

Supplementary information

In-situ construction of vanadium dioxide and MXene heterostructure towards high-capacity ammonium ion storage

Zeyu Cao, Jinyao Yang, Hang Ren, Jingyuan Zhang, Ying Yang, Guoyin Zhu, Yizhou Zhang, and Shengyang Dong*

Institute of Advanced Materials and Flexible Electronics (IAMFE), School of Chemistry and Materials Science, Nanjing University of Information Science and Technology, Nanjing 210044, China.

E-mail: dongsyst@nuist.edu.cn

1. Experiment section

1.1 Material preparation

VO₂@V₂C MXene is prepared by in-situ partial oxidation of V₂C MXene. Typically, 0.1 g of V₂C MXene (Nanjing Muke) was added to deionized water of 30 mL, and then 0.3 mL hydrogen peroxide (30%, Aladdin) was added. Subsequently, the mixture was transferred into a Teflon liner high pressure reactor and kept at 180 °C for 6, 12 and 24 h, respectively. Next, the precipitate was filtered and dried at 80 °C for 12 h under a vacuum condition. All the reagents are analytical-grade without further purification.

1.2 Material characterization

The morphology was characterized using scanning electron microscopy (SEM, ZEISS, Gemini300S) and transmission electron microscopy (TEM, JEOL, JEM-2100F). The crystal structure was measured by X-ray diffraction (XRD) which was obtained by using a Rigaku Ultra 250 detector with Cu K α radiation (1.5406 Å, 40 kV 40 mA). X-ray photoelectron spectroscopy (XPS; Perkin-Elmer PHI 550 spectrometer, Al, K α x-ray, 1486.6 eV) was used to determine the chemical composition. The Fourier transform infrared spectroscopy (FT-IR) were collected on Shimadzu IR Prestige-21.

1.3 Electrochemical measurements

The active material, acetylene black and polyvinylidene fluoride were mixed and ground in the weight ratio of 7:2:1 in N-methyl-2-pyrrolidone (NMP) to form a slurry, and coated on carbon cloth. The mass loading of the active substance was 1-1.5 mg cm⁻² after drying at 80 °C under vacuum for 12 h. Then 0.5 M CH₃COONH₄ (NH₄Ac) aqueous solution was prepared as the electrolyte, Ag/AgCl (1 M KCl) as the reference electrode, and assembled three-electrode cell for the electrochemical performance test. Cyclic voltammetry (CV) was performed at an electrochemical workstation (CorrTest CS-350). Galvanostatic charge/discharge (GCD) tests and galvanostatic intermittent titration technique (GITT) were performed using LANBTS cell test system. The GITT was employed to figure out the diffusion coefficient of NH₄⁺ by pulses of 10 min at a current density of 100 mA g⁻¹, followed by relaxing one hour.

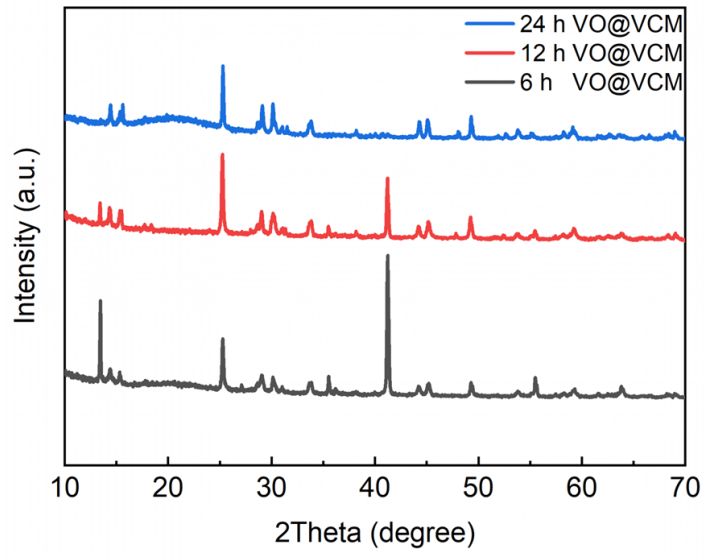


Fig. S1 XRD patterns of VO@VCM at different hydrothermal time.

