Pressure-Induced Modulation of Electronic and Optical Properties of Surface O-Functionalized Ti$_2$C MXene

Xiao-Hong Li,* Li Shan-Shan, Hong-Ling Cui, and Rui-Zhou Zhang

ABSTRACT: Functionalized MXenes have gained increasing interest in the fields of thermoelectric materials, hydrogen storage, and so forth. In this work, pressure-induced band modulation and optical properties of the Ti$_2$CO$_2$ monolayer are investigated by using density functional theory with the hybrid (HSE06) functional. The calculation reveals that Ti$_2$CO$_2$ MXenes under pressure are stable because of the positive $E_{\text{coh}}$. Ti$_2$CO$_2$ undergoes a semiconductor-to-metal phase transition at about 7 GPa. The metallization of Ti$_2$CO$_2$ mainly results from the Ti-d state. Research indicates that there exist strong interactions between Ti-d and C-p, and Ti-d and O-p states, which are further confirmed by the charge analysis. In addition, the absorption is enhanced in the visible region with increasing pressure. We also observed some new absorption peaks in the visible region.

1. INTRODUCTION

Lithium-ion batteries (LIBs) have been the promising energy storage devices in portable electronic devices and smart grids. However, the safety issues and the high cost seriously hindered the development of LIBs. Recently, two-dimensional (2D) materials have received great interest because of their wide applications in LIBs, catalysis (ECs), and so forth.

2D materials designated as $M_nX_{n-1}$ (MXenes) have outstanding electrochemical and mechanical properties and are extensively used in battery electrode materials. MXenes are obtained by etching the A layer from MAX phases ($M_{n+1}AX_n$). Here, M is an early transition metal, $n = 1, 2, 3$, and X is C or N. In the etching process, some functional groups are left on the MXene. Therefore, the formula of functionalized MXenes is $M_{n+1}X_nT_x$ ($T = F, O,$ and OH and $x$ is the termination number). Recent studies have presented the wide applications of MXenes as the anode material, optical device, and so forth.

Previous research indicated that MXenes with O or OH surface groups have a more stable structure, and the OH group can be changed to an O group at high temperature. For these reasons, O-functionalized Ti$_2$C MXenes are extensively investigated. Among all potential MXene phases, Ti$_2$C is one of the thinnest MXenes and has the biggest superfacial area per weight, which makes it become one of the most potential electrode materials.

Guo et al. thought that the O termination on the Ti$_2$C surface can enhance the mechanical properties. Gao et al. reported the adsorption behavior of mercury on the Ti$_2$CO$_2$ monolayer. Theoretical investigation indicated that the calculated band gaps of the Ti$_2$CO$_2$ monolayer with the Perdew–Burke–Ernzerhof (PBE) and Heyd–Scuseria–Ernzerhof (HSE06) functionals are 0.24 and 0.88 eV, respectively, and exhibits superhigh carrier mobility and thermal stability. In addition, Ti$_2$CO$_2$ has the highest hole mobility among MXenes. Nayak et al. investigated the electronic structure and lattice vibrational dynamics of MoS$_2$ under pressure in experiment and theory. Pressure is an important parameter to effectively alter the distance and interaction between atoms. Experimental research indicates that a high-pressure technique can improve the conductivity of some LIBs. However, up to now, the related properties under pressure are still unavailable for the Ti$_2$CO$_2$ monolayer.

Table 1. Cohesive Energy $E_{\text{coh}}$ of the Ti$_2$CO$_2$ Monolayer under Pressure

| pressure (GPa) | $E_{\text{coh}}$ (eV/atom) |
|---------------|----------------------------|
| 0             | 3.572                      |
| 1             | 3.566                      |
| 2             | 3.552                      |
| 3             | 3.531                      |
| 4             | 3.501                      |
| 5             | 3.463                      |
| 6             | 3.415                      |
| 7             | 3.358                      |

Received: May 23, 2020
Accepted: August 11, 2020
Published: August 25, 2020

https://dx.doi.org/10.1021/acsomega.0c02435
ACS Omega 2020, 5, 22248–22254

This is an open access article published under an ACS AuthorChoice License, which permits copying and redistribution of the article or any adaptations for non-commercial purposes.
Structural variation has a great effect on 2D materials and can make 2D materials show great diversity. The diversity makes it possible to develop next-generation electronics with specific functionalities. Ti$_2$CO$_2$ has a moderate indirect band gap, and using it in optical devices can interrupt efficient light emission. Hence, indirect-to-direct band engineering can improve the light emission in optical devices. We investigated the band modulation of Ti$_2$CO$_2$ under pressure in the present work. The semiconductor-to-metal transition occurs at 7 GPa. The optical properties under pressure are also explored.

