MXene/Graphene Heterostructures as High-Performance Electrodes for Li Ion Batteries

Yun-Ting Du, Xiang Kan, Feng Yang, Liyong Gan, and Udo Schwingenschlögl

ACS Appl. Mater. Interfaces, **Just Accepted Manuscript** • DOI: 10.1021/acsami.8b10729 • Publication Date (Web): 30 Aug 2018Downloaded from <http://pubs.acs.org> on September 5, 2018**Just Accepted**

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

MXene/Graphene Heterostructures as High-Performance Electrodes for Li Ion Batteries

Yun-Ting Du^{†,‡}, Xiang Kan^{*,†}, Feng Yang[†], Li-Yong Gan^{*,‡}, and Udo Schwingenschlög[§]

[†]Key Laboratory of Advanced Technology of Materials (Ministry of Education), Superconductivity and New Energy R&D Center, Southwest Jiaotong University, Chengdu, Sichuan 610031, China

[‡]School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China

[§]King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division (PSE), Thuwal 23955-6900, Saudi Arabia

Keywords: MXene, MXene/Graphene heterostructure, flexible Li-ion battery, twist structure, first-principles calculations

Abstract: Recently, MXene/graphene heterostructures have been successfully fabricated and found to exhibit outstanding performance as electrodes for Li ion batteries. However, insights into the mechanism behind the encouraging experimental results are missing. We use first-principles calculations to systematically investigate the electrochemical properties of MXene/graphene heterostructures, choosing Ti_2CX_2 ($X = F, O, \text{ and } OH$) as representative MXenes. Our calculations disclose that the presence of graphene not only avoids restacking effects of MXene layers but also enhances the electric conductivity, Li adsorption strength (while maintaining a high Li mobility), and mechanical stiffness. These favorable attributes collectively lead to the excellent performance of MXene/graphene electrodes observed experimentally. While the Ti_2CO_2 /graphene heterostructure is proposed to be the most promising candidate within the studied materials, the developed comprehensive understanding is of significance also for future rational design of MXene-based electrodes.

1. Introduction

The two-dimensional (2D) early transition metal carbides and nitrides, known as MXenes, recently receive great interest in material research due to their intriguing mechanical and electronic properties. Since the successful exfoliation of the first MXene, $\text{Ti}_3\text{C}_2\text{X}_y$ (X denotes the surface functional group), experimental and theoretical studies have identified a wide range of potential applications, including metal-ion batteries,¹⁻³ supercapacitors,⁴ bio-sensors,⁵ hydrogen production,⁶⁻⁷ oxygen production,⁸ and water purification.⁹ Intensive research activities on Li ion batteries are the result of excellent electric conductivity, high Li storage capability, and hydrophilicity of the surfaces.¹⁰ However, restacking of MXene layers is inevitable during electrode preparation and significantly hinders the ion transport and electrolyte infiltration.¹¹ Moreover, the stretchability of MXenes combined with a strong anisotropy of the mechanical properties severely hampers the fabrication of flexible electrodes.¹²

The emerging class of van der Waals heterostructures, consisting of different 2D materials, provides novel properties and unexpected opportunities to design and manipulate nanoelectronic devices.¹³⁻¹⁵ In particular, integration of graphene with other 2D materials can be used to tackle challenges related to wearable energy conversion and energy storage, owing to a high intrinsic flexibility.¹⁶ Thus, combining MXenes with graphene appears to be a feasible way to flexible MXene-based electrodes. Only recently advanced assembly techniques for 2D materials make it possible to fabricate MXenes/graphene hybrids with outstanding electrochemical performance.¹⁷⁻²² However, research on the mechanisms behind these encouraging experimental properties is still in an early stage. Despite studies of the interfaces between graphene and MXene monolayers^{23,24}, there is a lack of comprehensive insight into the consequences of integrating MXenes with graphene for the electrode performance, which currently precludes a rational design.

In the present work, we employ first-principles calculations to systematically study how the presence of graphene, to prevent restacking effects, impacts the electrochemical properties of MXene electrodes, choosing as representative MXenes the thinnest 2D titanium carbides, Ti_2CX_2 ($X = \text{F}, \text{O}, \text{and OH}$). The developed fundamental understanding of $\text{Ti}_2\text{CX}_2/\text{graphene}$ (X/G) heterostructures is expected to aid the rational design of MXene-based flexible Li ion batteries.

