Supporting Information

**Monoclinic VO$_2$(D) hollow nanospheres with super-long cycle life for aqueous zinc ion batteries**

**Experimental Section**

*Preparation of vanadyl oxalate precursor:* 3.56 g of oxalic acid (C$_2$H$_2$O$_4$.2H$_2$O) was dissolved in 100 mL deionized water to form a transparent solution. Then, 2.0 g of commercial V$_2$O$_5$ powder was added to the above solution, and the mixture was stirred at 60 °C for a certain time. The color of solution transformed from yellow to green and then blue, suggesting V$^{5+}$ was reduced to V$^{4+}$. Finally, the blue solution was dried in an air oven at 75 °C for 2 days to obtain the vanadyl oxalate precursor.

*Preparation of VO$_2$(D) hollow nanospheres:* 60 mg of vanadyl oxalate precursor obtained above was dispersed into the mixed solvent of CH$_3$OH (48 mL) and H$_2$O (12 mL). After completely dissolution, the resulting solution was transferred into a 100 mL Teflon-sealed autoclave, and heated at 200 °C for 24 h. After cooling down to room temperature naturally, the produced precipitates were collected by filtration, and washed with deionized water and absolute ethanol several times. Finally, the product was dried in vacuum at 60 °C for 12 h.

*Material characterizations:* Crystallographic phases of samples were measured by X-ray power diffraction (D-500, Siemens) using Cu Kα radiation. The
morphologies of the products were tested by scanning electron microscope (SEM, JSM-6360LV) and transmission electron microscope (TEM, JEM-2100F). X-ray photoelectron spectroscopic (XPS) was performed on Phi Quantum 2000 spectrophotometer with Al Kα radiation for verifying the element valence state.

Electrochemical characterizations: Electrochemical measurements were conducted using CR2025 coin cell. The cathode was prepared by pressing a mixture of 70 wt.% active material, 20 wt.% super P and 10 wt.% PTFE onto titanium mesh, the mass loading was about 1.2-1.5 mg cm⁻² except that in Fig. 5b and 5c (2.5-2.8 mg cm⁻²). Zn metal foil was used as the anode, and 3 M ZnSO₄ aqueous solution as electrolyte. The charge-discharge cycles and rate performance were tested on Neware battery-testing instrument. The cyclic voltammetry (CV, voltage range: 0.2-1.5 V) and electrochemical impedance spectroscopy (EIS) tests were carried out on CHI 660E electrochemical workstation. The EIS were performed in a frequency range of 10⁻² to 10⁶ Hz with an amplitude of 5 mV.
**Fig. S1** The crystal structure of monoclinic VO$_2$(D).
Fig. S2 Raman spectrum of VO$_2$(D).
Fig. S3 (a,b) The EIS spectra of the assembled Zn/VO$_2$(D) battery after different cycles, among which the current density during the cycling was controlled at (a) 0.1 A g$^{-1}$ and (b) 10 A g$^{-1}$. (c) The equivalent circuit diagram that can be used to model these EIS spectra.
Fig. S4 Discharge curve in the 5th cycle at 0.1 A g\(^{-1}\).

The average discharge voltage is calculated as following [1]:

\[
\overline{U} = \frac{1}{Q_t} \int_0^{Q_t} U \, dQ
\]  

(1)

where \( U \) and \( Q \) are the potential and the discharge capacity respectively, and \( Q_t \) is the total capacity.
Fig. S5 E vs. t profiles of VO$_2$(D) electrode for a single GITT and linear behavior of the transient voltage changes E vs. $\tau^{1/2}$ during the discharge (a,b) and the charge (c,d) process.

**Detailed test process:** prior to GITT measurement, the assembled cells were charged/discharged at 0.1 A g$^{-1}$ for 5 cycles to activate the battery. In GITT test, the cell was charged or discharged with a test current density of 0.05 A g$^{-1}$ for an interval of 10 min, followed by an open circuit stand for 90 min, allowing the cell voltage to relax to its steady-state value. The procedure was repeated until the battery reached to the cut off voltage (1.5 or 0.2 V).

**Detailed calculation method:** considering the linear relationship between transient voltage changes E vs. $\tau^{1/2}$ (Fig. S5b and S5d), the diffusion coefficient of Zn$^{2+}$ can be calculated by the simplified equation [2,3]:
\[
D_{\text{Zn}} = \frac{4}{\pi \tau} \left( \frac{m_B v_m}{M_B S} \right)^2 \left( \frac{\Delta E_S}{\Delta E_\tau} \right)^2
\]  

(1)

