Supporting Information

Interstratification-assembled 2D black phosphorene and V₂CT_x

MXene as superior anodes for boosting potassium-ion storage

Xinming Wu*, Han Wang, Zhilin Zhao, , Bin Huang

(School of Materials Science and Chemical Engineering, Xi'an Technological University, Xi'an 710032, P. R. China)

Measurements and Characterization

The microstructure of the samples, including BPE, V_2CT_x and BPE@ V_2CT_x , were investigated with scanning electron microscope (Novatm Nano SEM 430, Fei Company) at an accelerating voltage of 5 kV and transmission electron microscope (TEM, Jem 2010, Fei Tecnai g20). The BPE@ V₂CT_x nanosheets were investigated by atomic force microscope (AFM, FM-Nanoview 1000), and high-resolution transmission electron microscopy (HRTEM, JEM-2100) equipped with energy dispersive spectrometry (EDS) at an acceleration voltage of 200 kV, respectively. The crystalline structure of BPE, V₂CT_x and BPE@ V₂CT_x were carried out on a XRD-7000S/L diffractometer at a scanning rate of 6°/min and a scanning range of 2-60°. To determine the surface elemental compositions of the samples, the X-ray photoelectron spectra (XPS) was performed on Thermo Escalab 250 (USA) photoelectron spectrometer using Al Ka X-rays as the excitation source. The chemical structure analyses of samples were carried out on fourier transforms infrared spectra (FTIR, WQF-31) with the wavenumber between 4000 and 400 cm⁻¹. Zeta potential measurements were measured with a Zetasizer Nano ZS apparatus from Malvern Instruments. The specific surface areas and total pore volumes were obtained employing Brunauer-Emmett-Teller (BET) method (Nitrogen adsorption-desorption

^{*} Corresponding author: XM. Wu (🖂), Tel: +8613720456279; fax: +86 29 88173324

[.] E-mail address: Aimar_wu@xatu.edu.cn.

isotherms were performed using a micromeritics KUBO-X1000 surface area and porosity analyzer). Raman spectroscopy (Raman) was performed on a Renishaw microRaman spectroscopy with wave between 100 and 800 cm⁻¹.

The ex situ XRD test was carried out as follows: Firstly, two steel plates of about 5*5 cm are selected as the fixtures of the battery, with a circular hole with a diameter of 2 cm in the middle of the steel plate for X-ray transmission. Screws are installed around the steel plate to fix the battery. Secondly, Mylar membrane with excellent light transmittance is selected as the carrier of electrode material to adhere to the steel plate in advance, and a hollow plastic pad is used to fix the membrane in the middle. At the same time, the copper foil and aluminum foil with holes in the middle are used as the collector of the anode and the cathode of the battery, which are fixed in advance. The BPE@V₂CT_x electrode material adopts pulping and coating process. Firstly, the prepared anode materials are coated on the copper foil (the copper foil with holes in the middle can prevent the diffraction peak of Cu in the XRD pattern from covering up the peak of the cathode material). Next, the anode material, plastic pad, separator, electrolyte, and potassium foil are placed in sequence in the glove box on the Mylar die of the steel plate. Finally, put another steel plate on the top and fix it with nuts. It should be noted that during the preparation process, there should be no contact between steel plate and collector (copper foil and aluminum film) to avoid short circuit.

Electrochemical performance measurements

First, the BPE@ V₂CT_x electrodes were prepared by BPE@ V₂CT_x (80 wt%), acetylene black (15 wt%) and polyvinyl alcohlo (PVA, 5 wt%) dissolved in N-methyl-2-pyrrolidinone (NMP) to form a homogenous slurry, and then the slurry was coated onto Cu foil substrate and dried at 85 °C for 8 h, and the average mass loading of the electrode is about 0.8-1.0 mg or 0.76-0.89 mg cm⁻². Next, the BPE@ V₂CT_x electrodes were assembled into 2025 coin-cell by using fresh potassium foils as the reference electrode, Whatman glass fiber (GF/D) as the separator and 0.8 M KPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 vol) as the electrolyte.

Cyclic voltammetry (CV) curves between 0.01 and 3.0 V at various scan rates from

0.1 to 1.0 mV s⁻¹ and electrochemical impedance spectroscopy (EIS) were obtained on an electrochemical workstation (Biologic VMP3). Galvanostatic chargingdischarging (GCD) tests were performed on an electrochemical workstation (Donghua Instruments Co., DH7000) with a potential range of 0.01-3.0 V at room temperature.

