Supporting Information

Simultaneous derivatization and exfoliation of multilayered $Ti_3C_2T_x$ MXene into amorphous TiO_2 nanosheets for stable K-ion storage

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Experimental Section

Materials Preparation

Synthesis of multilayered Ti$_3$C$_2$T$_x$

The synthesis method was adapted from a previous report using the molten-salt approach **[S1]**. Typically, Ti$_3$AlC$_2$ (200~300 mesh) and CuBr$_2$ were mixed with a molar ratio of 1:6. And the mixture was transferred into a corundum crucible that was placed in a tube furnace filled with argon gas. The mixture was heated at 600°C for 6 hours, followed by a natural cooling procedure to room temperature. During this procedure, Al atoms layers in Ti$_3$AlC$_2$ were etched by melt CuBr$_2$, obtaining the multilayered Ti$_3$C$_2$T$_x$. Note that, the CuBr$_2$ was reduced to Cu that remained as impurities in the obtained multilayered Ti$_3$C$_2$T$_x$, which could be removed upon the conversion of multilayered Ti$_3$C$_2$T$_x$ into a-2D-TiO$_2$@C (see details below).

Synthesis of a-2D-TiO$_2$@C.

1g of the obtained multilayered Ti$_3$C$_2$T$_x$ was dispersed in 100 mL of (NH$_4$)$_2$S$_2$O$_8$ aqueous solution (0.5 mol L^{-1}) and stirred for 8 hours. The final product was collected by centrifugation and washing with deionized water and ethanol for at least three times, respectively, followed by vacuum-drying at 80°C overnight. During the oxidation, multilayered Ti$_3$C$_2$T$_x$ was simultaneously exfoliated and derived into a-2D-TiO$_2$@C. Meanwhile, the residual Cu impurities were oxidized into soluble Cu^{2+}, which was removed in the washing steps.

Materials Characterization

X-ray photoelectron spectroscopy (XPS) measurements were performed using a

Thermo Scientific K-Alpha spectrometer with Al Kα radiation. Thermogravimetric analysis was carried out using a Thermal analyzer (Netzsch, TG209 F3) in the air atmosphere with a heating rate of 5 °C min^{-1} from room temperature to 600 °C. Scanning electron microscopy (SEM) images were acquired using a Sirion microscope with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained using a Thermo Fisher Talos F200X microscope with an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were recorded using a Haoyuan DX-2700BH diffractometer. Raman spectra were collected using a WITec Alpha 300R spectrometer with a laser wavelength of 532 nm at a power of 0.14 mW. Nitrogen adsorption-desorption isotherms were recorded using a Micromeritics ASAP 2460 analyzer. Inductively coupled plasma optical emission spectrometer (ICP-OES) tests were performed using Thermo Fisher iCAP PRO.

Electrochemical Measurements

CR2032 coin-type cells were assembled in an argon-filled glove box for both half cells and full cells. In half cells, K metal foils and a-2D-TiO$_2$@C were used as the counter electrodes and working electrodes, respectively. In full cells, a-2D-TiO$_2$@C and Prussian blue (KPB) were employed as anode electrodes and cathode electrodes, respectively. To prepare a-2D-TiO$_2$@C electrodes, active materials (a-2D-TiO$_2$@C), conductive additive (carbon black), and binder (sodium carboxy methyl cellulose) were mixed in solvent (deionized water) with the mass ratio of 7:2:1 to form a homogenous slurry. The slurry was coated on Cu foil and then vacuum-dried

