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## Ti<sub>3</sub>BN monolayer: the MXene-like material predicted by first-principles calculations†

Dandan Wang,<sup>a</sup> ZhongHui Sun,<sup>ab</sup> DongXue Han,<sup>\*a</sup> Lei Liu<sup>c</sup> and Li Niu<sup>a</sup>

The discovery of graphene and other two-dimensional (2D) materials has set the foundation for exploring and designing novel single layered sheets. The family of 2D materials encompasses a wide selection of compositions including almost all the elements of the periodic table and they have the potential to play a fundamental role in the future of electronics, composite materials and energy technology. Therefore, searching for new 2D materials is a big challenge in materials science. In this work, we theoretically designed a monolayer of Ti<sub>3</sub>BN following the strategy of “atomic transmutation”. The Ti<sub>3</sub>BN monolayer can be considered as three Ti-atomic layers being interleaved with one N-atomic layer and one B-atomic layer, in the sequence of Ti<sub>1</sub>-N-Ti<sub>2</sub>-B-Ti<sub>3</sub>. The moderate cohesive energy, positive phonon frequencies and high melting point are the best guarantees for good stability of Ti<sub>3</sub>BN. Based on a global minimum structures search using the particle-swarm optimization (PSO) method, Ti<sub>3</sub>BN is the lowest energy structure in 2D space, which holds great promise for the realization of layered Ti<sub>3</sub>BN in experiment. Based on density functional theory (DFT) calculations, Ti<sub>3</sub>BN is intrinsically metallic and its electronic properties can be modulated by varying the surface groups, such as OH or F-termination. If realized in experiment, it may find applications in many aspects.

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### 1. Introduction

Since graphene was realized experimentally in 2004,<sup>1</sup> 2D materials have attracted significant interest and a large variety of freestanding monolayer solids have been successfully fabricated, such as hexagonal boron nitride (h-BN),<sup>2</sup> metal chalcogenides (MoS<sub>2</sub>, WS<sub>2</sub>),<sup>3,4</sup> silicene<sup>5</sup> and so on. Due to their unique electronic, chemical, and mechanical properties, those 2D materials have found wide applications in supercapacitors,<sup>6</sup> solar cells,<sup>7</sup> lithium ion batteries<sup>8</sup> and water splitting application<sup>9</sup> and other areas of energy and environment.

Recently, a new family of graphene-like 2D materials termed as MXenes were successfully synthesized by selectively extracting the “A” element from the layered MAX phases (A is an A-group element, mostly Al or Si) in the aqueous HF.<sup>10</sup> MAX phases are a large (>60 members) family of layered ternary early transition-metal carbides, nitrides, and carbonitrides with P6<sub>3</sub>/mmc symmetry.<sup>11</sup> To date, several MXenes have been

synthesized successfully, including Ti<sub>3</sub>C<sub>2</sub>,<sup>12</sup> Ti<sub>2</sub>C,<sup>13</sup> Ta<sub>4</sub>C<sub>3</sub>,<sup>14</sup> V<sub>2</sub>C,<sup>15</sup> TiNbC,<sup>16</sup> Nb<sub>2</sub>C<sup>17</sup> and Mo<sub>2</sub>C.<sup>18</sup>

With the increasing interest in MXenes, a mass of experimental and theoretical efforts related to their synthesis, structures, properties and potential applications have been made experimentally and theoretically.<sup>19,20</sup> Among the as-synthesized MXene phases, the most studied MXene is Ti<sub>3</sub>C<sub>2</sub>, prepared by immersing Ti<sub>3</sub>AlC<sub>2</sub> in HF solutions at room temperature.<sup>12</sup> Ti<sub>3</sub>C<sub>2</sub> was predicted theoretically to be good electrical conductors and its electrical conductivities can be tuned by different surface terminations.<sup>21</sup> What's more, Ti<sub>3</sub>C<sub>2</sub> have been proved to be very promising as anode materials for Li-ion batteries and as hydrogen storage media.<sup>22,23</sup>

Motivated by the Ti<sub>3</sub>C<sub>2</sub> monolayer, which is composed of three Ti-atomic layers being interleaved with two C-atomic layers, herein we designed a new 2D material of Ti<sub>3</sub>BN by performing density functional theory (DFT) calculations following the strategy of “atomic transmutation”, which means substituting certain types of elements with their neighboring elements in the periodic table but the total number of valence electrons is kept unchanged.<sup>24,25</sup> A major breakthrough has been made in finding and designing novel materials. For example, if one were to substitute the oxide ions in ZnO with N and F, one would ultimately obtain Zn<sub>2</sub>NF whose conduction and valence band edges are more favorable for water splitting.<sup>26</sup> When two C atoms in graphene were transmuted with one B atom and one N atom, h-BN with wide band gap and new functionalities will be obtained.<sup>27</sup> Therefore Ti<sub>3</sub>BN monolayer

<sup>a</sup>State Key Laboratory of Electroanalytical Chemistry, c/o Engineering Laboratory for Modern Analytical Techniques, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun, 130022, Jilin, P. R. China. E-mail: dxhan@ciac.ac.cn; Fax: +86 4318526 2800; Tel: +86 4318526 2425