2. Computational Details

First-principles calculations are performed using the Vienna Ab Initio Simulation Package (projector augmented wave method) with an energy cutoff of 500 eV.²⁵ The Perdew-Burke-Ernzerhof exchange correlation functional is employed. Slab models with a vacuum space of at least 29 Å are created to avoid unphysical interaction between periodically repeated images. Since the studied heterostructures are asymmetric, a dipole correction is used.²⁶ Furthermore, the van der Waals correction of Grimme (D2)²⁷ is adopted to model the interaction at the interface. The Brillouin zone is sampled on a Monkhorst-Pack $\mathbf{k}$ -mesh ($2 \times 2 \times 1$ in the structural optimization and $3 \times 3 \times 1$ in the electronic structure calculations) and the structures are optimized until all the atomic forces have declined below 0.02 eV/Å. The Li ion diffusion properties are evaluated by the climbing image nudged elastic band method.²⁸

3. Results and Discussion

Generally, as-fabricated MXenes are terminated by O-containing and/or F functional groups.²⁹ Thus, we focus on monolayer Ti_2CF_2 , Ti_2CO_2 , and $\text{Ti}_2\text{C}(\text{OH})_2$, for which optimized in-plane lattice constants of 3.051, 3.030, and 3.067 Å are obtained (2.467 Å for graphene), respectively, consistent with previous studies.^{30,31} In order to minimize the lattice mismatch, commensurate

heterostructures of 4×4 Ti_2CX_2 with 5×5 graphene are built, resulting in a lattice mismatch of only 1.1% for F/G, 1.7% for O/G, and 0.5% for OH/G. For each heterostructure, we consider the six stacking modes, I to IV, shown in Figure 1a (compare the vertical dashed lines), adopting always the lattice constant of Ti_2CX_2 to avoid any strain effect on Ti_2CX_2 . The interfacial binding energy is defined as $E_B = E_H - E_M - E_G$, where E_H , E_M , and E_G are the total energies of the heterostructure, MXene, and graphene, respectively. The obtained values per C atom as function of the interlayer distance are shown in Figure 1b. In each case the formation of the heterostructure is exothermic, suggesting structural stability, and the energy profiles of the six stacking modes almost coincide. Mode II is slightly favorable for F/G and O/G, and mode IV for OH/G. The corresponding binding energies are -41 , -86 , and -153 meV per C atom, respectively, and the optimal interlayer distances are 2.99, 3.10, and 2.20 Å. The planar geometries of Ti_2CX_2 and graphene remain largely intact with corrugations below 0.05 Å. These results indicate weak interfacial interaction (insensitive to the stacking mode) similar to the $\text{MoS}_2/\text{graphene}$ and $\text{MnO}_2/\text{graphene}$ heterostructures.^{32,33} This implies that graphene is able to effectively separate MXene layers and avoid restacking effects, rendering more electroactive sites accessible in the electrodes.

To explore the modifications of the electronic states of Ti_2CX_2 and graphene in the heterostructure, band structures are calculated for the favorable stacking modes: II-F/G, II-O/G, and IV-OH/G. They are shown in Figures 2a-c. It turns out that the main electronic features of each component are well preserved in all heterostructures due to the weak interfacial interactions. The Dirac point of graphene remains in the vicinity of the Fermi level in the case of F/G, while it shifts remarkably in the cases of O/G (strong p-doping) and OH/G (strong n-doping). To unravel the different doping behaviors, we show in Figures 2d-e the charge

redistributions at the interfaces. It is seen that a significant amount of charge shifts from graphene to the MXene in O/G (accepted by the O-1 layer at the interface) and in the opposite direction in OH/G (donated by both the OH-1 and Ti-1 layers). Similarly strong charge transfer previously has been found in weakly coupled $\text{Ti}_2\text{CX}_2/\text{MoS}_2$ heterostructures.³⁴ The fact that the amount of transferred charge follows the order $\text{OH/G} > \text{O/G} > \text{F/G}$ rationalizes the observed trend of the binding energy in the three heterostructures (see above). Monolayer Ti_2CF_2 and $\text{Ti}_2\text{C}(\text{OH})_2$ are known to be metallic,³³ while monolayer Ti_2CO_2 is semiconducting.³⁵ According to Figures 2a-c, the electrical conductivity is higher in F/G and OH/G as compared to the isolated MXenes, due to the graphene states, and metallicity arises in O/G.

