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The abbreviation of composite name in the text and figures are not unified, where PDDA-NPCNs/Ti₃C₂ for those in figures, and PDDA-NPCN/Ti₃C₂ in the text. We have revised all of them to "PDDA-NPCN/Ti₃C₂". Besides, the ESI files also make corresponding changes.

Supporting information

Self-Assembled Ti₃C₂ MXene and N-Rich Porous Carbon hybrids as Superior Anodes for High-Performance Potassium-Ion Batteries

Methods

Preparation of ex-Ti₃C₂ nanosheets. Ti₃AlC₂ powders (High purity) were purchased from 11 Technology Co., Ltd. Ex-Ti₃C₂ nanosheets were synthesized via etching of Ti₃AlC₂ powder.¹ Typically, 2.0 g LiF (Alfa Aesar, 98.5%) was dissolved in 9 M HCl solution (Beijing Chemical Factory, 40 mL). After stirring for 30 min, 2.0 g Ti₃AlC₂ was slowly added into the mixture solution under magnetic stirring, which was maintained stirring at 35 °C for 24 h. Then, the resultant was repeatedly washed with deionized water and centrifuged until the pH of the supernatant was approximately 6, and the clay-like sediment was obtained. Next, the sediment was dispersed in 500 mL of deionized water and bath sonicated for 1 h under Ar flow, followed by centrifugation at 3500 rpm for 1 h. Finally, the dark green supernatant was freeze-drying for 24 h, whose concentration was calculated by filtering a known volume of the suspension and measuring the weight of the film after dried. Herein, the dark green supernatant labeled as ex-Ti₃C₂.

Preparation of PDDA-NPCNs. Typically, 11.2 g hexamine (HMT, Adamas-beta) and 24.7 g cadmium nitrate (Cd(NO₃)₂·4H₂O) were dissolved in 560 and 340 mL ethanol solution, respectively. Then, the solution of Cd(NO₃)₂·4H₂O was added dropwise to the HMT solution, and white precipitates were immediately generated, indicating the formation of Cd-HMT metal-HMT frameworks (MHFs). The mixed solution was further kept still for 24 h for yielding enough Cd-HMT MHFs. Afterwards, the Cd-HMT MHFs were obtained by centrifugation and washed by alcohol several times to remove unreactive sources, and then dried at 80 °C overnight in the oven. Finally, the Cd-HMT MHFs was directly carbonized at 800 °C for 2 h in Ar atmosphere at a heating rate of 3 °C min⁻¹, and the corresponding functional 2D N-rich porous carbon nanosheets (NPCNs) were obtained. Next, NPCNs were first decorated with poly(diallyldimethylammonium chloride) (PDDA) to gain a positively charge surface. In detail, 2.149 g PDDA 35% solution, 0.363 g tris, 0.173 g NaCl and 150 mL H₂O were added into a vial and sonicated for 5 min, forming a mixture aqueous. Then, NPCNs were immersed in the stirring mixture aqueous and subjected to probe sonication for 30 minutes, followed by filtering and washing with deionized water three times to remove the redundant PDDA, and then freeze-drying for 24 h. Herein, the NPCNs were functionalized with PDDA labeled as PDDA-NPCNs.

Fabrication of PDDA-NPCNs/Ti₃C₂ hybrids. The PDDA-NPCNs/Ti₃C₂ hybrids were synthesized via an electrostatic attraction self-assembly process. Typically, ex-Ti₃C₂ and PDDA-NPCNs suspensions with a quality feeding rate of 2:1 were controllably dropped into a beaker simultaneously, respectively. After both kinds of solutions were completely added, the mixed solution was sonicated for 1 h and then stirred for another 12 h, centrifuged with copious deionized water, and then freeze-drying for 24 h to obtain the PDDA-NPCNs/ex-Ti₃C₂ Herein, the PDDA-NPCNs/ex-Ti₃C₂ was labeled as PDDA-NPCNs/Ti₃C₂. The prepared PDDA-NPCNs/Ti₃C₂ hybrids with three different mass ratios were denoted as PDDA-NPCNs/Ti₃C₂₋₁, PDDA-NPCNs/Ti₃C₂₋₂ and PDDA-NPCNs/Ti₃C₂₋₃ by controlling ex-Ti₃C₂ and PDDA-NPCNs suspensions with the quality feeding rates of 1.0:1, 2.0:1 and 3.0:1.

