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Electronic Supplementary Information (ESI)

A lamellar V_2O_3@C composite for aluminium-ion battery displaying long cycle life and low-temperature tolerance

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Experimental section

Synthesis of V-NDC precursor: The V-NDC precursor was synthesized through a two-step hydrothermal method. 3 mmol VO_2 and 1.5 mmol 1,4-naphthalene formic acid (H_2NDC, Aladdin) were dissolved in 30 mL of ultra-pure water at room temperature. The solution was stirred vigorously for 1.5 h. The uniformly mixed solution was transferred to a 50 mL polytetrafluoron reactor and maintained at 180 °C for 24 h. At last, the sample was collected, washed for three times. The product was placed in an oven at 60 °C for drying.

Synthesis of book-like lamellar V_2O_3@C: The as-prepared V-NDC precursor (0.1-0.2 g) was put loosely in a ceramic boat and calcined for 4 h under argon atmosphere in a tubular furnace. The calcining temperature was 800 °C, and the heating rate was 2 °C min^{-1}. After cooling down, the V_2O_3@C composites were obtained.

Characterization: The crystal structure was determined using XRD (Bruker D8 Advance, Copper target, Kα X-ray wavelength 1.5418 Å), field emission scanning electron microscopy (SEM, Hitachi S-8100) and transmission electron microscopy (TEM, Ht-7700, TecnaiG2 20S-Twin). In order to observe the lattice spacing, a high-resolution transmission electron microscope (HRTEM) was used. Energy dispersive X-ray spectroscopy (EDX) was used for elemental mapping to determine the elements, and the composition was analyzed by X-ray photoelectron spectroscopy (XPS, EscalAB250). The sample powders were vacuum-dried for 2 h, and then a piece of sample was prepared by pressing into a small tablet. After that, the sample tablet was put on a holder with double-sided adhesive for testing. The standard peak position of carbon at 284.8 eV was used to calibrate. In order to demonstrate the presence of carbon coating, Raman spectroscopy (Renishaw in Via) was used to measure the chemical state of the carbon layer at 532 nm. The mass content of carbon was determined by thermogravimetric analysis (TGA, Setaram Labsys Evo SDT Q600). Prior to the BET test, the sample was degassed at 120 °C for 12 h in a vacuum to remove water adsorbed on the surface, and then physical adsorption isotherms (adsorption-desorption branch) were recorded in nitrogen at 77 K using a specific surface area tester (ASAP Micromeritics Tristar 2460).

Electrochemical tests: The samples were first mixed with the book-like lamellar V_2O_3@C (70 wt%) and conductive carbon black (20 wt%),, then PVDF (polyvinylidene fluoride, 10 wt%) was added in a ratio of 7:2:1. NMP (n-methylpyrrolidone, 6.54 wt %) was used as diluent to disperse the mixture. The evenly-mixed slurry was coated on a carbon paper, dried in a vacuum oven at 80 °C for 24 h, and cut into 12 mm discs. The counter electrode was aluminum, while the diaphragm was fiberglass. The composition of the electrolyte was $AlCl_3$:[EMIm]Cl=1.3:1, and the electrolyte volume/mass=62.5 μL mg^{-1}. The water and oxygen levels were less than 0.01 ppm in the glove box (MIKROUNA, Super1220/750/900). The cycling and rate-performance were measured by using the galvanostatic charge-discharge mode. The tests were carried out on a battery tester (NEWARE, CT-4008). When the voltage range was 0.01-2.0 V, Electrochemical workstation (CHI660e) was used to test cyclic voltammetry and electrochemical impedance spectra.