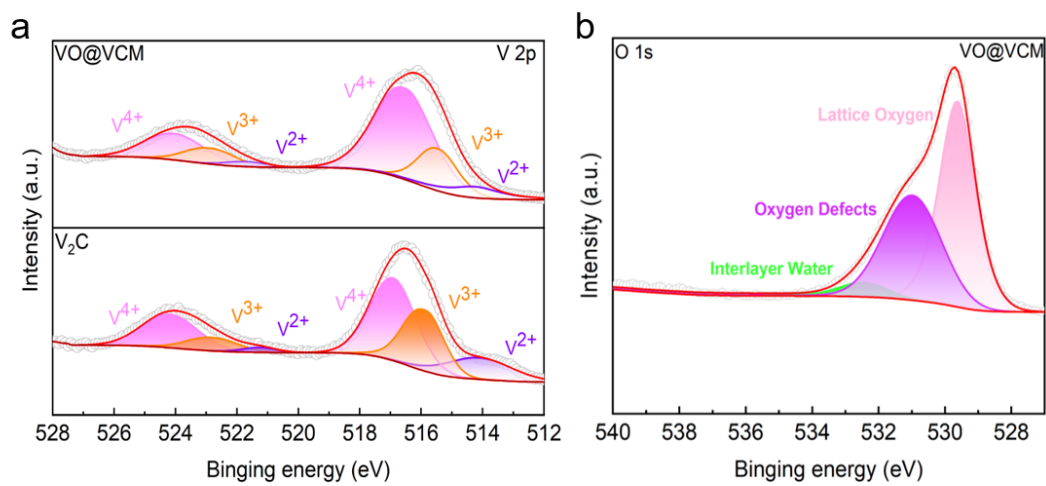


Fig. S2 XPS of (a) V 2p and (b) O 1s.

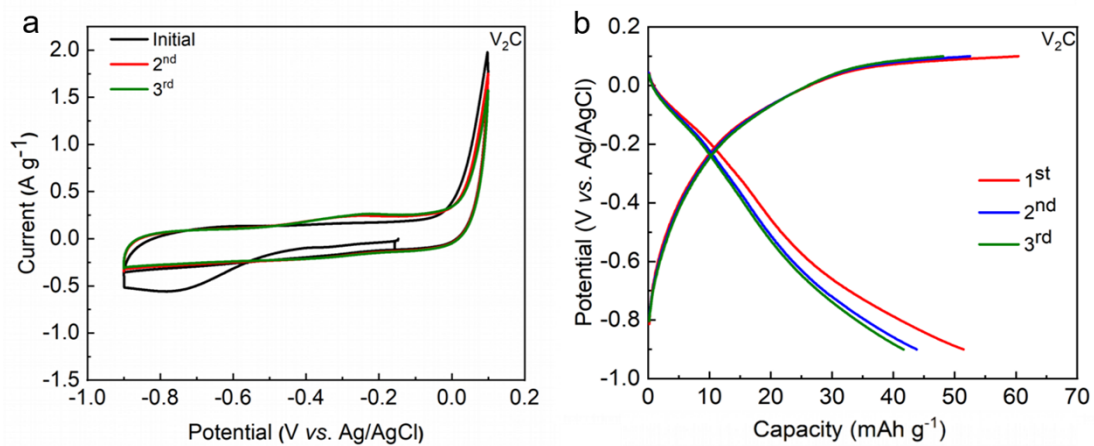


Fig. S3 (a) CV at $1\ mV\ s^{-1}$ and (b) GCD curves at $100\ mA\ g^{-1}$ of V_2C MXene.

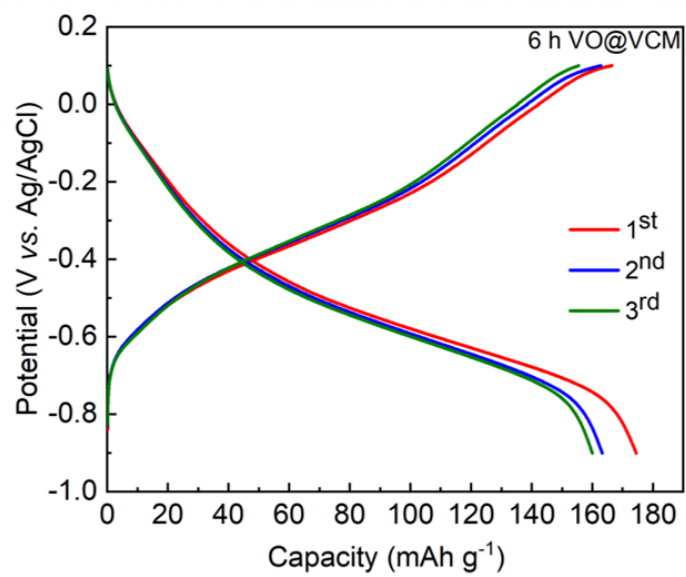


Fig. S4 First three GCD curves of 6h VO@VCM.

