	3.21	2.24 (2.12)	2.84	8.91	88.56	68.74	5.01	4.15	0.41	M	1.97	9.01	2.10
$\text{Ti}_3\text{C}_2\text{-F}_2$	3.07	2.18 (2.07)	2.16	7.20	90.77	90.39	7.33	4.84	0.69	M	3.40	17.42	3.98
$\text{Ti}_3\text{C}_2\text{-Cl}_2$	3.18	2.22 (2.11)	2.49	7.97	88.70	79.11	5.34	4.50	0.56	M	3.61	12.97	3.16
$\text{Ti}_3\text{C}_2\text{-Br}_2$	3.24	2.24 (2.12)	2.62	8.21	87.81	76.11	4.46	4.11	0.52	M	3.36	11.8	2.96
$\text{Ti}_3\text{C}_2\text{-I}_2$	3.33	2.29 (2.15)	2.49	8.49	86.46	72.81	3.18	3.56	0.42	M	3.05	10.45	2.66

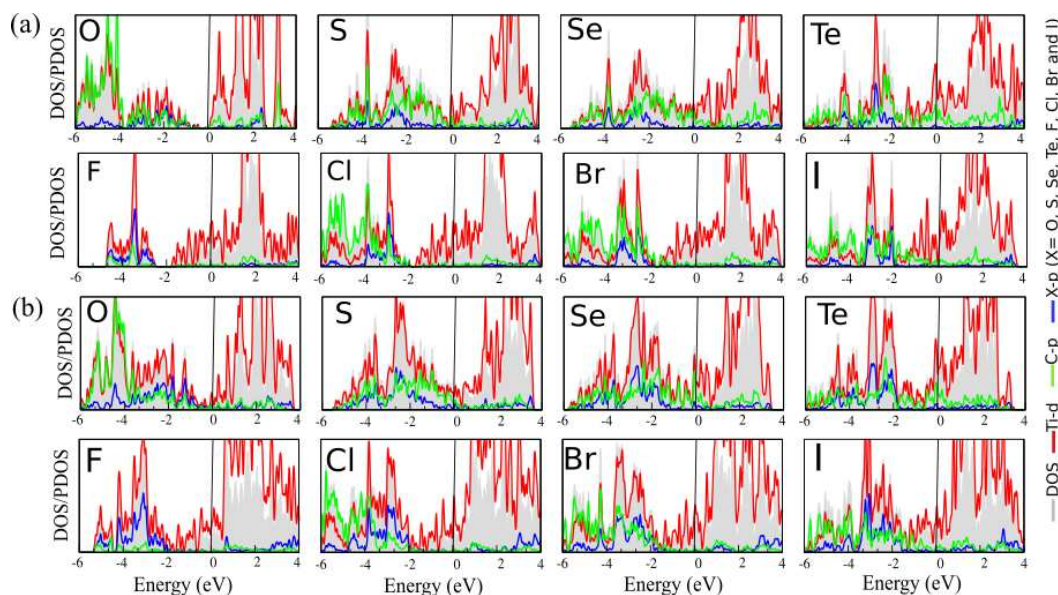


**Fig. 4** Electronic band structure of functionalized  $\text{Ti}_2\text{C}$  (top) and  $\text{Ti}_2\text{CO}_2$  (bottom) monolayers. Corresponding DOS and PDOS, indicated in top of electronic band structures. Zero of energy is set at the Fermi energy.

K points as shown in the corresponding band structures around the Fermi energy. Therefore, the semi-metallic behavior can be obtained upon external fields by tuning the energy of the Dirac cones.

To clearly see the nature and contribution of atomic orbitals to the formation of electronic bands of the functionalized MXene monolayers, we have also calculated the PDOS of the function-

alized monolayers as depicted in Fig. 5. Focusing on the case of  $\text{Ti}_2\text{C-O}_2$ , we can see that the  $p$ -orbitals of Ti atoms contribute greatly to the formation of electronic bands, especially in the conduction band. Besides, the contribution of the C- $p$  orbital to the electronic band, especially the valence band, is significant. As illustrated in Fig. 5(a), in the high energy region of the valence band, from  $-4$  eV to  $-6$  eV, the contribution of C- $p$  orbital is



**Fig. 5** DOS and PDOS of functionalized  $\text{Ti}_2\text{C}$  (top) and  $\text{Ti}_3\text{C}_2$  (bottom) monolayers. Zero of energy is set at the Fermi energy.