Materials characterization. The crystalline structures were characterized on a Rigaku D/Max-KA X-ray diffractometer equipped with a Cu K α source (λ =1.5406 Å). Fourier transform infrared (FTIR) characterization was carried out on Bruker spectrometer (TENSOR 27). Raman spectra were recorded on a JY HR800 micro Raman spectrometer with a 633 nm laser as the excitation source. The exfoliated nanosheets were investigated by atomic force microscope (AFM, FM-Nanoview 1000). The morphologies, microstructures and elemental components of those materials were characterized by field emission scanning electron microscopy (FESEM, SU-70), and high-resolution transmission electron microscopy (HRTEM, JEM-2100) equipped with energy dispersive spectrometry (EDS) at an acceleration voltage of 200 kV, respectively. Chemical compositions of the samples were further characterized by high-resolution X-ray photoelectron spectroscopy (XPS) recorded with an ESCALAB 250 instrument equipped with a 150 W Al K α probe beam. Zeta potential measurements were measured with a Zetasizer Nano ZS apparatus from Malvern

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PDDA-NPCN/Ti ₃ C ₂ -2 and PDDA-
NPCN/Ti ₂ C ₂ -3

Instruments. Nitrogen adsorption-desorption isotherms were performed using a micromeritics KUBO-X1000 surface area and porosity analyzer.

Electrochemical measurements. The working electrodes were prepared by active materials (80 wt%), acetylene black (Super-P, 10 wt%) and poly(vinyl difluoride) (PVDF, 10%) dissolved in N-methyl-2-pyrrolidinone (NMP) to form a homogenous slurry. Then the slurry was coated onto Cu foil substrate and dried at 80 °C for 12 h, and the average mass loading of the electrode is about 1.0-1.2 mg or 0.83-0.99 mg cm⁻². Next, the working 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 by volume) as the electrolyte. Galvanostatic charging/discharging (GCD) tests were performed on a LAND CT2001A instrument (Wuhan, China) with a potential range of 0.01-3.0 V at room temperature. 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) with the frequency range between 100 KHz and 10.0 mHz were tested on an electrochemical workstation (PARSTAT2273).

DFT calculations. First-principles calculations were carried out based on density functional theory (DFT). The structural optimization and absorption energy calculations were conducted by using Vienna Ab-initio Simulation Package (VASP) code.²⁻⁵ The projector augmented wave (PAW) method was performed considering spin-polarized calculations.⁶ The exchange correlation functional was described by Perdew-Burke-Ernzerhof (PBE) type of generalized gradient approximation (GGA). A plane wave basis set with an energy cutoff of 520 eV was used throughout the calculations.⁷ The K-points mesh of $3\times3\times1$ was performed in Ti₃C₂, NPCNs and NPCNs/Ti₃C₂ adsorption systems. The structure was optimized until the force convergence was 0.05 eV/Å in this work. The difference charge density was used to analyze the charge transfer between K and Ti₃C₂, NPCNs or NPCNs/Ti₃C₃⁸

To analyze interactions between K and Ti_3C_2 , NPCNs or NPCNs/ Ti_3C_2 , the adsorption energies have been calculated by the following equation:

 $E_a = E_{t+K} - (E_t + E_K)$

where E_a means the adsorption energy, E_{t+K} means the total energy of adsorption structure, E_t means the total energy of Ti₃C₂, NPCNs or NPCNs/Ti₃C₂ structure, and E_K means the total energy of the K.

The difference charge density was calculated by the following equation:

 $\Delta\rho(r)=\rho_{t^+\!K}(r)-\rho_t(r)-\rho_K(r)$

Where $\rho_{t+K}(r)$ means the charge density of adsorption structure, $\rho_t(r)$ is the charge density of Ti₃C₂, NPCNs or NPCNs/Ti₃C₂ structure, and $\rho_K(r)$ is the charge density of K.

