

Supporting Information

Hierarchical Porous Metallic V₂O₃@C for Advanced Aqueous Zinc-Ion Batteries

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Materials synthesis

All chemicals were purchased from Sinoreagent and used without any further treatment.

Preparation of V-CPs and P-V₂O₃@C

Typically, 2.3 mmol of vanadyl acetylacetonate (VO(acac)₂) and 3 mmol of 1,4-Benzenedicarboxylic acid (BDC) were dissolved in 50 mL of ethanol absolute (GR, $\geq 99.8\%$), a homogeneous solution was formed by continuous stirring for 30 minutes. The mixed solution was transferred to 100 mL Teflon-lined autoclave and then heated to 180 °C for 12 h. The V-CPs microspheres were collected from the solution by centrifugation and washed with methanol four times and then dried at 80 °C for 12 h in an oven. The V-CPs powders were transferred to tube furnace under N₂ flow and pyrolysis at 700 °C for 1 h with a heating rate of 5 °C min⁻¹, the porous P-V₂O₃@C microsphere was obtained.

Preparation of MIL-47(V) and V₂O₃@C

Typically, 3 mmol of VCl₃ and 3 mmol of 1,4-Benzenedicarboxylic acid (BDC) were dissolved in 50 mL of ethanol absolute (GR, $\geq 99.8\%$), a homogeneous solution was formed by continuous stirring for 30 minutes. The mixed solution was transferred to 100 mL Teflon-lined autoclave and then heated to 120 °C for 48 h. The light green MIL-47(V) was collected from the solution by centrifugation and washed with methanol four times and then dried at 60 °C for 12 h in an oven. The MIL-47(V) powders were transferred to tube furnace under N₂ flow and pyrolysis at 500 °C for 1 h with a heating rate of 5 °C min⁻¹, the black V₂O₃@C was obtained.

Materials characterization

The microstructures of P-V₂O₃@C and V₂O₃@C were acquired on a field emission scanning electron microscope (FESEM, Zeiss Sigma) operated at an accelerating voltage of 10.0 kV. Transmission electron microscopy (TEM) images of the samples were obtained with a JEOL2010 microscope, operated at an acceleration voltage of 200 kV. To analyze the crystal phases of the samples, powder X-ray diffraction (XRD) patterns were recorded on a Rigaku SmartLab X-ray diffractometer-9KW with Cu-K α radiation (1.5418 Å). X-ray photoelectron spectroscopy (XPS) was performed in vacuum with a Kratos Axis Ultra X-ray photoelectron spectrometer using an excitation source of monochromatic Al K α radiation at 15 kV and 150 W. The surface areas and pore structure of the samples were measured by N₂ adsorption/desorption experiments on a Micromeritics Accelerated Surface Area and Porosimetry System (ASAP2460). Raman scattering spectra were taken on a Renishaw System 2000 spectrometer using the 514.5 nm line of Ar⁺ for excitation.

Electrochemical measurements

The electrochemical performance of P-V₂O₃@C and V₂O₃@C sample was evaluated using the CR2032-type coin cells. The working electrodes prepared by mixing the active materials, carbon black and polyvinylidene fluoride (PVDF, 5 wt% in NMP) with a weight ratio of 70:20:10 in 1-Methyl-2-pyrrolidinone (NMP). The resulting slurry was scraped onto stainless steel mesh (250 mesh) and dried in vacuum at 80 °C for 12 h. The mass loading of the electrode materials is about 2 mg cm⁻². The 2032-type coin cell assembled in open air with a zinc plate (100 μ m, thick) as the anode, glass

fiber was used as the separator and 3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ aqueous electrolyte. Galvanostatic cycling test of the assembled cells was conducted on a BTS 400 system (Shenzhen, China) in the voltage range of 0.3-1.5 V (vs. Zn^{2+}/Zn) at different current density. Galvanostatic Intermittent Titration Technique (GITT) was employed to determine the Zn^{2+} ion diffusion coefficients in V_2O_3 cathode. In our GITT study, a cell was charged or discharged at 100 mA g^{-1} rate for 10 min, followed by a 20 min open circuit step to allow relaxation back to equilibrium.