more dominant than that of other atomic orbitals, including Ti- $p$  orbital. From the PDOS in Fig. 5(a), we can see that opening the band gap of  $\text{Ti}_2\text{C-O}_2$  could be caused by the hybridization of  $d$ -orbital of carbon atoms and  $p$ -orbital of oxygen atoms. For the other configurations, the contribution of Ti- $d$  orbitals to the formation of electronic bands is distinctly prominent, that is similar to the case of  $\text{Ti}_2\text{C-O}_2$ . In addition, the  $p$ -orbital of atom X atoms also contributes significantly to the electronic bands, especially the valence band. The Ti orbitals are dominating at the Fermi energy with a considerable contribution of C orbitals in the cases of X=S, Se and Te. The  $\text{Ti}_2\text{C-Te}_2$  monolayer has a metallicity character more than  $\text{Ti}_2\text{C-S}_2$  and  $\text{Ti}_2\text{C-Se}_2$  monolayers due to its number of electrons. The band structures and DOS/PDOS of  $\text{Ti}_2\text{C-X}_2$  (X=S, Se, Te) are in good agreement with published in a previous theoretical study<sup>86</sup>. For halogen atoms (X=F, Cl, Br, I), Fig. 5(a), the contribution of C orbitals at the Fermi energy is very small as compared to the chalcogen atoms (X=S, Se, Te). The DOS/PDOS of  $\text{Ti}_3\text{C}_2\text{-X}_2$  is very similar to the corresponding DOS/PDOS of  $\text{Ti}_2\text{C-X}_2$  (Fig. 5(b)). In addition, the contribution of X=F, Cl, Br and I orbitals in  $\text{Ti}_3\text{C}_2\text{-X}_2$  monolayer is larger than the corresponding contribution in the  $\text{Ti}_2\text{C-X}_2$  monolayer.

### 3.2 Mechanical properties

Using the harmonic approximation, we explore the linear-elastic properties of the proposed monolayers in terms of their in-plane stiffness and Poisson's ratio values. The in-plane stiffness is known as the measure of the rigidity of a 2D material. For the bare monolayers of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$ , the elastic constants are isotropic and the in-plane stiffness values are found to be 130 N/m and 231 N/m, respectively, which correspond well with a previous study<sup>85</sup>. This indicates that increasing the number of C and Ti layers in the monolayer structure increases the stiffness of the materials. After surface functionalization, it is found that halide atoms increase the stiffness, while Se and Te chalcogenides

weaken the rigidity of the monolayer. Apparently, the highest in-plane stiffness is calculated for oxygen-saturated monolayers (272 and 375 N/m for  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$ , correspondingly). As the atomic radius increases from O to Te, in-plane stiffness possesses a decreasing trend in both monolayers. In addition, a similar trend is found when  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers are saturated with halide atoms. Notably, the fluorinated and oxygenated monolayers of  $\text{Ti}_3\text{C}_2$  are stiff materials with in-plane stiffness values comparable to that of graphene (340 N/m). As a result, it is important to mention that surface functionalization of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  can tune their elastic properties depending on the type of

**Table 2** The elastic parameters of bare and functionalized monolayers; the in-plane stiffness,  $C$ ; and Poisson's ratio,  $\nu$ ).

	$C$ (N/m)	$\nu$
$\text{Ti}_2\text{C}$	130	0.23
$\text{Ti}_2\text{C-O}_2$	272	0.31
$\text{Ti}_2\text{C-S}_2$	176	0.24
$\text{Ti}_2\text{C-Se}_2$	89	0.20
$\text{Ti}_2\text{C-Te}_2$	17	0.93
$\text{Ti}_2\text{C-F}_2$	220	0.31
$\text{Ti}_2\text{C-Cl}_2$	177	0.27
$\text{Ti}_2\text{C-Br}_2$	177	0.25
$\text{Ti}_2\text{C-I}_2$	167	0.22
$\text{Ti}_3\text{C}_2$	231	0.17
$\text{Ti}_3\text{C}_2\text{-O}_2$	375	0.29
$\text{Ti}_3\text{C}_2\text{-S}_2$	267	0.27
$\text{Ti}_3\text{C}_2\text{-Se}_2$	161	0.59
$\text{Ti}_3\text{C}_2\text{-Te}_2$	78	0.80
$\text{Ti}_3\text{C}_2\text{-F}_2$	349	0.25
$\text{Ti}_3\text{C}_2\text{-Cl}_2$	294	0.24
$\text{Ti}_3\text{C}_2\text{-Br}_2$	294	0.24
$\text{Ti}_3\text{C}_2\text{-I}_2$	276	0.22

