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Mechanistic insights into the pseudocapacitive performance of bronze-type vanadium dioxide with mono/multi-valent cations intercalation

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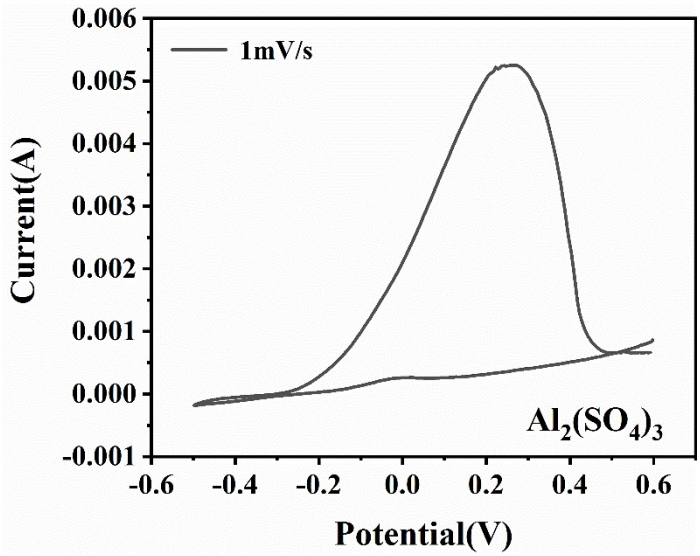

Fig. S1 Cyclic voltammetry curve of VO_2(B) cycled in 1 M $Al_2(SO_4)_3$ electrolyte measured at 1 mV/s scan rate.

Table S1. Solvothermal reaction conditions used to optimize the pseudocapacitive performance of as-synthesized VO_2(B) electrodes.

Sample No. / Reaction conditions	1-0	1-1	1-2	1-3	1-4
Volume ratio of water/ethylene glycol	3 : 2	1 : 1	2 : 3	3 : 2	3 : 2
Reaction time (h)	6	6	6	7	8

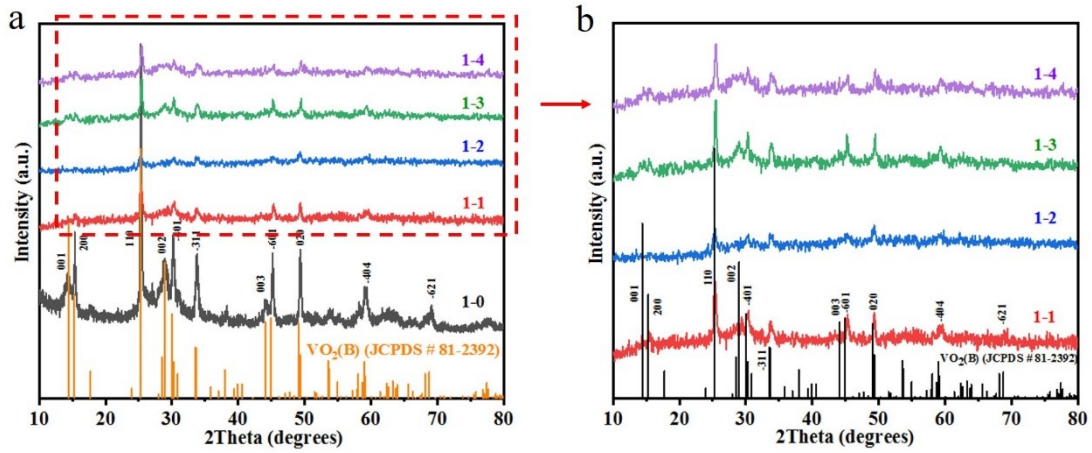

Fig. S2 XRD patterns of vanadium dioxides (Sample 1-0 to 1-4) prepared with different solvothermal reaction conditions.

