Supporting Information


H$_2$V$_3$O$_8$ Nanowire/Graphene Electrodes for Aqueous Rechargeable Zinc Ion Batteries with High Rate Capability and Large Capacity

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Figure S1. XRD spectrum of the as-prepared H$_2$V$_3$O$_8$ NW/graphene powder.
Figure S2. XPS spectra of carbon element. a, XPS of C 1s of the graphene oxide powder. b, XPS of C 1s of the H$_2$V$_3$O$_8$ NW/graphene composite.
Figure S3. Structural and morphological characterizations of the pure $\text{H}_2\text{V}_3\text{O}_8$ NW. a, XRD pattern indicates no impurity in the sample. b, SEM image shows the uniform NW size and morphology the pure $\text{H}_2\text{V}_3\text{O}_8$ NW sample. c, TEM image shows the clean surface of the $\text{H}_2\text{V}_3\text{O}_8$ NWs. d, HRTEM image of the pure $\text{H}_2\text{V}_3\text{O}_8$ NW.

Figure S4. BET curves of $\text{H}_2\text{V}_3\text{O}_8$ NW/graphene composite and pure $\text{H}_2\text{V}_3\text{O}_8$ NWs.
Figure S5. SEM image of the pristine H$_2$V$_3$O$_8$ NW/graphene electrode. The graphene film in the electrode builds additional conductive pathway between H$_2$V$_3$O$_8$ NWs and conductive additive.

Figure S6. The thermogravimetry curves of H$_2$V$_3$O$_8$ NW/graphene composite and pure H$_2$V$_3$O$_8$ NWs. The weight loss before 350 °C was the dehydration process primarily from the H$_2$V$_3$O$_8$ crystals and yielded V$_3$O$_7$. After 350 °C, a slight weight increase was due to the oxidation of V$_3$O$_7$ to V$_2$O$_5$ (black curve). From the H$_2$V$_3$O$_8$/graphene sample (red curve), a significant weight loss between 350 and 420 °C was observed. This can be attributed to the decomposition of graphene, which typically decompose at ~400 °C.$^{[1-3]}$ The curve then became flat and parallel to the black curve. Therefore, we can safely estimate that the difference at the high-temperature parallel region between these two curves was corresponding to the amount of graphene in the composite. Thus, the mass fraction of graphene in the composite was estimated to be 4.7 wt.%.
Figure S7. SEM image of the cross section of an as-fabricated electrode.

Figure S8. Electrochemical performance of the pure H$_2$V$_3$O$_8$ NW electrode. a, The cycling performance of the H$_2$V$_3$O$_8$ NW/graphene composite and pure H$_2$V$_3$O$_8$ NWs electrodes at 1/3 C rate. b, The rate capability of the electrode at C rate range from 1/3 C to 5 C.
Figure S9. a, The XRD spectra of the H$_2$V$_3$O$_8$ NW/graphene electrode before and after 2000 cycles at 20C. b, The magnification of Figure S9a between 7° - 14°.
Figure S10. EIS spectrum of the electrodes after different cycles. H$_2$V$_3$O$_8$ NW/graphene electrode after 1$^{\text{st}}$ (black) and 150$^{\text{th}}$ (red) discharge and pure H$_2$V$_3$O$_8$ NW electrode after 1$^{\text{st}}$ (yellow) and 150$^{\text{th}}$ (blue) discharge.

Figure S11. XRD shift of the (200) peak of the H$_2$V$_3$O$_8$ NW/graphene electrode at different charge-discharge stage.
Figure S12. HRTEM image of the NWs remained the pure $\text{H}_2\text{V}_3\text{O}_8$ phase.

Figure S13. a, STEM image of the $\text{H}_2\text{V}_3\text{O}_8$ NW. b, Crystal structure of $\text{H}_2\text{V}_3\text{O}_8$ viewed along the [100] direction.
Density functional theory (DFT) calculations

DFT calculations were performed with the Vienna Ab-initio Simulation Package (VASP) using a plane wave basis set, the GGA-Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and the projector augmented wave (PAW) method. Rotationally invariant in GGA+$U$ was employed\cite{4} to correct the strong electronic correlation among localized V 3d electrons. Parameters $U_{\text{eff}} = U - J = 3.25$ eV was used. The same $U_{\text{eff}}$ was applied on Zn. The charge state of Zn is assumed to be $+2$, which is achieved by a homogenous charge background in the calculation. In DFT calculations, $2 \times 1 \times 1 104$ atom supercell was used with kinetic energy cutoff of 520 eV and $4 \times 4 \times 2$ Monkhorst-Pack $k$-mesh. The Hellmann-Feynman forces were converged to 0.001 eV/Å. This DFT relaxation gave the potential ground state of Zn position at the global energy minimum. In the real case, particularly during fast electrochemical reactions at relatively low temperature, Zn$^{2+}$ ions can be kinetically trapped at neighboring local minimums. Therefore, this DFT calculation cannot give precise atomic location of the kinetically stabilized system. Instead, it provides a support to valid the interaction sites of Zn$^{2+}$ ions.

Figure S14. 2D Gaussian fitting with projected V interatomic distances marked (red squares) and additional potential Zn HAADF signals located inside the V quasi-hexagon (white arrow).

2D Gaussian fitting

To achieve sub-pixel location of the atomic column position, each V atomic column was fit to a 2D Gaussian function by the standard Levenberg-Marquart $L^2$-norm minimization method,
following approaches used by Yankovich. The function form for the fitting was

$$z(x, y) = z_0 + A \exp \left( \frac{1}{2(1-c^2)} \left( \frac{x-x_0}{x_w} \right)^2 + \left( \frac{y-y_0}{y_w} \right)^2 - \frac{2c(x-x_0)(y-y_0)}{x_w y_w} \right),$$

where $z_0, A, c, x_w, y_w, x_0$ and $y_0$ are fitting parameters. The column position is $(x_0, y_0)$.

Table S1. The lattice parameters calculated from the XRD curves.

<table>
<thead>
<tr>
<th>sample</th>
<th>$a$ (nm)</th>
<th>$b$ (nm)</th>
<th>$c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$V$_3$O$_8$/graphene</td>
<td>1.693(1)</td>
<td>0.936(5)</td>
<td>0.364(5)</td>
</tr>
<tr>
<td>Pure H$_2$V$_3$O$_8$</td>
<td>1.693(2)</td>
<td>0.935(7)</td>
<td>0.364(6)</td>
</tr>
</tbody>
</table>

Table S2. Zn/V compositions obtained from XPS analysis for the pristine and fully discharged/charged electrodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Pristine electrode</th>
<th>discharged to 0.2V</th>
<th>Charged to 1.6 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn atom/V atom</td>
<td>0</td>
<td>2.11/3</td>
<td>0.30/3</td>
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</table>

References