Where, \(D_{\text{Zn}}\) (cm\(^2\) s\(^{-1}\)) is the chemical diffusion coefficient of Zn\(^{2+}\), \(\tau\) (s) is the pulse duration of constant current, \(m_B\) (g), \(M_B\) (g mol\(^{-1}\)), and \(v_m\) (cm\(^3\) mol\(^{-1}\)) correspond to the quality, molar mass, and molar volume of the active material, respectively, \(S\) (cm\(^2\)) is the contacting area of electrode with electrolyte (taken as the geometric area of electrode for better comparison with literatures), \(\Delta E_S\) is the voltage change of the termination voltage of two adjacent relaxation steps, \(\Delta E_\tau\) is the voltage difference during the current pulse subtracting the IR drop.
Fig. S6 Ex-situ XRD patterns of VO$_2$(D) collected in the second cycle at various discharged/charged states.
Fig. S7 TEM and HRTEM images of the VO$_2$(D) electrodes in pristine (a, d), fully discharged (b, e), and charged states (c, f).
Fig. S8 Galvanostatic discharge/charge curves of VO$_2$(D) in (a) pH 4 H$_2$SO$_4$ electrolyte and (b) 0.1 M Zn(CF$_3$SO$_3$)$_2$ electrolytes with different water content.
Fig. S9 Ex-situ XRD patterns for VO$_2$(D) cycled in 0.1 M Zn(CF$_3$SO$_3$)$_2$ electrolytes with pure AN and pure H$_2$O.
Fig. S10 XPS patterns of VO$_2$(D) collected in pristine and fully discharged/charged states.
**Table S1** Comparison of electrochemical performance of the VO$_2$(D) electrodes with previously reported vanadium based oxides cathode for ZIBs.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Rate capability</th>
<th>Cycling performance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$_{0.25}$V$_2$O$_5$:nH$_2$O</td>
<td>1M ZnSO$_4$</td>
<td>300/0.3; 260/2.4</td>
<td>211/81%/2.4/1000</td>
<td>[4]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$</td>
<td>0.5M Zn(AC)$_2$</td>
<td>97/0.05; 58/1</td>
<td>72/74%/0.05/100</td>
<td>[5]</td>
</tr>
<tr>
<td>LiV$_3$O$_8$</td>
<td>1M ZnSO$_4$</td>
<td>256/0.016; 29/1.67</td>
<td>150/75%/0.133/65</td>
<td>[6]</td>
</tr>
<tr>
<td>H$_2$V$_3$O$_8$</td>
<td>3M Zn(CF$_3$SO$_3$)$_2$</td>
<td>423.8/0.1; 113.9/5</td>
<td>136.1/94.3%/5/1000</td>
<td>[7]</td>
</tr>
<tr>
<td>VS$_2$</td>
<td>1M ZnSO$_4$</td>
<td>190.3/0.05; 115.5/2</td>
<td>110.9/98%/0.5/200</td>
<td>[8]</td>
</tr>
<tr>
<td>Zn$_3$V$_2$O$_5$(OH)$_2$:2H$_2$O</td>
<td>1M ZnSO$_4$</td>
<td>213/0.05; 76/3</td>
<td>101/68%/0.2/300</td>
<td>[9]</td>
</tr>
<tr>
<td>V$_2$O$_5$:nH$_2$O</td>
<td>3M Zn(CF$_3$SO$_3$)$_2$</td>
<td>372/0.3; 319/15</td>
<td>~213/71%/6/900</td>
<td>[10]</td>
</tr>
<tr>
<td>K$_2$V$<em>6$O$</em>{16}$:2.7H$_2$O</td>
<td>ZnSO$_4$</td>
<td>239.2/0.1; 178.0/6</td>
<td>154/82%/6/500</td>
<td>[11]</td>
</tr>
<tr>
<td>LVO-250</td>
<td>2M ZnSO$_4$</td>
<td>470/0.5; 170/10</td>
<td>192/-/-/10/1000</td>
<td>[12]</td>
</tr>
<tr>
<td>(NH$<em>4$)$<em>2$V$</em>{10}$O$</em>{25}$:8H$_2$O</td>
<td>3M Zn(CF$_3$SO$_3$)$_2$</td>
<td>228.8/0.1; 123.6/5</td>
<td>~111/90.1%/5/5000</td>
<td>[13]</td>
</tr>
<tr>
<td>Na$_{0.33}$V$_2$O$_5$</td>
<td>3M Zn(CF$_3$SO$_3$)$_2$</td>
<td>367.1/0.1; 96.4/2</td>
<td>218.4/93%/1.0/1000</td>
<td>[14]</td>
</tr>
<tr>
<td>VO$_2$(B)</td>
<td>3M Zn(CF$_3$SO$_3$)$_2$</td>
<td>274/0.1; 133/10</td>
<td>105/79.0%/10/10000</td>
<td>[15]</td>
</tr>
<tr>
<td>VO$_2$(B)</td>
<td>3M Zn(CF$_3$SO$_3$)$_2$</td>
<td>357/0.043; 171/51.2</td>
<td>250/91.2%/0.85/300</td>
<td>[16]</td>
</tr>
<tr>
<td>VO$_2$(D)</td>
<td>2M ZnSO$_4$</td>
<td>-</td>
<td>~50/15%/0.043/50</td>
<td></td>
</tr>
<tr>
<td>VO$_2$(D)</td>
<td>3M ZnSO$_4$</td>
<td>442/0.1; 200/20</td>
<td>298/81%/3/1200</td>
<td></td>
</tr>
</tbody>
</table>

Explanation of the above data implications: take the first Zn$_{0.25}$V$_2$O$_5$:nH$_2$O as an example, i) Rate capability, 300/0.3; 260/2.4 present that 300 mAh g$^{-1}$ at 0.3 A g$^{-1}$, and 260 mAh g$^{-1}$ at a high rate of 2.4 A g$^{-1}$; ii) Cycling performance, 211/81%/2.4/1000 present that 211 mAh g$^{-1}$ (capacity retention of 81%) was retained at 2.4 A g$^{-1}$ after 1000 cycles.
References