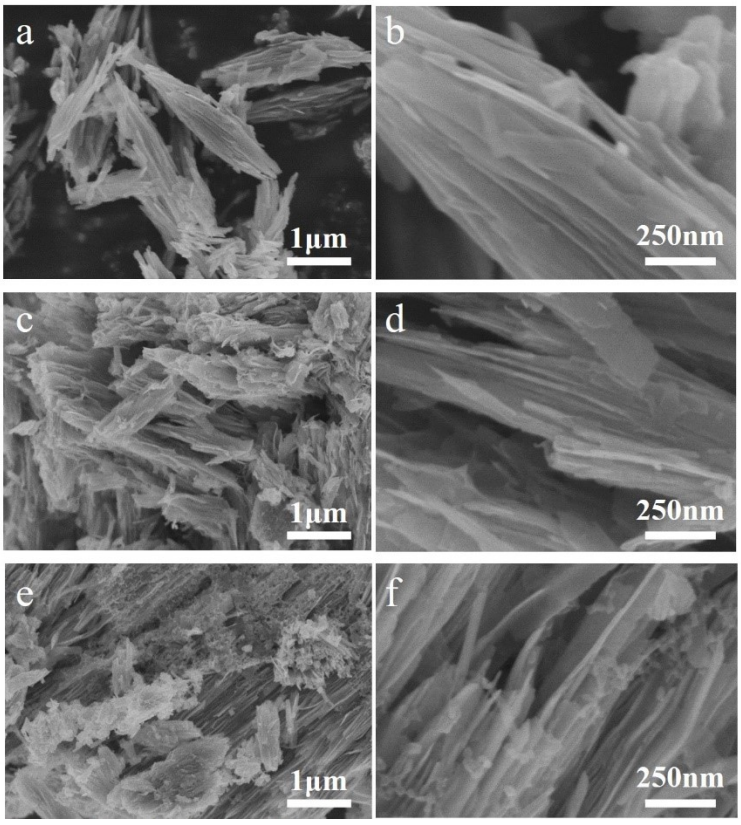

Fig. S3 SEM images of vanadium dioxides (Sample 1-0 to 1-2) prepared with different solvothermal reaction conditions.

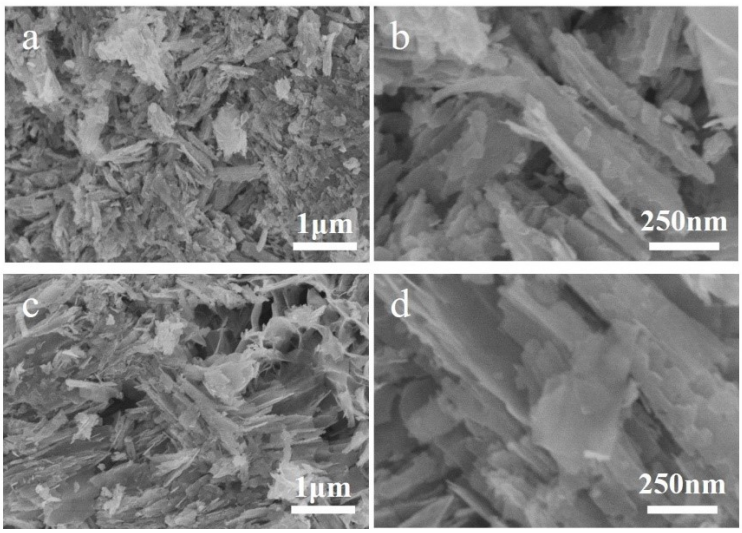

Fig. S4 SEM images of vanadium dioxides (Sample 1-3 to 1-4) prepared with different solvothermal reaction conditions.