at 80°C for 12 h. The preparation of KPB cathode electrodes was similar to that of a-2D-TiO$_2$@C ones, except that KPB was used as active materials, polyvinylidene fluoride was used as the binder, and N-methylpyrrolidone was used as the solvent. In addition, the KPB-based slurry was coated on Al foil, followed by vacuum-drying at 80°C for 12 h. The coated Cu foils and Al foils were punched into small discs with diameters of 12 and 10 mm, respectively. The average mass loadings of active materials are approximately 0.6 mg cm^{-2} (for KPB) and 1 mg cm^{-2} (for a-2D-TiO$_2$@C). The electrolyte and separator were 4M KFSI in EC/DEC (1:1, volume ratio) and glass fiber membrane (Whatman, GF/D), respectively. 70 μL of electrolyte was used for each full cell. The specific capacity of full cells was calculated based on the mass of KPB. Galvanostatic charge-discharge (GCD) tests were performed on a Neware battery test system (MIHW-200-160CH). Cyclic voltammetry (CV) was conducted on an electrochemical workstation (CHI660E, Shanghai Chenhua Instruments) in the voltage range of 0.01-3.0 V. Full cells were tested in the voltage range of 1.1-3.6 V. All cells were stood for 24h before testing. All electrochemical tests were carried out at 25°C.
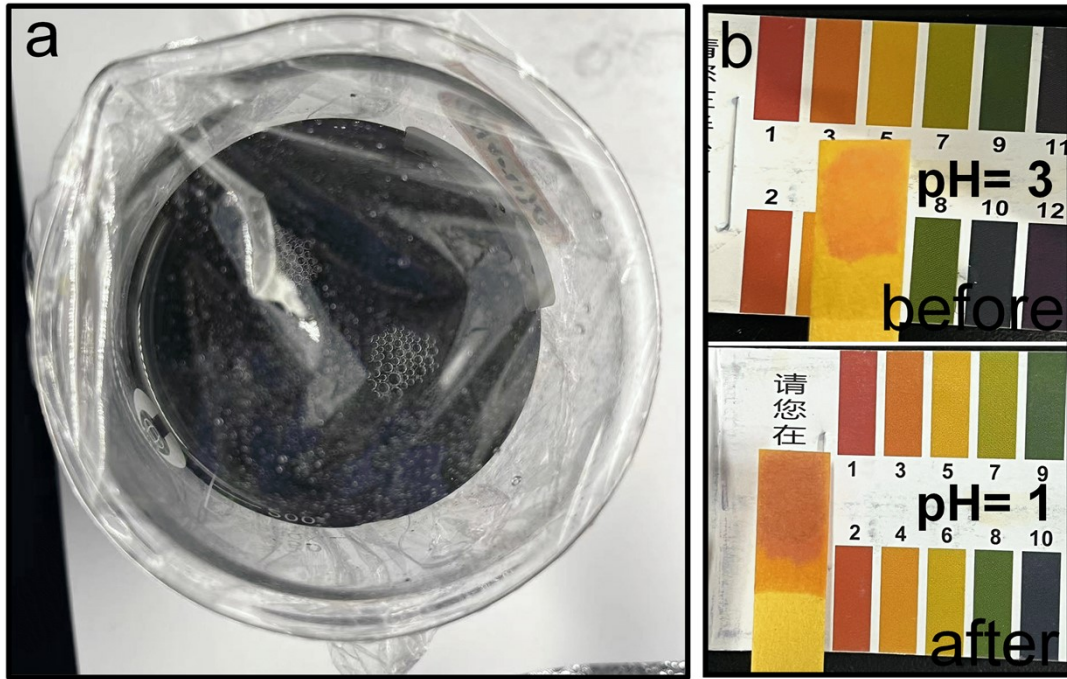
Fig S1. (a) Bubbles produced during the reaction (without stirring), (b) pH tests before and after the reaction.
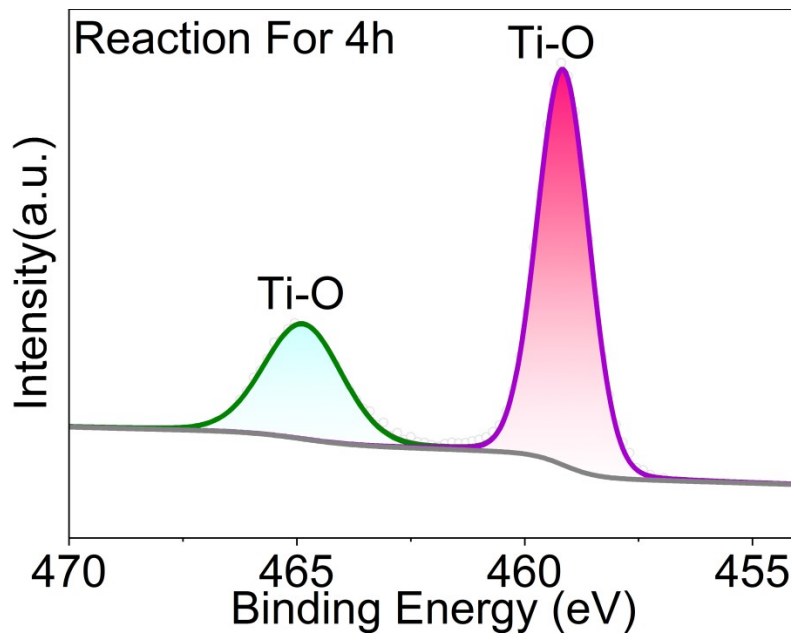