2. RESULTS AND DISCUSSION

2.1. Structural Properties. Figure 1a presents the Ti$_2$AlC MAX phase. Etching Al atoms from Ti$_2$AlC can produce the Ti$_2$C monolayer. Figure 1b,c presents the O-terminated Ti$_2$C MXene (Ti$_2$CO$_2$), from the top and side views. Previous studies indicate that the position of the etched-away Al atoms is energetically more favorable for the O-site. Figure 1d presents the calculated HSE06 band structure of the Ti$_2$CO$_2$ MXene. The band gap calculated with the HSE06 hybrid functional is 0.9012 eV, which is consistent with the theoretical result of Xie et al.

Cohesive energy ($E_{\text{coh}}$) is defined as the energy required to separate a solid to isolated atoms. For the Ti$_2$CO$_2$ monolayer, $E_{\text{coh}}$ is calculated using the equation

$$E_{\text{coh}} = \frac{2E_{\text{atm}}(\text{Ti}) + E_{\text{atm}}(\text{C}) + 2E_{\text{atm}}(\text{O}) - E_{\text{tot}}(\text{Ti}_2\text{CO}_2)}{5}$$

where $E_{\text{tot}}$ is the electronic total energy of the Ti$_2$CO$_2$ monolayer and $E_{\text{atm}}$ is the energy of isolated atoms Ti, C, and O, respectively. The larger the $E_{\text{coh}}$ the more stable the crystal structure.

Table 1 lists the calculated $E_{\text{coh}}$ for the Ti$_2$CO$_2$ monolayer under pressure. From Table 1, positive $E_{\text{coh}}$ indicates the stability of Ti$_2$CO$_2$ MXenes under pressure. In order to have a comparison, we further calculated the $E_{\text{coh}}$ of Ti$_2$C MXenes at zero pressure, which is 1.441 eV/atom. This shows that Ti$_2$CO$_2$ MXenes are more stable than Ti$_2$C MXenes. Previous studies reported the $E_{\text{coh}}$ of FeB$_6$ (5.56 eV/atom), Al$_2$C (4.49 eV/atom), and Be$_2$C monolayers (4.86 eV/atom). The $E_{\text{coh}}$ of Ti$_2$CO$_2$ MXenes under pressure is smaller when compared with that of FeB$_6$, Al$_2$C, and Be$_2$C. This indicates that the chemical bonds between Ti and O atoms are not so stronger than those in FeB$_6$, Al$_2$C, and Be$_2$C.

2.2. Band Gap Modulation. Figure 2 presents the band structures of Ti$_2$CO$_2$ under pressure. No magnetism is found for Ti$_2$CO$_2$ MXenes under pressure. From Figure 1d, there is a 0.9012 eV band gap at zero pressure. The band gap decreases gradually with the increase in pressure and becomes zero when the pressure increases to 7 GPa. This indicates that Ti$_2$CO$_2$ under pressure undergoes a semiconductor-to-metal transition. We further examine the energy per atom to investigate the electronic properties under pressure. The energy under pressure $E_p = (E_{\text{pressure}} - E_{\text{nonpressure}})/n$, $n$ is the number of atoms in the unit cell. Figure 3 presents band gap and energy under pressure. With the increase in pressure, the energy increases and the band gap decreases gradually. At about 7 GPa, Ti$_2$CO$_2$ has a semiconductor-to-metal transition.

Figure 4 presents the partial density of states (PDOS) under pressure. The dashed vertical lines indicate the Fermi level ($E_F$). From Figure 4, we can see that Ti$_2$CO$_2$ below 7 GPa exhibits a semiconductor nature with a small band gap. The Ti-3d state provides the main contribution to the conduction band under pressure, while C-p and O-p states have little contribution. The mixture of Ti-d, C-p, and O-p states provides the main contribution to the valence band under pressure, indicating the strong interaction between Ti-d and C-p, and Ti-d and O-p states. In the energy range of −7 to −5 eV, the main contribution is from the O-p state, with little from Ti-d, Ti-p, and C-p states.
The PDOS of Ti-d, Ti-p, C-p, and O-p states is presented in Figure 5. We found that (1) Ti-p and O-p states have little contribution at EF, while Ti-d and C-p states have the main contribution. (2) PDOS shapes of Ti-d, Ti-p, O-p, and C-p under pressure changed distinctly. First, the Ti-d state has two peaks at about 1.5 eV (labeled in Figure 5). The two peaks under pressure split into several peaks. Second, DOS values of the Ti-d state under pressure at EF increase, while DOS values of the C-p state are nearly constant. This implies that the Ti-d state results in the metallization of Ti$_2$CO$_2$. Third, the peak of the C-p state at about 3.5 eV splits into two visible peaks, and the obvious changes of Ti-p and O-p states make several peaks converged in the energy range of −2 to −7 eV and −4.5 to −5.5 eV, respectively.