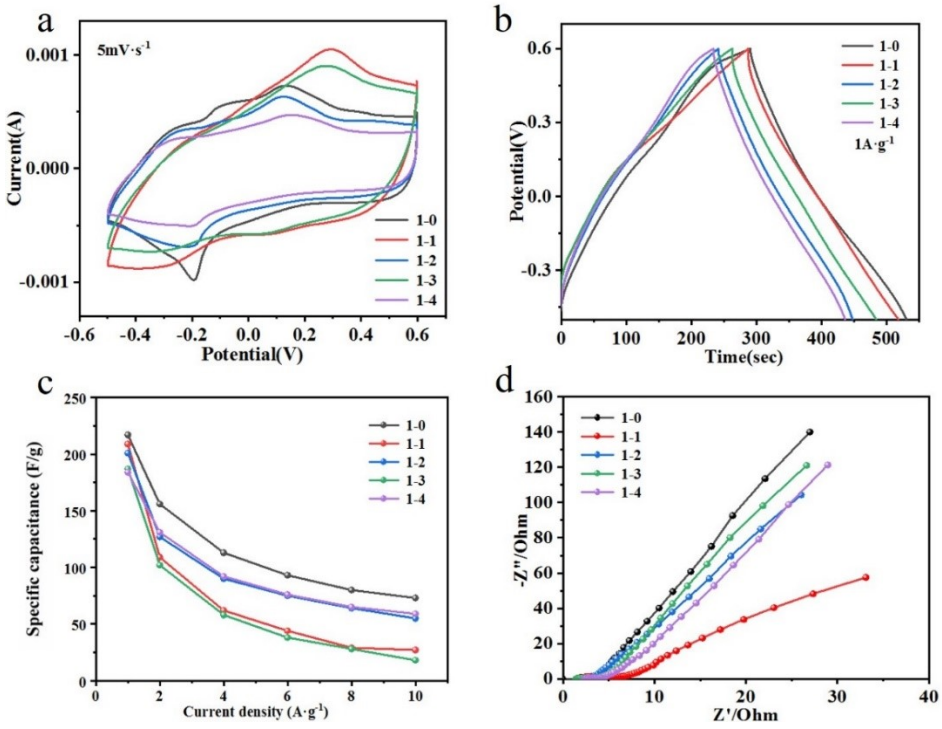

Fig. S5 Electrochemical measurements of vanadium dioxides (Sample 1-0 to 1-4) prepared with different solvothermal reaction conditions. (a) cyclic voltammetry curves measured at 5 mV/s scan rate, (b) galvanostatic charge-discharge curves measured at 1 A/g current density, (c) specific capacitances at various current densities, (d) Nyquist plots.

Table S2. Summary of specific capacitances and rate capabilities of vanadium dioxides (Sample 1-0 to 1-4) prepared with different solvothermal reaction conditions.

Samples	1-0	1-1	1-2	1-3	1-4
Specific capacitances (F/g)	217.6	209.8	201.0	200.7	183.3
Capacitance retention with ×10 increased current density (%)	33.6	12.9	27.4	9.6	32.0

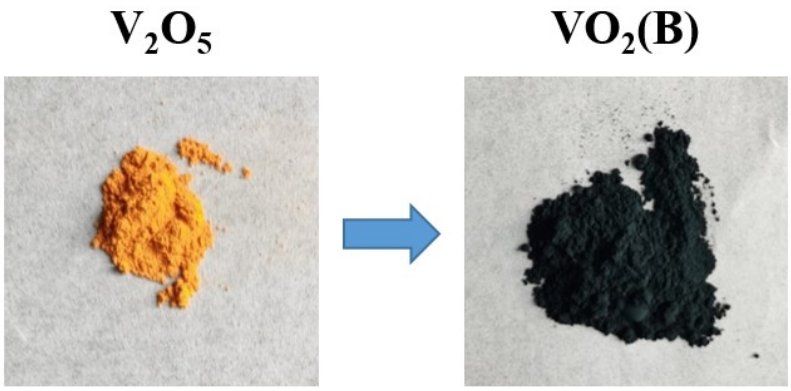

Fig. S6 Color variation from yellow to dark blue after solvothermal reduction reaction indicates the transformation of V_2O_5 to pure phase $VO_2(B)$.