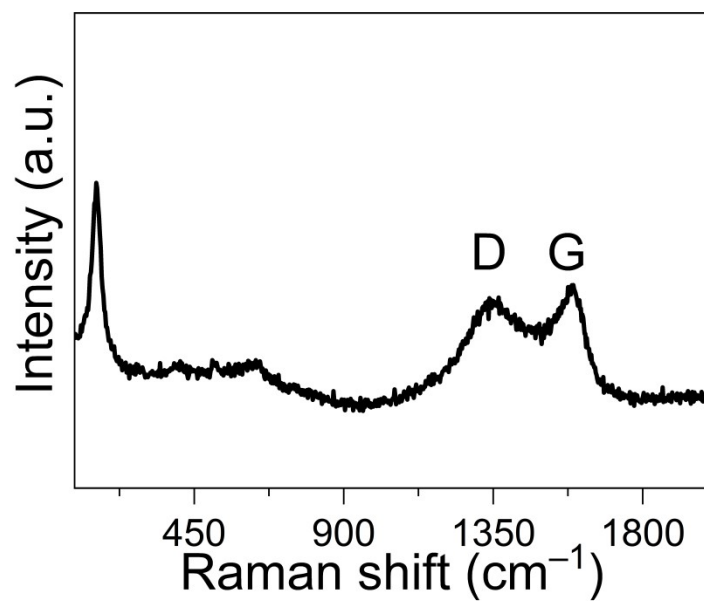**Fig S2.** Ti 2p XPS spectrum of intermediate product (react for 4h).
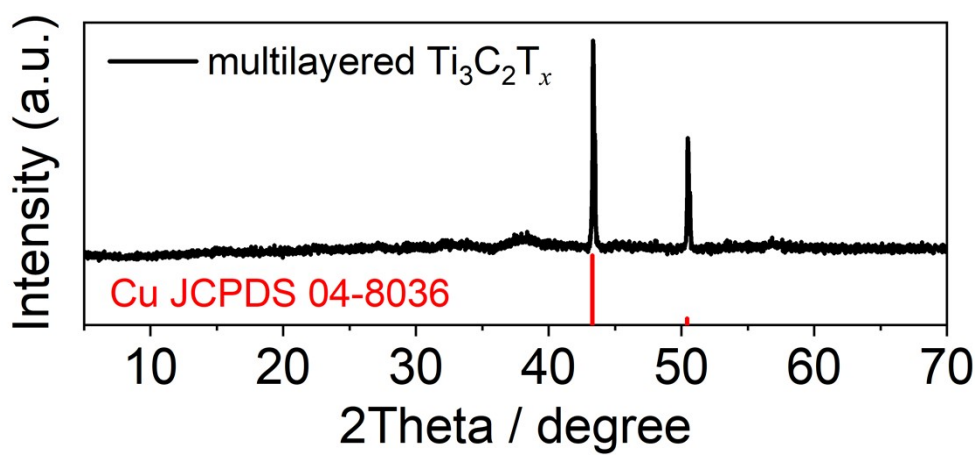
Fig S3. Raman spectrum of a-2D-TiO$_2$@C.
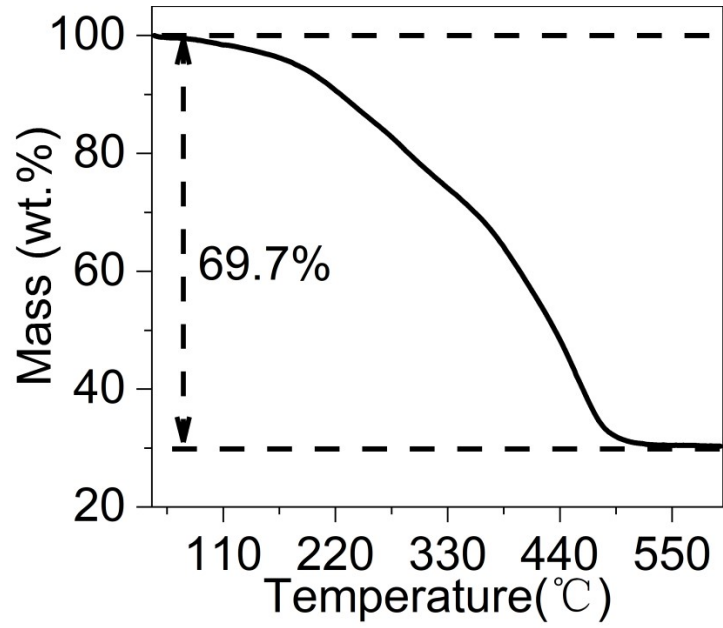

Fig S4. XRD pattern of multilayered Ti$_3$C$_2$T$_x$.