2.3. Optical Properties. We know that Ti$_2$CO$_2$ has the band gap under the pressure from 0 to 6 GPa with the indirect band gap range of 0.0958−0.9012 eV. For the materials with zero band gap, the photoactivated electrons and holes within materials can recombine easily and accomplish photocatalytic reactions, which shows that the material cannot be utilized for photocatalytic applications. Hence, we further investigated the optical properties under pressure from 0 to 6 GPa.

For the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, we can obtain the real part $\varepsilon_1(\omega)$ from the imaginary part $\varepsilon_2(\omega)$. The absorption coefficient $a(\omega)$ can be obtained from the equation:

$$a(\omega) = \sqrt{2\omega \left[ \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]}^{1/2} \quad (2)$$
Figure 6 presents the $\varepsilon_2(\omega)$ for Ti$_2$CO$_2$ under pressure. There is a very strong peak in the visible region (about 2.5 eV). The strong peak is considered as the charge transfer between Ti-d and C-p, and Ti-d and O-p in Figure 4. The peak of $\varepsilon_2(\omega)$ at about 2.5 eV gradually increases with increasing pressure (2.6053, 2.7767, 2.8967, 3.1770, 3.3985, and 3.6652 for 0, 1, 2, 3, 4, 5, and 6 GPa, respectively), which corresponds to electron excitation. Hence, we think that the charge transfer under pressure between Ti-d and C-p, and Ti-d and O-p states is strengthened in the visible region. The second peak is not so strong and appears at about 5.5 eV, which mainly derived from the interaction of Ti-d and C-p states.

Figure 7 presents the optical absorption of Ti$_2$CO$_2$ under pressure. The strongest absorption zone between 0 and 3 eV is at 2.5 eV. The maximum peaks of the absorption spectrum in this range increase with increasing pressure, and the absorption is enhanced in the visible region. A valley occurs at 4 eV under zero pressure, and the valley (labeled in Figure 7) gradually declines and becomes steep with increasing pressure. This indicates that the absorptions under pressure at 4 eV are the lowest, with the maximum and minimum absorptions for 0 and 6 GPa, respectively. Then, the absorption fluctuantly increases with increasing pressure and reaches the maximum at about 7 eV, with the maximum and minimum absorption for 6 and 0 GPa, respectively.

2.4. Charge Analysis. In order to gain deep insight into electronic distribution, the atomic charge and bond length under pressure are investigated and listed in Table 2. It is noted that O and C atoms gain more electrons from Ti atoms for Ti$_2$CO$_2$ under pressure. With the increasing pressure, the charge donated by Ti atom decreases, while the accepted charge by C and O atoms also decreases. The bond lengths of
O–Ti and C–Ti bonds become shorter with increasing pressure, so the covalent characteristics of Ti–O and Ti–C bonds are stronger, which is consistent with the analysis of DOS.

3. CONCLUSIONS

In summary, we investigated the electronic and optical properties of Ti$_2$CO$_2$ under pressure theoretically. The negative $E_{coh}$ confirms the stability of Ti$_2$CO$_2$ under pressure. Ti$_2$CO$_2$
undergoes the semiconductor-to-metal transition at about 7 GPa. The metallization of Ti$_2$CO$_2$ mainly results from the Ti-d state. The Ti3d state provides the main contribution to the conduction band, and the valence band is contributed from Ti-d, C-p, and O-p states. The absorption under pressure is enhanced, and some new absorption peaks occur in the low-energy region.