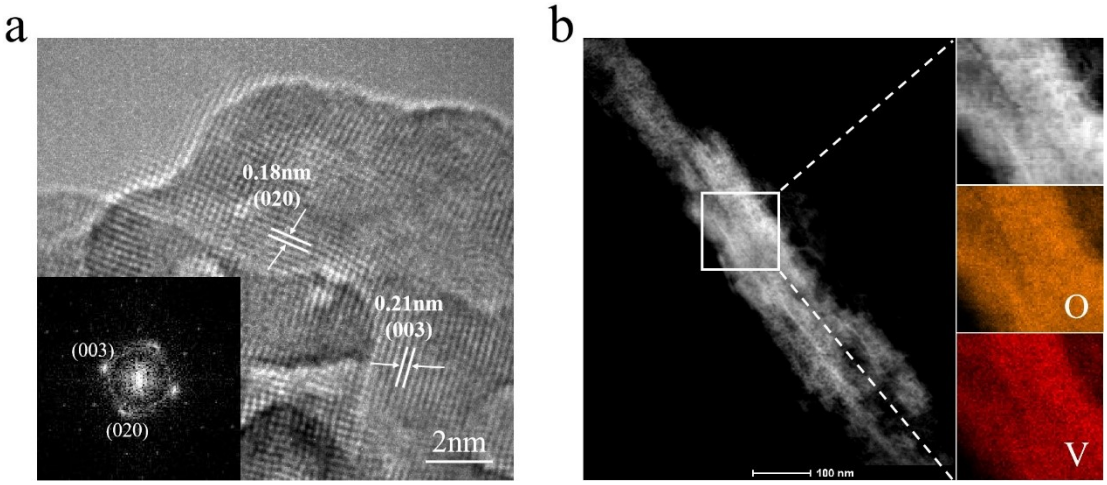

Fig. S7 (a) HRTEM image of $VO_2(B)$ with the corresponding fast Fourier transform (FFT) pattern in the inset, (b) HAADF-STEM image and EDS elemental mapping of V and O.

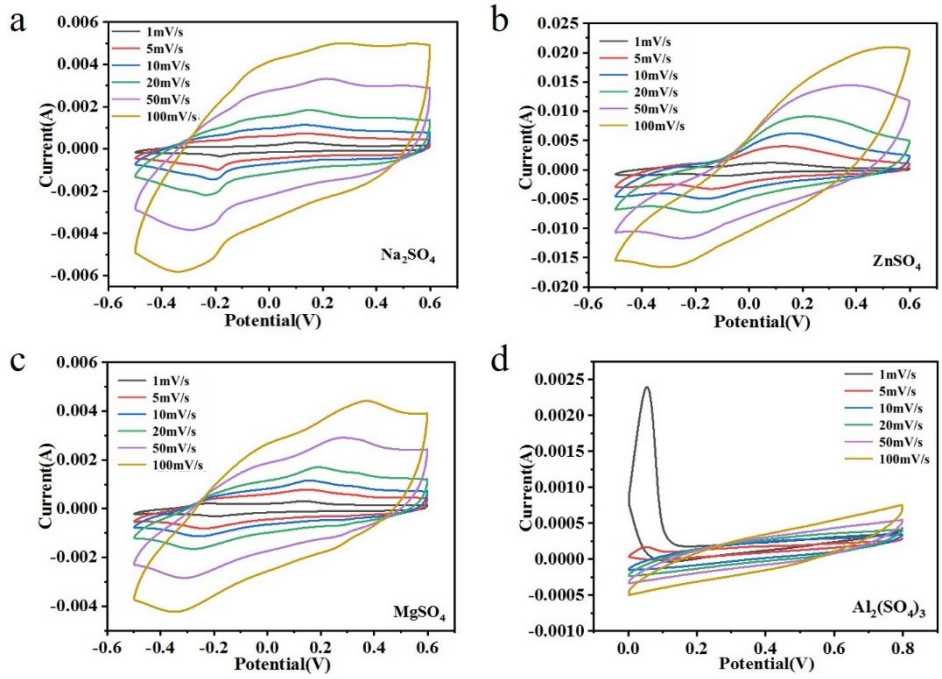

Fig. S8 Cyclic voltammetry curves of VO_2(B) cycled in Na_2SO_4, $MgSO_4$, $ZnSO_4$ and $Al_2(SO_4)_3$ electrolytes at various scan rates from 1 to 100 mV/s.