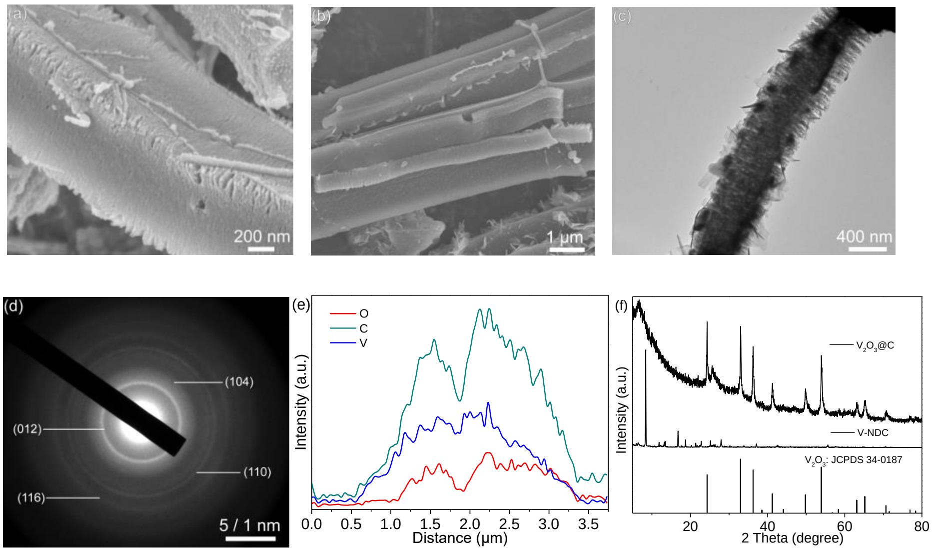

Fig. S1 (a) SEM image of the book-like lamellar V_2O_3@C calcined at 600 °C; (b) SEM image, (c) TEM image, (d) SAED pattern, and (e) line-scanning curves of V_2O_3@C calcined at 800 °C. (f) XRD patterns of V-NDC and V_2O_3@C.

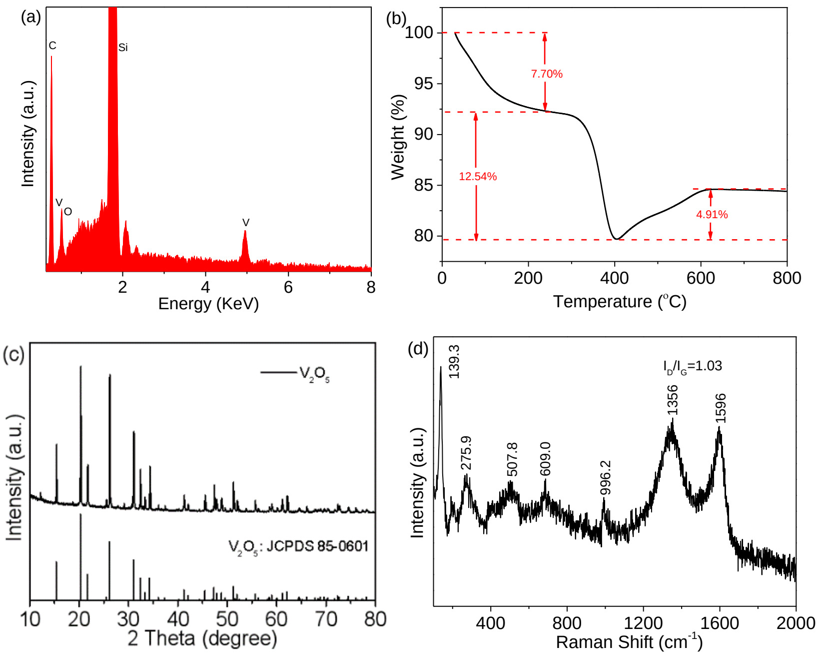

Fig. S2 (a) EDS spectrum and (b) TGA curve of V_2O_3@C. (c) XRD pattern of the sample after TGA measurement. (d) Raman spectrum of V_2O_3@C.

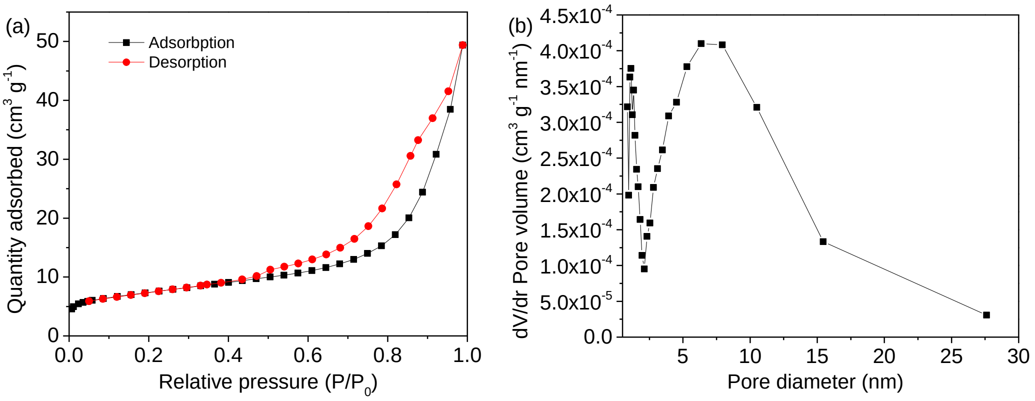

Fig. S3 (a) Adsorption-desorption isothermal and (b) pore-size distribution of V_2O_3@C.

