Supporting Information

VS_4 with chain crystal structure used as an intercalation cathode for an aqueous Zn-ion battery

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Experimental Section

Synthesis of VS_4 nanoparticles:

In a typical process, 0.35 g of ammonium metavanadate (NH_4VO_3) was added into 30 mL of deionized water. Then the suspension was heated to 60 °C to form a clear pale-yellow solution. Then, 30 mL of 0.6 M thioacetamide (TAA) dissolved in ethylene glycol (EG) was added in the above solution. Finally, the homogeneous solution was transferred into a Teflon-lined stainless steel autoclave with a capacity of 100 mL. The autoclave was heated and maintained at 160 °C for 16 h. The precipitate product was rinsed with a centrifuge by deionized water and ethanol for several times and dried in a vacuum oven at 60 °C.

Materials Characterization:

The morphology, microstructure, and crystal phase composition of the prepared samples were characterized by field-emission scanning electron microscopy (FE-SEM, JSM-6700F), transmission electron microscopy (TEM, JEM-2100F), and X-ray diffraction (XRD, PANalytical X'PertPRO), respectively. X-ray photoelectron spectroscopy (VG Multiab-2000) using a PHI Quantum 2000 XPS system with a monochromatic Al Kα source and charge neutralizer were performed to analyze the valence and bonding information of V, S and Zn elements. The element contents were determined by the energy dispersive spectroscopy (EDS, EDAX genesis 7000).

Electrochemical Characterization:

All the electrochemical measurements were conducted by employing an electrochemical workstation (CHI660E). The VS_4-Zn battery was assembled in a pouch cell with a separator (NKK) in 1 M $ZnSO_4$ solution. The cathode VS_4 was connected as a working electrode, and the Zn anode electrode as both reference and counter electrodes.

DFT calculation:

The energies of VS_4 and the structures of Zn_xVS_4 with different Zn^{2+} insertion content x (from 0 to 1) were computed using DFT with implementation in the Vienna ab Initio Simulation Package (VASP). The plane wave cutoff energy was fixed at 400 eV. All of the structures were fully optimized and relaxed to ground state. The self-consistent field convergence criterion was set to be 10^{-4} The pristine VS_4 has lattice parameters of α=90°, β=100.72°, γ=90°, a=7.44Å, b=12.1664 Å and c = 11.93150 Å. To reduce the influence of geometry changes on the formation energy, the relative formation energy per VS_4 unit was defined as

$$\Delta E_F = E(Zn_xVS_4) - E(Zn_{x-1/n}VS_4) - (E(Zn_{1/n}VS_4) - E(VS_4))$$

where $E(Znx VS_4)$ is the lowest energy state with x Zn^{2+} ions (x = 1/n to 1) inserted into the VS_4, and $E(VS_4)$ is the energy of pristine VS_4. Since we carried out DFT calculations based on the supercell of V_8S_{32}, the value of n, which represents the number of VS_4 cell, is 8.

Table S1. Comparison of the top five lattice spaces for VS_2 and VS_4.

(h, k, l) VS_2	**(h, k, l) VS_4**
(001), 5.76 Å	(011), 7.84 Å
(002), 2.88 Å	(002), 5.95 Å
(100), 2.79 Å	(110), 5.61 Å
(011), 2.51 Å	(020), 5.21 Å
(012), 2.00 Å	(-112), 4.45 Å

Table S2. Parameters of cell volume and d space with different x value.

x value	**Cell volume Å^3**	**d space Å**
0	1061.2598	5.9662
0.125	1187.4092	6.5261
0.25	1193.6443	6.6212
0.375	1199.66	6.6690
0.5	1213.23	6.7783
0.625	1226.738	6.7572
0.75	1232.6317	6.8541
0.875	1273.6632	6.9727
1	distortion	distortion