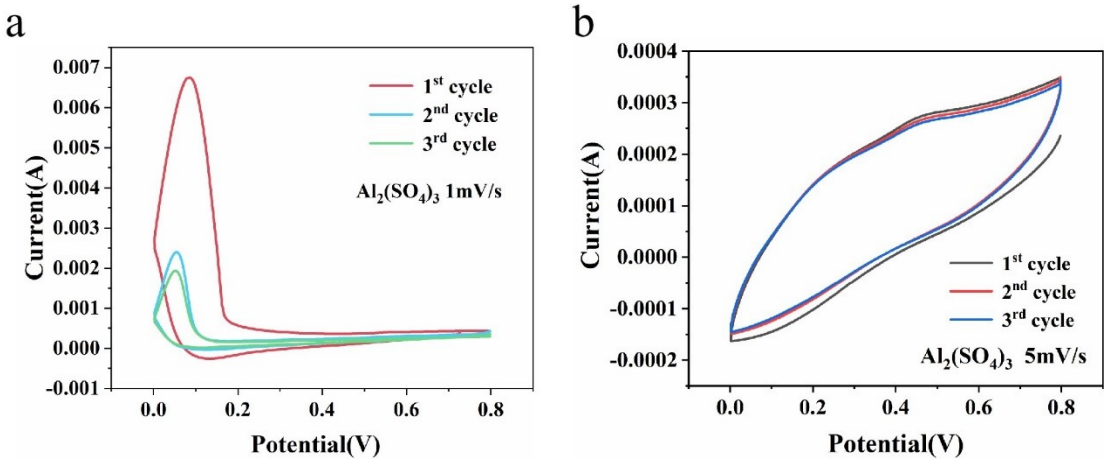

Fig. S9 Cyclic voltammetry curves of VO_2(B) cycled in $Al_2(SO_4)_3$ electrolyte at (a) 1 mV/s and (b) 5 mV/s.

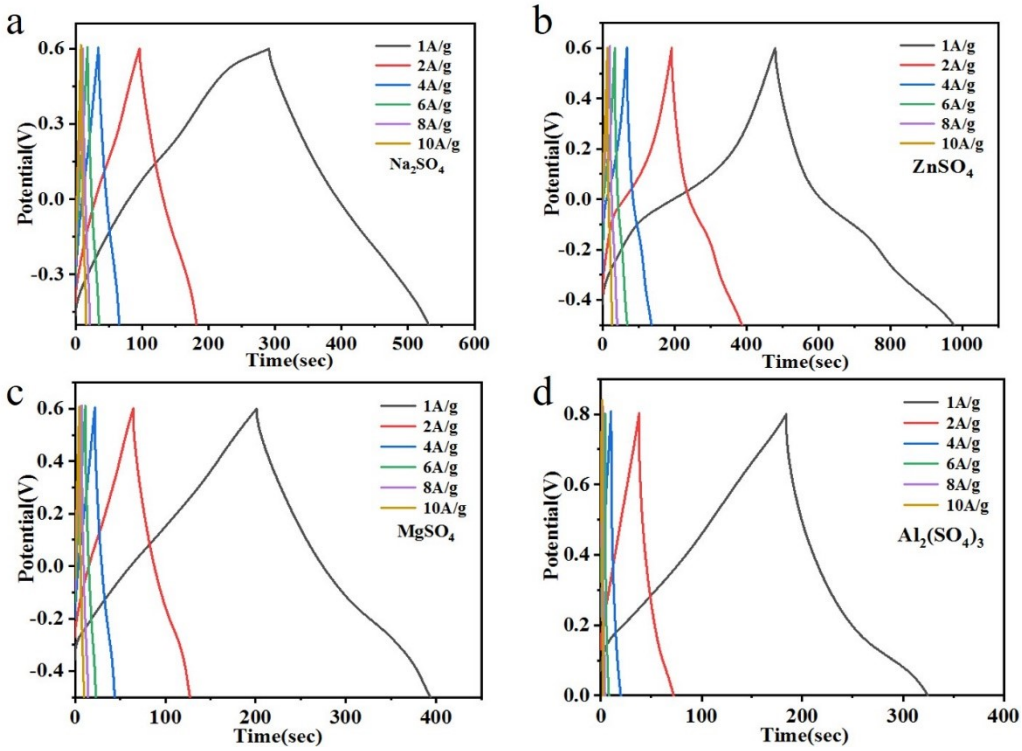

Fig. S10 Galvanostatic charge-discharge curves of VO_2(B) cycled in Na_2SO_4, $MgSO_4$, $ZnSO_4$ and $Al_2(SO_4)_3$ electrolytes at different current densities from 1 to 10 A/g.

Table S3. Summary of the specific capacitances of VO_2(B) cycled in Na_2SO_4, $MgSO_4$, $ZnSO_4$ and $Al_2(SO_4)_3$ electrolytes at different current densities from 1 to 10 A/g.

