

Supporting Information

H₂V₃O₈ Nanowires as High-Capacity Cathode Materials for Magnesium-Based Battery

*Han Tang,¹ Nuo Xu,² Cunyuan Pei,¹ Fangyu Xiong,¹ Shuangshuang Tan,¹ Wen Luo,¹ Qinyou An^{*1} and Liqiang Mai^{*1,3}*

¹State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Hubei, Wuhan 430070, China

²School of Chemistry, Chemical Engineering and Life Sciences, Wuhan University of Technology, Hubei, Wuhan 430070, China.

³Department of Chemistry, University of California, Berkeley, California 94720, United States

*E-mail: anqinyou86@whut.edu.cn; mlq518@whut.edu.cn.

Experimental section

Synthesis of H₂V₃O₈ nanowires

A facile, one-step hydrothermal method which was ameliorated from our previous work was applied.¹ Briefly, V₂O₅ sol and aniline were mixed with molar ratio of 30:1 under constant stirring. After stirred for 1 h, polyethylene glycol (PEG-4000) was added into the above solution until the concentration reached 1.7 g/L. Then, the above solution was transferred to the Teflon-lined stainless steel autoclave and kept under 180 °C for 48 h. Dark green products could be prepared after washed by deionized water and ethanol, respectively. Finally, the H₂V₃O₈ nanowires were obtained by drying the hydrothermal product at 80 °C for 8 h in vacuum.

Material characterization

X-ray diffraction (XRD) measurements were performed to investigate the crystallographic information using a Bruker D8 Advance X-ray diffractometer with a non-monochromated Cu K α X-ray source. Scanning electron microscopy (SEM) images were collected with a Jeol JSM-7100F field emission scanning electron microscope at an acceleration voltage of 15 kV. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded with a Jeol JEM-2100F scanning transmission electron microscope/energy dispersive X-ray spectroscopy (EDX) microscope. Raman spectra were obtained using a Renishaw IN VIA micro-Raman spectroscopy system. Fourier transform-infrared (FTIR) transmittance spectra were recorded using a Nicolet 60-SXB IR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed using a VG MultiLab 2000 instrument.

Preparation of electrolytes

All the preparation process operated in the glove box full filled with the argon and both moisture and oxygen concentrations were under 0.1 ppm. The all-phenyl complex (APC) electrolytes were prepared according to Oren Mizrahi et al.² The tetrahydrofuran (THF, Aldrich, 99.9%) was mixed with molecular sieve (4 Å molecular sieves) for one week to reduce the trace amounts of water. The first step, 0.0667 g aluminum chloride (Aldrich, 99.99%) powder was added into 15 ml THF very slow and carefully with vigorous stirring,

this step last about 2 h. Next, the above solution was added dropwise into 5 ml phenyl magnesium chloride (Macklin, 2 M solution in THF) with vigorous stirring, this step continued about 1 h. After stirred about 12 h, the 0.25 M APC was obtained. Finally, corresponding LiCl powder was added into 0.25 M APC with vigorous stirring and it last about 12 h to obtain hybrid $\text{Mg}^{2+}/\text{Li}^+$ electrolyte.

Fabrication of battery and the electrochemical measurements

The synthetic $\text{H}_2\text{V}_3\text{O}_8$ nanowires, acetylene black, and polytetrafluoroethylene (PTFE) were mixed in a weight ratio of 8:1:1 and then grinded in agate mortar sufficiently about 30 min. Next they were put into roller press and pushed into disks with an area about 0.5 cm^2 with a loading of $\sim 1.5 \text{ mg cm}^{-2}$. Finally, the disks of cathode material was dried in the vacuum drying oven about 12 h. To three-electrode cell, the material was pushed on stainless steel meshes with a mass loading about 1.5 mg cm^{-2} . Activated carbon (AC) clothes are both used as counter and reference electrode. The potential of AC cloth was measured to be 0.12 V vs ferrocene/ferrocenium, i.e. 2.4 V vs Mg/Mg^{2+} .³ The working electrodes were operated within -1.2 to 0.7 V vs AC, equivalent to 1.2 to 3.1 V vs Mg/Mg^{2+} . When tested the electrolyte property, Pt foil was used as working electrode and Mg foils are used as counter and reference electrodes. Galvanostatic charge/discharge cycling, cyclic voltammetry were measured using a potentiostat (Bio-Logic VMP-3). To coin cell, the glass microfibre membrane was chosen as the separator. Mg metal was polished with sandpaper and pushed into disks as anode before use. These parts were assembled orderly by CR2016 coin cells in glove box. Galvanostatic charging/discharging tests of the cells were carried out with the potential region of 0.5–2 V (vs Mg/Mg^{2+}) on a multichannel battery testing system (LAND). Cyclic voltammetry (CV) of the cells was recorded using an electrochemical analyzer (Autolab PGSTAT302 and CHI 760D).