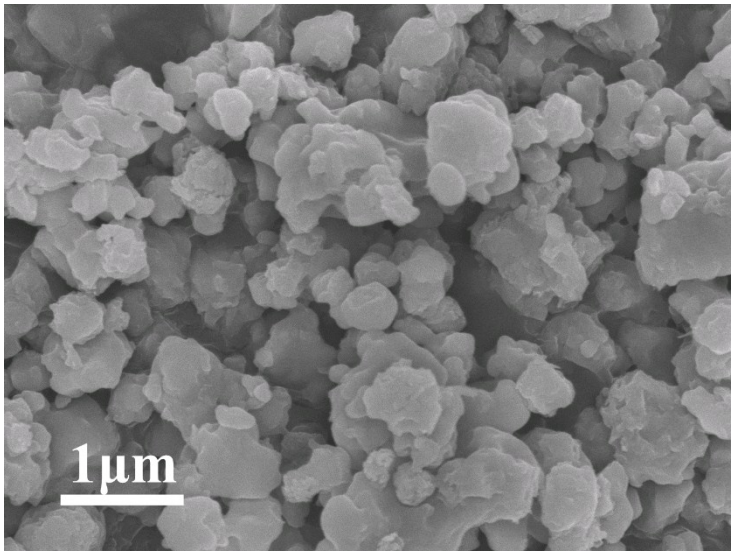

Figure S1. SEM image of prepared VS_4 nanoparticles.

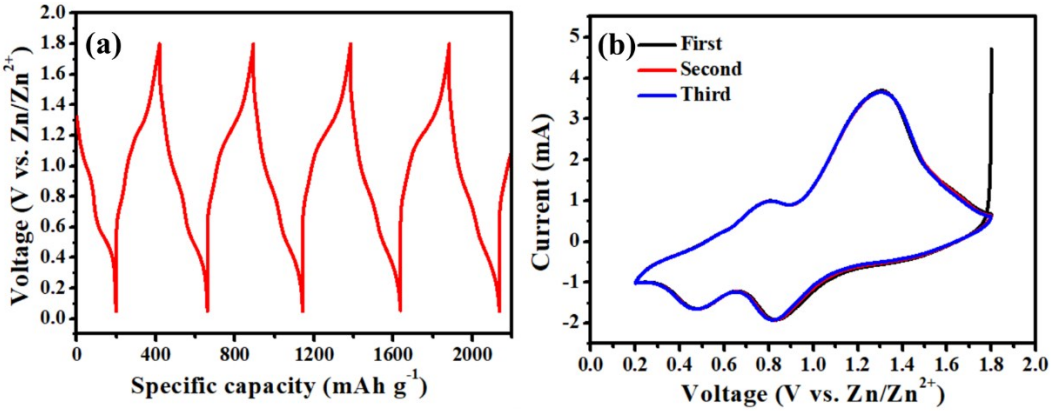

Figure S2. (a) Galvanostatic charge and discharge curves of VS_4-Zn battery at the current density of 1 A g^{-1}. (b) CV curves of the VS_4-Zn battery at the scan rate of 0.8 mV s^{-1}.

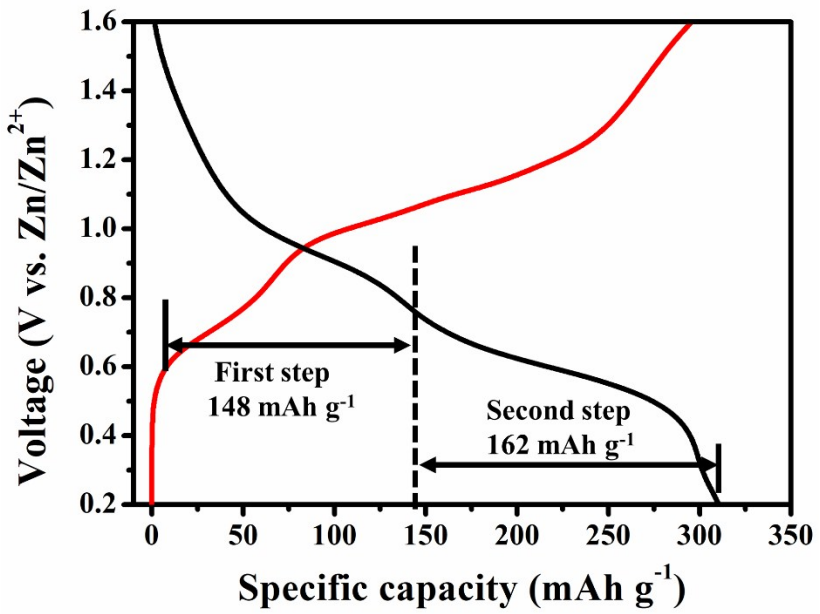

Figure S3. Charge and discharge curves of VS_4 at 0.1 A g^{-1}.