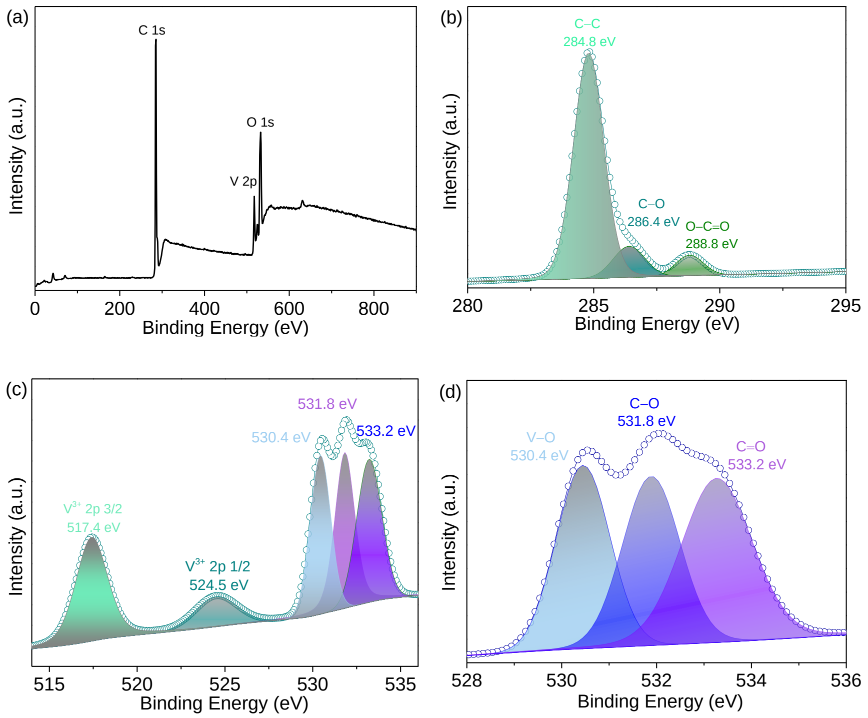

Fig. S4 XPS spectra of V_2O_3@C: (a) full survey spectrum, (b) C 1s, (c) V 2p, and (d) O 1s.

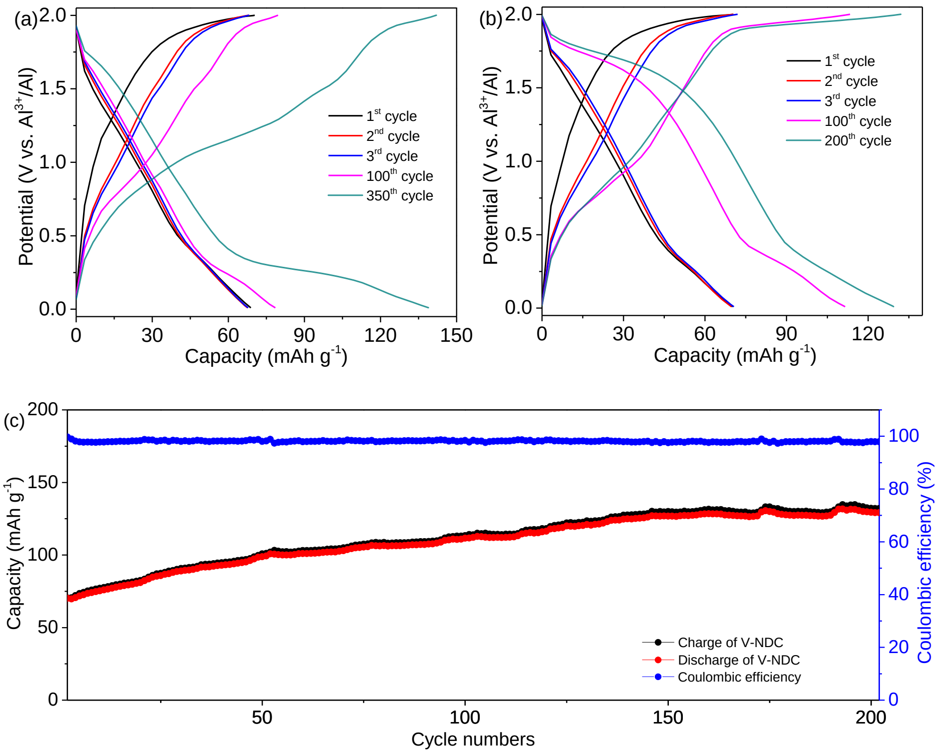

Fig. S5 (a) Charge-discharge curves of V-NDC at 0.3 A g^{-1}. (b) Charge-discharge curves and (c) cycling performance of V-NDC with a loading of 2.23 mg cm^{-2} cycling at 0.2 A g^{-1}.