adatoms. On the other hand, we calculate the Poisson's ratio, which is defined as the ratio of the transverse contraction strain to the longitudinal extension, and the results are presented in Table 2. Our results for the Poisson's ratio of bare  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers are: 0.23 and 0.17, respectively, i.e., these values are close to that of graphene (0.16) due to the presence of C atoms in the structures. It is found out that as the atomic mass of the halide atom increases from F to I, the Poisson's ratio decreases for both structures. In contrast, as the atomic mass of the chalcogenide atom from S to Te increases, the Poisson's ratio values are found to increase due to less mechanical stability of the functionalized monolayer. In both monolayers of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$ , the Te-functionalized structures exhibit a very high Poisson's ratio values, which are still in the 2D limit. The high Poisson's ratios of these monolayers indicate the high flexibility of the monolayers along the unstretched direction.

## 4 Conclusion

We have investigated the structural, electronic, and mechanical properties of functionalized  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  monolayers by means of ab-initio calculations. Our results revealed that monolayers of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  are dynamically stable metallic structures. Phonon band dispersion calculations showed the two-surface functionalization of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  via chalcogenides (S, Se, and Te), halides (F, Cl, Br, and I), and oxygen atoms results in dynamically stable novel functionalized monolayer materials. Electronic band dispersions and the corresponding density of states calculations have indicated that all the functionalized monolayer structures preserve the metallic nature of both  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  except for  $\text{Ti}_2\text{C}-\text{O}_2$ , which possess an indirect semiconductor behavior via full-surface oxygen passivation. Moreover, it has been shown that although, halide passivated  $\text{Ti}_3\text{C}_2$  structures are still metallic, there exist multiple Dirac-like cones around the Fermi-level, which indicates that semi-metallic behavior can be obtained upon external effects by tuning the energy of the Dirac cones. Moreover, the calculated linear-elastic parameters indicated that the functionalization plays a crucial role in tuning the mechanical properties of stiff monolayers of bare  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$ . This theoretical study opens a new door for exploration and will stimulate further experimental research on these exciting materials in future.

## 5 Conflicts of interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

## 6 Acknowledgments

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## References

- 1 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Electric field effect in atomically thin carbon films, *Sci.*, 306, 666-669, 2004.