4. COMPUTATIONAL DETAILS

All calculations were performed using density functional theory (DFT) implemented in the plane-wave VASP code. The HSE06 hybrid functional is used. The generalized gradient approximation of the PBE scheme is used to optimize the structure through relaxing the lattice parameters a and b and the position of all the atoms until the convergence tolerance of force on each atom is less than 1.0 × 10$^{-6}$ eV/Å. The orbits of Ti (3d$^{4s^2}$), C (2s$^2$2p$^2$), and O (2s$^2$2p$^2$) for Ti, C, and O are treated as valence electrons, respectively. The pressure was imposed in the direction parallel to the Ti$_2$CO$_2$ plane. The plane wave cutoff energy is 700 eV. A large vacuum layer of 25 Å is imposed on both sides to simulate the isolated monolayer. A 25 × 25 × 1 k-point mesh is used during optimization and a 103-points grid is utilized for obtaining the reliable energy band. The spin polarization and vdW interaction are taken into consideration.

■ AUTHOR INFORMATION

Corresponding Author
Xiao-Hong Li — College of Physics and Engineering, Henan University of Science and Technology, Luoyang 471023, China; Henan Key Laboratory of Photoelectric Energy Storage Materials and Applications, Luoyang 471023, China; orcid.org/0000-0003-2450-4476; Phone: +86-379-6526265; Email: lorna639@yeah.net, lorna639@126.com

Authors
Li Shan-Shan — College of Physics and Engineering, Henan University of Science and Technology, Luoyang 471023, China
Hong-Ling Cui — College of Physics and Engineering, Henan University of Science and Technology, Luoyang 471023, China
Rui-Zhou Zhang — College of Physics and Engineering, Henan University of Science and Technology, Luoyang 471023, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c02435

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The research was supported by the Innovation Team of Henan University of Science and Technology (2015XTD001).

Table 2. Atomic Charge (e$^\text{\text{a}}$) and Bond Length (Å) of Ti$_2$CO$_2$ under Pressure

| pressure (GPa) | atomic charge | bond length |
|---------------|---------------|-------------|
|               | C  | O  | Ti | r$_{C-N}$ | r$_{O-N}$ |
| 0             | -1.504 | -0.985 | 1.735 | 2.188 | 1.980 |
| 1             | -1.504 | -0.975 | 1.724 | 2.171 | 1.968 |
| 2             | -1.503 | -0.965 | 1.715 | 2.160 | 1.960 |
| 3             | -1.500 | -0.956 | 1.706 | 2.151 | 1.954 |
| 4             | -1.497 | -0.947 | 1.697 | 2.140 | 1.947 |
| 5             | -1.490 | -0.937 | 1.682 | 2.130 | 1.940 |
| 6             | -1.481 | -0.927 | 1.666 | 2.121 | 1.934 |
| 7             | -1.471 | -0.918 | 1.654 | 2.111 | 1.929 |