Computational methods

The calculation process adopted the method reported in the previous literature [1-3]. The theoretical potassium binding energies and diffusion barriers were calculated based on density functional theory (DFT) by employing the Vienna Ab initio Simulation Package (VASP) with the projector augmented wave. The exchange-correlation interaction of electrons within the generalized gradient approximation (GGA) was treated the Perdew-Burke-Ernzerhof scheme. The Grimme empirical correction scheme was employed due to the van der Waals interaction. The Monkhorst-Pack k-point mesh of $3 \times 3 \times 1$ was used to investigate the properties of all studies in the Brillouin zone. To ensure enough area for potassium atoms to move, a $3 \times 2 \times 1$ supercell of BPE and $4 \times 3 \times 1$ supercell of V₂CT_x were used. The climbing image nudged elastic band (CI-NEB) method was chosen to identify the minimum energy path (MEP) and saddle points between the initial and final positions, and compute the migration energy barrier.



Fig. S1 SEM images of (a) the V₂CTx, (b, c) the et- V₂CTx and (d) the ex-V₂CTx



Fig.S2 AFM image of the ex-V₂CTx sheets and the corresponding height profiles

As is show in Fig.S1, it exhibits the typical morphology of the V_2CT_x , which contains rough surface and dense axial lamination. After etching, the microstrcture of et- V_2CT_x have changed a lot, presenting an accordion-like structure (Fig.S1b-c) similar to other MXenes [23]. This multi-layer et- V_2CT_x was further delaminated into

single or few-layer ex-V₂CTx nanosheets via sonication (Fig. 1d). From the Fig.S2, the atomic force microscopy (AFM) image of the ex-V₂CTx sheets and the corresponding height profiles exhibit a flat surface with the average thickness of the nanosheets is around 3.15 nm. It can be seen that the Fig.S4(a-b) exhibits the low and high resolution SEM images of BPE nanosheets which are restacked by a sequence of nanosheets with various thicknesses. Fig.S4(c-d) presented the cross-sectional and top-view TEM images of BPE, which futher demonstrated the self-restacked sheet-like microstructure of BPE nanosheets.



Fig.S3 Amplification of XRD pattern of BPE@V₂CT_x (red line) and V₂CT_x MXene (blue line) in the low-angle range



Fig. S4 SEM images (a, b) and TEM images (c, d) of BPE



Fig.S5 Amplification of XRD pattern of BPE@ V_2CT_x (red line) and BPE (yellow line) in the low-angle range



Fig.S6 Raman spectra of BPE and ct-BPE nanosheets on SiO₂/Si substrate

Fig.S3 show the XRD pattern of BPE@V₂CT_x and V₂CT_x MXene in the lowangle range. It can be seen that at $2\theta = 7.8$, the XRD diffraction peaks correspond to the crystalline phase of (002). However, after BPE was embedded in V₂CT_x MXene, the diffraction peak moves to the left compare to the V₂CT_x MXene, revealing the increase of average layer distance after self-assembly compared with their individual counterparts. Fig.S5 show the XRD pattern of BPE@V₂CT_x and BPE in the low-angle range. From the diffraction patterns of BPE, at $2\theta = 17.1$, the XRD diffraction peaks correspond to the crystalline phase of (020). When BPE was embedded in V₂CTx MXene, the intensity of peak dramatically decreased and the diffraction peak moves to the left compared with the BPE, which demonstrating that the low crystallinity of BPE and the increase of average layer distance. As show in Fig.S6, the Raman spectra of BPE nanosheets depict three identical Raman peaks. Raman peak located at 362cm⁻¹ 1 , 344cm⁻¹ and 368cm⁻¹ correspond to the in-plane Ag¹ 1 B_{2g} and Ag² modes respectively. However the Ag¹ 1 B_{2g} and Ag² Raman peak positions of BPE removed to left compared with ct-BPE, suggesting the thickness of ct-BPE was reduced.