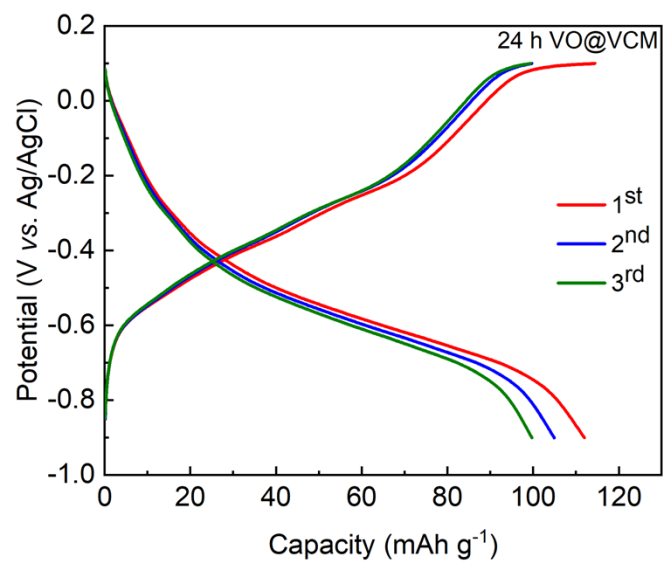


Fig. S5 First three GCD curves of 24h VO@VCM.

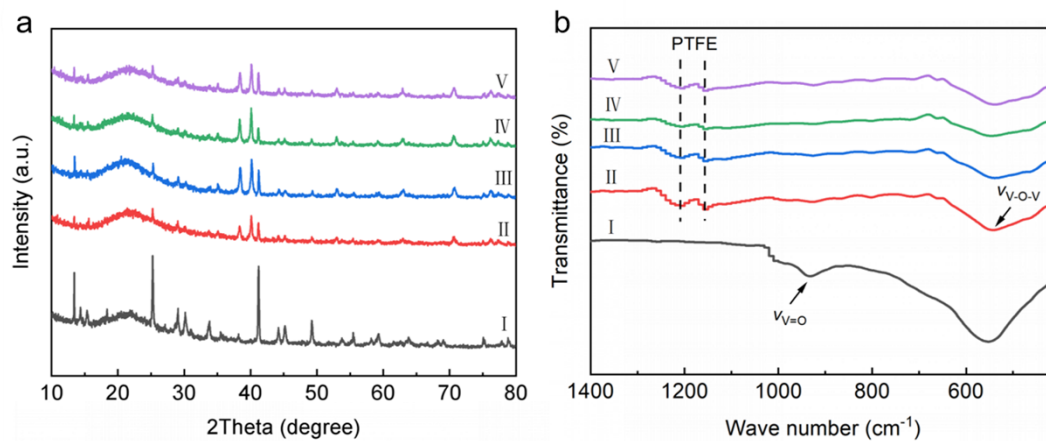


Fig. S6 (a) Ex situ XRD patterns. (b) Ex situ FT-IR spectroscopy.

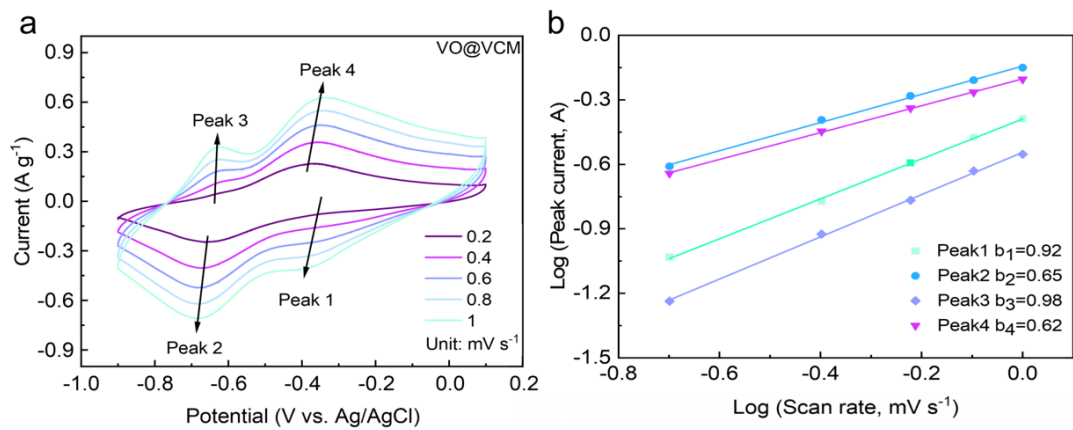


Fig. S7 (a) CV curves at different scan rates from 0.2 to 1.0 mV s^{-1} . (b) $\log(i)$ versus $\log(v)$ plots at redox peaks.