<sup>b</sup>University of Chinese Academy of Sciences, Beijing, 100049, P. R. China

<sup>c</sup>State Key Laboratory of Luminescence and Applications, CIOMP, Chinese Academy of Sciences, No. 3888 Dongnanhu Road, Changchun, 130033, Jilin, P. R. China

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can be thought of as obtained by substituting the two C-atomic layers of  $\text{Ti}_3\text{C}_2$  monolayer with one nitrogen-atomic layer and one boron-atomic layer, respectively, in consideration of that nitrogen and boron are two nearest-neighbors of carbon in the periodic table and  $\text{Ti}_3\text{BN}$  is isoelectronic to  $\text{Ti}_3\text{C}_2$ .

## 2. Computational method

DFT calculations were performed within the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation<sup>28</sup> and the projected augmented wave (PAW) method<sup>29,30</sup> as implemented in the Vienna *ab initio* simulation package (VASP). To reach convergence criteria for both energy and forces, a special  $k$ -point sampling with a  $k$ -point separation of  $0.04 \text{ \AA}^{-1}$  is applied for the Brillouin-zone integration and the cutoff energy for the plane wave basis set is 408 eV. The ground state geometries of the 2D  $\text{Ti}_3\text{BN}$  are obtained with all the atomic positions relaxed until their residual forces are less than  $0.01 \text{ eV \AA}^{-1}$ . In building the monolayer models, a vacuum thickness of  $15 \text{ \AA}$  is adopted to avoid the interactions between adjacent layers. The phonon dispersion curves of  $\text{Ti}_3\text{BN}$  monolayer was calculated using the density functional perturbation theory (DFPT)<sup>31,32</sup> as implemented in the PHONOPY program interfaced with VASP. To obtain the accurate electronic properties of  $\text{Ti}_3\text{BN}$  monolayer, hybrid functional calculations using Hetero-Scuseria–Ernzerhof (HSE06) functional<sup>33</sup> have been employed.

The thermal stability of  $\text{Ti}_3\text{BN}$  monolayer was assessed by first-principles molecular dynamics (MD) calculations using the PAW pseudo-potential and PBE functional as implemented in VASP.<sup>34</sup> For each temperature, a preheating for 1 ps was applied for the initial geometry structure. And the MD calculations were in NVT ensemble, lasting for 10 ps with a time step of 1.0 fs. To control the temperature, Nosé–Hoover method was applied.<sup>35</sup>

The global minimum structure for  $\text{Ti}_3\text{BN}$  monolayer was searched by particle-swarm optimization (PSO) method within the evolution algorithm which was implemented in CALYPSO code.<sup>36–38</sup> The population size was set as 30, and the number of generation was maintained at 25. Unit cells containing 5, 10, and 15 atoms were considered. The structure relaxations during the PSO searching were carried by using PBE functional as implemented in VASP.

## 3. Results and discussion

### 3.1 Structural properties and stability of $\text{Ti}_3\text{BN}$ monolayer

The optimized structure of our designed  $\text{Ti}_3\text{BN}$  monolayer is shown in Fig. 1(a). Similar with  $\text{Ti}_3\text{C}_2$  monolayer,  $\text{Ti}_3\text{BN}$  monolayer is crystallized in the space group  $P3m1$  (no. 156) and each unit cell contains five atoms, all in different atomic planes with the sequence of  $\text{Ti}_1\text{-N-Ti}_2\text{-B-Ti}_3$ . To avoid the interactions between the  $\text{Ti}_3\text{BN}$  monolayer and its periodic images along the normal direction, a vacuum layer of  $15 \text{ \AA}$  is used and the calculated lattice constants for the unit cell are  $a = b = 3.095 \text{ \AA}$ . In  $\text{Ti}_3\text{BN}$  monolayer, the length of  $\text{Ti}_1\text{-N}$  and  $\text{N-Ti}_2$  bonds ( $2.054$  and  $2.195 \text{ \AA}$ ) are shorter than those of corresponding  $\text{Ti-C}$  bonds ( $2.064$  and  $2.212 \text{ \AA}$ )<sup>19,20</sup> in  $\text{Ti}_3\text{C}_2$  monolayer, while the  $\text{Ti}_2\text{-B}$  and  $\text{B-Ti}_3$  bond lengths are  $2.249$  and  $2.117 \text{ \AA}$ ,