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Supporting Figures



Figure S1. (a-b) AFM image and thickness profile of ex-Ti₃C₂ nanosheet.



Figure S2. (a) SEM, (b) TEM images and XRD pattern of layered bulk Cd-HMT MHFs. (d) SEM, (e-f) TEM images, (g) ED pattern and (h-i) AFM image and thickness profile of the resulting PDDA-NPCNs.

SEM and TEM images of Cd-HMT MHFs (Fig. S2a-b) show a typical rodlike morphology. XRD pattern (Fig. S2c) shows the main diffraction peaks of Cd-HMT MHFs at 12.8°, 16.3° and 20.6° are consistent, suggesting that the pure phase of the Cd-HMT MHFs are formed. After pyrolysis and surface modified, the layered bulk Cd-HMT MHFs is successfully converted to 2D N-rich porous carbon nanosheets (NPCNs). Typically, SEM image (Fig. S2d) shows that the wrinkled NPCNs with a lateral size of several micrometers are obtained. TEM image (Fig. S2e) shows that the PDDA-NPCNs exhibit network morphology similar to a highly crumpled paper. The crumpled NPCNs are extremely thin and almost transparent to the electron beam, which is indeed comparable to those reported for the graphene nanosheets. HRTEM image (Fig. S2f) shows that the PDDA-NPCNs mainly consist of amorphous carbon with a typical disordered structure. The porosity structure can result from the evaporation of elemental Cd nanoparticles, which are generated by the reduction of carbon during the annealing process.⁹ Note that the PDDA-NPCNs contain more active sites and defects on the surface.¹⁰ Moreover, the diffraction rings in the ED pattern (Fig. S2g) tend to a polycrystalline phase.



Figure S3. HRTEM images of PDDA-NPCNs/Ti₃C, T stands for ex-Ti₃C₂ and C is PDDA-NPCNs. Inset shows ED pattern of PDDA-NPCNs/Ti₃C, flocculation.



Figure S4. XPS spectra of ex-Ti₃C₂, PDDA-NPCNs and PDDA-NPCNs/Ti₃C₂ hybrids, respectively. (a-b) High-resolution

Comment [C]: PDDA-NPCN/Ti₃C₂ Comment [C]: PDDA-NPCN/Ti₃C₂ Comment [C]: PDDA-NPCN/Ti₃C₂ spectra of O 1s and F 1s.

The O 1s spectra of ex-Ti₃C₂ nanosheets (**Fig. S4a**) located at 529.7 and 531 eV could be assigned to Ti-O and Ti-OH groups.¹¹ Moreover, deconvolution of the O 1s region of PDDA-NPCNs displays three peaks at 531.6, 532.7 and 534.6 eV, which should be indexed to C=O, C-OH and -COOH bonds.¹² However, there are significant changes for the strength and position of these peaks in PDDA-NPCNs/Ti₃C₂ demonstrating the PDDA-NPCNs/Ti₃C₃ hybrids are synthesized successfully. The component in the F 1s region of ex-Ti₃C₂ nanosheets (**Fig. S4b**) is located at 684.6 eV, corresponding to Ti-F surface functional group.¹¹ Nevertheless, the Ti-F peak shifts to lower binding energy of 684.3 eV in PDDA-NPCNs/Ti₃C₂ which further confirms the PDDA-NPCNs/Ti₃C₃ hybrids are synthesized successfully.



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Figure S5. FTIR spectra of ex-Ti₃C₂, PDDA-NPCNs and PDDA-NPCNs/Ti₃C₂ hybrids.

As shown in **Fig. S5**, FTIR spectra of ex-Ti₃C₂ nanosheets terminated with -O, -OH and -F surface functional groups exhibit a broad band around 3439 cm⁻¹, corresponding to the -OH stretching vibration. Another three obvious bands at 1628, 1384 and 1093 cm⁻¹ correspond to the stretching vibration of C=O, O-H and C-F, respectively. Particularly, the peaks at 616 and 460 cm⁻¹ could be assigned to the Ti-O and Ti-F bonds vibration.^{11, 13} FTIR spectra of PDDA-NPCNs exhibit three characteristic peaks at 1630, 1382 and 1168 cm⁻¹, which correspond to the C=C, -CH₂ and C-N/C-O species, respectively.¹⁰ Obviously, almost all the surface functional groups of ex-Ti₃C₂ and PDDA-NPCNs can be clearly demonstrated in the PDDA-NPCNs/Ti₃C₂ material, suggesting the PDDA-NPCNs/Ti₃C₂ hybrids are synthesized successfully.