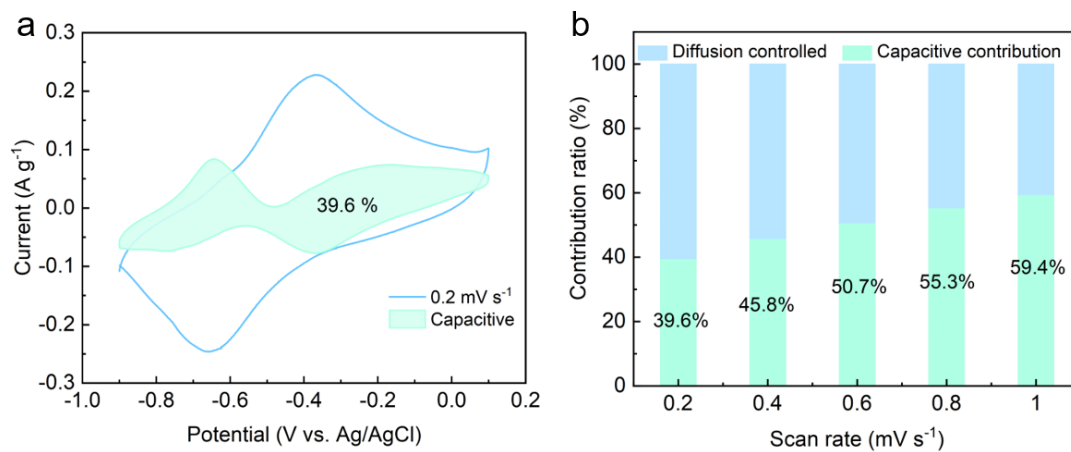


Fig. S8 (a) Capacitive contribution displayed in the shaded section at a scan rate of 1 mV s⁻¹. (b) The contribution percentage of diffusion-controlled capacities and capacitive capacities.

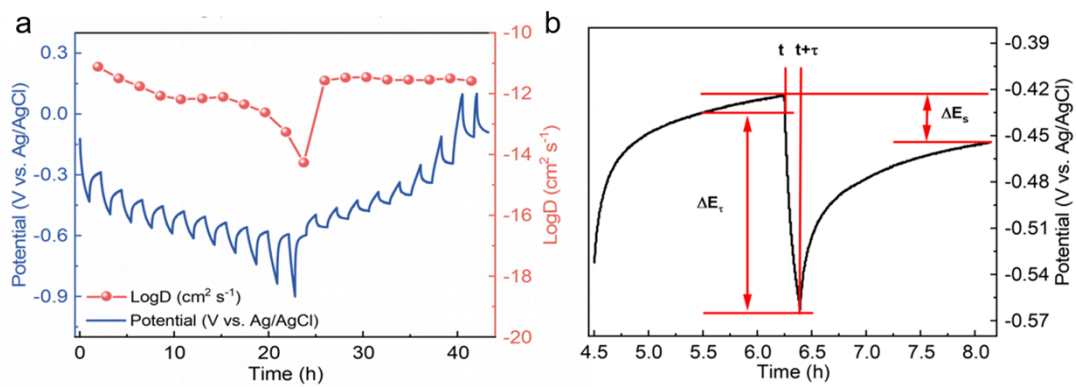


Fig. S9 (a) GCD curves in the GITT and the corresponding diffusion coefficient. (b)

Current step diagram, τ is 10 min.

Table S1. Comparison with previous reported anode materials for ammonium ion storage.

Anode material	Potential range	Electrolyte	Capacity (mAh g ⁻¹)/specific current (mA g ⁻¹)	Ref.
This work	-0.9-0.1 V vs. Ag/AgCl	0.5 M NH ₄ Ac	200/100	
		1.0 M NH ₄ Ac	147.7/100	
PNNI	-0.9 to 0.2 V vs. Ag/AgCl	0.5 M (NH ₄) ₂ SO ₄	155.6/100	S1
		1.0 M NH ₄ Cl	183.6/100	
HATP-PT COF	-1.0 to 0.3 V vs. SCE	2.0 m NH ₄ OTf@S	108.5/200	S2
K _{0.38} (H ₂ O) _{0.82} MoS ₂	-0.4-0.8 V vs. Ag/AgCl	0.5 M (NH ₄) ₂ SO ₄	50.7/500	S3
<i>h</i> -MoO ₃	-0.5-0.75 V vs. SCE	1 M NH ₄ Cl	115/1000	S4
V ₂ CT _x MXene	-1.0 to -0.1 V vs. Ag/AgCl	0.5 M NH ₄ Ac	115.9/1000	S5

References

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