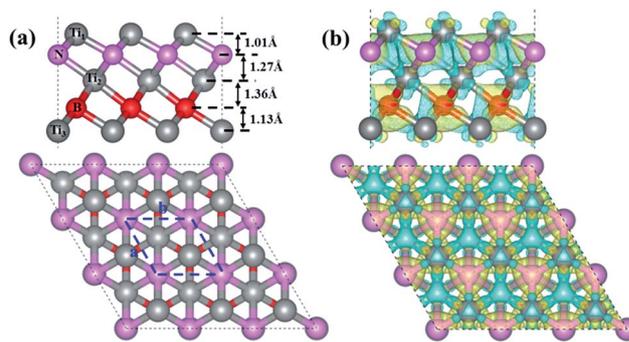


Fig. 1 (a) Side (upper) and top (lower) views of the optimized structure of monolayer  $\text{Ti}_3\text{BN}$ . A  $3 \times 3 \times 1$  supercell is used in the projection, and the blue dash lines denote a unit cell where  $a$ ,  $b$  represents the lattice constants. Gray, pink and red balls represent Ti, N and B atoms, respectively. (b) Side (upper) and top (lower) views of the isosurface of the deformation charge density of monolayer  $\text{Ti}_3\text{BN}$  with the isovalue of  $0.008 \text{ \AA}^{-3}$ . The blue (yellow) smooth shadings denote electron depletion (accumulation).

respectively, longer than those of corresponding  $\text{Ti-C}$  bonds in  $\text{Ti}_3\text{C}_2$  monolayer. The thickness of  $\text{Ti}_3\text{BN}$  monolayer is  $4.78 \text{ \AA}$  with the atomic layer distances of  $1.01$ ,  $1.27$ ,  $1.36$  and  $1.13 \text{ \AA}$ , respectively.

To elucidate the chemical bonding and stabilization mechanism of  $\text{Ti}_3\text{BN}$  monolayer, the deformation electronic density<sup>39</sup> has been calculated. As shown in Fig. 1(b), there is remarkable electron transfer from Ti atoms to N atoms and from Ti atoms to B atoms, indicating the electronically stabilization in the  $\text{Ti}_3\text{BN}$  monolayer. Bader charge analysis shows that the net charges on N and B atom are  $-1.65 \text{ e}$  and  $-1.57 \text{ e}$  and those on  $\text{Ti}_1$ ,  $\text{Ti}_2$ , and  $\text{Ti}_3$  atom are  $0.97 \text{ e}$ ,  $1.34 \text{ e}$  and  $0.91 \text{ e}$ , respectively. The electron localization function<sup>39</sup> of  $\text{Ti}_3\text{BN}$  monolayer is also calculated to highlight the electron distribution. As seen from the isosurfaces of electron localization functions presented in Fig. S1,<sup>†</sup> the electrons are completely delocalized around the Ti atoms, and widely distributed in the N and B frameworks, which also suggests the electron transfer from Ti atoms to N and B atoms.

Although  $\text{Ti}_3\text{BN}$  monolayer possesses similar structure properties with  $\text{Ti}_3\text{C}_2$  monolayer, the question whether  $\text{Ti}_3\text{BN}$  monolayer is as stable as  $\text{Ti}_3\text{C}_2$  or not need to be answered. The cohesive energy of  $\text{Ti}_3\text{BN}$  monolayer is a useful argument for evaluating its stability, defined as  $E_{\text{coh}} = (xE_{\text{Ti}} + yE_{\text{N}} + zE_{\text{B}} - E_{\text{Ti}_3\text{BN}})/(x + y + z)$ , where  $E_{\text{Ti}}$ ,  $E_{\text{N}}$ ,  $E_{\text{B}}$  and  $E_{\text{Ti}_3\text{BN}}$  are the total energies of a single Ti atom, a single N atom, a single B atom and  $\text{Ti}_3\text{BN}$  monolayer,  $x$ ,  $y$  and  $z$  are the number of Ti, N, and B atoms in the supercell, respectively. Based on our DFT calculations, the cohesive energy of  $\text{Ti}_3\text{BN}$  monolayer is  $7.46 \text{ eV}$  per atom, which is a little smaller than that of graphene ( $7.95 \text{ eV}$  per atom)<sup>40</sup> and higher than that of  $\text{Ti}_3\text{C}_2$  (about  $7.00 \text{ eV}$ ).<sup>13</sup> The relatively large cohesive energy of  $\text{Ti}_3\text{BN}$  monolayer indicates that  $\text{Ti}_3\text{BN}$  monolayer is a stable phase with strong chemical bonds. What's more, the small cohesive energy difference between  $\text{Ti}_3\text{BN}$  monolayer and  $\text{Ti}_3\text{BN}$  bulk ( $7.46 \text{ eV}$  per atom *vs.*  $7.82 \text{ eV}$  per atom) means that it's favorable to obtain  $\text{Ti}_3\text{BN}$  monolayer from its bulk phase. The elastic constants of  $\text{Ti}_3\text{BN}$  monolayer were



then calculated to be  $C_{11} = C_{22} = 202.11 \text{ N m}^{-1}$ ,  $C_{12} = C_{21} = 59.24 \text{ N m}^{-1}$ , which satisfy the mechanical stability criteria, indicating that the  $\text{Ti}_3\text{BN}$  monolayer is also mechanically stable.