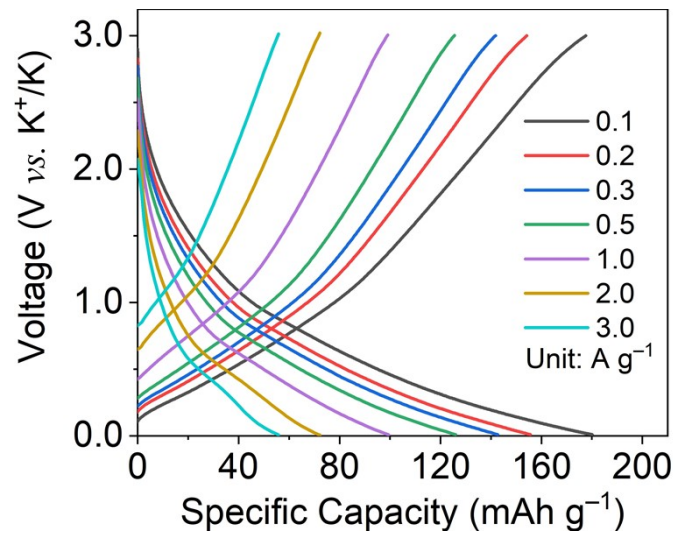**Fig S5.** TGA curve of a-2D-TiO$_2$@C under air atmosphere.

Fig S6. GCD curves of a-2D-TiO$_2$@C in half cells at different current densities.

Table S1. Comparison between a-2D-TiO$_2$@C and other TiO$_2$-based anode materials performances in K-ion batteries.

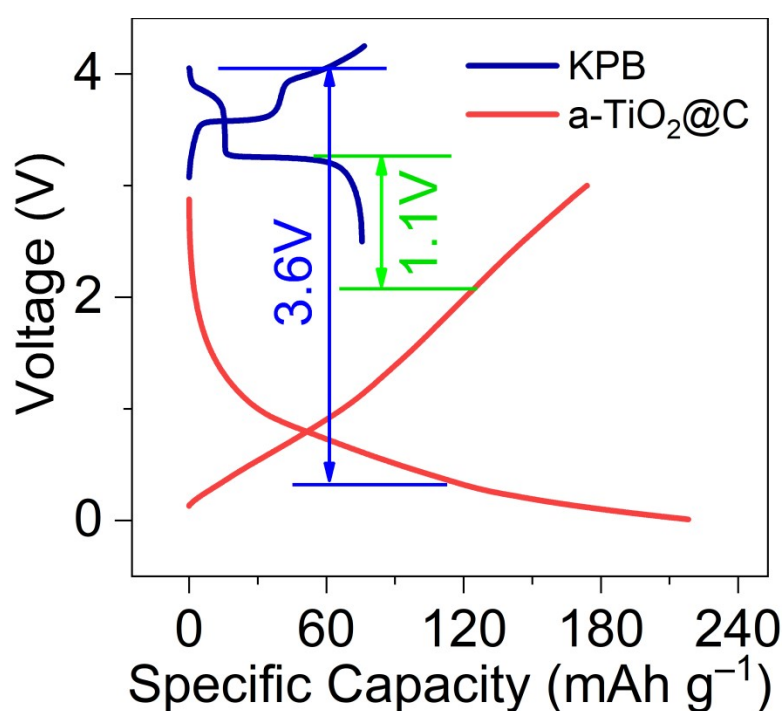| TiO$_2$-based Material	Current density (A g^{-1})	Cycle number (n)	Specific capacity (mAh g^{-1})	Reference
a-2D-TiO$_2$@C	1.0	2000	96.1	**Our work**
MOF derived TiO$_2$@C	0.2	300	153	**[S2]**
LL-KTO	0.1	1800	201	**[S3]**
TiO$_2$/C	0.05	1000	259	**[S4]**
TiO$_2$/RGO	1	1000	85	**[S5]**
TiO$_2$/CN	0.05	500	193.2	**[S6]**

Fig S7. GCD profiles of a-2D-TiO$_2$@C anode and KPB cathode in half cells at 0.1 A g^{-1}.
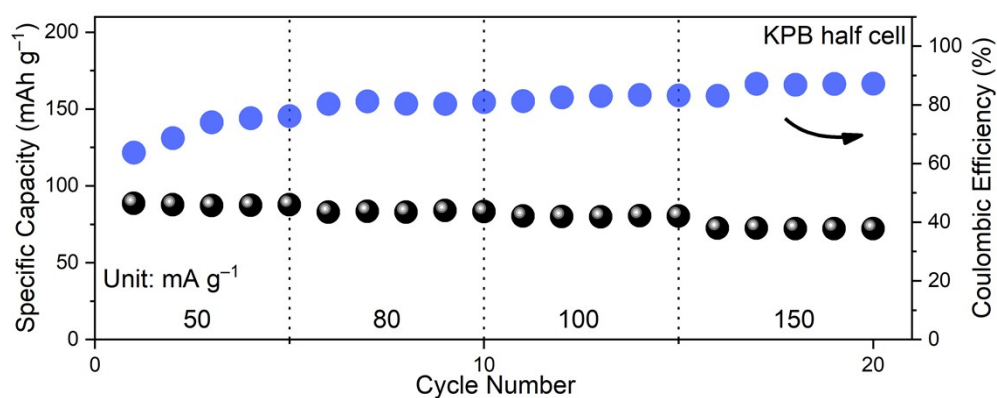