In the first step: $VS_4 + xZn^{2+} + 2xe^- \leftrightarrow Zn_xVS_4$ ($x = 0.49$)
In the second step: $Zn_xVS_4 + yZn^{2+} + 2ye^- \leftrightarrow Zn_{x+y}VS_4$ ($y = 0.54$)

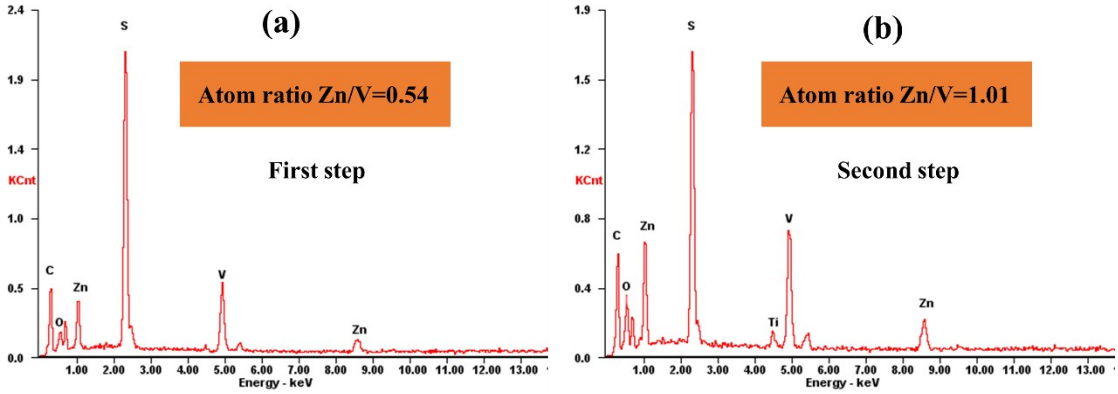

Figure S4. Zn and V ratio characterized by EDS for the first (a) and second (b) discharge steps.

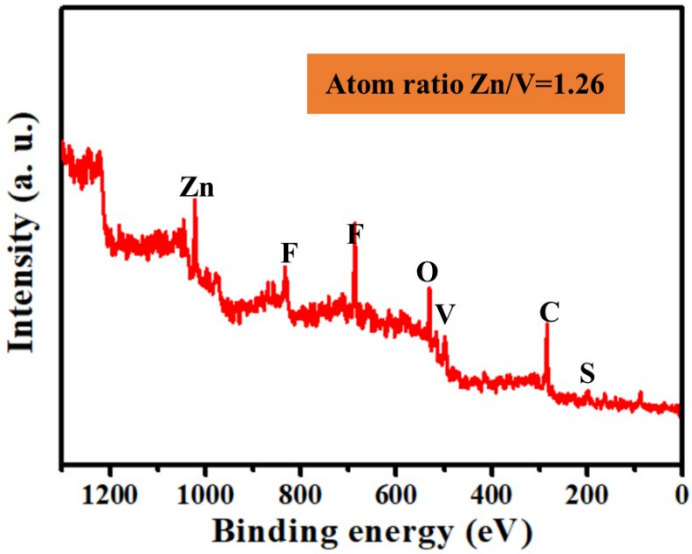

Figure S5. Zn and V ratio characterized by XPS survey spectrum for discharged VS_4.

Table S3. Capacity and cycle performance comparison of our work with the other related reports.

Materials	electrolyte	Current (mA g^{-1})/capacity (mAh g^{-1})	Cycle times/capacity retention	Ref.
VS_4	1 M $ZnSO_4$	100 / 310 250 / 260 1000 / 209 2500 / 135	500 / 85%	(our work)
V_2O_5	0.5 M AN-$Zn(TFSI)_2$	14.4 / 170 288 / 130	120 / 97%*	37
VS_2	1 M $ZnSO_4$	50 / 190.3 200 / 145.3 500 / 136.8 1000 / 121.5 2000 / 115.5	200 / 98%	24
$Zn_3V_2O_7(OH)_2 \cdot 2H_2O$	1 M $ZnSO_4$	50 / 200 100 / 166 500 / 122 1000 / 84 2000 / 75	300 / 68%	20
LiV_3O_8	1 M $ZnSO_4$	16 / 256 266 / 148 533 / 79 1066 / 47	65 / 86%*	38
$Na_{1.1}V_3O_{7.9}$	1 M $Zn(CF_3SO_3)_2$	300 / 220 1000 / 84.8	500 / 84.8%	40
$K_2V_8O_{21}$	2 M $ZnSO_4$	300 / 247	300 / 83%	39
$Zn_{0.25}V_2O_5 \cdot nH_2O$	1 M $ZnSO_4$	300 / 282	1000 / 81%	8
$Na_3V_2(PO_4)_3$	0.5 M $Zn(CH_3COO)_2$	50 / 97 1000 / 58	100 / 74%	21

* Estimated value