The first principle calculations

The first principle calculations based on projector-augmented-wave (PAW) pseudopotential approximations and Perdew-Burke-Ernzerhof (PBE) exchange correlation function implemented in Vienna Ab-initio Simulation Package (VASP). A Monkhorst-Pack k-point grid is employed. The plane-wave energy cutoff is chosen as 600eV. All the lattice parameters and the ionic positions are fully optimized until the force is less than $5\text{E-}4 \text{ eV/\AA}$. Then, the optimized structure was adopted to calculate the density of states (DOS) and the differential charge state.

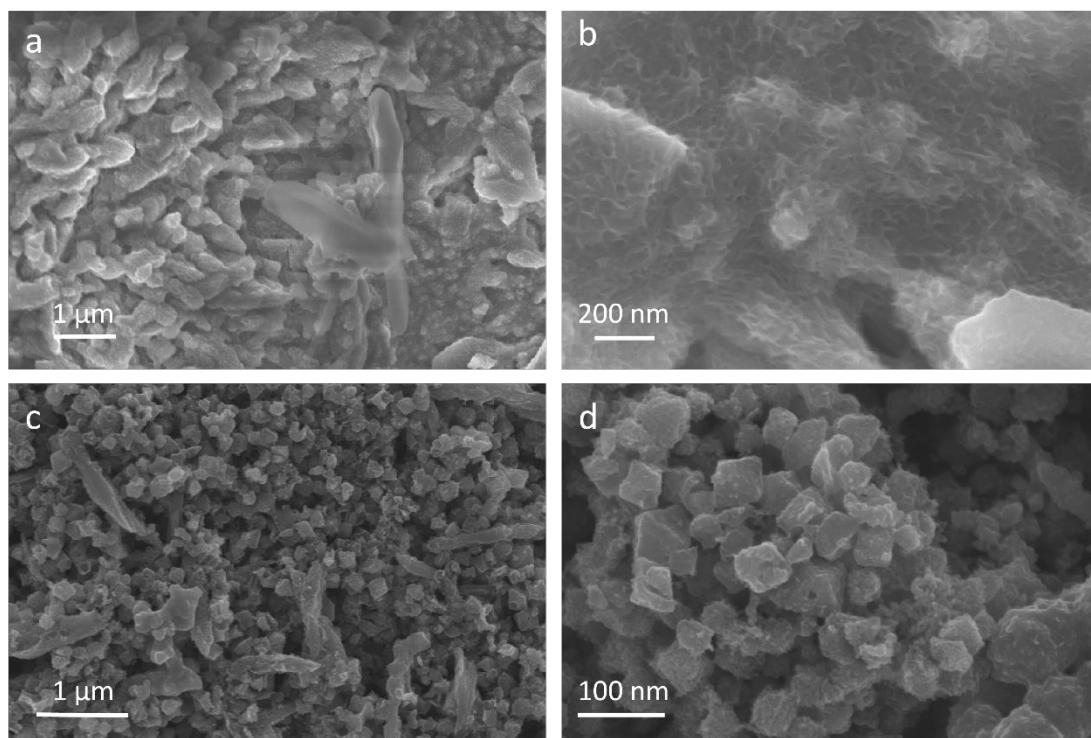


Figure S1. SEM images of MIL-47(V) at (a) low resolution and (b) high resolution.

SEM images of $V_2O_3@C$ at (c) low resolution and (d) high resolution.

Table S1. The contents of C, O and V in P- $V_2O_3@C$ and $V_2O_3@C$.