Table S1.	Textural	properties	of the as-pre	nared ex-Ti ₂ C ₂	PDDA-NPCNs and	PDDA-NPCNs/Ti ₂ C ₂	materials respectively
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material	Surface area (m ² g ⁻¹)	Pore size (nm)	Pore volume (m ³ g ⁻¹)	Micro-pore volume (m ³ g ⁻¹)	Meso-pore volume (m ³ g ⁻¹)
ex-Ti ₃ C ₂	44.20	8.51	0.188	0.016	0.172
PDDA-NPCNs	740.30	4.53	1.675	0.285	1.390
PDDA-NPCNs/Ti ₃ C ₂	147.87	10.94	0.809	0.053	0.756

To investigate the structure, such as surface area, pore size distribution and pore volume, N₂ adsorptiondesorption analysis is performed as shown in **Fig. S6**. From the BET results of PDDA-NPCNs in **Fig. S6a**, a typical type IV isotherm shown with a hysteresis in high pressure range (P/P₀~1) corresponds to the existence of meso-pores, and rapid rise of adsorption at low pressure range (P/P₀~0) reveals the existence of a large amount of microspores. Actually, the pore volume of micro-pores and meso-pores are 0.285 and 1.39 cm³ g⁻¹ respectively. PDDA-NPCNs possess high surface area of 740.30 m² g⁻¹, which could contribute to rapid electrolyte absorption during cycling process. The pore-size distribution curve based on BJH method in **Fig. S6b** presents narrow pore-size distribution concentrated on 4.0 nm, indicating that there are large amount of mesopores within this range. Meanwhile, the HK curve in **Fig. S6c** for PDDA-NPCNs demonstrates most of the micro-pores distributed at about 0.55 nm. Moreover, ex-Ti₃C₂ and **PDDA-**NPCNs/Ti₃C₂ hybrids exhibit a type IV isotherm with an obvious hysteresis loop, indicating the presence of mesoporous characteristics. However, the ex-Ti₃C₂ manosheets display surface area of only 44.2 m² g⁻¹ and pore volume of 0.188 cm³ g⁻¹. The PSD plots of ex-Ti₃C₂ material concentrated on 8.51 nm.



Figure S7. CV curves of (a) ex-Ti₃C₂, (b) PDDA-NPCNs and (c) PDDA-NPCNs/Ti₃C₃ anodes for PIBs in the potential range of 0.01-3.00 V (vs. K⁺/K) at a scan rate of 0.1 mV s⁻¹, respectively.

CV profiles for the first five cycles of $ex-Ti_3C_2$ anode are illustrated in **Fig. S7a**, and the cathodic scan in the first cycle is different from the following cycles. The cathodic reduction peaks at 1.39 and 0.51 V in the initial cycle are observed while disappear in the subsequent cycles, 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.¹⁴⁻¹⁶ The broad anodic peaks at 0.56 and 2.8 V can be attributed to K⁺ extraction from Ti_3C_2 layers, and the reversible reactions between the K⁺ and surface functional groups. In the following cycles, CV curves exhibit excellent reproducibility, indicative of exceptional electrochemical reversibility of ex-Ti₃C₂ anode for PIBs.