Compared to Ti_2CX_2 electrodes, the X/G heterostructures offer advantages in electrical conductivity and electrolyte infiltration, which may improve the electrochemical performance. To investigate the Li ion adsorption and diffusion, we first address, as a benchmark, the adsorption of a single Li atom on the individual MXenes. It turns out that the Li atom prefers location at the hollow site above a C atom. We find adsorption energies (calculated using bulk Li as reference state) of -1.01 eV for Ti_2CF_2 , -2.15 for Ti_2CO_2 , and -0.11 eV for $\text{Ti}_2\text{C}(\text{OH})_2$, consistent with previous reports.³⁶ The charge transfer can be quantitatively estimated by Bader charge analysis,³⁷ see the results in Table 1. Li acts as electron donor and becomes almost fully ionized. Following the order of electronegativity, the charge transfer decreases from F to O and further to OH termination, reflecting a gradual weakening of the Coulomb attraction and therefore partially explaining the observed trend of the adsorption energy. The fact that Li bonds stronger to O than F is due to an enhanced covalency contribution.³⁸ These results suggest that the Coulomb and covalent components collectively determine the Li adsorption strength on Ti_2CX_2 .

We next study the Li adsorption properties of the heterostructures to evaluate the role of graphene. In agreement with previous computational results,^{39,40} we find for pristine graphene that adsorption of Li is favorable at the center site of the hexagon, however, being endothermic by 0.10 eV. In principle, in the heterostructures Li can be adsorbed at the Ti_2CX_2 side, graphene side, or interface. We investigate the adsorption sites shown in Figure 3a and give in Figures 3b-d results for the two most favorable sites, H_C and $\text{H}_{\text{C-I}}$. For all heterostructures, the adsorption energy at the H_C site is similar to that obtained for the pristine MXene, as the distance to graphene is large. On the other hand, the $\text{H}_{\text{C-I}}$ site is energetically favorable with significantly higher adsorption energies (−1.64, −2.34, and −0.85 eV for F/G, O/G, and OH/G, respectively), pointing to an unexpected collective effect that enhances the adsorption strength in the presence of graphene. In particular, the heterostructures proposed in the present work thus can prevent formation of metallic Li and improve the safety and cycling stability of MXene-based Li ion batteries. In order to address the bonding behavior of Li, we visualize in Figure 4 the charge redistribution upon Li adsorption on Ti_2CF_2 and in F/G. Substantial charge depletion is visible around Li. The redistribution patterns are very similar for adsorption on Ti_2CF_2 and at the Ti_2CF_2 side of F/G. On the other hand, adsorption at the interface of F/G results in distinct charge transfer to graphene (see also Table 1), which accounts for the enhanced Li adsorption behavior of the heterostructures.

The charging/discharging rate, which determines the performance of Li ion batteries, depends on both the electrical and ionic conductivities. Having shown that combination of Ti_2CX_2 with graphene enables higher electrical conductivity, we next turn our attention to the ionic conductivity, i.e., the mobility of the Li ions. Figure 5a shows, as an example, results for the relative energy along the favorable diffusion paths of a Li ion on Ti_2CF_2 and at the interface of

F/G. Results for the diffusion barriers are summarized in Figure 5b for all the materials under investigation. We focus on Li diffusion at the interface of *X*/G to explore how the stronger adsorption, as compared to the pristine MXenes, impacts the mobility. For the pristine MXenes our diffusion barriers agree well with previous theoretical results.³⁶ The corresponding values for the heterostructures turn out to be less than 150 meV higher. While the stronger adsorption thus slows down the Li diffusion, the diffusion barriers are still comparable to those found on other 2D materials,^{41,42} suggesting that the heterostructures are suitable for electrodes of Li ion batteries. Support for this conjecture comes from an estimation of the diffusion coefficient as $D = a^2 v^* \exp(-\Delta E/k_B T)$, where a , v^* , ΔE , k_B , and T are the distance between adjacent sites (1.8 Å), the hopping frequency (10^{13} s^{-1}), the diffusion barrier, the Boltzmann constant, and the absolute temperature (300 K). For Ti_2CX_2 the values fall in the range from 1.2×10^{-9} to $2.0 \times 10^{-7} \text{ cm}^2/\text{s}$ and for *X*/G in the range from 1.3×10^{-11} to $3.9 \times 10^{-9} \text{ cm}^2/\text{s}$. Therefore, the Li diffusion is faster than the ultrafast Na diffusion in bulk NaZnSb ($\sim 10^{-14} \text{ cm}^2/\text{s}$), for example,⁴³ indicating that reliable Li transport can be expected. Our results are consistent with the observation of fast ion diffusion by electrochemical impedance spectroscopy.¹⁸