- 2 D. Pacile, J. C. Meyer, C. O. Girit, and A. Zettl, The two-dimensional phase of boron nitride: Few-atomic-layer sheets and suspended membranes, *Appl. Phys. Lett.*, 92, 133107, 2008.
- 3 B. Lalmi, O. Hamid, H. Enriquez, A. Kara, S. Vizzini, B. Ealet, and B. Aufray, Epitaxial growth of a silicene sheet, *Appl. Phys. Lett.*, 97, 223109, 2010.
- 4 H. Liu, T. N. Adam, Zh. Zhen, Zh. Luo, X. Xu, D. Tomanek, and P. D. Ye. Phosphorene: an unexplored 2D semiconductor with a high hole mobility, *ACS Nano*, 8, 4033-4041, 2014.
- 5 C. Ataca, H. Sahin, and S. Ciraci, Stable, single-layer  $\text{MX}_2$  transition-metal oxides and dichalcogenides in a honeycomb-like structure, *J. Phys. Chem. C*, 116, 8983-8999, 2012.
- 6 Y. Dong, Z.-S. Wu, W. Ren, H.-M. Cheng, and X. Bao, Graphene: A Promising 2D Material for Electrochemical Energy Storage, *Sci.* 62, 724-40 2017.
- 7 V. Berry, Impermeability of graphene and its applications, *Carbon N. Y.*, 62, 1-10, 2013.
- 8 K. Einalipour Eshkalak, S. Sadeghzadeh, and F. Molaei, C&A: Physical Processes in Nanomaterials and Nanostructures Interfacial Thermal Resistance Mechanism for Polyaniline ( $\text{C}_3\text{N}$ )-Graphene Heterostructure, *J. Phys. Chem. C*, 2020.
- 9 A. Bafekry, C. Stampfl, and M. Ghergherehchi, Strain, electric-field and functionalization induced widely tunable electronic properties in  $\text{MoS}_2/\text{BC}_3/\text{C}_3\text{N}$  and/van der Waals heterostructures, *Nanotechnol.*, 31, 295202, 2020.
- 10 X. Li and H. Zhu, Two-dimensional  $\text{MoS}_2$ : Properties, preparation, and applications, *J. Mater.*, 1, 33-44, 2015.
- 11 C. Cong, J. Shang, Y. Wang, and T. Yu, Optical properties of 2D semiconductor  $\text{WS}_2$ , *Adv. Opt. Mater.*, 6, 1, 1700767, 2018.
- 12 H. Tan, Y. Fan, Y. Zhou, Q. Chen, W. Xu, and J. H. Warner, Ultrathin 2D photodetectors utilizing chemical vapor deposition grown  $\text{WS}_2$  with graphene electrodes, *ACS Nano*, 10, 8, 7866-7873, 2016.
- 13 A. Bafekry, M. Faraji, M. M Fadlallah, B. Mortazavi, A. A. Zibari, A. B. Khatibani, Ch. V. Nguyen, M. Ghergherehchi, D. Gogova, Point Defects in a Two-Dimensional  $\text{ZnSnN}_2$  Nanosheet: A First-Principles Study on the Electronic and Magnetic Properties, *J. Phys. Chem. C* 125 , 13067-13075, 2021.
- 14 A. Bafekry, M. Yagmurcukardes, B. Akgenc, M. Ghergherehchi, B. Mortazavi, First-principles investigation of electronic, mechanical and thermoelectric properties of graphene-like  $\text{XB}_i$  ( $\text{X} = \text{Si, Ge, Sn}$ ) monolayers *Phys. Chem. Chem. Phys.* 23, 12471-12478, 2021.
- 15 A. Bafekry, C. Stampfl, M. Faraji, M. Yagmurcukardes, M.M. Fadlallah, H.R. Jappor, M. Ghergherehchi, S.A.H. Feghhi, A Dirac-semimetal two-dimensional  $\text{BeN}_4$ : Thickness-dependent electronic and optical properties *Appl. Phys. Lett.* 118 , 203103, 2021.
- 16 M. Faraji, A. Bafekry, D. Gogova, D.M. Hoat, M. Gherghere-