The kinetic stability of  $\text{Ti}_3\text{BN}$  monolayer has been further confirmed by its phonon dispersion along the high-symmetry directions in the first Brillouin zone. As shown in Fig. 2(a), there is no appreciable imaginary frequency in the phonon dispersion curves, implying the good kinetic stability of  $\text{Ti}_3\text{BN}$  monolayer. The highest frequency of  $\text{Ti}_3\text{BN}$  monolayer is  $653.60 \text{ cm}^{-1}$ , higher than that of the widely studied  $\text{MoS}_2$  monolayer ( $473 \text{ cm}^{-1}$ )<sup>40</sup> and silicene ( $580 \text{ cm}^{-1}$ ).<sup>40</sup> The high frequency suggests that the related bonds in  $\text{Ti}_3\text{BN}$  monolayer are strong.

Finally, the thermal stability of  $\text{Ti}_3\text{BN}$  monolayer was investigated by first-principles molecular dynamics (MD) calculations. A  $5 \times 5$  supercell containing 125 atoms was used here and three individual MD calculations for  $\text{Ti}_3\text{BN}$  monolayer at temperatures of 500 K, 800 K, and 1000 K were performed. Fig. 3 presents the snapshots of  $\text{Ti}_3\text{BN}$  monolayer at the end of 10 ps MD calculations. These snapshots show that  $\text{Ti}_3\text{BN}$  monolayer can maintain its structural integrity throughout a 10 ps dynamical calculation up to 800 K, however will be disrupted at the temperature of 1000 K. Those results reveal that the  $\text{Ti}_3\text{BN}$  monolayer has good thermal stability and the melting point of  $\text{Ti}_3\text{BN}$  monolayer is between 800 K and 1000 K.

### 3.2 Global minimum search for $\text{Ti}_3\text{BN}$ monolayer in 2D space

Although  $\text{Ti}_3\text{BN}$  monolayer has good stability based on the above results, the doubt about that the  $\text{Ti}_3\text{BN}$  monolayer is a local minimum or a global minimum needs to be solved. It's well known that the global minimum structure is more likely to be realized experimentally. Therefore, we carried out a global search for the lowest energy structure of  $\text{Ti}_3\text{BN}$  monolayer in the 2D space by adopting the first-principles based particle-swarm optimization method. After 25 generations, three low-energy structures for 2D  $\text{Ti}_3\text{BN}$  were obtained, labelled as  $\text{Ti}_3\text{BN-I}$ ,  $\text{Ti}_3\text{BN-II}$ , and  $\text{Ti}_3\text{BN-III}$  in the order of increasing energy.

As shown in Fig. 4, in which the relative energy per atom is presented, the global minimum structure is  $\text{Ti}_3\text{BN-I}$ , which is

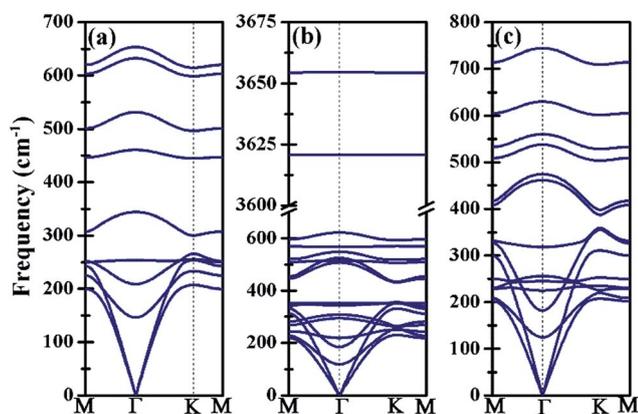


Fig. 2 Phonon dispersion curves of (a) bare  $\text{Ti}_3\text{BN}$  monolayer; (b)  $\text{Ti}_3\text{BN}(\text{OH})_2\text{-IV}$  monolayer; (c)  $\text{Ti}_3\text{BNF}_2\text{-I}$  monolayer.

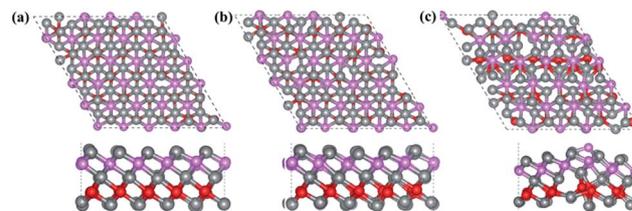


Fig. 3 Top (upper) and side (lower) views of snapshots of the  $\text{Ti}_3\text{BN}$  monolayer equilibrium structures at the end of 10 ps MD simulations: (a) 500 K, (b) 800 K, and (c) 1000 K. Gray, pink and red balls represent Ti, N and B atoms, respectively.

just the above discussed  $\text{Ti}_3\text{BN}$  monolayer. Interestingly,  $\text{Ti}_3\text{BN-II}$  is also crystallized in the space group  $P3m1$  (no. 156). The geometric construction, thickness, atomic layer distances of  $\text{Ti}_3\text{BN-II}$  is similar with that of  $\text{Ti}_3\text{BN-I}$ , while the biggest difference between them is the N-atomic layer just located above the B-atomic layer and the  $\text{Ti}_1$ -atomic layer above the  $\text{Ti}_3$ -atomic layer in  $\text{Ti}_3\text{BN-II}$  monolayer. The length of  $\text{Ti}_1\text{-N}$ ,  $\text{N-Ti}_2$ ,  $\text{Ti}_2\text{-B}$ , and  $\text{B-Ti}_3$  bond in  $\text{Ti}_3\text{BN-II}$  monolayer is  $2.043 \text{ \AA}$ ,  $2.202 \text{ \AA}$ ,  $2.254 \text{ \AA}$ , and  $2.116 \text{ \AA}$ , respectively. Considering structure  $\text{Ti}_3\text{BN-III}$ , it is  $0.057 \text{ eV}$  per atom higher in energy than  $\text{Ti}_3\text{BN-I}$ . This high energy might be due to the more nonbonding electrons of  $\text{Ti}_1$  atoms.