Fig. S7 (a, b) Top-view SEM image of BPE@V₂CT_x, (c, d) Cross-sectional SEM images of BPE@ V₂CT_x



Fig.S8 (a, b) Top-view TEM images of BPE@ V_2CT_x and (c, d) Cross-sectional

TEM images of BPE@ V2CTx



Fig.S9 SEM image of BPE@ V_2CT_x and the corresponding elemental mapping images of V, C and P elements, respectively



Fig.S10 The corresponding high resolution spectra in the O 1s of BPE@V₂CT_x



Fig.S11 The corresponding high resolution spectra in the F 1s of BPE@V₂CT_x



Fig. S12 FTIR spectra of the V_2CT_x , BPE and BPE@ V_2CT_x



Fig. S13 (a) Nitrogen adsorption-desorption isotherms and (b) the pore diameter distribution for the mesopores and micropores of the BPE, V_2CT_x and BPE@ V_2CT_x materials

	Surface	Pore	Pore	Micro-pore	Meso-pore
Material	area (m² g-	size	volume	volume (m³ g	volume (m³ g-
	1)	(nm)	(m ³ g ⁻¹)	¹)	1)
BPE	35.20	5.52	0.175	0.012	0.168
V ₂ CT _x	82.60	8.91	0.708	0.048	0.726
BPE@V ₂ CT _x	121.20	11.84	0.958	0.225	1.128

Table.S1 Textural properties of the BPE, V2CTx and BPE@V2CTx materials

Fig.S7 shows the top-view and cross-sectional SEM image of BPE@V₂CT_x, the SEM image of BPE@V₂CT_x displays a typical stacked layer-by-layer morphology. As show in Fig.S8, the top-view TEM image of BPE@V₂CT_x exhibit that BPE and V₂CT_x were superimposed together (Fig. S8(a-b)). From the Fig.S8(c-d), It can be seem clearly that BPE was embedded into V₂CT_x which presenting an accordion-like structure. SEM image of BPE@V₂CT_x and the corresponding elemental mapping images of V, C and P elements also demonstrated that BPE were uniformly dispersed in the V₂CT_x(Fig. S9). XPS measurement results show that P-OH_x P-O_x V-OH_x V-

O and V-F appeared in the XPS band spectrum of O 1s and F 1s, demonstrating that BPE@V₂CT_x has been successfully synthesized(Fig.S10 and S11). FTIR tests were performed on the V₂CT_x, BPE and BPE@V₂CT_x, as shown in Fig.S12. It can be seen from the Fig.S3 that the BPE@V₂CT_x contains –OH_x C=O_x P=O_x C-F_x V-O and V-F bonds, which further proves that BPE@V₂CT_x was successfully synthesized. Fig. S13 and Table.S1 show the nitrogen adsorption-desorption isotherms and the pore diameter distribution for the mesopores and micropores of the BPE, V₂CT_x and BPE@V₂CT_x materials. When the relative pressure (P/P₀) of 0.973 occurred on the desorption curve indicates that the pore size distribution is concentrated at this time, BPE@V₂CT_x possess a specific surface area of about 121.20 m² g⁻¹ and the pore size is 11.84 nm, so that BPE@V₂CT_x has a larger amount of mesoporous compare with the BPE and V₂CT_x [30].



Fig.S14 (a) CV curves of BPE anode in the potential range of 0.01-3.0 V (vs. K⁺/K) at a scan rate of 0.1 mV s⁻¹, (b) Initial five galvanostatic charge/discharge profiles at 0.1 A g⁻¹ for the BPE anode

CV curves of BPE anode as show in Fig.S14 (a), in the first cathodic scan, the irreversible peak at 0.31 V, while vanishes in the subsequent scans which can be ascribed to the combined effects of the formation of solid electrolyte interface (SEI) layer, and the reactions between the K⁺ and surface functional groups. During the subsequent cycles, the CV curves overlap, revealing the excellent reversibility of the electrode. As can be seen from Fig.S14(b), all the constant current charge-discharge

curves show excellent symmetry, revealing that the electrode material has fast chargedischarge efficiency and excellent electrochemical reversibility, which is consistent with the CV curves of BPE anode results. However, the BPE electrode achieves a high first discharge capacity of 2450 mAh g⁻¹, the capacity less the 453 mAh g⁻¹ after five cycles.



Fig.S15 (a) CV curves of V₂CT_x anode in the potential range of 0.01-3.0 V (vs. K⁺/K) at a scan rate of 0.1 mV s⁻¹, (b) Initial five galvanostatic charge/discharge profiles at 0.1 A g⁻¹ for the V₂CT_x anode

CV curves of V₂CTx anode as show in Fig.S15 (a), in the first cathodic cycle, the irreversible peak at 0.61 V, while disappear in the subsequent cycle which can be ascribed to the combined effects of SEI layer, and the reactions between the K⁺ and surface functional groups. In the following cycles, CV curves of V₂CT_x anode exhibit good reproducibility, combine with charge-discharge curves of V₂CT_x anode, demonstrating that the electrode material has excellent electrochemical reversibility.



