Supplementary Information (SI) for ChemComm.

Supporting Information

Experimental

1. Synthesis

V_2CT_x MXene was prepared by etching V_2AlC using a NaF and HCl solution. Specifically, 1.0 g of V_2AlC (400 mesh, purity > 98%, purchased from Foshan Xinxene Technology Co., Ltd.) was gradually added to a solution containing 1.0 g of NaF (purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.) and 20 mL of HCl (36.0%-38.0%, purchased from Guangdong Guangshi Reagent Technology Co., Ltd.) in a Teflon container. The mixture was transferred to a hydrothermal reactor and etched at 90 °C for 72 h. After etching, the resulting suspension was centrifuged at 4500 r/min and washed repeatedly with deionized water. The supernatant was discarded after each centrifugation cycle until the pH of the supernatant reached approximately 7. Finally, the black precipitate was dried at 60°C for 12 h to remove residual moisture, yielding the final V_2CT_x powder.

The VCT@Na electrode was fabricated via a mechanical mixing method, and the equipment used was a precision manual press (J03-0.3A). Metallic Na and V_2CT_x powder were combined at a mass ratio of 10:1. The V_2CT_x powder was incrementally and mechanically rolled into metallic Na until fully incorporated. The resultant composite was pressed into thin sheets and used as electrodes for electrochemical measurements. Each electrode was cut into a disc with the diameter of 14 mm. Bare Na electrodes were directly prepared by cutting metallic Na into a disc with the diameter of 14 mm.

For the fabrication of full cell, we used NVP (purchased from Dongguan Canrd Co., Ltd.) as cathode material. For the preparation of electrode, the NVP, Super P, and polyvinylidene fluoride (PVDF) were mixed in an 8:1:1 mass ratio. An appropriate amount of N-methyl-2-pyrrolidone was added to form a uniform slurry, which was then coated onto Al foil. After drying, the electrode was punched into a disc with the diameter of 14 mm for full cell assembly. Generally, the loading of NVP active material on each disc was 1.5 mg. For the high loading condition, the loading of NVP active material on each disc was 13.35 mg.

2. Characterization

The morphology of V_2CT_x was characterized using scanning electron microscopy (SEM, SU8220) and transmission electron microscopy (TEM, JEM 2100F). The crystal structure of V_2CT_x was analyzed by X-ray diffraction (XRD, PANalytical X'Pert PRO, Cu-Kα, λ = 0.15418 nm), Raman spectra (inVia-58P056) using a 532 nm laser excitation source. The surface chemical states of V_2CT_x were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). Optical microscopy (Leica) was employed to examine the morphology of separators and electrode surfaces. For in situ observations, a portable optical microscope was integrated with an electrochemical reaction cell, enabling real-time analysis of sodium deposition on electrodes at a current density of 1 mA cm^{-2} during open-cell operation.

3. Electrochemical measurement

All electrochemical performance tests were conducted using CR2032 coin cells assembled in an argon-filled glovebox (Etelus Lab2000, H_2O < 0.1 ppm, O_2 < 0.1 ppm). Glass fiber was used as the separator. The electrolyte comprised 1 M $NaClO_4$ dissolved in a 1:1 volume ratio of ethylene carbonate/propylene carbonate with 5% fluoroethylene carbonate additive. Symmetrical cells were constructed using identical electrodes on both sides, while asymmetric cells used carbon paper as the counter electrode and either bare Na or VCT@Na as the working electrode, forming bare Na||CP and VCT@Na||CP configurations. Full cells were assembled with either bare Na or VCT@Na as the anode paired with an NVP cathode. The cycling performance of cells were evaluated by a Neware BTS-4000 battery test system at 0.5 mA cm^{-2}/0.5 mAh cm^{-2} except as otherwise noted. For full cells, cycling performance were conducted within a voltage range of 2.5-3.7 V, and CV was performed on a CHI660E electrochemical workstation. EIS was conducted using a Princeton VersaSTAT3 workstation at a frequency range of 0.01~10 kHz with a 10 mV AC perturbation.