Materials	C	O	V
P- $V_2O_3@C$	56.98	31.64	11.38
$V_2O_3@C$	53.54	30.85	15.61

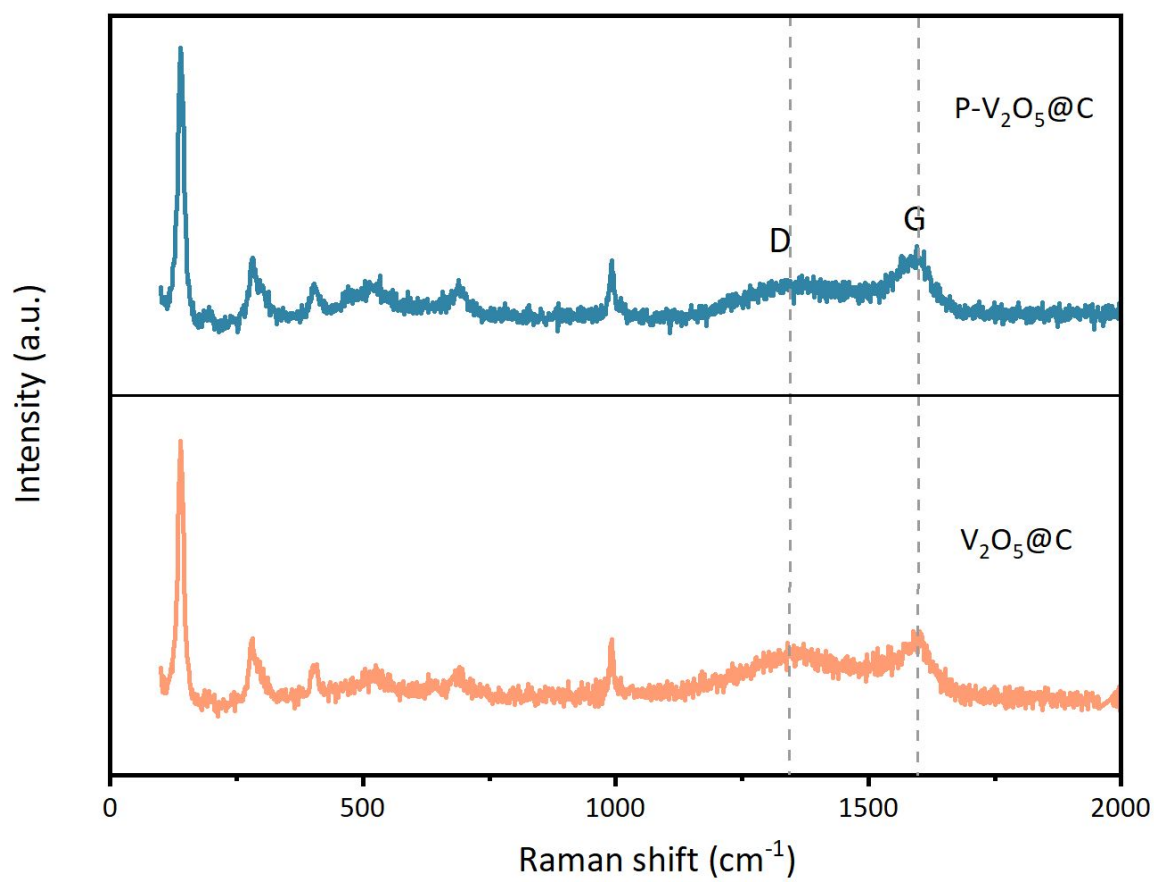


Figure S2. The Raman spectrum of P-V₂O₃@C and V₂O₃@C.