Fig.S16 (a) CV curves at various scan rates and (b) relationship between log (*i*) vs. log(v) for the BPE anode



Fig.S17 (a) CV curves at various scan rates and (b) relationship between log (*i*) vs. $\log (v)$ for the V₂CT_x anode

Fig.S16 and Fig.S17 show the CV curves at different scan rates and relationship between log (*i*) vs. log (*v*) for the BPE and V_2CT_x anode respectively. The following equations describe the relationship between the measured currents (*i*) and the scan rates (*v*):

$$i = av^b (0.5 \le b \le 1)$$

$$\log i = b \log v + \log a$$

where the b value reflect the K^+ storage behaviors. When b = 0.5 stands for a diffusion-controlled process, and b = 1 stand for a capacitive process free of diffusion

limitations. From the Fig.S16(b), The b value for the BPE anode material is about 0.76. Similarity, from the Fig.S17(b), The b value for the V_2CT_x anode material is around 0.67, revealing that capacitive behaviors is very important for potassium-ion storage.



Fig. S18 *ex situ* SEM images of BPE@V₂CT_x anode at fully charge state after 500 cycles, the corresponding elemental mappings of V, C, O, F, P and K.

Fig. S18 show the SEM images of BPE@V₂CT_x anode, corresponding elemental mappings and the typical EDS spectrum after 500 cycles. It can be seen that morphology of the BPE@V₂CT_x anode material has not change after 500 cycles, which demonstrates that the cycling stability of the BPE@V₂CT_x. The elements of V, C, O, F, P and K are equally distributed among the whole BPE@V₂CT_x anode, which further further proving successful potassiation of the BPE@V₂CT_x anode.



Fig. S19 Ex situ XPS spectra of the BPE@V₂CT_x anode at different states during the first potassiation/depotassiation process. (a) Full spectra. (b-e) High-resolution spectra of V 2p, P 2p, C1s and O 1s.

Fig.S19 show the Ex situ XPS spectra of the BPE@V₂CT_x anode at different states, revealed that the fresh BPE@V₂CT_x anode is made up V, O, V, K, C and P. The new peaks at the binding energies of 289 and 371 eV are assigned to the K 2p and K 2s during the first potassiation/depotassiation process. As show in Fig.S19(b)

indicated that the V 2p peaks get lower binding energy after discharged to 0.01 V, proving the valence states of V has channges. The binding energy of V 2p peaks recove to their initial state after after discharged to 3.0 V, indicating the reversibility of the charge/discharge process. As we all know, the O 1s spectra are used to analyze the composition of the SEI layer. From the Fig.S19(e), the peaks at the binding energies of 530.3 eV, SEI component can be observed. However, the peak shows weaker intensity after discharged to 0.01 V, and when discharged to 3.0 V, the peak disappear, which further verified that the potassium storage mechanism of the BPE@V₂CT_x anode.



Fig. S20 Initial five galvanostatic charge/discharge profiles at 0.1 A g^{-1} for the BPE@V₂CT_x anode: (a) 1:1 and (b) 3:1

From the initial five galvanostatic charge/discharge profiles at 0.1 A g⁻¹ for the BPE@V₂CT_x (1:1) anode (Fig.S20(a)), it can be seen that compared with the capacity of BPE@V₂CT_x (2:1), the capacity of BPE@V₂CT_x (1:1) is obviously reduced, which may be attributed to the decrease in the amount of V₂CT_x, leading to the decrease in the active site of the hybrid electrode and thus affecting the electrochemical performance. Compared with the BPE@V₂CT_x (2:1) capacity, the capacity of BPE@V₂CT_x (3:1) is not significantly different, which could be attributed to the fact that the capacity of the hybrid electrode did not increase significantly as the amount of V₂CT_x was increased (Fig.S20(b)).

Table.S2 The adsorption energy of BPE, V₂CTx and BPE@V₂CTx anode with K

Materials	K position	E _{ad} (eV)
BPE	Н	-1.82
V ₂ C(OH) ₂	T _V	-1.258
VCE	$T_{\rm H}$	-1.208
V ₂ CF ₂	T_{V}	-2.817
	H _p	-1.525
BPE@ V ₂ C(OH) ₂	Н	-1.586
	H _T	-1.196
	H _p	-1.496
BPE@ V ₂ CF ₂	Н	-2.312
	H _T	-2.096

atom adsorbed at representative positions in Fig.7(a).