Generally, drastic structural changes during the charging/discharging process can lead to fracture of the electrode material, eventually resulting in capacity fading.⁴⁴ To examine the mechanical behavior of the heterostructures, we calculate the stiffness $C_{2D} = 2\Delta E_H/[A(\Delta L/L)^2]$, where ΔE_H and ΔL are the total energy and lattice constant changes under strain, respectively, A being the area and L the lattice constant without strain. Studying biaxial lattice expansion or compression of $\Delta L/L = 3\%$, we obtain for Ti_2CF_2 , Ti_2CO_2 , and $\text{Ti}_2\text{C}(\text{OH})_2$ values of 146, 302, and 231 N/m, respectively. In the heterostructures (i.e., in contact with graphene) the stiffness is remarkably enhanced to 607, 662, and 634 N/m, exceeding even the value reported for the

phosphorene/G heterostructure (464 N/m).⁴⁵ The excellent in-plane flexibility renders the heterostructures under study highly promising for flexible and wearable Li ion batteries.

As the ion specific capacity is crucial for battery electrodes, we determine how many Li ions can be adsorbed by each material. The MXenes turn out to reach saturation at Li/Ti₂CF₂/Li, Li/Ti₂CO₂/Li, and Li_{0.25}/Ti₂C(OH)₂/Li_{0.25} configurations with specific capacities of 368, 383, and 95 mAh/g, respectively, consistent with previous results,⁴⁶ and open circuit voltages (OCVs) of 0.27, 1.52, and 0.08 V. While we already know that the lithiation of the heterostructures starts at the interface, saturation is reached in the case of Li/Ti₂CF₂/Li/C_{3.125}/Li_{0.3125}, Li/Ti₂CO₂/Li_{1.5}/C_{3.125}/Li_{0.3125}, and Li_{0.25}/Ti₂C(OH)₂/Li_{0.75}/C_{3.125}/Li_{0.3125} configurations, none of them showing significant structural deformations. F/G provides a slightly (by 0.06 V) reduced OCV and inherits 92% of the capacity of the parent MXene. O/G loses 0.4 V of OCV but achieves an impressive specific capacity of 426 mAh/g, exceeding that of the commercial graphite anode (372 mAh/g).⁴⁷ Finally, OH/G maintains the OCV of the parent MXene and provides a roughly doubled specific capacity of 196 mAh/g. The actual specific capacities may be even higher due to the possibility of multilayer Li adsorption on MXenes.⁴⁸ We obtain for O/G even at the highest Li content a small change of only 2.6% for the interlayer distance, suggesting high structural stability.

Fabrication processes of van der Waals heterostructures often result in interlayer twisting, and the structural and electronic properties may depend on the twist angle.⁴⁹⁻⁵¹ Thus, we study the possible influences for a selected heterostructure, O/G, choosing the $3\times\sqrt{13}$ (O/G-t1), $\sqrt{13}\times\sqrt{19}$ (O/G-t2), and $\sqrt{19}\times 2\sqrt{7}$ (O/G-t3) structures with lattice mismatches of 2.2%, 1.6%, and 1.1% and twist angles of 10.9°, 5.2°, and -2.2°, respectively, see Figure 6. We obtain binding energies of -42, -44, and -47 meV per C atom, respectively, slightly lower than in the case without twist.

Figures 7a-c show close similarity to Figure 2b. It turns out that Li is absorbed only slightly stronger at the interface than in the case without twist, see Table 1. According to Figure 5c, the diffusion barrier remains also almost the same. We can conclude that twisting does not critically affect the electronic properties and Li intercalation/diffusion behavior of the heterostructures under investigation.

4. Conclusions

Employing first-principles calculations, we have systematically studied the Li adsorption properties of prototypical MXene/graphene heterostructures for potential applications as electrodes in Li ion batteries. As the interfacial interaction is found to be weak, insertion of graphene can be used to avoid restacking of MXene layers, facilitating rapid ion transport for fast charging and discharging. It turns out that the heterostructures provide enhanced electric conductivity and Li adsorption strength, while maintaining high Li mobility. In addition, an excellent mechanical stiffness guarantees structural stability during lithiation. Collectively, these features explain the superior electrochemical performance found in recent experiments. Our results indicate that the O/G heterostructure, due to its high Li specific capacity, is the most promising electrode material for high performance MXene-based Li ion batteries.

AUTHOR INFORMATION

Corresponding Author

*Email: xiangkan@swjtu.edu.cn; ganly@scut.edu.cn

Notes

The authors declare no competing financial interest.