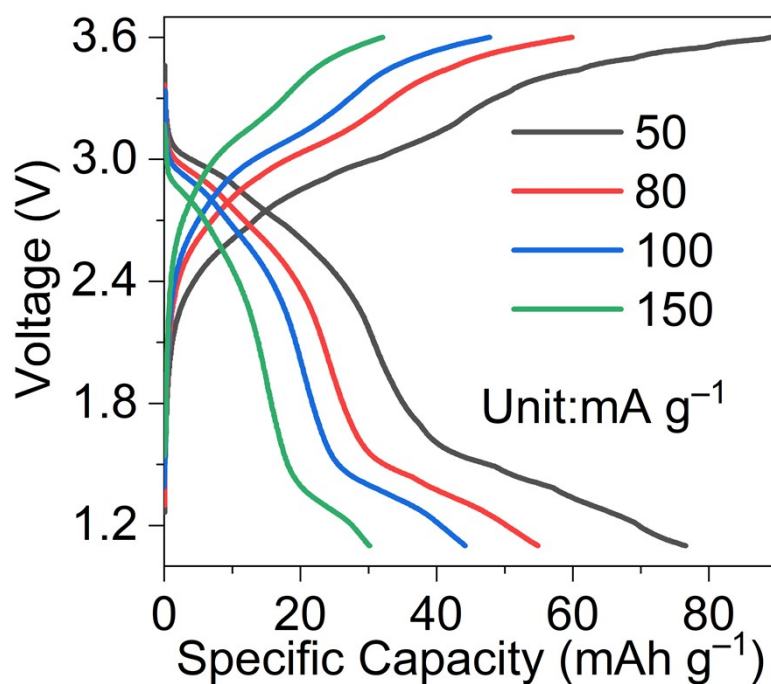**Fig S8.** Rate performance of KPB-based half cells at different current densities.

Fig S9. GCD curves of KPB‖a-2D-TiO$_2$@C full cells at different current densities.
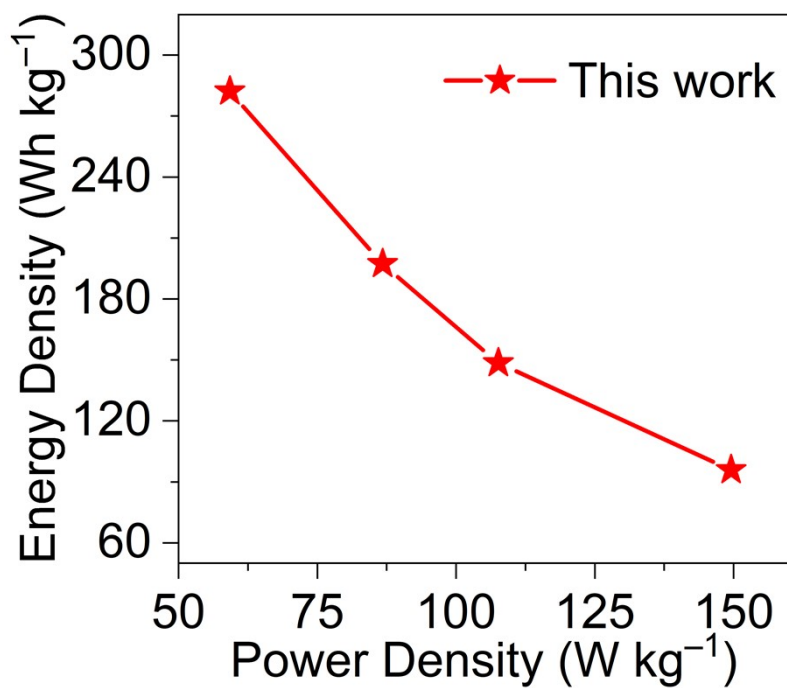

Fig S10. Ragone plots for KPB‖a-2D-TiO$_2$@C full cells.

Reference

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