Table.S3 Potassium storage performance comparison between present works with those of previously reported MXene-based and 2D anodes materials.

Electrode material	Voltage range(V)	Current density(mA g- ¹)	Initial CE(%)	mAh g ⁻¹ (Cycling Stability)	Ref#
Ti ₃ C ₂	0.01-3.5	100	43.0	45(30.8%after120	1
5-2				cycles)	
a-Ti ₃ C ₂	0.01-3.0	20	27.1	98(72.1% after 20	2
				cycles)	
Ti₃CNT _z	0.005-3.0	20	28.4	75(37.1% after	3
				100 cycles)	
MXene@Sb	0.01-1.2	50	57.3	516.8(65.3% after	4
				100 cycles)	
MoSe2/MXene@C	0.01-3.0	200	54.4	355(55.4% after	5
			54.4	100 cycles)	

	0.01.2.0	100	42 1	342.8(90.9% after	6	
N doped porous C	0.01-3.0	100	43.1	500 cycles)		
Granhite	0.01.1.5	140	56 /	100(50.8% after	7	
Grapinte	0.01-1.5	140	50.4	50 cycles)		
P,O doped	0.01-3.0	50	22.6	150(88.2% after	8	
graphene	0.01-5.0	50	22.0	175 cycles)	0	
N doned norous C	0.001-3.0	50	30.3	296.8(84.9% after	9	
iv doped porous e	0.001-5.0	50	50.5	100 cycles)		
N doned granhene	0.01-3.0	50	37 3	320(90.8% after	10	
it uspeu gruphene	0.01 5.0	20	51.5	60 cycles)		
Expanded graphite	0.01-3.0	50	81.6	228(105.1% after	11	
Expanded gruphice	0.01 5.0	20	01.0	200cycles)		
Hard carbon	0 001-3 0	50	25.0	230.6(76.1% after	12	
	0.001-3.0		20.0	100cycles)		
Activated carbon	0.01-2.0	200	74.3	100.3(63.0% after	13	
				100 cycles)		
N,O doped porous	0.01-3.0	50	38.7	266(76.0% after	14	
С	0.01 5.0			100 cycles)		
Carbon	0.01-3.0	200	50.2	270(91.2% after	15	
nanoparticles				300 cycles)	10	
PDDA-	0.01-3.0	100	65.2	429.4(63.0% after	16	
NPCN/Ti ₃ C ₂				300 cycles)		
MXene / MoS ₂	0.01-2.5	50	66.5	252.6(86.6% after	19	
				50 cycles)		
TiO _x N _v /C	0.01-3.0	200	/	125(98.4% after	20	
				100 cycles)		
M-NTO	0.01-3.0	200	51	191(99.82% after	21	
				150 cycles)		
BPE@V ₂ CT _x	0.01-3.0	100	80.2	570(99.5% after	This	

Table.S4 Long-term cycling performance comparison between present works with those of previously reported anodes materials

Electrode material	Voltage	Current density(mA g [_]	Reversible capacity(mAh g ⁻	Cycling	Ref#
	range(V)	1)	1) 1)	number(N)	
a-Ti ₃ C ₂	0.01-3.0	200	42	500 cycles	2
MXene@Sb	0.01-1.2	500	21.3	500 cycles	4
MoSe ₂ /MXene@C	0.01-3.0	1000,2000,5000	317, 243, 207	300 cycles	5
N doped porous C	0.01-3.0	1000,2000,5000	226.1,194.0,144.4	1000 cycles	6
P,O doped graphene	0.01-3.0	500,1000,2000	385,235,160	600 cycles	8
N doped porous C	0.001-3.0	500	121.3	1000 cycles	9
N doped graphene	0.01-3.0	500	150.0	500 cycles	10
Hard carbon	0.001-3.0	1050	123	1100 cycles	12
N,O doped porous C	0.01-3.0	1000	104.3	1000 cycles	14
Carbon nanoparticles	0.01-3.0	1000	190	4000 cycles	15
PDDA- NPCN/Ti ₃ C ₂	0.01-3.0	1000,2000	252.2,151.2	2000 cycles	16
Graphitic carbons	0.25-2.0	2000	95	1000 cycles	17
CNFs	0.005-3.0	279	170	1900 cycles	18
MXene / MoS ₂	0.01-2.5	200	145.5	50 cycles	19
TiO _x N _y /C	0.01-3.0	200	150	1250 cycles	20
M-NTO	0.01-3.0	2000	101	62 cycles	21