Acknowledgement

This study was financially supported by the National Natural Science Foundation of China (No. 11504303). The authors thank the National Supercomputing Center in Guangzhou for computational resources (Tianhe II supercomputer) and technical support. The research reported in this publication was supported by funding from King Abdullah University of Science and Technology (KAUST).

References

- (1) Naguib, M.; Come, J.; Dyatkin, B.; Presser, V.; Taberna, P.-L.; Simon, P.; Barsoum, M. W.; Gogotsi, Y., MXene: A Promising Transition Metal Carbide Anode for Lithium-Ion Batteries. *Electrochem. Commun.* **2012**, 16, 61-64.
- (2) Naguib, M.; Halim, J.; Lu, J.; Cook, K. M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W., New Two-Dimensional Niobium and Vanadium Carbides as Promising Materials for Li-Ion Batteries. *J. Am. Chem. Soc.* **2013**, 135, 15966-15969.
- (3) Yu, Y. X., Prediction of Mobility, Enhanced Storage Capacity, and Volume Change During Sodiation on Interlayer-Expanded Functionalized Ti_3C_2 MXene Anode Materials for Sodium-Ion Batteries. *J. Phys. Chem. C* **2016**, 120, 5288-5296.
- (4) Rakhi, R. B.; Ahmed, B.; Hedhili, M. N.; Anjum, D. H.; Alshareef, H. N., Effect of Postetch Annealing Gas Composition on the Structural and Electrochemical Properties of Ti_2CT_x MXene Electrodes for Supercapacitor Applications. *Chem. Mater.* **2015**, 27, 5314-5323.
- (5) Liu, H.; Duan, C.; Yang, C.; Shen, W.; Wang, F.; Zhu, Z., A Novel Nitrite Biosensor Based on the Direct Electrochemistry of Hemoglobin Immobilized on MXene- Ti_3C_2 . *Sens. Actuators B-Chem.* **2015**, 218, 60-66.

- (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) Gao, G.; O'Mullane, A. P.; Du, A., 2D MXenes: A New Family of Promising Catalysts for the Hydrogen Evolution Reaction. *ACS Catal.* **2017**, 7, 494-500.
- (8) Liu, J. H.; Kan, X.; Amin, B.; Gan, L.-Y.; Zhao, Y., Theoretical Exploration of the Potential Applications of Sc-Based MXenes. *Phys. Chem. Chem. Phys.* **2017**, 19, 32253-32261.
- (9) Ren, C. E.; Hatzell, K. B.; Alhabeb, M.; Ling, Z.; Mahmoud, K. A.; Gogotsi, Y., Charge- and Size-Selective Ion Sieving Through $\text{Ti}_3\text{C}_2\text{T}_x$ MXene Membranes. *J. Phys. Chem. Lett.* **2015**, 6, 4026-4031.
- (10) Lukatskaya, M. R.; Mashtalir, O.; Ren, C. E.; Dall'Agnese, Y.; Rozier, 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.
- (11) Zhao, M. Q.; Ren, C. E.; Ling, Z.; Maria, R. L.; Zhang, C.; Katherine, L. V. A.; Michel, W. B.; Yury, G., Flexible MXene/Carbon Nanotube Composite Paper with High Volumetric Capacitance. *Adv. Mater.* **2015**, 27, 339-345.
- (12) Peng, Q.; Hu, K.; Sa, B.; Zhou, J.; Wu, B.; Hou, X.; Sun, Z., Unexpected Elastic Isotropy in a Black Phosphorene/ TiC_2 Van Der Waals Heterostructure with Flexible Li-Ion Battery Anode Applications. *Nano Res.* **2017**, 10, 3136-3150.
- (13) Geim, A. K.; Grigorieva, I. V., Van Der Waals Heterostructures. *Nature* **2013**, 499, 419-425.
- (14) Novoselov, K. S.; Mishchenko, A.; Carvalho, A.; Castro Neto, A. H., 2D Materials and Van Der Waals Heterostructures. *Science* **2016**, 353, aac9439.