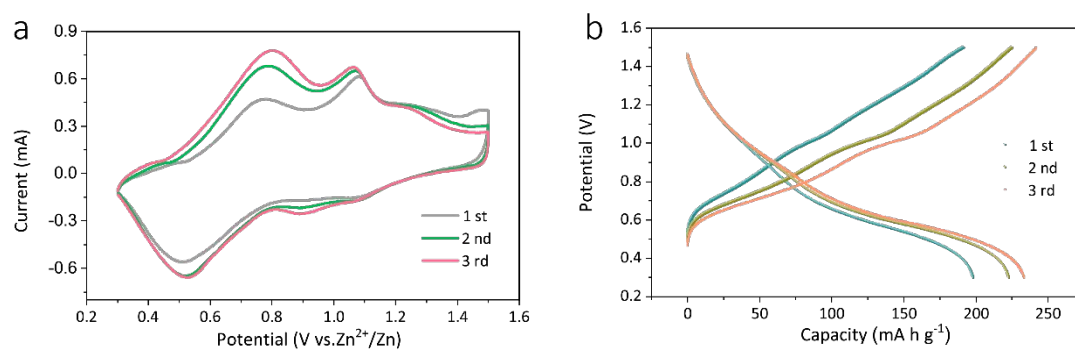


Figure S3. (a) CV and (b) charge-discharge curves for the initial three cycles of V₂O₃@C.

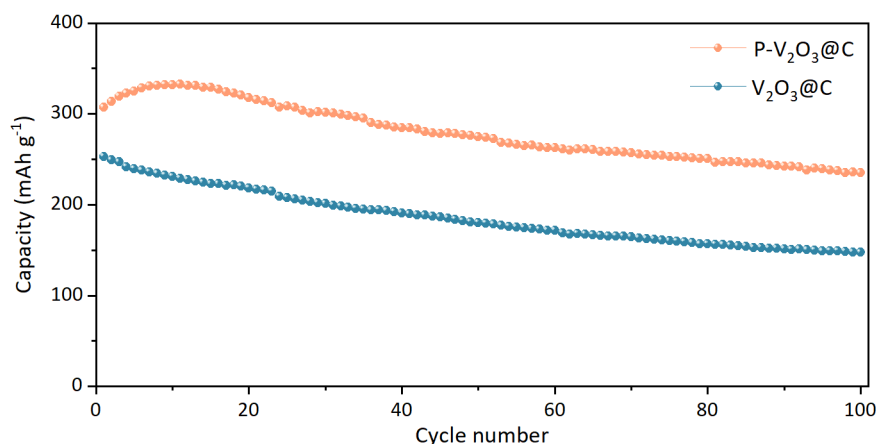


Figure S4. Long-term cycling performance at a current rate of 100 mA g⁻¹.

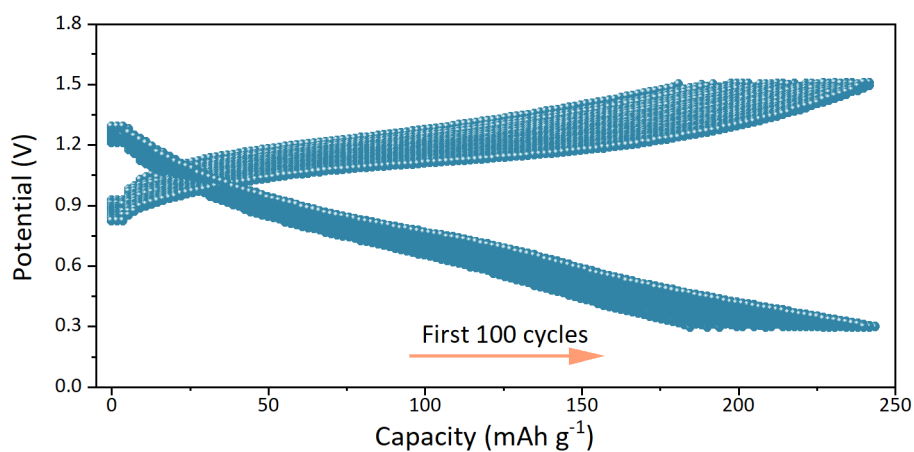


Figure S5. The charge and discharge profiles in the first 100 cycles.