MXene@Ni-Mn LDH	0.01-1.7	1000,2000,4000	56,48,41	5000 cycles	22
Ti ₃ C ₂ T _x MXene	0.01-3.0	200	242	1000 cycles	23
VN/PC//Ti ₃ C ₂ T _x	0.01-2.0	1000	/	10000 cycles	24
BP/G/PA-Am	0.01-3.0	200	1280	300 cycles	25
BP/Ti ₃ C ₂	0.01-3.0	100,500	774.4,649	200 cycles	26
BP-G/PANI	0.01-2.0	4000	520	1000 cycles	27
BP/AB// Li ₂ S/P ₂ S ₅	0.01-2.5	1470	500	150 cycles	28
PVA@BP	0.01-1.5	/	212.8	100 cycles	29
BP/PANa	0.01-2.0	500	1500	25 cycles	30
BP@TiO2	0.01-2.0	500	982	100 cycles	31
DROVCT	0.01.2.0	200, 2000	501 202	2000 aval	This
BPE@V ₂ CT _x	0.01-3.0	200, 2000	501, 292	SUUU CYCIES	work



Fig.S21 (a) Energy barrier and diffusion path of one K^+ diffusion on the V₂CF₂ surface of BPE/V₂CF₂, (b) Energy barrier of one K^+ diffusion on the surface of BPE and on the BPE surface of BPE/V₂CF₂.



Fig.S22 (a) Energy barrier and diffusion path of one K⁺ diffusion on the V₂C(OH)₂ surface of BPE/V₂C(OH)₂, (b) Energy barrier of one K⁺ diffusion on the surface of BPE and on the BPE surface of BPE/(OH)₂.

Fig.S20 and Fig.S21 show the energy barrier and diffusion path of K atom diffusion on different material surfaces. The energy barrier of one K⁺ diffusion on the V₂CF₂ surface of BPE/V₂CF₂ and the energy barrier of one K⁺ diffusion on the BPE surface of BPE/V₂CF₂ are lower than that of a K atom diffusing along the surface of V₂CF₂ and BPE (Fig.S21), which demonstates that K⁺ diffusion kinetics was enhanced in the hybrid. Besides, the energy barrier of one K⁺ diffusion on the BPE/V₂C(OH)₂ is lower than BPE/V₂CF₂ (Fig.S22), proving that K⁺ diffusion in the BPE/V₂C(OH)₂ is faster compared with BPE/V₂CF₂.



Fig.S23 Galvanostatic intermittent titration technique (GITT) result for the V_2CT_x , BPE and BPE/ V_2CT_x anode measured at a current density of 0.1 A g⁻¹ in the second cycle, followed by a 1200 s of relaxation to achieve equilibrium potential (the cell was pre-cycled at the same current for 1 time before this measurement).



Fig.S24 Corresponding K⁺ diffusion coefficient at different discharge/charge states of the V_2CT_x , BPE and BPE/ V_2CT_x anode in the second cycle

References

- [1] Y. Xie, Y. Dall'Agnese, M. Naguib, Y. Gogotsi, M. W. Barsoum, H. L. Zhuang and P. R. Kent, Prediction and Characterization of MXene Nanosheet Anodes for Non-Lithium-Ion Batteries, *ACS Nano*, 2014, 8, 9606-9615.
- [2] P. Lian, Y. Dong, Z.-S. Wu, S. Zheng, X. Wang, W. Sen, C. Sun, J. Qin, X. Shi and X. Bao, Alkalized Ti₃C₂ MXene Nanoribbons with Expanded Interlayer Spacing for High-Capacity Sodium and Potassium Ion Batteries, *Nano Energy*, 2017, 40, 1-8.
- [3] M. Naguib, R. A. Adams, Y. Zhao, D. Zemlyanov, A. Varma, J. Nanda and V. G. Pol, Electrochemical performance of MXenes as K-ion battery anodes, *Chem. Commun.*, 2017, 53, 6883-6886.
- [4] Y. Tian, Y. An, S. Xiong, J. Feng and Y. Qian, General Constructing Robust,

Flexible and Freestanding MXene@Metal Anodes for High-Performance Potassium-Ion Batteries, *J. Mater. Chem. A*, 2019, 7, 9716-9725.