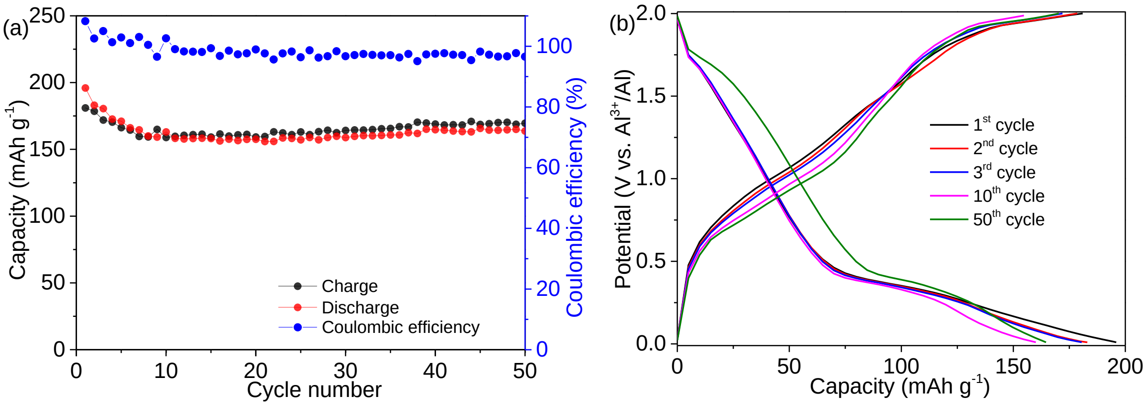

Fig. S6 (a) Capacity and (b) charge-discharge curves of pure V_2O_3 at 0.3 A g^{-1}.

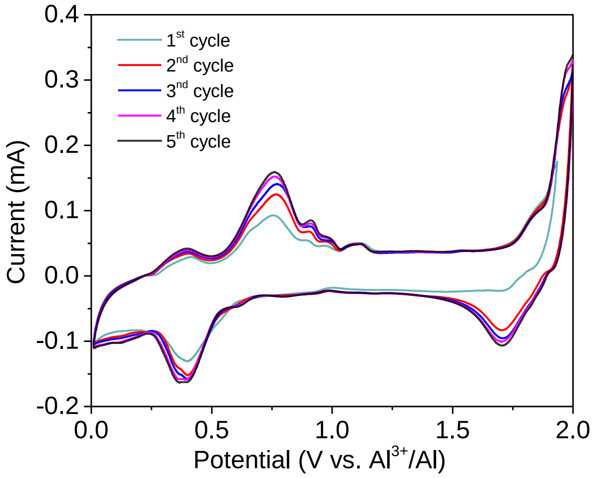

Fig. S7 CV profiles of V-NDC at a scanning rate of 0.1 mV s^{-1}.

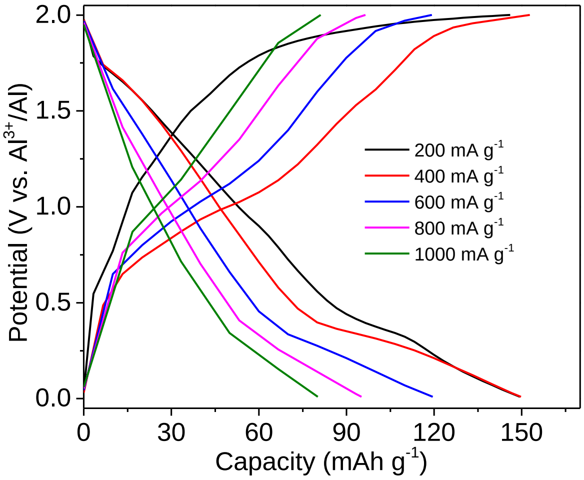

Fig. S8 Charge-discharge profiles of V_2O_3@C during rate-performance measurements.

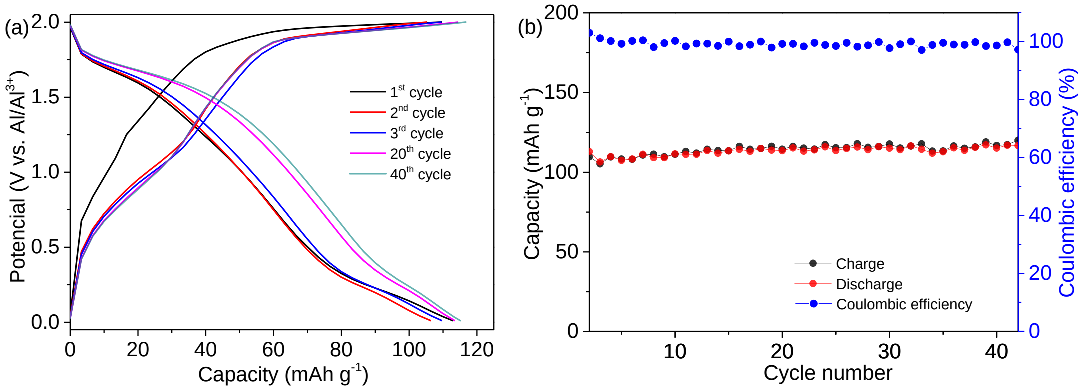

Fig. S9 (a) Charge-discharge profiles and (b) cycling performance of V-NDC at –10 °C.