- (15) Liu, Y.; Weiss, N. O.; Duan, X.; Cheng, H.-C.; Huang, Y.; Duan, X., Van Der Waals Heterostructures and Devices. *Nat. Rev. Mater.* **2016**, 1, 16042.
- (16) Bonaccorso, F.; Colombo, L.; Yu, G. H.; Stoller, M.; Tozzini, V.; Ferrari, A. C.; Ruoff, R. S.; Pellegrini, V., Graphene, Related Two-Dimensional Crystals, and Hybrid Systems for Energy Conversion and Storage. *Science* **2015**, 347, 1246501.
- (17) Yang, Q.; Xu, Z.; Fang, B.; Huang, T.; Cai, S.; Chen, H.; Liu, Y.; Gopalsamy, K.; Gao, W.; Gao, C., MXene/Graphene Hybrid Fibers for High Performance Flexible Supercapacitors. *J. Mater. Chem. A* **2017**, 5, 22113-22119.
- (18) Yan, J.; Ren, C. E.; Maleski, K.; Hatter, C. B.; Anasori, B.; Urbankowski, P.; Sarycheva, A.; Gogotsi, Y., Flexible MXene/Graphene Films for Ultrafast Supercapacitors with Outstanding Volumetric Capacitance. *Adv. Funct. Mater.* **2017**, 27, 1701264.
- (19) Wu, X.; Wang, Z.; Yu, M.; Xiu, L.; Qiu, J., Stabilizing the MXenes by Carbon Nanoplatelet for Developing Hierarchical Nanohybrids with Efficient Lithium Storage and Hydrogen Evolution Capability. *Adv. Mater.* **2017**, 29, 1607017.
- (20) Yue, Y.; Liu, N.; Ma, Y.; Wang, S.; Liu, W.; Luo, C.; Zhang, H.; Cheng, F.; Rao, J.; Hu, X.; Su, J.; Gao, Y., Highly Self-Healable 3D Microsupercapacitor with MXene-Graphene Composite Aerogel. *ACS Nano* **2018**, 12, 4224-4232.
- (21) Cedric, C.; Mohamed, A.; Katherine, L. V. A.; Narendra, K.; Luisa, G.; Adriana, M. N.-S.; Babak, A.; Husam, N. A.; Yury, G., Asymmetric Flexible MXene-Reduced Graphene Oxide Micro-Supercapacitor. *Adv. Electron. Mater.* **2018**, 4, 1700339.
- (22) Ma, Z.; Zhou, X.; Deng, W.; Lei, D.; Liu, Z., 3D Porous MXene (Ti₃C₂)/Reduced Graphene Oxide Hybrid Films for Advanced Lithium Storage. *ACS Appl. Mater. Interfaces* **2018**, 10, 3634-3643.

- (23) Paul, P.; Chakraborty, P.; Das, T.; Nafday, D.; Saha-Dasgupta, T., Properties at the Interface of Graphene and Ti_2C MXene. *Phys. Rev. B* **2017**, 96, 035435.
- (24) Aierken, Y.; Sevik, C.; Gülseren, O.; Peetersa F. M.; Çakır D., MXenes/Graphene Heterostructures for Li Battery Applications: A First Principles Study. *J. Mater. Chem. A* **2018**, 6, 2337-2345.
- (25) Kresse, G.; Hafner, J., Ab initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, 47, 558-561.
- (26) Kresse, G.; Furthmüller, J., Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, 6, 15-50.
- (27) Grimme, S., Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* **2006**, 27, 1787-1799.
- (28) Henkelman, G.; Uberuaga, B. P.; Jónsson, H., A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths. *J. Chem. Phys.* **2000**, 113, 9901-9904.
- (29) Naguib, M.; Kurtoglu, M.; Presser, V.; Lu, J.; Niu, J.; Heon, M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W., Two-Dimensional Nanocrystals Produced by Exfoliation of Ti_3AlC_2 . *Adv. Mater.* **2011**, 23, 4248-42453.
- (30) Chan, K. T.; Neaton, J. B.; Cohen, M. L., First-Principles Study of Metal Adatom Adsorption on Graphene. *Phys. Rev. B* **2008**, 77, 235430.
- (31) Xie, Y.; Kent, P. R. C., Hybrid Density Functional Study of Structural and Electronic Properties of Functionalized $\text{Ti}_{n+1}\text{X}_n$ ($\text{X} = \text{C}, \text{N}$) Monolayers. *Phys. Rev. B* **2013**, 87, 235441.
- (32) Ma, Y.; Dai, Y.; Guo, M.; Niu, C.; Huang, B., Graphene Adhesion on MoS_2 Monolayer: An Ab Initio Study. *Nanoscale* **2011**, 3, 3883-3887.