Current density (A/g)	Specific capacitance (F/g)			
	Na^+	Zn^{2+}	Mg^{2+}	Al^{3+}
1	218	460	180	151
2	147	371	120	60
4	109	274	88	19
6	89	219	74	11
8	76	181	65	
10	71	158	59	

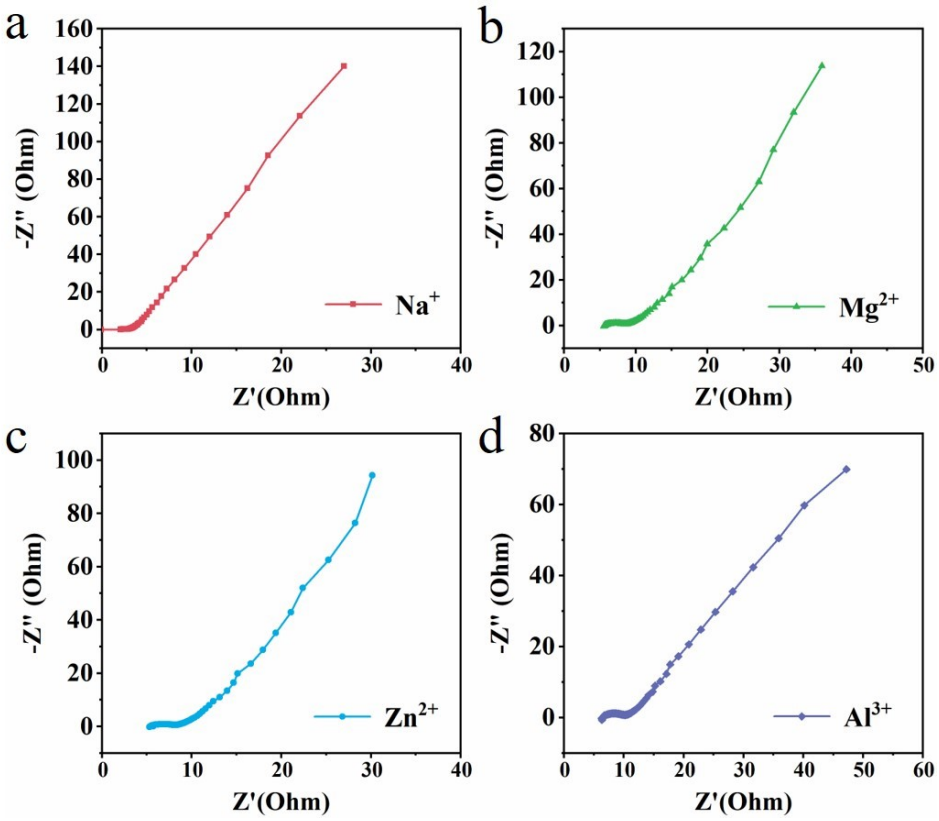

Fig. S11 Nyquist plots of VO_2(B) cycled in (a) Na_2SO_4, (b) $MgSO_4$, (c) $ZnSO_4$ and (d) $Al_2(SO_4)_3$ electrolytes.

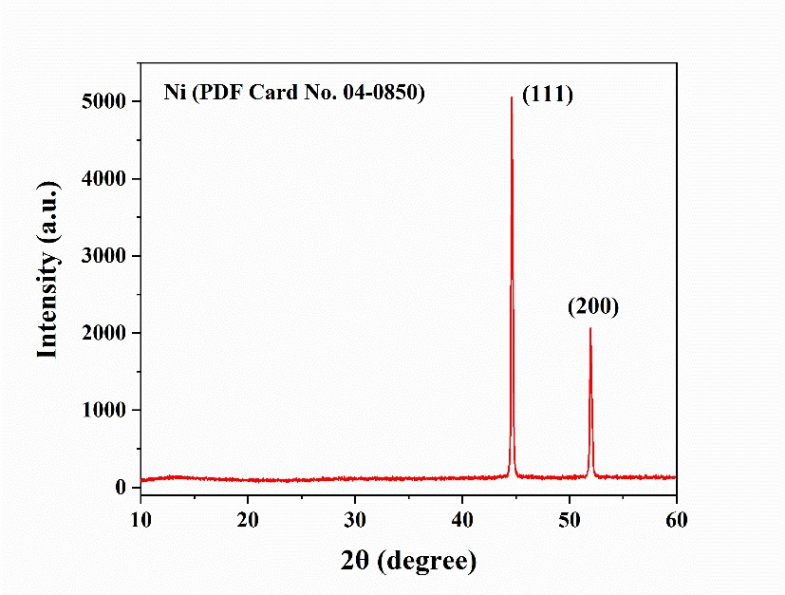

Fig. S12 XRD pattern of the pure nickel foam.