### 3.3 Electronic properties of $\text{Ti}_3\text{BN}$ monolayer

Since  $\text{Ti}_3\text{BN-I}$  monolayer holds great potential to be realized in experiment, does it have intriguing properties and promising applications? To figure out this issue, we have studied the electrical properties of the  $\text{Ti}_3\text{BN-I}$  monolayer using the hybrid density functional calculations. Fig. 5 illustrates the band structure and partial density of state (PDOS) of  $\text{Ti}_3\text{BN-I}$  monolayer. Obviously, a conduction band and a valence band across through the Fermi level, indicating that  $\text{Ti}_3\text{BN}$  monolayer has metallic properties. The PDOS analysis shows that mainly the Ti-3d states, especially the 3d states of Ti atoms from surface atomic layer, contribute to the high density of electron states around the Fermi level. Note that the high density of states near the Fermi level means available carriers which are beneficial to the high electric conductivity of the  $\text{Ti}_3\text{BN}$  monolayer.

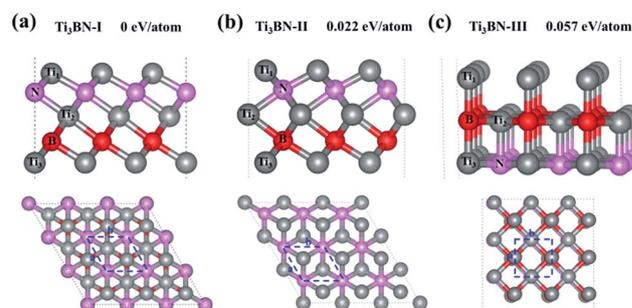


Fig. 4 Side (upper) and top (lower) views of low-energy 2D structures of  $\text{Ti}_3\text{BN}$  obtained from the PSO calculations. For Comparison, the relative energy per atom is given. The blue dash lines denote a unit cell where  $a$ ,  $b$  represents the lattice constants. Gray, pink and red balls represent Ti, N and B atoms, respectively.



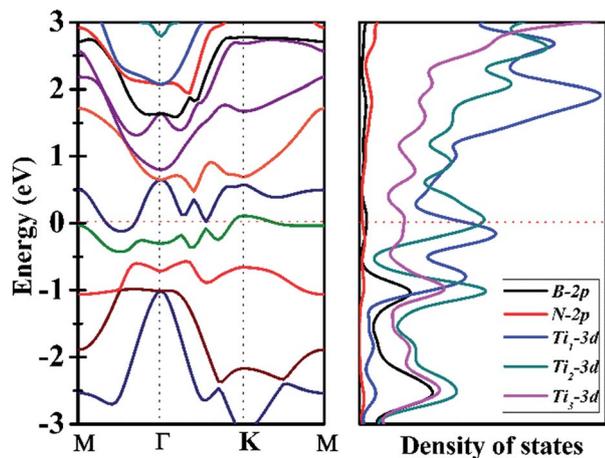


Fig. 5 Band structure (left) and partial density of states (PDOS) of  $\text{Ti}_3\text{BN-I}$  monolayer obtained from hybrid functional calculations. For reference, the Fermi level is set at 0 eV.  $\text{Ti}_1$  and  $\text{Ti}_3$  represent the Ti atoms from the surface Ti-atomic layer and  $\text{Ti}_2$  denotes the Ti atoms from inner Ti-atomic layer.

### 3.4 Surface modification of $\text{Ti}_3\text{BN}$ monolayer by OH and F termination

Moreover, the high DOS at the Fermi level mainly originated from  $\text{Ti}_1$  and  $\text{Ti}_3$  atoms indicates the high activity of surface Ti atoms, suggesting the feasibility in the surface modification and even in composite materials for  $\text{Ti}_3\text{BN}$  monolayer. For example, our theoretical studies have shown that the electronic properties of  $\text{Ti}_3\text{BN}$  can be tuned by surface functional groups ( $-\text{OH}$ ,  $-\text{F}$ ). Herein, four possible geometry structures of  $\text{Ti}_3\text{BN}$  monolayer with hydroxylated, and fluorinated surfaces are considered, as presented in Fig. 6. The top views of  $\text{Ti}_3\text{BNF}_2\text{-I}$  and  $\text{Ti}_3\text{BNF}_2\text{-II}$  configurations are depicted in Fig. S2.† In configuration I, all the  $-\text{OH}$  or  $-\text{F}$  groups are located above the hollow sites between the three neighboring C/B atoms or point directly toward the  $\text{Ti}_2$  atoms on both sides of  $\text{Ti}_3\text{BN}$  monolayer. In configuration II, all the  $-\text{OH}$  or  $-\text{F}$  groups are oriented above