- [5] H. Huang, J. Cui, G. Liu, R. Bi and L. Zhang, Carbon Coated MoSe₂/MXene Hybrid Nanosheets for Superior Potassium Storage, *Acs Nano*, 2019, 13, 3448-3456.
- [6] D. Li, X. Ren, Q. Ai, Q. Sun, L. Zhu, Y. Liu, Z. Liang, R. Peng, P. Si, J. Lou, J. Feng and L. Ci, Facile Fabrication of Nitrogen-Doped Porous Carbon as Superior Anode Material for Potassium-Ion Batteries, *Adv. Energy Mater.*, 2018, 8, 1802386.
- [7] Z. Jian, W. Luo and X. Ji, Carbon Electrodes for K-Ion Batteries, J Am. Chem. Soc., 2015, 137, 11566-11569.
- [8] G. Ma, K. Huang, J. S. Ma, Z. Ju, Z. Xing and Q. C. Zhuang, Phosphorus and oxygen dual-doped graphene as superior anode material for room-temperature potassium-ion batteries, *J. Mater. Chem. A*, 2017, 5, 7854-7861.
- [9] X. Qi, K. Huang, X. Wu, W. Zhao, H. Wang, Q. Zhuang and Z. Ju, Novel fabrication of N-doped hierarchically porous carbon with exceptional potassium storage properties, *Carbon*, 2018, 131, 79-85.
- [10] Z. Ju, P. Li, G. Ma, Z. Xing, Q. Zhuang and Y. Qian, Few layer nitrogen-doped graphene with highly reversible potassium storage, *Energy Storage Mater.*, 2018, 11, 38-46.
- [11] Y. An, H. Fei, G. Zeng, L. Ci, B. Xi, S. Xiong and J. Feng, Commercial expanded graphite as a low-cost, long-cycling life anode for potassium-ion batteries with conventional carbonate electrolyte, *J. Power Sources*, 2018, 378, 66-72.
- [12] J. Yang, Z. Ju, Y. Jiang, Z. Xing, B. Xi, J. Feng and S. Xiong, Enhanced Capacity and Rate Capability of Nitrogen/Oxygen Dual-Doped Hard Carbon in Capacitive Potassium-Ion Storage, *Adv. Mater.*, 2018, 30, 1700104.
- [13] Z. Tai, Q. Zhang, Y. Liu, H. Liu and S. Dou, Activated carbon from the graphite with increased rate capability for the potassium ion battery, *Carbon*, 2017, 123, 54-61.

- [14] Y. Sun, H. Xiao, H. Li, Y. He, Y. Zhang, Y. Hu, Z. Ju, Q. Zhuang and Y. Cui, Nitrogen/Oxygen Co-doped Hierarchically Porous Carbon for High-Performance Potassium Storage, *Chem. Eur. J.*, 2019, 25, 7359-7365.
- [15] Q. Gan, J. Xie, Y. Zhu, F. Zhang, P. Zhang, Z. He and S. Liu, Sub-20 nm Carbon Nanoparticles with Expanded Interlayer Spacing for High-Performance Potassium Storage, ACS Appl. Mater. Interfaces, 2019, 11, 930-939.
- [16] Z. T. Wu, T. X. Shang, Y. Q. Deng, Y. Tao and Q. H. Yang, Self-assembled Ti₃C₂ MXene and N-rich porous carbon hybrids as superior anodes for highperformance potassium-ion batteries, *Adv. Sci.*, 2020, 7, 1903077.
- [17] A. P. Cohn, N. Muralidharan, R. Carter, K. Share, L. Oakes and C. L. Pint, Durable Potassium Ion Battery Electrodes from High-Rate Cointercalation into Graphitic Carbons, *J. Mater. Chem. A*, 2016, 4, 14954-14959.
- [18] R. A. Adams, J. M. Syu, Y. Zhao, C. T. Lo, A. Varma and V. G. Pol, Binder-free N- and O- Rich Carbon Nanofiber Anodes for Long Cycle Life K-ion Batteries, *ACS Appl. Mater. Interfaces*, 2017, 9, 17872-17881.
- [19] J. H. Li, B. L. Rui, W. X. Wei, P. Nie, L. M. Chang, Z. Y. Le, M. Q. Liu, H. R. Wang, L. M. Wang and X. G. Zhang, Nanosheets assembled layered MoS₂/MXene as high performance anode materials for potassium ion batteries, *J. Power Sources*, 2020, 449, 227481.
- [20] M. L. Tao, G. Y. Du, Y. Q. Zhang, W. Gao, D. Y. Liu, Y. S. Luo, J. Jiang, S. J. Bao and M. W. Xu, TiO_xN_y nanoparticles/C composites derived from MXene as anode material for potassium-ion batteries, *Chem. Eng. J.*, 2019, 369, 828-933.
- [21] Y. F. Dong, Z. S. Wu, S. H. Zheng, X. H. Wang, J. Q. Qin, S. Wang, X. Y. Shi and X. H. Bao. Ti₃C₂ MXene-Derived Sodium/Potassium Titanate Nanoribbons for High-Performance Sodium/Potassium Ion Batteries with Enhanced Capacities, *ACS Nano*, 2017, 11, 4792-4800.
- [22] W. D. Wang, D. M. Jiang, X. Chen, K. Xie, Y. Jiang and Y. Wang. A sandwichlike nano-micro LDH-MXene-LDH for high-performance supercapacitors, *Appl. Surf. Sci.*, 2020, 515.