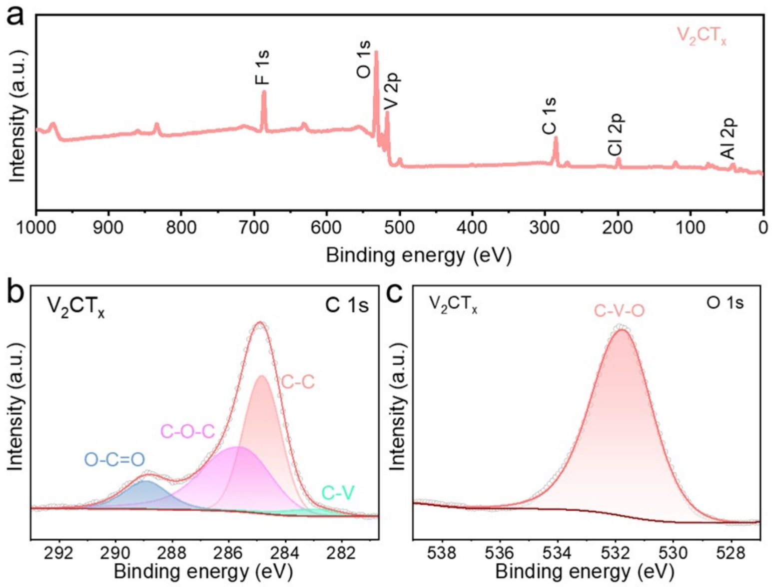

Figure S1 (a) Survey, (b) C 1s and (c) O 1s XPS spectra of V_2CT_x

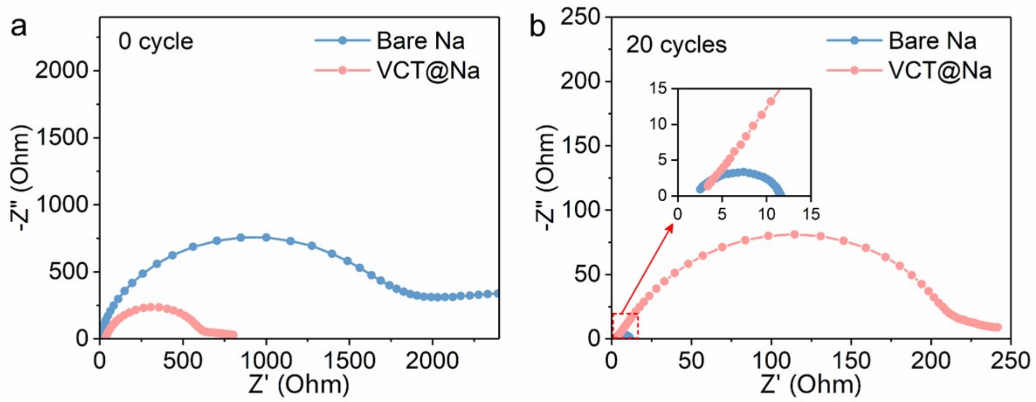

Figure S2 EIS curves of bare Na||bare Na and VCT@Na||VCT@Na cells (a) before cycling and (b) after 20 cycles at 0.5 mA cm^{-2}/0.5 mAh cm^{-2}

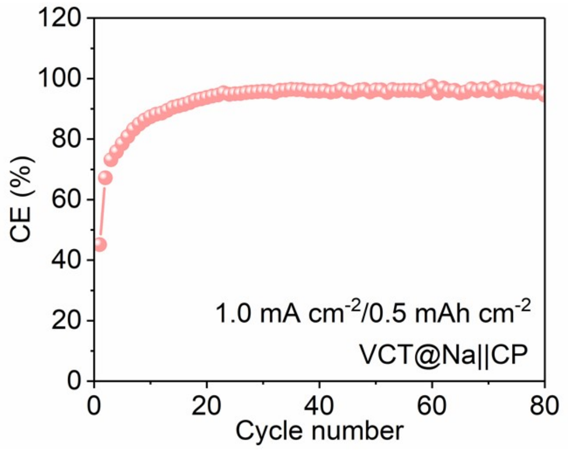

Figure S3 CE of VCT@Na||CP cell at 1.0 mA cm^{-2}/0.5 mAh cm^{-2}

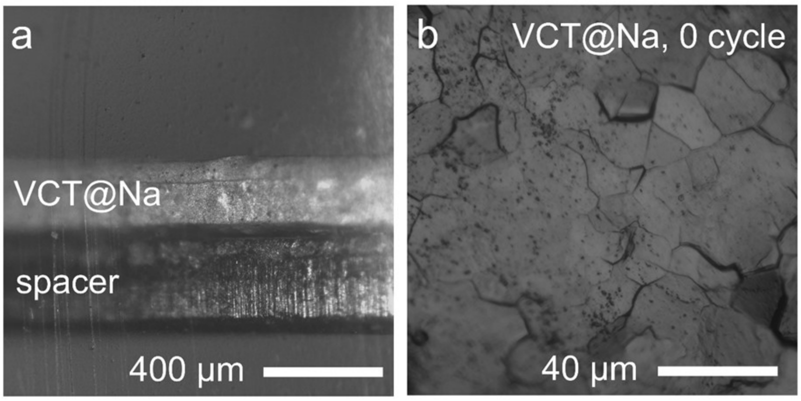

Figure S4 (a) Cross-sectional view and (b) top view optical microscope images of VCT@Na before cycling