- (33) Gan, L.-Y.; Zhang, Q.; Guo, C.-S.; Schwingenschlögl, U.; Zhao, Y., Two-Dimensional MnO₂/Graphene Interface: Half-Metallicity and Quantum Anomalous Hall State. *J. Phys. Chem. C* **2016**, 120, 2119-2125.
- (34) Gan, L.-Y.; Zhao, Y.-J.; Huang, D.; Schwingenschlögl, U., First-Principles Analysis of MoS₂/Ti₂C and MoS₂/Ti₂CY₂ (Y = F and OH) All-2D Semiconductor/Metal Contacts. *Phys. Rev. B* **2013**, 87, 245307.
- (35) 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.
- (36) Xie, Y.; Dall'Agnese, Y.; Naguib, M.; Gogotsi, Y.; Barsoum, M. W.; Zhuang, H. L.; Kent, P. R. C., Prediction and Characterization of MXene Nanosheet Anodes for Non-Lithium-Ion Batteries. *ACS Nano* **2014**, 8, 9606-9615.
- (37) Bader, R., *Atoms in Molecules: A Quantum Theory*. Oxford University Press: New York, **1990**.
- (38) Zhu, J.; Chroneos, A.; Eppinger, J.; Schwingenschlögl, U., S-functionalized MXenes as Electrode Materials for Li-Ion Batteries. *Appl. Mater. Today* **2016**, 5, 19-24.
- (39) Lee, E.; Persson, K. A., Li Absorption and Intercalation in Single Layer Graphene and Few Layer Graphene by First Principles. *Nano Lett.* **2012**, 12, 4624-4628.
- (40) Jaber-Ansari, L.; Puntambekar, K. P.; Tavassol, H.; Yildirim, H.; Kinaci, A.; Kumar, R.; Saldaña, S. J.; Gewirth, A. A.; Greeley, J. P.; Chan, M. K. Y.; Hersam, M. C., Defect Evolution in Graphene upon Electrochemical Lithiation. *ACS Appl. Mater. Interfaces* **2014**, 6, 17626-17636.

- (41) Mukherjee, S.; Banwait, A.; Grixti, S.; Koratkar, N.; Singh, C. V., Adsorption and Diffusion of Lithium and Sodium on Defective Rhenium Disulfide: A First Principles Study. *ACS Appl. Mater. Interfaces* **2018**, 10, 5373-5384.
- (42) Mukherjee, S.; Kavalsky, L.; Singh, C. V., Ultrahigh Storage and Fast Diffusion of Na and K in Blue Phosphorene Anodes. *ACS Appl. Mater. Interfaces* **2018**, 10, 8630-8639.
- (43) Nie, A.; Gan, L.-Y.; Cheng, Y.; Tao, X.; Yuan, Y.; Sharifi, A. S.; He, K.; Asayesh, A. H.; Vasiraju, V.; Lu, J.; Mashayek, F.; Klie, R.; Vaddiraju, S.; Schwingenschlögl, U.; Shahbazian, Y. R., Ultrafast and Highly Reversible Sodium Storage in Zinc-Antimony Intermetallic Nanomaterials. *Adv. Funct. Mater.* **2016**, 26, 543-552.
- (44) Shu, H.; Li, F.; Hu, C.; Liang, P.; Cao, D.; Chen, X., The Capacity Fading Mechanism and Improvement of Cycling Stability in MoS₂-Based Anode Materials for Lithium-Ion Batteries. *Nanoscale* **2016**, 8, 2918-2926.
- (45) Guo, G. C.; Wang, D.; Wei, X. L.; Zhang, Q.; Liu, H.; Lau, W. M.; Liu, L. M., First-Principles Study of Phosphorene and Graphene Heterostructure as Anode Materials for Rechargeable Li Batteries. *J. Phys. Chem. Lett.* **2015**, 6, 5002-5008.
- (46) 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.
- (47) Armand, M.; Tarascon, J. M., Building Better Batteries. *Nature* **2008**, 451, 652-657.
- (48) 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.

- (49) Wang, Y.; Ni, Z.; Liu, L.; Liu, Y.; Cong, C.; Yu, T.; Wang, X.; Shen, D.; Shen, Z., Stacking-Dependent Optical Conductivity of Bilayer Graphene. *ACS Nano* **2010**, 4, 4074-4080.
- (50) Wang, K.; Huang, B.; Tian, M.; Ceballos, F.; Lin, M.-W.; Mahjouri-Samani, M.; Boulesbaa, A.; Puretzky, A. A.; Rouleau, C. M.; Yoon, M.; Zhao, H.; Xiao, K.; Duscher, G.; Geohegan, D. B., Interlayer Coupling in Twisted WSe₂/WS₂ Bilayer Heterostructures Revealed by Optical Spectroscopy. *ACS Nano* **2016**, 10, 6612-6622.
- (51) Ding, Y.; Wu, R.; Abidi, I. H.; Wong, H.; Liu, Z.; Zhuang, M.; Gan, L.-Y.; Luo, Z., Stacking Modes-Induced Chemical Reactivity Differences on Chemical Vapor Deposition-Grown Trilayer Graphene. *ACS Appl. Mater. Interfaces* **2018**, 10, 23424-23431.