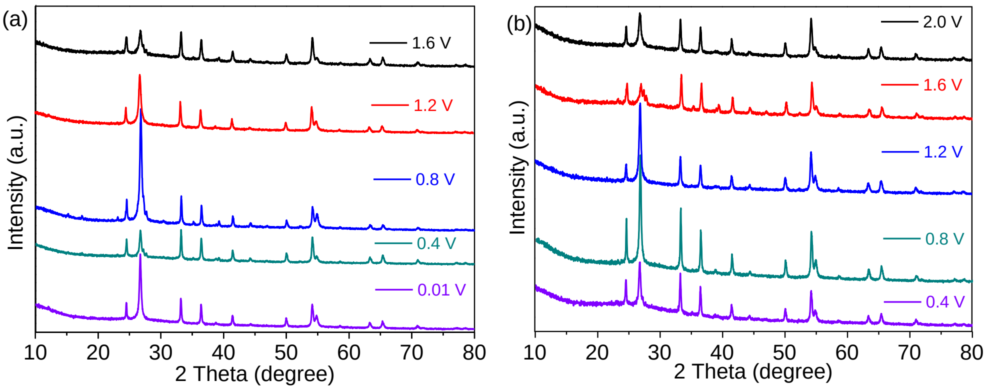

Fig. S10 *Ex-situ* XRD patterns of V_2O_3@C composite at different potentials during (a) discharge and (b) charge.

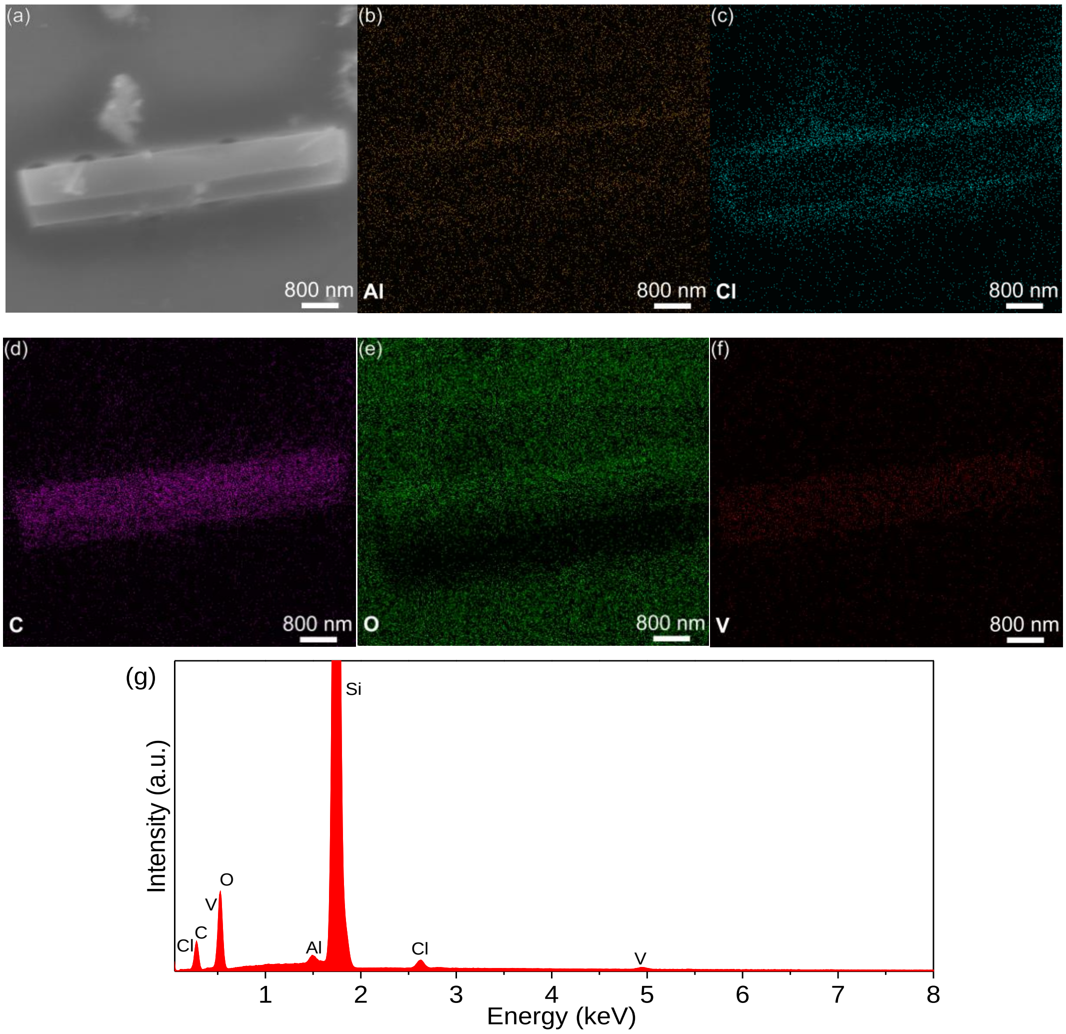

Fig. S11 (a) SEM image, (b-f) Al, Cl, C, O, V elemental mapping images and (g) EDS spectrum of V_2O_3@C after 50 cycles at 0.3 A g^{-1}.