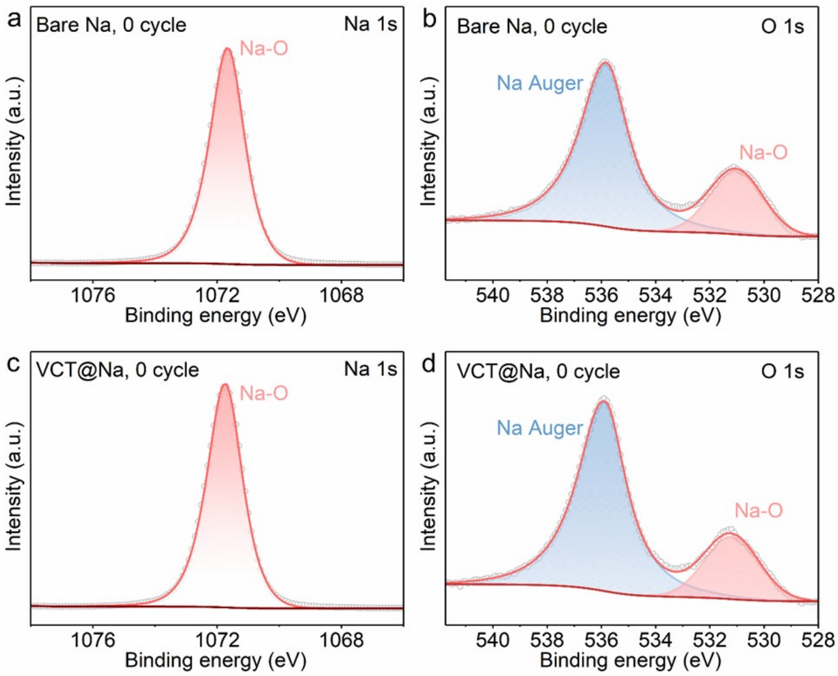

Figure S5 XPS spectra of Na 1s and O 1s of bare Na and VCT@Na before cycling

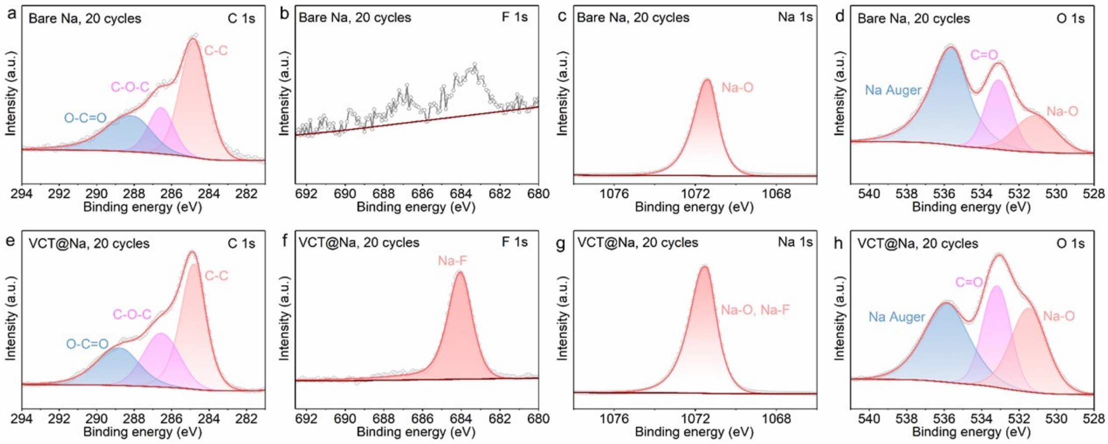

Figure S6 XPS spectra of C 1s, F 1s, Na 1s and O 1s of bare Na and VCT@Na after 20 cycles at 0.5 mA cm^{-2}/0.5 mAh cm^{-2}

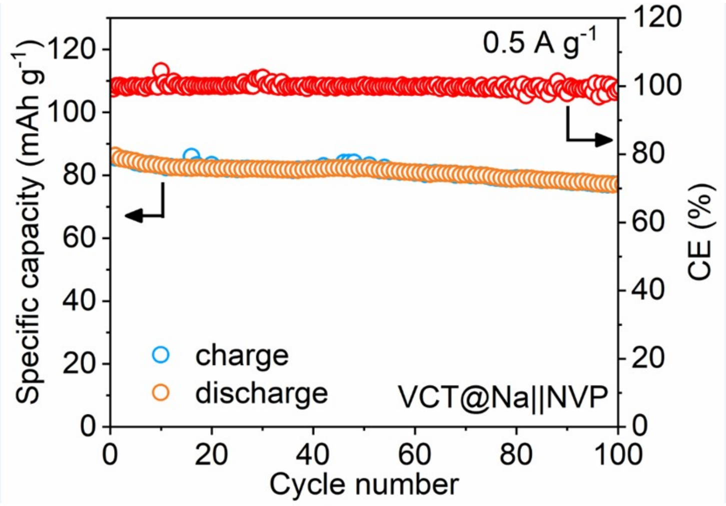

Figure S7 Cycling performance of VCT@Na||NVP cell under high loading condition at 0.5 A g^{-1}

Table S1 Cycling performance at different current densities and capacities for metal Na

Materials	Current density (mA cm^{-2})	Capacity (mAh cm^{-2})	Cycle time (h)	Polarization voltage (mV)	Reference
3D-Na_3Bi@Na	1	1	>700	~80	1
Na-CF	0.5	1	300	-	2
Na/carbon composites	1	1	200	-	3
Na@O-CF	1	1	200	<100	4
Na@r-GO	0.25	0.0625	300	-	5
VCT@Na	**0.5**	**0.5**	**>500**	**~90**	**This work**

References

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