■ REFERENCES

1. Wen, J.; Yu, Y.; Chen, C. A review on lithium-ion batteries safety issues: Existing problems and possible solutions. Mater. Express 2012, 2, 197–212.
2. Wang, H.; Si, C.; Zhou, J.; Sun, Z. Vanishing schottky barriers in blue phosphorene/MXene heterojunctions. J. Phys. Chem. C 2017, 121, 25164–25171.
3. Wang, X.; Kajiyama, S.; Inuma, H.; Hosono, E.; Oro, S.; Moriguchi, I.; Okubo, M.; Yamada, A. Pseudocapacitance of MXene nanosheets for high-power sodium-ion hybrid capacitors. Nat. Commun. 2015, 6, 6544–6560.
4. Qiao, J.; Kong, X.; Hu, Z.-X.; Yang, F.; Ji, W. High-mobility transport anisotropy and linear dichroism in few-layer black phosphorus. Nat. Commun. 2014, 5, 4475.
5. Zhang, H.; Yang, G.; Zuo, X.; Tang, H.; Yang, Q.; Li, G. Computational studies on the structural, electronic and optical properties of graphene-like MXenes (M$_i$C$_{x}$T$_y$ = Ti, Zr, Hf; T = O, F, OH) and their potential applications as visible-light driven photocatalysts. J. Mater. Chem. A 2016, 4, 12913–12920.
6. Ling, C.; Shi, L.; Ouyang, Y.; Wang, J. Searching for highly active catalysts for hydrogen Evolution reaction based on O-terminated MXenes through a simple descriptor. Chem. Mater. 2016, 28, 9026–9032.
7. Hu, M.; Li, Z.; Zhang, H.; Hu, T.; Zhang, C.; Wu, Z.; Wang, X. Self-assembled Ti$_2$C/Ti MXene film with high gravimetric capacitance. Chem. Commun. 2015, 51, 13531–13533.
8. Dall’Agne, Y.; Taberna, P. L.; Gototis, Y.; Simon, P. Two-dimensional vanadium carbide (MXene) as positive electrode for sodium-ion capacitors. J. Phys. Chem. Lett. 2015, 6, 2305–2309.
9. Bai, Y.; Srikantan, N.; Chua, C. K.; Zhou, K. Density functional theory study of M$_{n}$AX$_{n}$ phases: A review. Crit. Rev. Solid State Mater. Sci. 2019, 44, 56–107.
10. Naguib, M.; Mochalin, V. N.; Barsoum, M. W.; Gogotsi, Y. 25th Anniversary Article: MXenes: A New Family of Two-Dimensional Materials. Adv. Mater. 2014, 26, 992–1005.
11. Magne, D.; Mauchamp, V.; Celerier, S.; Chartier, P.; Cabioch, T. Spectroscopic evidence in the visible-ultraviolet energy range of surface functionalization sites in the multilayer Ti3C2 Mxene. Phys. Rev. B: Condens. Matter Mater. Phys. 2015, 91, 204109.
12. Tang, Q.; Zhou, Z.; Shen, P. Are MXenes Promising anode materials for Li ion batteries? Computational studies on electronic properties and Li storage capability of Ti$_2$C$_x$ and Ti$_2$C$_x$(X = F, OH) monolayer. J. Am. Chem. Soc. 2012, 134, 16909–16916.
13. Xie, Y.; Naguib, M.; Mochalin, V. N.; Barsoum, M. W.; Gogotsi, Y.; Yu, X.; Nam, K.-W.; Yang, X.-Q.; Kolesnikov, A. I.; Kent, P. R. C. Role of surface structure on Li-Ion energy storage capacity of two dimensional transition metal carbides. J. Am. Chem. Soc. 2014, 136, 6385–6394.
14. Zhang, X.; Lei, J.; Wu, D.; Zhao, X.; Jing, Y.; Zhou, Z. A Ti-anchored Ti$_2$CO$_2$ monolayer (MXene) as a single-atom catalyst for CO oxidation. J. Mater. Chem. A 2016, 4, 4871–4876.
15. Wang, X.; Lu, X.; Liu, B.; Chen, D.; Tong, Y.; Shen, G. Flexible Energy-Storage Devices: Design Consideration and Recent Progress. Adv. Mater. 2014, 26, 4763–4782.
16. Ghidiu, M.; Lukatskaya, M. R.; Zhao, M.-Q.; Gogotsi, Y.; Barsoum, M. W. Conductive two-dimensional titanium carbide clay with high volumetric capacitance. Nature 2014, 516, 78–81.
17. Eames, C.; Islam, M. S. Ion intercalation into two-dimensional transition-metal carbides: global screening for new high-capacity battery materials. J. Am. Chem. Soc. 2014, 136, 16270–16276.
18. Lukatskaya, M. R.; Mashtalir, O.; Ren, C. E.; Dall’Agne, Y.; ROisier, P.; Taberna, P. L.; Naguib, M.; Simon, P.; Barsoum, M. W.; Gogotsi, Y. Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide. Science 2013, 341, 1502–1505.
19. Guo, Z.; Zhou, J.; Si, C.; Sun, Z. Flexible two-dimensional Ti +1Cn (n = 1, 2 and 3) and their functionalized MXenes predicted by density functional theories. Phys. Chem. Chem. Phys. 2015, 17, 15348–15354.
(20) Gao, X.; Zhou, Y.; Tan, Y.; Cheng, Z.; Yang, B.; Ma, Y.; Shen, Z.; Jia, J. Exploring adsorption behavior and oxidation mechanism of mercury on monolayer Ti2CO2 (MXenes) from first principles. Appl. Surf. Sci. 2019, 464, 53−60.

(21) Xie, Y.; Kent, P. R. C. Hybrid density functional study of structural and electronic properties of functionalized Ti2C, and dissociation during the oxidation of monolayer Ti2C. Phys. Rev. B: Condens. Matter Mater. Phys. 2013, 87, 235441.

(22) Lai, S.; Jeon, J.; Jang, S. K.; Xu, J.; Choi, Y. J.; Park, J.-H.; Hwang, E.; Lee, S. Surface group modification and carrier transport properties of layered transition metal carbides (TiCTx, T = OH, −F and −O). Nanoscale 2015, 7, 19390−19396.