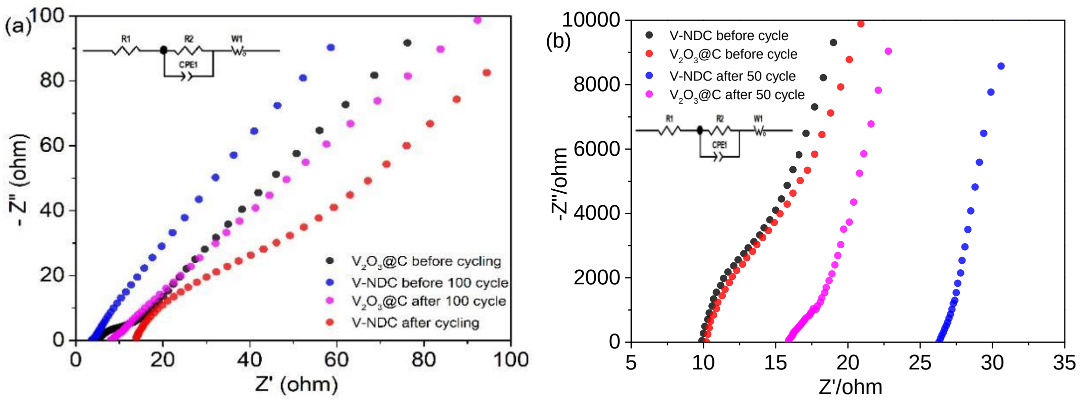

Fig. S12 EIS spectra of different samples at (a) room temperature and (b) –10 °C.

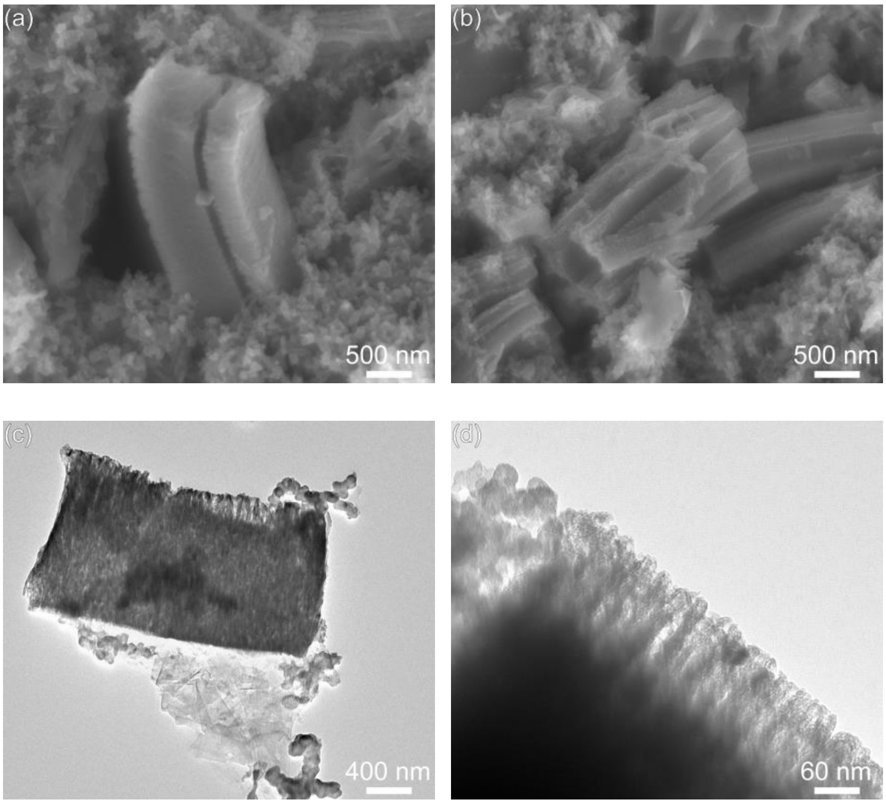

Fig. S13 (a,b) SEM images, (c,d) TEM images of V_2O_3@C after 50 cycles at 0.3 A g^{-1} at –10 °C.