- hchi, Ch. V. Chuong, S.A.H. Fegghi, Novel two-dimensional ZnO<sub>2</sub>, CdO<sub>2</sub> and HgO<sub>2</sub> monolayers: a first-principles-based prediction, *N. J. Chem.* 45, 9368-9374, 2021.
- 17 M. Khazaei, M. S. Bahramy, N. S. Venkataramanan, H. Mizuseki, and Y. Kawazoe, Chemical engineering of prehydrogenated C and BN-sheets by Li: Application in hydrogen storage, *J. Appl. Phys.*, 106, 94303, 2009.
  - 18 L. Ci, L. Song, Ch. Jin, D. Jariwala, D. Wu, Y. Li, A. Srivastava, Z. F. Wang, K. Storr, and L. Balicas, Atomic layers of hybridized boron nitride and graphene domains, *Nat. Mater.*, 9, 430-435, 2010.
  - 19 H. Wang, J. T. Robinson, X. Li, and H. Dai, Solvothermal reduction of chemically exfoliated graphene sheets, *J. Am. Chem. Soc.*, 131, 9910-9911, 2009.
  - 20 R. Ibragimova, M. J. Puska, and H.-Komsa, pH-Dependent Distribution of Functional Groups on Titanium-Based MXenes, *ACS Nano*, 13, 9171-9181, Aug. 2019.
  - 21 M. M. Fadlallah, A. A. Maarouf, U. Schwingenschlogl, U. Eckern, Unravelling the interplay of geometrical, magnetic and electronic properties of metal-doped graphene nanomeshes, *J. Phys.: Condens. Matter* 29, 055301 2017.
  - 22 W. Zhang, D. Chang, Q. Gao, Ch. Niu, Ch. Li, F. Wang, X. Huang, C. Xia, and Y. Jia, Interlayer coupling and external electric field tunable electronic properties of a 2D type-I tellurene/MoS<sub>2</sub> heterostructure, *J. Mater. Chem. C*, 6, 10256-10262, 2018.
  - 23 D. M. Hoat, T. V Vu, M. M. Obeid, and H. R. Jappor, Tuning the electronic structure of 2D materials by strain and external electric field: case of GeI<sub>2</sub> monolayer, *Chem. Phys.*, 527, 110499, 2019.
  - 24 D. Akinwande, Ch. J. Brennan, J. S. Bunch, Ph. Egberts, J. R. Felts, H. Gao, R. Huang, J.-S. Kim, T. Li, and Y. Li, A review on mechanics and mechanical properties of 2D materials- Graphene and beyond, *Extrem. Mech. Lett.*, 13, 42-77, 2017.
  - 25 R. Kumar, E. Joanni, R. K. Singh, D. Singh, and S. A. Moshkalev, Recent advances in the synthesis and modification of carbon-based 2D materials for application in energy conversion and storage, *Prog. Energy Combust. Sci.*, 67, 115-157, 2018.
  - 26 L. Tang, X. Meng, D. Deng, and X. Bao, Confinement catalysis with 2D materials for energy conversion, *Adv. Mater.*, 31, 1901996, 2019.
  - 27 X. Zhang, L. Hou, A. Ciesielski, and Samorñ, 2D materials beyond graphene for high-performance energy storage applications, *Adv. Energy Mater.*, 6, 1600671, 2016.
  - 28 Y. Peng, Y. Li, Y. Ban, and W. Yang, Two-dimensional Metal-Organic Framework Nanosheets for Membrane-Based Gas Separation, *Angew. Chemie*, 129, 9889-9893, 2017.
  - 29 A. K. Singh, K. Mathew, H. L. Zhuang, and R. G. Hennig, Computational screening of 2D materials for photocatalysis, *J. Phys. Chem. Lett.*, 6, 1087-1098, 2015.
  - 30 R. Irshad, K. Tahir, B. Li, Z. Sher, J. Ali, and S. Nazir, A revival of 2D materials, phosphorene: Its application as sensors, *J. Ind. Eng. Chem.*, 64, 60-69, 2018.