CV curves for PDDA-NPCNs anode as shown in **Fig. S7b**, in the first cathodic scan, the irreversible peak at 0.48 V, which vanishes in the subsequent scans, can be attributed to the decomposition of the electrolyte and formation of the SEI layer.¹² Subsequently, a broad peak is observed between 0 and 1.0 V, which can be ascribed to the combined effects of the reactions between the K^+ and N functional groups, and the insertion of

Comment [C]: PDDA-NPCN/Ti₃C₂ Comment [C]: PDDA-NPCN/Ti₃C₂ Comment [C]: PDDA-NPCN/Ti₃C₂ Comment [C]: PDDA-NPCN/Ti₃C₂ K^+ into the carbon structure.^{17, 18} In the following anodic scans, a broad peak is observed between 0.2 and 0.9 V, which is ascribed to the combined effects of the extraction of K^+ from the carbon layers, and the reversible reactions between the K^+ and N functional groups. During the subsequent cycles, the CV curves overlap, indicating the good reversibility of the electrode.

As depicted in **Fig. S7c**, the cathodic scan of PDDA-NPCNs/Ti₃C₂ anode in the first cycle is different from the following cycles. A broad peak is observed between 0 and 1.5 V in the first cathodic process, which can be ascribed to the combined effects of the reactions between the K⁺ and surface functional groups, the decomposition of electrolyte and formation of the SEI layer, and the stepwise insertion of K⁺ into the Ti₃C₂ and NPCNs to form K-intercalated compound.^{14, 15, 18-20} In the following anodic scans, a broad peak is observed between 0.2 and 1.0 V, which is ascribed to the combination of multiple charge storage mechanisms with the stepwise extraction of the K⁺ from K-intercalated compound and Ti₃C₂ layers, and the reversible reactions between the K⁺ and surface functional groups. Importantly, during the subsequent cycles, the CV curves almost overlap, suggesting a potentially stable cycling capability.



Figure S8. Rate performance at different current densities for PDDA-NPCNs/Ti₃C₂-1, PDDA-NPCNs/Ti₃C₂-2 and PDDA-NPCNs/Ti₃C₂-3 anodes.

Table S2 Potassium storage performance comparison between present works with those of previously reported Ti_3C_2 -based and carbonaceous anodes materials.

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Electrode material	Voltage	Current density	/ Initial	Cycling Stability(mAh g ⁻¹)	Ref
	range (V)	(mA g ⁻¹)	CE (%)		#
Ti ₃ C ₂	0.01-3.5	100	43.0	45 (30.8% after120 cycles)	14
a-Ti ₃ C ₂	0.01-3.0	20	27.1	98 (72.1% after 20 cycles)	15
Ti ₃ CNT _z	0.005-3.0	20	28.4	75 (37.1% after 100 cycles)	16
MXene@Sb	0.01-1.2	50	57.3	516.8 (65.3% after 100 cycles)	21
MoSe ₂ /MXene@C	0.01-3.0	200	54.2	355 (55.4% after 100 cycles)	22
N doped porous C	0.01-3.0	100	43.1	342.8 (90.9% after 500 cycles)	12
Graphite	0.01-1.5	140	56.4	100 (50.8% after 50 cycles)	23
RGO	0.01-2.0	10	50	150 (88.2 after 175 cycles)	18
P,O doped graphene	0.01-3.0	50	22.6	474 (83.7% after 50 cycles)	24
N doped porous C	0.001-3.0	50	30.3	296.8 (84.9% after 100 cycles)	25
N doped graphene	0.01-3.0	50	37.3	320 (90.8% after 60 cycles)	26
Expanded graphite	0.01-3.0	50	81.6	228 (105.1% after 200 cycles)	27
Hard carbon	0.001-3.0	50	25.0	230.6 (76.1% after 100 cycles)	28
Activated carbon	0.01-2.0	200	74.3	100.3 (63.0% after 100 cycles)	29
PNHC	0.01-3.0	200	56.9	360.6 (80.1% after 100 cycles)	19

Comment [C]: PDDA-NPCN/Ti₃C₂

Comment [C]: PDDA-NPCN/Ti₃C₂-1, PDDA-NPCN/Ti₃C₂-2 and PDDA-NPCN/Ti₃C₂-3

N,O doped porous C	0.01-3.0	50	38.7	266 (76.0% after 100 cycles)	30
Carbon nanoparticles	0.01-3.0	200	50.2	270 (91.2 after 300 cycles)	31
This work	0.01-3.0	100	65.2	429.4 (63.0 after 300 cycles)	

Comment [C]: PDDA-NPCN/Ti₃C₂

Table S3 Long-term cycling performance comparison between present works with those of previously reported anodes materials.