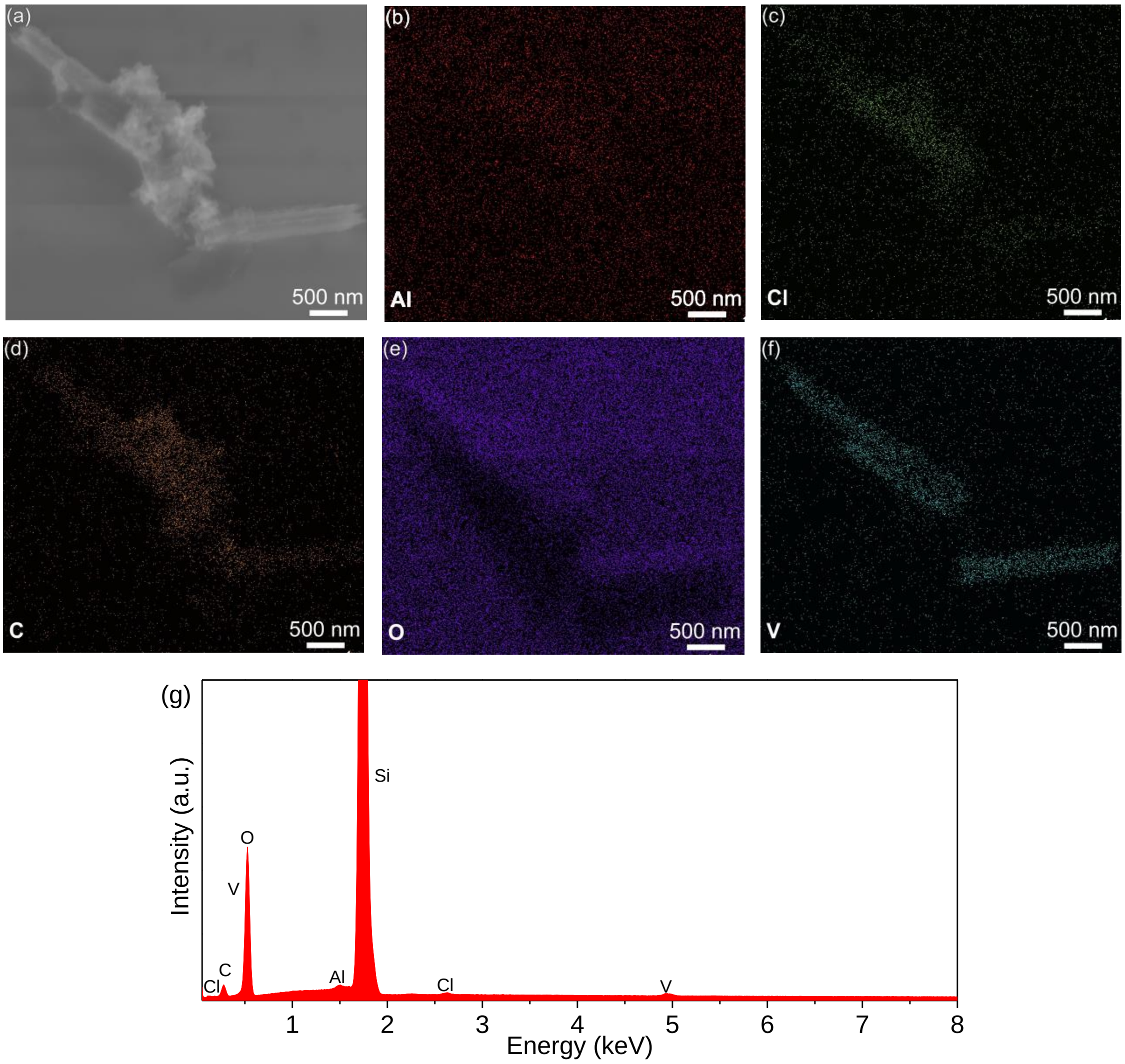

Fig. S14 (a) SEM images, (b-f) elemental mapping and (g) EDS spectrum of V_2O_3@C after 50 cycles at 0.3 A g^{-1} at –10 °C.