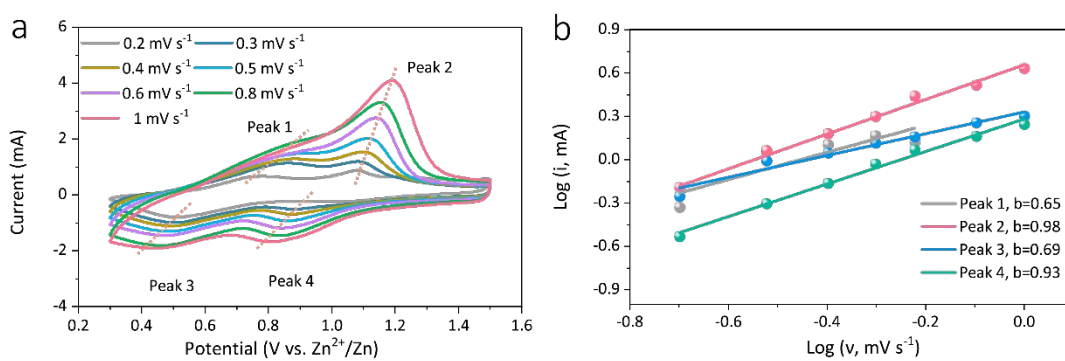


Figure S6. (a) CV curves of V₂O₃@C at different scan rates. (b) Log *i* versus log *v* plots of V₂O₃@C based on the CV profiles at different scanning rates.

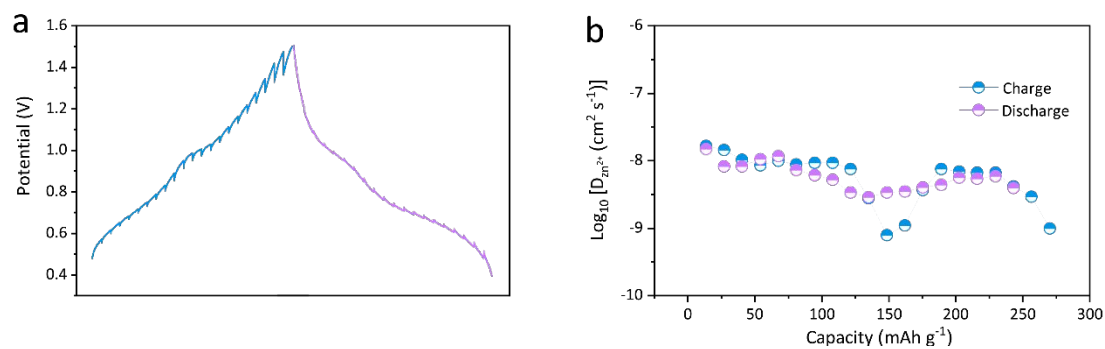


Figure S7. (a) GITT curves at a current density of 100 mA g^{-1} and (b) the corresponding Zn^{2+} diffusion coefficient during the charge-discharge scan of $\text{V}_2\text{O}_3@\text{C}$.

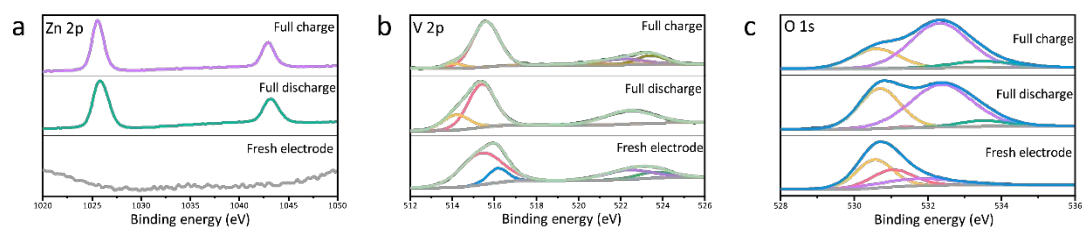


Figure S8. High-resolution XPS spectra of (a) Zn 2p, (b) V 2p and (c) O 1s of the P- $\text{V}_2\text{O}_3@\text{C}$ electrode at the pristine state and full first discharge (0.3 V) and charge state (1.5 V).