  - 31 S. Feng, Z. Lin, X. Gan, R. Lv, and M. Terrones, Doping two-dimensional materials: ultra-sensitive sensors, band gap tuning and ferromagnetic monolayers, *Nanoscale Horizons*, 2, 72-80, 2017.
  - 32 L. Prozorovska and R. Kidambi, State-of-the-Art and Future Prospects for Atomically Thin Membranes from 2D Materials, *Adv. Mater.*, 30, 1801179, 2018.
  - 33 J. L. Hart, K. Hantanasirisakul, A. C. Lang, B. Anasori, D. Pinto, Y. Pivak, J. Tijn van Omme, S. J. May, Y. Gogotsi, M. L. Taheri, Control of MXenes' electronic properties through termination and intercalation, *Nat Commun* 10, 522 (2019).
  - 34 M. Khazaei, A. Ranjbar, M. Arai, T. Sasaki, and S. Yunoki, Electronic properties and applications of MXenes: a theoretical review, *J. Mater. Chem. C*, 5, 2488-2503, 2017.
  - 35 M. Naguib et al., Two-dimensional nanocrystals produced by exfoliation of Ti<sub>3</sub>AlC<sub>2</sub>, *Adv. Mater.*, 23, 4248-4253, 2011.
  - 36 J. Luo, X. Tao, J. Zhang, Y. Xia, H. Huang, L. Zhang, Y. Gan, Ch. Liang, and W. Zhang, Sn<sup>4+</sup> ion decorated highly conductive Ti<sub>3</sub>C<sub>2</sub> MXene: promising lithium-ion anodes with enhanced volumetric capacity and cyclic performance, *ACS Nano*, 10, 2, 2491-2499, 2016.
  - 37 F. Shahzad, M. Alhabeib, Ch. B. Hatter, B. Anasori, S. M. Hong, Ch. M. Koo, and Y. Gogotsi, Electromagnetic interference shielding with 2D transition metal carbides (MXenes), *Sci.*, 353, 1137-1140, 2016.
  - 38 J. Liu, H. B. Zhang, R. Sun, Y. Liu, Zh. Liu, A. Zhou, and Zh. Yu, Hydrophobic, Flexible, and Light weight MXene Foams for High-Performance Electromagnetic-Interference Shielding, *Adv. Mater.*, 29, 1-6, 2017.
  - 39 J. Zhu, E. Ha, G. Zhao, Y. Zhou, D. Huang, G. Yue, L. Hu, N. Sun, Y. Wang, and L. Y. S. Lee, Recent advance in MXenes: A promising 2D material for catalysis, sensor and chemical adsorption, *Coord. Chem. Rev.*, 352, 306-327, 2017.
  - 40 F. Alimohammadi, M. Sharifian Gh, N. H. Attanayake, A. C. Thenuwara, Y. Gogotsi, B. Anasori, and D. R. Strongin, Antimicrobial properties of 2D MnO<sub>2</sub> and MoS<sub>2</sub> nanomaterials vertically aligned on graphene materials and Ti<sub>3</sub>C<sub>2</sub> MXene, *Langmuir*, 34, 7192-7200, 2018.
  - 41 K. Rasool, M. Helal, A. Ali, C. E. Ren, Y. Gogotsi, and K. A. Mahmoud, Antibacterial activity of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene, *ACS Nano*, 10, 3, 3674-3684, 2016.
  - 42 R. Pandey, K. Rasool, V. E. Madhavan, B. Aissa, Y. Gogotsi, and K. A. Mahmoud, Ultrahigh-flux and fouling-resistant membranes based on layered silver/MXene (Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>) nanosheets, *J. Mater. Chem. A*, 6, 8, 3522-3533, 2018.
  - 43 M. Khazaei, A. Ranjbar, M. Ghorbani-Asl, M. Arai, T. Sasaki, Y. Liang and S. Yunoki, Nearly free electron states in MXenes, *Phys. Rev. B*, 2016, 93, 205125.
  - 44 X. Sheng, Y. Zhao, L. Zhang, and X. Lu, Properties of two-dimensional Ti<sub>3</sub>C<sub>2</sub> MXene/thermoplastic polyurethane nanocomposites with effective reinforcement via melt blending, *Compos. Sci. Technol.*, 181, 107710, 2019.
  - 45 G. Gao, A. Omullane, and A. Du, 2D MXenes: a new family