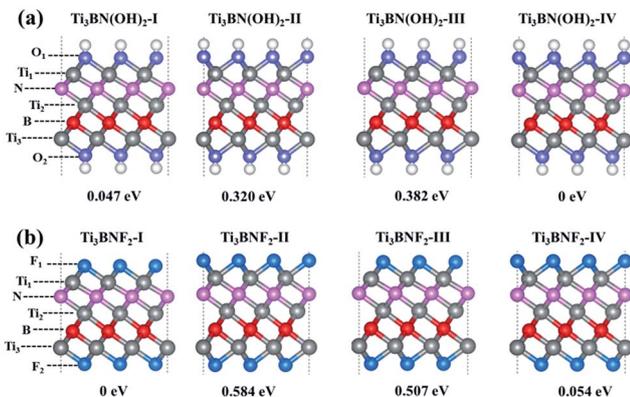


Fig. 6 Side views of optimized geometries of the hydroxylated and fluorinated  $\text{Ti}_3\text{BN}$  monolayer: (a)  $\text{Ti}_3\text{BN}(\text{OH})_2$ ; (b)  $\text{Ti}_3\text{BNF}_2$ . Gray, pink and red balls represent Ti, N and B atoms, respectively. The H, O, and F atoms are indicated by white, purple, and cyan balls.

the topmost sites of C and B atoms on the two sides of  $\text{Ti}_3\text{BN}$  monolayer, respectively. Afterwards, we can view the asymmetric arrangement of configuration III and IV as the combination of configuration I and II.

The structural stability of different  $\text{Ti}_3\text{BN}(\text{OH})_2$  and  $\text{Ti}_3\text{BNF}_2$  configurations can be estimated by comparing their relative total energies. For  $\text{Ti}_3\text{BN}(\text{OH})_2$ , configuration IV is energetically most favorable.  $\text{Ti}_3\text{BN}(\text{OH})_2\text{-IV}$  is energetically lower than  $\text{Ti}_3\text{BN}(\text{OH})_2\text{-I}$ ,  $\text{Ti}_3\text{BN}(\text{OH})_2\text{-II}$  and  $\text{Ti}_3\text{BN}(\text{OH})_2\text{-III}$  by 0.047, 0.320, and 0.382 eV per unit cell, respectively. While for  $\text{Ti}_3\text{BNF}_2$ , configuration I is energetically most favorable, with its energy lower than that of  $\text{Ti}_3\text{BNF}_2\text{-II}$ ,  $\text{Ti}_3\text{BNF}_2\text{-III}$  and  $\text{Ti}_3\text{BNF}_2\text{-IV}$  by 0.584, 0.507, and 0.054 eV per unit cell, respectively. Phonon dispersions of  $\text{Ti}_3\text{BN}(\text{OH})_2\text{-IV}$  and  $\text{Ti}_3\text{BNF}_2\text{-I}$  has been further calculated to investigate their kinetic stability, as shown in Fig. 2(b) and (c). As expected, there are no imaginary frequencies in the phonon dispersion curves. The phonons at about  $3654.56\text{ cm}^{-1}$  and  $3620.86\text{ cm}^{-1}$  for  $\text{Ti}_3\text{BN}(\text{OH})_2\text{-IV}$  should be dominated by the OH groups, and the phonons at about  $744.73\text{ cm}^{-1}$  for  $\text{Ti}_3\text{BNF}_2\text{-I}$  should be due to the F groups. These high-frequency phonons indicate the strong bond nature of the related bonds (Ti–O and Ti–F).

In comparison with bare  $\text{Ti}_3\text{BN}$ , the OH or F-terminated  $\text{Ti}_3\text{BN}$  monolayer have smaller lattice constants. With terminal groups, the bond lengths of N– $\text{Ti}_2$  and  $\text{Ti}_2\text{–B}$  shrink, while the bonds between the  $\text{Ti}_1\text{–N}$  and B– $\text{Ti}_3$  are elongated except the  $\text{Ti}_1\text{–N}$  bonds of  $\text{Ti}_3\text{BNF}_2\text{-I}$  and  $\text{Ti}_3\text{BNF}_2\text{-III}$ . Those results imply that the surface groups strongly interact with the original  $\text{Ti}_3\text{BN}$  block, in accordance with the corresponding phonon dispersions. For clearance, the calculated lattice constants and bond lengths are presented in Table S1.†

Though the  $\text{Ti}_3\text{BN}$  monolayer is metallic, its hydroxylated or fluorinated derivatives may be narrow-gap semiconductors or metals, depending on the geometrical arrangements of surface F and OH groups. Seen from Fig. 7(a), for  $\text{Ti}_3\text{BN}$  with surface OH