Table 1. Li adsorption on Ti_2CX_2 and the X/G heterostructures (compare Figure 3a for the adsorption sites): Adsorption energy (E_{ad}); Bader charges of Li (Q_{Li}) and the adjacent X (Q_{X}), Ti (Q_{Ti}), and C (Q_{C}) atoms; equilibrium interlayer distance (D) in the heterostructures.

System	Site	E_{ad} (eV)	Q_{Li} ($ e $)	Q_{X} ($ e $)	Q_{Ti} ($ e $)	Q_{C} ($ e $)	D (Å)
Ti_2CF_2	H_{C}	−1.01	+0.89	−0.77	+1.47	-	-
Ti_2CO_2	H_{C}	−2.15	+0.88	−1.11	+1.68	-	-
$\text{Ti}_2\text{C}(\text{OH})_2$	H_{C}	−0.11	+0.76	−0.85	+1.48	-	-
F/G	H_{C}	−1.06	+0.90	−0.77	+1.48	−0.02	3.01
	$\text{H}_{\text{C-I}}$	−1.64	+0.87	−0.76	+1.50	−0.19	3.07
O/G	H_{C}	−2.00	+0.88	−1.12	+1.69	−0.09	3.06
	$\text{H}_{\text{C-I}}$	−2.34	+0.86	−1.12	+1.69	−0.13	3.11
O/G-t1	$\text{H}_{\text{C-I}}$	−2.48	+0.86	−1.11	+1.69	−0.10	3.07
O/G-t2	$\text{H}_{\text{C-I}}$	−2.46	+0.86	−1.09	+1.68	−0.08	3.03
O/G-t3	$\text{H}_{\text{C-I}}$	−2.44	+0.86	−1.11	+1.68	−0.09	3.03
OH/G	H_{C}	−0.12	+0.78	−0.84	+1.48	−0.12	2.21
	$\text{H}_{\text{C-I}}$	−0.85	+0.86	−0.70	+1.52	−0.16	2.18

Figure 1. (a) Side views of the six stacking modes considered in this study. (b) Binding energy per C atom as function of the interlayer distance. The equilibrium positions are marked by stars.

Figure 2. Band structure of (a) F/G, (b) O/G, and (c) OH/G weighted with the contributions of graphene to the eigenstates (red dots). Dirac points are highlighted by blue circles. The Fermi level is set to zero energy. Charge redistribution at the interface of (d) F/G, (e) O/G, and (f) OH/G. Cyan and yellow isosurfaces represent charge depletion and accumulation, respectively. The isosurface value is 4×10^{-4} electrons/ $\text{\AA}^3$.

Figure 3. (a) Adsorption sites for Li on X/G . (b-d) Adsorption energies of Li on Ti_2CX_2 (black), graphene (blue), and the heterostructures (red).

Figure 4. Charge redistribution upon Li adsorption on (a) Ti₂CF₂ and Li adsorption at the (b) Ti₂CF₂ side and (c) interface of F/G. Cyan and yellow isosurfaces represent charge depletion and accumulation, respectively. The isosurface value is 10⁻² electrons/Å³.

Figure 5. (a) Energy profiles for Li diffusion on Ti_2CF_2 (black) and at the interface of F/G (red). Insets show the migration paths. (b) Energy barriers for Li diffusion on Ti_2CX_2 (black) and at the interface of X/G (red).

Figure 6. Heterostructures with twist angles of (a) 0° (O/G), (b) 10.9° (O/G-t1), (c) 5.2° (O/G-t2), and (d) -2.2° (O/G-t3).

Figure 7. Band structure of (a) O/G-t1, (b) O/G-t2, and (c) O/G-t3 weighted with the contributions of graphene to the eigenstates (red dots). Dirac points are highlighted by blue circles. The Fermi level is set to zero energy. (d) Charge redistribution at the interface of O/G-t1. Cyan and yellow isosurfaces represent charge depletion and accumulation, respectively. The isosurface value is 4×10^{-4} electrons/ $\text{\AA}^3$.

Graphical Abstract