- of promising catalysts for the hydrogen evolution reaction, *ACS Catal.*, 7, 494-500, 2017.
- 46 Z. Hemmat, P. Yasaei, J. F. Schultz, L. Hong, L. Majidi, A. Behranginia, L. Verger, N. Jiang, M. W. Barsoum, and R. F. Klie, Tuning thermal transport through atomically thin  $Ti_3C_2T_x$  MXene by current annealing in vacuum, *Adv. Funct. Mater.*, 29, 19, 1805693, 2019.
  - 47 S. Sarikurt, D. CakÅsr, M. Keceli, and C. Sevik, The influence of surface functionalization on thermal transport and thermoelectric properties of MXene monolayers, *Nanoscale*, 10, 8859-8868, 2018.
  - 48 M. Khazaei, M. Arai, T. Sasaki, Ch.-Y. Chung, N. S. Venkataramanan, M. Estili, Y. Sakka, and Y. Kawazoe, Novel Electronic and Magnetic Properties of Two-Dimensional Transition Metal Carbides and Nitrides, *Adv. Funct. Mater.*, 23, 2185-2192, 2013.
  - 49 J. L. Hart, K. Hantanasirisakul, A. C. Lang, B. Anasori, D. Pinto, Y. Pivak, J. T. v. Omme, Steven J. May, Y. Gogotsi, and M. L. Taheri. Control of MXenes electronic properties through termination and intercalation, *Nat. Commun.*, 10, 1, 2019.
  - 50 G. R. Berdiyrov, Effect of surface functionalization on the electronic transport properties of  $Ti_3C_2$  MXene, *Epl*, 111, 6, 2015.
  - 51 S. Li, J. He, Nachtigall, L. Grajciar, and F. Brivio, Control of spintronic and electronic properties of bimetallic and vacancy-ordered vanadium carbide MXenes via surface functionalization, *Phys. Chem. Chem. Phys.*, 21, 25802-25808, 2019.
  - 52 G. R. Berdiyrov, Optical properties of functionalized  $Ti_3C_2T_2$  (T= F, O, OH) MXene: First-principles calculations, *Aip Adv.*, 6, 5, 55105, 2016.
  - 53 H. Xu, A. Ren, J. Wu, and Z. Wang, Recent Advances in 2D MXenes for Photodetection, *Adv. Funct. Mater.*, 2000907, 2020.
  - 54 H. Kim, B. Anasori, Y. Gogotsi, and H. N. Alshareef, Thermoelectric Properties of Two-Dimensional Molybdenum-Based MXenes, *Chem. Mater.*, 29, 6472-6479, 2017.
  - 55 S. Kumar and U. Schwingenschlogl, Thermoelectric performance of functionalized  $Sc_2C$  MXenes, *Phys. Rev. B*, 94, 35405, 2016.
  - 56 H. Wang, J. Li, X. Kuai, L. Bu, L. Gao, X. Xiao and Y. Gogotsi, Enhanced rate capability of ion-accessible  $Ti_3C_2T_x$ -NbN hybrid electrodes, *Adv. Energy Mater.* 2020,10, 2001411.
  - 57 E. M. D. Siriwardane, I. Demiroglu, C. S., F. M. Peeters, and D. Cakir, Assessment of sulfur-functionalized MXenes for Li-ion battery applications, *J. Phys. Chem. C*, 1932-7447, 2020.
  - 58 L. Rui, L. Jianmin, L. Meng, Z. Qinghong, S. Guoying, L. Yaogang, H. Chengyi, and W. Hongzhi, A MXene-coated air permeable pressure-sensing fabric for smart wear, *ACS Appl. Mater. Interfaces*, 1944-8244, 2020.
  - 59 W. Y. Chen, S. Lai, C. Yen, X. Jiang, D. Peroulis, and L. A. Stanciu, Surface functionalization of TiCT MXene with highly reliable superhydrophobic protection for volatile organic compounds sensing, *ACS Nano*, 14, 11490-11501, 2020.
  - 60 Q. Zhao, M. Sereych, E. Precetti, C. E. Shuck, M. Harhay, R. Pang, C. Shan, and Y. Gogotsi, Adsorption of uremic toxins using  $Ti_3C_2T_x$  MXene for dialysate regeneration, *ACS Nano* 14, 11787-11798, 2020.
  - 61 A. Bafekry, M. Faraji, D.M. Hoat, M. Shahrokhi, M.M. Fadlallah, F. Shojaei, S. A. H. Fegghi, M. Ghergherehchi, D. Gogova,  $MoSi_2N_4$  single-layer: a novel two-dimensional material with outstanding mechanical, thermal, electronic and optical properties, *J. Phys. D: Appl. Phys.*, 54, 155303, 2021.
  - 62 A. Bafekry, B. Akgenc, M. Ghergherehchi, F.M. Peeters, Strain and electric field tuning of semi-metallic character  $WCrCO_2$  MXenes with dual narrow band gap, *J. Phys. Conde. Matter* 32 (25), 355504, 2021.
  - 63 A. Bafekry, C.V. Nguyen, C. Stampfl, B. Akgenc, M. Ghergherehchi, Oxygen Vacancies in the Single Layer of  $Ti_2CO_2$  MXene: Effects of Gating Voltage, Mechanical Strain, and Atomic Impurities *physica status solidi (b)*, 2000343, 2021.
  - 64 A. Bafekry, M. Faraji, M.M. Fadlallah, A.B. Khatibani, A. ab-dolahzadeh Ziabari, M. Ghergherehchi, Sh. Nedaei, S. Farjani Shayesteh, D. Gogova, Tunable electronic and magnetic properties of  $MoSi_2N_4$  monolayer via vacancy defects, atomic adsorption and atomic doping, *Appl. Surf. Sci.* 559, 149862, 2021.
  - 65 A Bafekry, C Stampfl, Band-gap control of graphenelike borocarbonitride g- $BC_6N$  bilayers by electrical gating, *Phys. Rev. B* 102, 195411, 2021.
  - 66 J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77, 3865, 1996.
  - 67 J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 78, 1396, 1997.
  - 68 G. Kresse and J. Hafner, Ab initio molecular dynamics for liquid metals, *Phys. Rev. B* 47, 558, 1993.
  - 69 G. Kresse and J. Hafner, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B* 49, 14251, 1994.
  - 70 S. J. Grimme, Semiempirical GGA-type density functional constructed with a long-range dispersion correction, *Comput. Chem.* 27, 1787, 2006.
  - 71 G. Henkelman, A. Arnaldsson, and H. Jonsson, A fast and robust algorithm for Bader decomposition of charge density, *Comput. Mater. Sci.* 36, 354, 2006.
  - 72 H.J. Monkhorst and J.D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B* 13, 12, 1976.
  - 73 D. Alfe, PHON: A program to calculate phonons using the small displacement method, *Comput. Phys. Commun.* 180, 2622, 2009.
  - 74 N. Zhang, Y. Hong, S. Yazdanparast, M. Asle Zaeem, Superior structural, elastic and electronic properties of 2D titanium nitride MXenes over carbide MXenes: a comprehensive