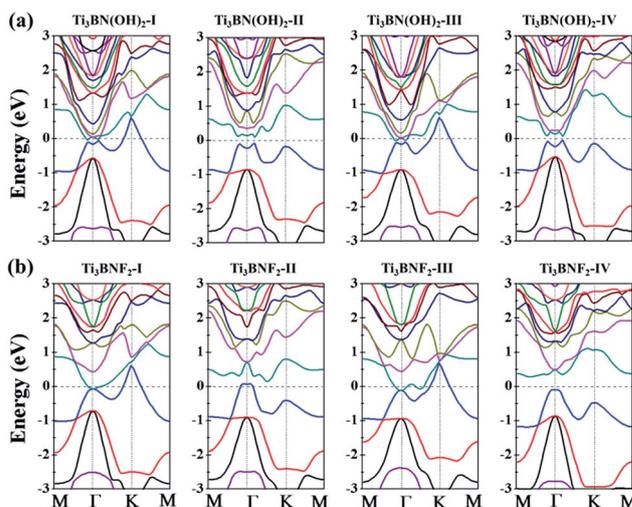


Fig. 7 Band structures of the hydroxylated and fluorinated  $\text{Ti}_3\text{BN}$  monolayer obtained from hybrid functional calculations: (a)  $\text{Ti}_3\text{BN}(\text{OH})_2$ ; (b)  $\text{Ti}_3\text{BNF}_2$ .



groups, the most favorable  $\text{Ti}_3\text{BN}(\text{OH})_2\text{-IV}$  has a semi-conducting character, with a direct band gap of 0.09 eV.  $\text{Ti}_3\text{BN}(\text{OH})_2\text{-II}$  also shows the electronic properties of direct semiconductor, and the band gap is 0.16 eV. However,  $\text{Ti}_3\text{BN}(\text{OH})_2\text{-I}$  and  $\text{Ti}_3\text{BN}(\text{OH})_2\text{-III}$  is metallic. For  $\text{Ti}_3\text{BN}$  with F-termination (Fig. 7(b)), the most stable configuration of  $\text{Ti}_3\text{BNF}_2\text{-I}$  and the metastable configuration of  $\text{Ti}_3\text{BNF}_2\text{-III}$  are metals. On the contrary, the band structures of  $\text{Ti}_3\text{BNF}_2\text{-II}$  and  $\text{Ti}_3\text{BNF}_2\text{-IV}$  demonstrate their indirect semiconducting characters, with the band gap of 0.07 eV and 0.37 eV, respectively. Those theoretical results prove that the electronic structure of  $\text{Ti}_3\text{BN}$  monolayer can be modulated by varying the surface functional groups.

## 4. Conclusions

In summary, we designed a new inorganic 2D material of  $\text{Ti}_3\text{BN}$  monolayer following the strategy of "atomic transmutation" by performing DFT calculations. In  $\text{Ti}_3\text{BN}$  monolayer, the Ti-B and Ti-N bonds are strong and the geometry structure is similar with the reported MXenes. The high cohesive energy, elastic constants, and absence of imaginary phonon frequencies prove that the  $\text{Ti}_3\text{BN}$  monolayer possess dynamic and mechanical stability. Particularly, MD simulation results verify that  $\text{Ti}_3\text{BN}$  monolayer can maintain its structural stability up to at least 800 K. The PSO method revealed that  $\text{Ti}_3\text{BN}$  monolayer is the global minimum structure in 2D space, suggesting the possibility to realize  $\text{Ti}_3\text{BN}$  monolayer in experiment. What's more, the electronic properties of  $\text{Ti}_3\text{BN}$  monolayer can be modified by varying the surface functional groups and their geometrical configurations. Therefore, if  $\text{Ti}_3\text{BN}$  is realized, it may find wide applications, such as in electrics, composite materials, Li-ion batteries and so on.