- [23] N. Sun, Z. R. X. Guan, Q. Z. Zhu, B. Anasori ,Y. Gogotsi and B. Xu, Enhanced Ionic Accessibility of Flexible MXene Electrodes Produced by Natural Sedimentation, *Micro Nano Lett.*, 2020, 12, 1700107-701.
- [24] S. Venkateshalu and A. N. Grace, Ti₃C₂T_x MXene and Vanadium nitride/Porous carbon as electrodes for asymmetric supercapacitors, *Electrochim. Acta.*, 2020, 341.
- [25] H. W. Zhang, Z. S. Lv, Q. H. Liang, H. R. Xia, Z. Q. Zhu, W. Zhang, X. Ge, P. Yuan, Q. Y. Yan and X. D. Chen, Highly Elastic Binders Incorporated with Helical Molecules to Improve the Electrochemical Stability of Black Phosphorous Anodes for Sodium Ion Batteries, *Batteries & Supercaps*, 2020, 3, 101-107.
- [26] H. Li, A. M. Liu, X. F. Ren, Y. F.Yang, L. G. Gao, M. Q. Fan and T. L.Ma, A black phosphorus/Ti₃C₂ MXene nanocomposite for sodium-ion batteries: a combined experimental and theoretical study, *Nanoscale*, 2019, 11, 19862-19869.
- [27] H. C. Jin, T. M. Zhang, C. H. Chuang, Y. R. Lu, T. S. Chan, Z. Z. Du, H. X.Ji and L. J. Wan, Synergy of Black Phosphorus-Graphite-Polyaniline Based Ternary Composite for Stable High Reversible Capacity Na-ion Battery Anodes, *ACS Appl. Mater. Interfaces*, 2019, 11, 16656-16661.
- [28] M. Nagao, A. Hayashi and M. Tatsumisago, All-solid-state lithium secondary batteries with high capacity using black phosphorus negative electrode, *J. Power Sources*, 2010, 196, 6902-6905.
- [29] S. A. Yang, M. L. Bo, C. Peng, Y. D. Li and Y. Li, Three-electrode flexible Zinc-Nickel battery with Black Phosphorus modified polymer electrolyte, *Mater. Lett.*, 2018, 15, 118-121.
- [30] M. Dahbi, N. Yabuuchi, M. Fukunishi, K. Kubota, K. Chihara, K. Tokiwa, X. F. Yu, H. Ushiyama, K. Yamashita, J. Y. Son, Y. T. Cui, H. Oji and S. Komaba, Black Phosphorus as a High-Capacity, High-Capability Negative Electrode for Sodium-Ion Batteries: Investigation of the Electrode/Electrolyte Interface, *Chem.*

Mater., 2016, 28, 1625-1635.

[31] Y. F. Luo, H. C. Wu, L. L. Liu, Q. Q. Li, K. L. Jiang, S. S. Fan, J. Li and J. P.Wang, TiO₂-Nanocoated Black Phosphorus Electrodes with Improved Electrochemical Performance, *ACS Appl. Mater. Interfaces*, 2018, 10, 36058-36066.