- first principles study, *2D Mater.* 5, 045004, 2018.
- 75 James, Arthur M and Lord, Mary P, *Macmillan's Chemical and Physical Data*, Macmillan, Basingstoke, 1992.
  - 76 Q. Wan , S. Li and J. Liu , First-Principle Study of Li-Ion Storage of Functionalized Ti<sub>2</sub>C Monolayer with Vacancies, *ACS Appl. Mater. Interfaces* 10 ,6369, 2018.
  - 77 M. Sternik and U. D. Wdowik, Probing the impact of magnetic interactions on the lattice dynamics of two-dimensional Ti<sub>2</sub>X (X = C, N) MXenes, *Phys. Chem. Chem. Phys.* 20 , 7754, 2018.
  - 78 P. Lv, Y.-L Li and J.-F. Wang, Monolayer Ti<sub>2</sub>C MXene: manipulating magnetic properties and electronic structures by an electric field *Phys. Chem. Chem. Phys.* 22, 11266, 2020.
  - 79 O. Mashtalir, M. Naguib, V.N. Mochalin, Y. Dall'Agnese, M. Heon, M.W. Barsoum, Y. Gogotsi, Intercalation and delamination of layered carbides and carbonitrides, *Nat. Commun.* 4, 1716, 2013.
  - 80 C. Shi, M. Beidaghi, M. Naguib, O. Mashtalir, Y. Gogotsi, and S. J. Billinge, Structure of Nanocrystalline Ti<sub>3</sub>C<sub>2</sub> MXene Using Atomic Pair Distribution Function, *Phys. Rev. Lett.* 112, 125501, 2020.
  - 81 U. Yorulmaz, İ.G. Demiroglu, D. Cakir, O. Gulseren, and Cem Sevik, A systematical ab-initio review of promising 2D MX-enemonolayers towards Li-ion battery applications, *J. Phys. Energy* 2, 032006, 2020.
  - 82 H. Zhang, G. Yang, X. Zuo, H. Tang, Q. Yangaand, G. Li, Computational studies on the structural, electronic and optical properties of graphene-like MXenes (M<sub>2</sub>CT<sub>2</sub>, M=Ti, Zr, Hf; T=O, F, OH) and their potential applications as visible-light, driven photocatalysts, *J. Mater. Chem. A* 4, 12913, 2016.
  - 83 Y. Xie, P. R. C. Kent, Hybrid density functional study of structural and electronic properties of functionalized Ti<sub>n</sub> + 1X<sub>n</sub> (X=C, N) monolayers, *Phys. Rev. B* 87, 235441, 2013.
  - 84 M. Khazaei, A. Ranjbar, M. Arai, T.o Sasaki, S. Yunoki, Electronic properties and applications of MXenes: a theoretical review, *J. Mater. Chem. C* 5, 2488, 2017.
  - 85 S. Wang, J.-X. Li, Y.-L. Du, C. Cui, First-principles study on structural, electronic and elastic properties of graphene-like hexagonal Ti<sub>2</sub>C monolayer, *Computational Materials Science* 83, 290, 2014
  - 86 D. Li, X. Chen, P. Xiang, H. Du, B. Xiao, Chalcogenated-Ti<sub>3</sub>C<sub>2</sub> MXene (X = O, S, Se and Te) as a high-performance anode material for Li-ion batteries, *Applied Surface Science* 501, 144221, 2020.
  - 87 A. N. Gandhi, H. N. Alshareef, U. Schwingenschlogl, Thermoelectric Performance of the MXenes M<sub>2</sub>CO<sub>2</sub> (M = Ti, Zr, or Hf), *Chem. Mater.* 28, 1647 2016.
  - 88 L. Li, Lattice dynamics and electronic structures of Ti<sub>3</sub> C<sub>2</sub> O<sub>2</sub> and Mo<sub>2</sub> TiC<sub>2</sub> O<sub>2</sub> (MXenes): The effect of Mo substitution, *Comput. Mater. Sci.* 124, 8 2016.