Electrode material	Voltage range	Current density	Reversible	Cycle	Ref
	(*)	(mA g ⁻¹)	capacity(mAh g ⁻¹)	number (N)	#
a-Ti ₃ C ₂	0.01-3.0	200	42	500 cycles	15
MXene@Sb	0.01-1.2	500	214.3	500 cycles	21
MoSe ₂ /MXene@C	0.01-3.0	1000, 2000, 5000	317, 243, 207	300 cycles	22
N doped porous C	0.01-3.0	1000, 2000, 5000	226.1, 194.0, 144.4	1000 cycles	12
P,O doped graphene	0.01-3.0	500,1000, 2000	385,235,160	600 cycles	24
N doped porous C	0.001-3.0	500	121.3	1000 cycles	25
N doped graphene	0.01-3.0	500	150.0	500 cycles	26
Hard carbon	0.001-3.0	1050	123	1100 cycles	28
PNHC	0.01-3.0	1000	270.4	1000 cycles	19
N,O doped porous C	0.01-3.0	1000	104.3	1000 cycles	30
Carbon nanoparticles	0.01-3.0	1000	190	4000 cycle	31
Graphitic carbons	0.25-2.0	2000	95	1000 cycles	32
CNFs	0.005-3.0	279	170	1900 cycles	33
This work	0.01-3.0	1000, 2000	252.2, 151.2	2000 cycles	

Table S4. The ion diffusion coefficient comparison between present works with those of previously reported anodes materials.

material	$D_{Li}/D_{Na}/D_K \ (cm^2 \ S^{-1})$	Technique	Ref#
Pure Si	$D_{li} - 4.2 \times 10^{-16}$	EIS	34
PG-Si	$D_{li} - 2.6 \times 10^{-15}$	EIS	34
Amorphous carbon	$D_{li} - 2.5 \times 10^{-15}$	EIS	35
np-Bi75Ni25	$D_{Na} - 4.3 \times 10^{-16}$	EIS	36
np-Bi ₅₀ Ni ₅₀	$D_{Na} - 7.6 \times 10^{-16}$	EIS	36
Sb@Co(OH)2	$D_{Na} - 8.2 \times 10^{-16}$	EIS	37
NCRO	$D_k - 10^{-13} \sim 10^{-12}$	GITT	38
ex-Ti ₃ C ₂	$D_k - 1.0 \times 10^{-14}$	EIS	This work
PDDA-NPCNs	$D_k - 2.0 \times 10^{-14}$	EIS	This work
PDDA-NPCNs/Ti ₃ C ₂	$D_k - 1.9 \times 10^{-14}$	EIS	This work



Figure S9. (a) CV curves of ex-Ti₃C₂ anode at various scan rates from 0.1 to 1.0 mV s⁻¹. **(b)** The corresponding *b*-value using the relationship between the peak current and scan rate.





Figure S10. (a) CV curves of PDDA-NPCNs anode at various scan rates from 0.1 to 1.0 mV s⁻¹. (b) The corresponding *b*-value using the relationship between the peak current and scan rate.



Figure S11. Charge transfer mechanism of PDDA-NPCNs/Ti₃C₂ anode.



Figure S12. Ex situ SEM images of (a-c) ex-Ti₃C₂, PDDA-NPCNs and PDDA-NPCNs/Ti₃C₂ anodes at fully charge state after

300 cycles.



Figure S13. Ex situ TEM images of PDDA-NPCNs/Ti₃C₂ anode at fully charge state after 300 cycles, the corresponding elemental mappings and the typical EDS spectrum of Ti, C, O, F, N and K.



Figure S14. Ex situ XPS spectra of the PDDA-NPCNs/Ti₃C₂ anode at different states during the first potassiation/depotassiation process. (a) Full spectra. (b-e) High-resolution spectra of Ti 2p, C1s, N 1s and O 1s.