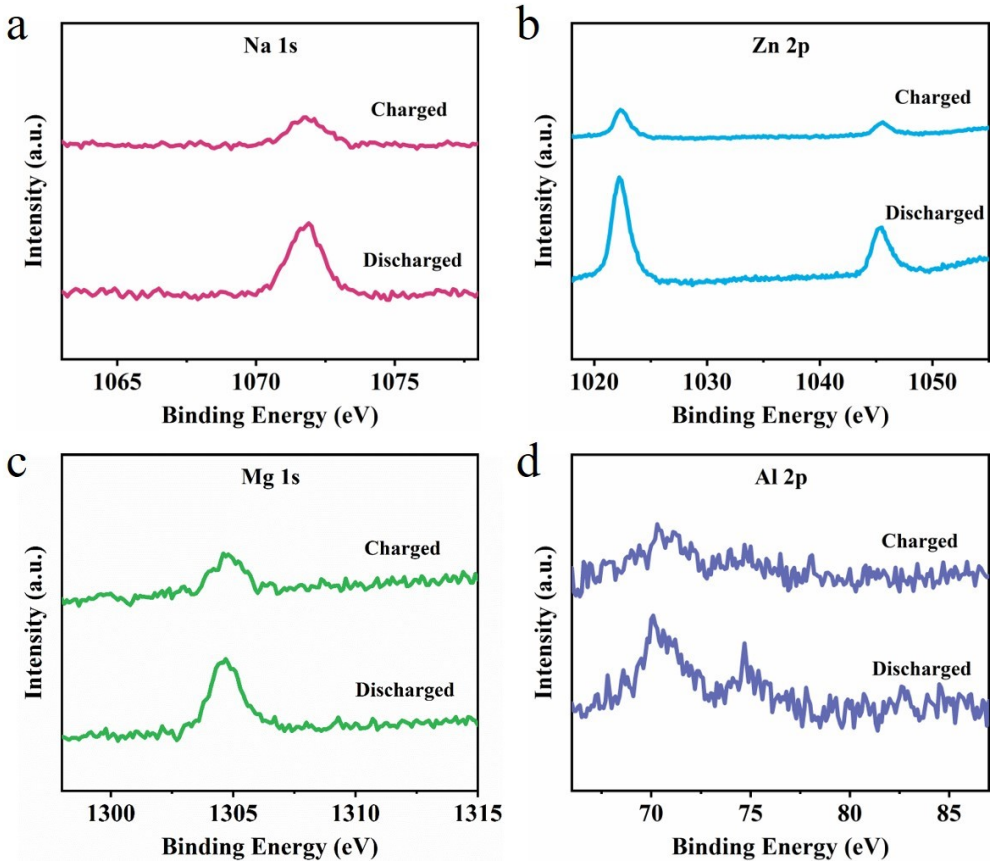

Fig. S13 High-resolution XPS spectra of (a) Na 1s, (b) Zn 2p, (c) Mg 1s, and (d) Al 2p at fully charged and discharged states.

Table S4. Summary of adsorption energy of Na, Mg, Zn and Al on VO_2(B)'s surfaces.

Electrolyte ions	Na	Mg	Zn	Al
Adsorption energy (eV)	-3.39	-4.78	-0.83	-8.17

Table S5. Summary of ΔE_{tol}, ΔE_{zpe}, ΔS and ΔG for standard Gibbs free energy change calculation during the formation process of $Zn_3(OH)_2V_2O_7$.

ΔE_{tol}	ΔE_{zpe}	ΔS	ΔG
-0.480883325	-0.267381	-0.22108313	-0.527181195