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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, *Science*, 2004, **306**, 666–669.
- 2 L. H. Li and Y. Chen, *Adv. Funct. Mater.*, 2016, **26**, 2594–2608.
- 3 L. Dominik and K. Andras, *ACS Nano*, 2012, **6**, 10070–10075.
- 4 B. Liu, W. J. Zhao, Z. J. Ding, I. Verzhbitskiy, L. J. Li, J. P. Lu, J. Y. Chen, G. Eda and K. P. Loh, *Adv. Mater.*, 2016, **28**, 6457–6464.
- 5 T. Li, C. Eugenio, C. Daniele, G. Carlo, F. Marco, D. Madan, M. Alessandro and A. Deji, *Nat. Nanotechnol.*, 2015, **10**, 227–231.
- 6 X. Y. Zhang, S. H. Sun, X. J. Sun, Y. R. Zhao, L. Chen, Y. Yang, W. Lu and D. B. Li, *Light: Sci. Appl.*, 2016, **5**, e16130.
- 7 W. Wei, K. Sun and Y. H. Hu, *J. Mater. Chem. A*, 2016, **4**, 12398–12401.
- 8 C. X. Peng, B. D. Chen, Y. Qin, S. H. Yang, C. Z. Li, Y. H. Zuo, S. Y. Liu and J. H. Yang, *ACS Nano*, 2012, **6**, 1074–1081.
- 9 H. L. Zhuang and R. G. Hennig, *Chem. Mater.*, 2013, **25**, 3232–3238.
- 10 S. Kajiyama, L. Szabova, K. Sodeyama, H. Iinuma, R. Morita, K. Gotoh, Y. Tateyama, M. Okubo and A. Yamada, *ACS Nano*, 2016, **10**, 3334–3341.
- 11 M. W. Barsoum, *Prog. Solid State Chem.*, 2000, **28**, 201–281.
- 12 M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi and M. W. Barsoum, *Adv. Mater.*, 2011, **23**, 4248–4253.
- 13 T. S. Zhao, S. H. Zhang, Y. Guo and Q. Wang, *Nanoscale*, 2016, **8**, 233–242.
- 14 M. Naguib, O. Mashtalir, J. Carle, V. Presser, J. Lu, L. Hultman, Y. Gogotsi and M. W. Barsoum, *ACS Nano*, 2012, **6**, 1322–1331.
- 15 M. Naguib, J. Halim, J. Lu, K. M. Cook, L. Hultman, Y. Gogotsi and M. W. Barsoum, *J. Am. Chem. Soc.*, 2013, **135**, 15966–15969.
- 16 O. Mashtalir, M. Naguib, V. N. Mochalin, Y. Dall'Agnese, M. Heon, M. W. Barsoum and Y. Gogotsi, *Nat. Commun.*, 2013, **4**, 1716–1723.
- 17 J. P. Hu, B. Xu, C. Y. Ouyang, Y. Zhang and S. Y. A. Yang, *RSC Adv.*, 2016, **6**, 27467–27474.
- 18 C. Xu, L. Wang, Z. Liu, L. Chen, J. K. Guo, N. Kang, X.-L. Ma, H.-M. Cheng and W. Ren, *Nat. Mater.*, 2015, **14**, 1135–1141.
- 19 S. K. Kim, Y.-J. Zhang, H. Bergstrom, R. Michalsky and A. Peterson, *ACS Catal.*, 2016, **6**, 2003–2013.
- 20 Q. Tang, Z. Zhou and P. Shen, *J. Am. Chem. Soc.*, 2012, **134**, 16909–16916.
- 21 S. Lai, J. Jeon, S. K. Jang, J. Xu, Y. J. Choi, J.-H. Park, E. Hwang and S. Lee, *Nanoscale*, 2015, **7**, 19390–19396.
- 22 D. Er, J. Li, M. Naguib, Y. Gogotsi and V. B. Shenoy, *ACS Appl. Mater. Interfaces*, 2014, **6**, 11173–11179.
- 23 Q. K. Hu, D. D. Sun, Q. H. Wu, H. Y. Wang, L. B. Wang, B. Z. Liu, A. G. Zhou and J. L. He, *J. Phys. Chem. A*, 2013, **117**, 14253–14260.
- 24 J.-H. Yang, Y. Zhang, W. J. Yin, X. G. Gong, B. I. Yakobson and S.-H. Wei, *Nano Lett.*, 2016, **16**, 1110–1117.
- 25 C. Zhang and Q. Sun, *J. Phys. Chem. Lett.*, 2016, **7**, 2664–2670.
- 26 Y. Kubota, K. Watanabe, O. Tsuda and T. Taniguchi, *Science*, 2007, **317**, 932–934.
- 27 S. R. Lingampalli, K. Manjunath, S. Shenoy, U. V. Waghmare and C. N. R. Rao, *J. Am. Chem. Soc.*, 2016, **138**, 8228–8234.
- 28 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 29 J. Furthmüller, J. Hafner and G. Kresse, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 15606.
- 30 G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758.
- 31 B. Stefano, S. De Gironcoli and A. Dal Corso, *Rev. Mod. Phys.*, 2001, **73**, 515.
- 32 A. Togo and I. Tanaka, *Scr. Mater.*, 2015, **108**, 1.



- 33 J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2003, **118**, 8207.
- 34 M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos, *Rev. Mod. Phys.*, 1992, **64**, 1045.
- 35 G. J. Martyna, M. L. Klein and M. E. Tuckerman, *J. Chem. Phys.*, 1992, **97**, 2635.
- 36 Y. C. Wang, J. Lv, L. Zhu and Y. M. Ma, *Comput. Phys. Commun.*, 2012, **183**, 2063–2070.
- 37 X. Y. Luo, J. H. Yang, H. Y. Liu, X. J. Wu, Y. C. Wang, Y. M. Ma, S.-H. Wei, X. G. Gong and H. J. Xiang, *J. Am. Chem. Soc.*, 2011, **133**, 16285–16290.
- 38 Y. C. Wang, M. S. Miao, J. Lv, L. Zhu, K. T. Yin, H. Y. Liu and Y. M. Ma, *J. Chem. Phys.*, 2012, **137**, 224108.
- 39 H. J. Zhang, Y. F. Li, J. H. Hou, K. X. Tu and Z. F. Chen, *J. Am. Chem. Soc.*, 2016, **138**, 5644–5651.
- 40 Y. F. Li, Y. L. Liao and Z. F. Chen, *Angew. Chem., Int. Ed.*, 2014, **53**, 7248–7252.