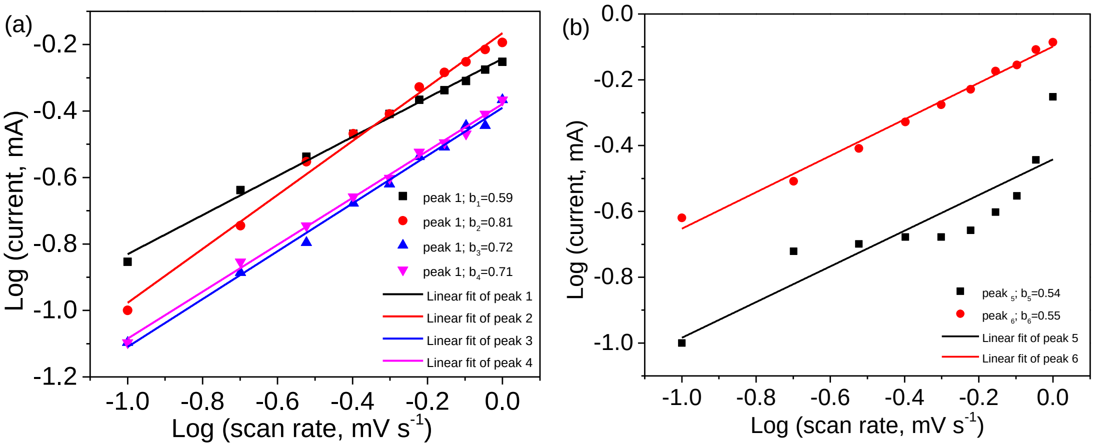

Fig. S15 The log(i) vs. log(v) of (a) oxidization and (b) reduction peaks.

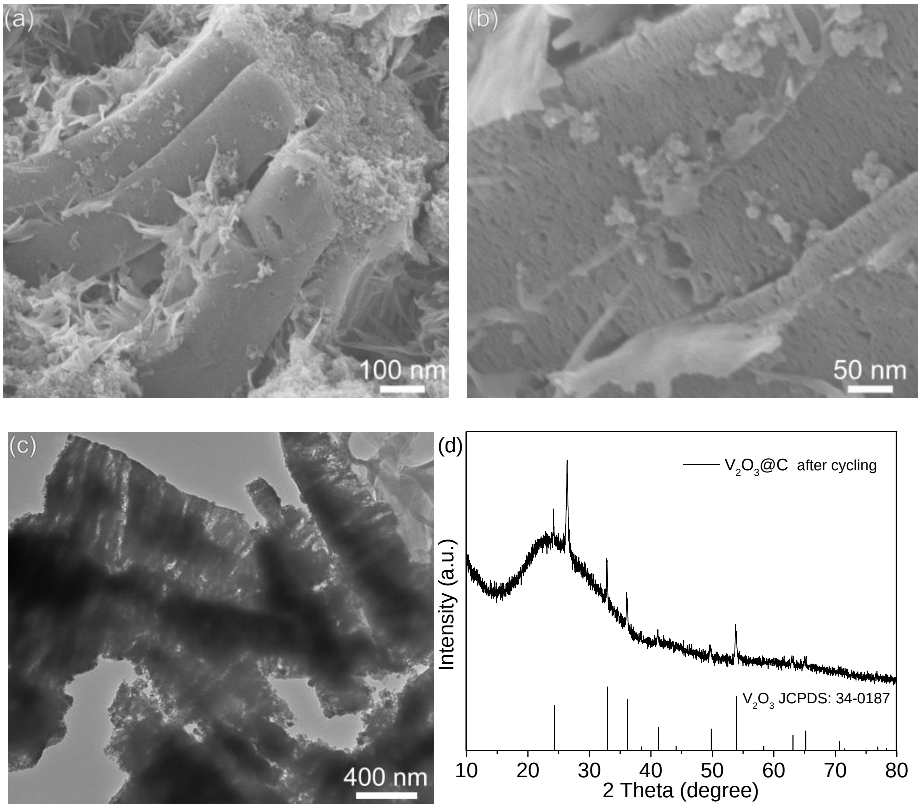

Fig. S16 (a,b) SEM images, (c) TEM images and (d) XRD pattern of V_2O_3@C after 100 cycles at 0.3 A g^{-1}.

Table S1. Comparison on the electrochemical performance of some Al-ion battery cathodes.

Composite	Cycling rate	Cycle number	Capacity (mAh g^{-1})	Ref.
Defect-free soft carbon	0.5 A g^{-1}	1000	77.7	1
Potassium-rich cryptomelane nanowires	0.02 A g^{-1}	60	109	2
One-Dimensional TiS_2 nanobelt arrays	1C	90	150	3
δ-MnO_2 nanofibers	0.1 A g^{-1}	15	59	4
Dense integration of graphene paper	2 A g^{-1}	8000	27.1	5

VO_2	0.05 A g^{-1}	100	116	6
$NiCo_2S_4$ nanosheet	0.2 A g^{-1}	1000	64	7
Co-P	0.2 A g^{-1}	400	85.1	8
Co_9S_8	0.2 A g^{-1}	250	120	9
WS_2	1 A g^{-1}	500	119	10
Graphene nanosheet	0.1 A g^{-1}	1640	90	11
TiO_2	100 C	4000	20	12
V_2O_3@C	0.3 A g^{-1}	500	242.5	This work

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