Ex situ XPS survey spectra as shown in **Fig. S14a** indicate that the fresh [PDDA-NPCNs/Ti₃C] anode is mainly composed of Ti, C, O, F and N. After the first potassiation/depotassiation process, the new peaks at the binding energies of 292 and 378 eV are assigned to the K 2p and K 2s.¹⁵ As displayed in the fresh anode (**Fig. S14b**), the Ti 2p3/2 and Ti 2p1/2components locate at 458.3 and 464.3 eV, respectively, which coincides with the previously reported studies.¹¹ When discharged to 0.01 V, the Ti 2p peaks shift to lower binding energies, implying the changes in the valence states of Ti from +4 to +3 or +2 during the potassiation process. When charged to 3.0 V, the Ti 2p peaks recover to their initial state, indicating the reversible redox reactions of the Ti⁴⁺/Ti³⁺ or Ti⁴⁺/Ti²⁺ couples. It is noteworthy that the Ti²⁺ cannot fully recover in the fully charged state, which indicates that the partial Ti²⁺ is irreversible and leads to the irreversible capacity during the first potassiation/depotassiation process.³⁹ As mentioned before, the sp2 carbon (C=C/C-C) at 284.7 eV in the C 1s

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spectra (Fig. S14c) correspond to graphite carbon. Therefore, the fully discharged PDDA-NPCNs/Ti₃C₂ anode shows weakest intensity for sp2 C, revealing the insertion of K⁺ in accordance with the ex situ Raman result. It should be noticed that the peaks for C 1s exhibit a 0.1 eV shift to higher binding energy at the fully discharged state, corresponding to the formation of C-K bonds.²³ However, the C 1s spectra become complicated and some new peaks appear associated with SEI component, which is due to the partial decomposition of the electrolyte.³⁹ When charged to 3.0 V, the C-K bonds are disconnected firstly, and K⁺ extracts from the anode. Furthermore, the binding energy of the sp2 carbon (C=C/C-C) does not shift back to initial state again, demonstrating that the K⁺ can partially be reversibly from the PDDA-NPCNs/Ti₃C₂ anode. After discharge 0.01V, the N 1s peak (Fig. S14d) shifts to higher binding energies compared with the fresh PDDA-NPCNs/Ti₃C₂ anode, indicating the interaction of K^+ within the conductive nature of the framework. More (significantly, when charged to 3.0 V, the N 1s peak recovers to their initial state, which clearly demonstrates the reversibility of the charge/discharge process. The O1s spectra are used to analyze the composition of the SEI layer. As illustrated in Fig. S14e, the existence of SEI component can also be observed, corresponding to the peak at 531.6 eV. As we know that the surface adsorption behavior appears from the initial discharge and continues in the cycles, it is further verified that the potassium storage mechanism of the $PDDA-NPCNs/Ti_3C_2$ anode in the high potential slope region is the adsorption behavior of the material surface rather than the interference caused by the SEI layer formation.



Figure S15. A possible electrochemical process of the PDDA-NPCNs/Ti₃C₂ anode during the potassiation/depotassiation process. The PDDA and water molecules between the layers are not shown here for clarity.

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 Comment [C]: PDDA-NPCN/Ti₃C₂

 Comment [C]: PDDA-NPCN/Ti₃C₂





Figure S16. The most stable adsorption configurations for a single K^+ adsorbed on the **(a)** Ti₃C₂, **(b)** NPCNs and **(c-d)** Different adsorption sites in NPCNs/Ti₃C₂ hybrids and **(e)** their corresponding adsorption energies. The PDDA and water molecules between the layers are not shown here for clarity.



Comment [C]: NPCN/Ti₃C₂

Figure S17. Calculated charge density differences for a single K^+ adsorbed on the (a) Ti_3C_2 , (b) NPCNs and (c-d) Different adsorption sites in NPCNs/Ti_3C_2 hybrids. Cyan and yellow regions show the depletion and accumulation of electrons, respectively. The PDDA and water molecules between the layers are not shown here for clarity.

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In order to unify the abbreviation of composite name in the text and figures, the ESI figures also make corresponding changes.



Figure S6.



Figure S8.



Figure S16.



Figure S17.