(23) Zha, X.-H.; Huang, Q.; He, J.; He, H.; Zhai, J.; Francisco, J. S.; Du, S. The thermal and electrical properties of the promising semiconductor MXene Hf2CO2. Nanoscale 2016, 8, 27971.

(24) Khazaei, M.; Arai, M.; Sasaki, T.; Chung, C.-Y.; Venkataramanan, N. S.; Estili, M.; Sakka, Y.; Kawazoe, Y. Novel electronic and magnetic properties of two-dimensional transition metal carbides and nitrides. Adv. Funct. Mater. 2013, 23, 2185−2192.

(25) Zha, X.-H.; Luo, K.; Li, Q.; Huang, Q.; He, J.; Wen, X.; Du, S. Role of the surface effect on the structural, electronic, and mechanical properties of the carbide MXenes. Europhys. Lett. 2015, 111, 26007.

(26) Gan, L.-Y.; Huang, D.; Schwingenschlögl, U. Oxygen adsorption and dissociation during the oxidation of monolayer Ti2C. J. Mater. Chem. A 2013, 1, 13672−13678.

(27) Zha, X.-H.; Zhou, J.; Zhou, Y.; Huang, Q.; He, J.; Francisco, J. S.; Luo, K.; Du, S. Promising electron mobility and high thermal conductivity in Sc2CT2 (T = F, OH) MXenes. Nanoscale 2016, 8, 6110−6117.

(28) Nayak, A. P.; Pandey, T.; Voiry, D.; Liu, J.; Moran, S. T.; Sharma, A.; Tan, C.; Chen, C.-H.; Li, L.-J.; Chhowalla, M.; Lin, J.-F.; Singh, A. K.; Akimwande, D. Pressure-dependent optical and vibrational properties of monolayer molybdenum disulphide. Nano Lett. 2015, 15, 346−353.

(29) Huang, Y.; He, Y.; Sheng, H.; Lu, X.; Dong, H.; Samanta, S.; Dong, H.; Li, X.; Kim, D. Y.; Mao, H.-k.; Liu, Y.; Li, H.; Li, H.; Wang, L. Li-ion battery material under high pressure: amorphization and enhanced conductivity of Li2TiO3. Nat. Sci. Rev. 2019, 6, 239−246.

(30) Peng, X.; Wei, Q.; Copple, A. Strain-engineered direct-indirect band gap transition and its mechanism in two-dimensional phosphor-ene. Phys. Rev. B: Condens. Matter Mater. Phys. 2014, 90, 085402.

(31) Liu, B.; Zhou, K. Recent progress on graphene-analogous 2D nanomaterials: Properties, modeling and applications. Prog. Mater. Sci. 2019, 100, 99−169.

(32) Eklund, P.; Rosen, J.; Persson, P. O. Å. Layered ternary M2A1X3 phases and their 2D derivative MXene: an overview from a thin-film perspective. J. Phys. D: Appl. Phys. 2017, 50, 113001−113014.

(33) Anasori, B.; Lukatskaya, M. R.; Gogotsi, Y. 2D metal carbides and nitrides (MXenes) for energy storage. Nat. Rev. Mater. 2017, 2, 16098−16117.

(34) Khazaei, M.; Ranjar, A.; Arai, M.; Sasaki, T.; Yunoki, S. Electronic properties and applications of MXenes: a theoretical review. J. Mater. Chem. C 2017, 5, 2488−2503.

(35) Balci, E.; Akkuş, U. O.; Berber, S. Band gap modification in doped MXene: Sc2CxF4. J. Mater. Chem. C 2017, 5, 5956−5961.

(36) Zhang, H.; Li, Y.; Hou, J.; Tu, K.; Chen, Z. FeB6 monolayers: the graphene-like material with hypercoordinate transition metal. J. Am. Chem. Soc. 2016, 138, 5644−5651.

(37) Li, Y.; Liao, Y.; Schleyer, P. V. R.; Chen, Z. Al2C monolayer: the planar tetracoordinate carbon global minimum. Nanoscale 2014, 6, 10784−10791.

(38) Li, Y.; Liao, Y.; Chen, Z. Be2C monolayer with quasi-Planar hexacoordinate carbons: a global minimum structure. Angew. Chem., Int. Ed. 2014, 53, 7248−7252.

(39) Tong, H.; Ouyang, S.; Bi, Y.; Umezawa, N.; Oshikiri, M.; Ye, J. Na-no-photocatalytic materials: Possibilities and challenges. Adv. Mater. 2012, 24, 229−251.