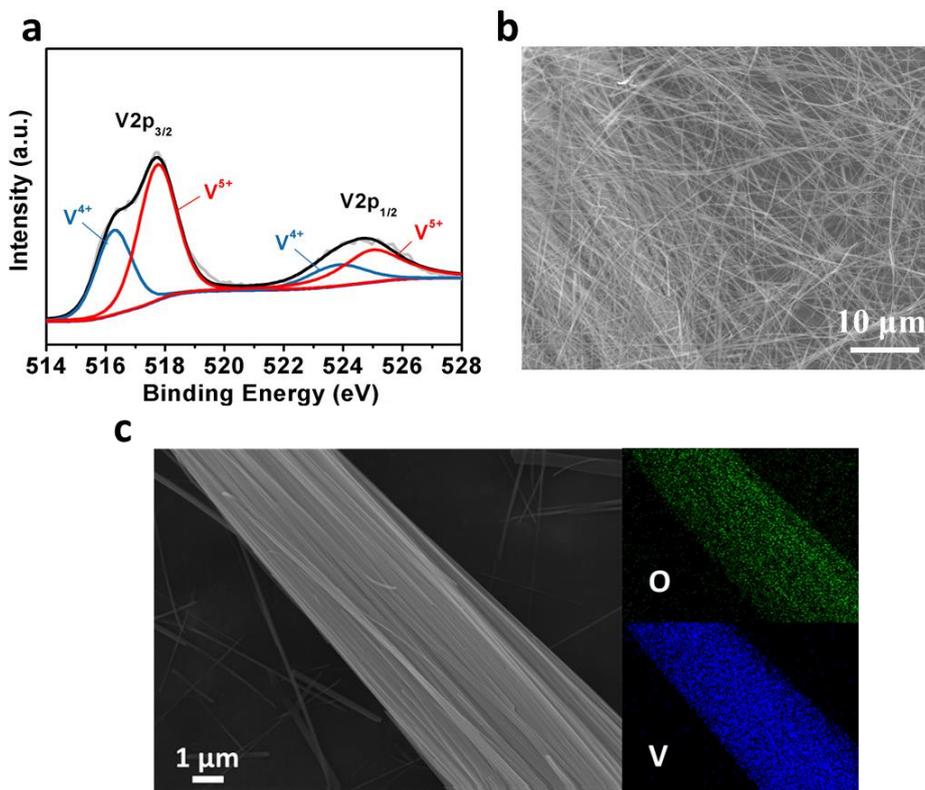


Figure S1. (a) XPS spectrum of vanadium element, (b) SEM images and (c) elemental mapping images of H₂V₃O₈.

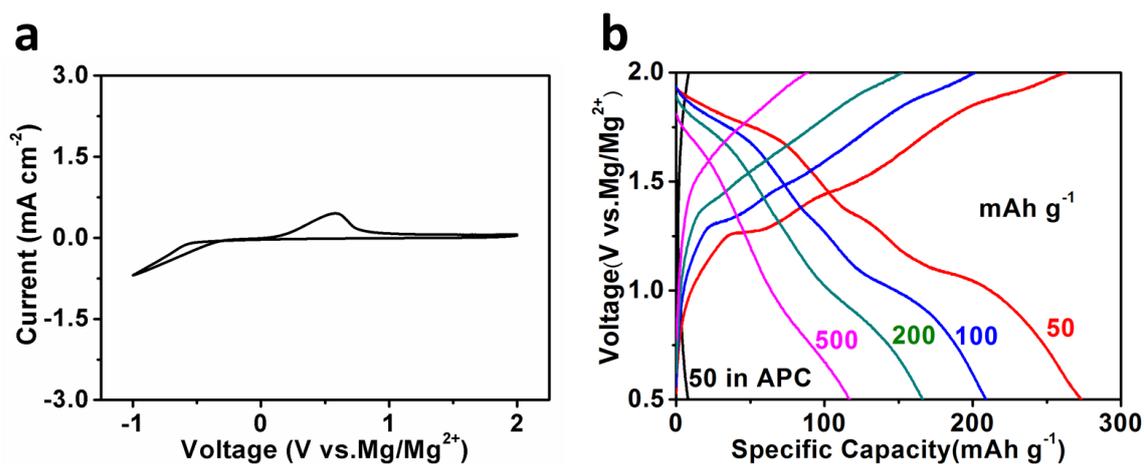


Figure S2. (a) CV curves of APC on SS working electrode with Mg as both counter and reference electrode. (b) Charge/discharge profiles of the H₂V₃O₈ nanowires at the current density of 50/100/200/500 mA g⁻¹ in hybrid Mg²⁺/Li⁺ battery and at the current density of 50 mA g⁻¹ in Mg battery.

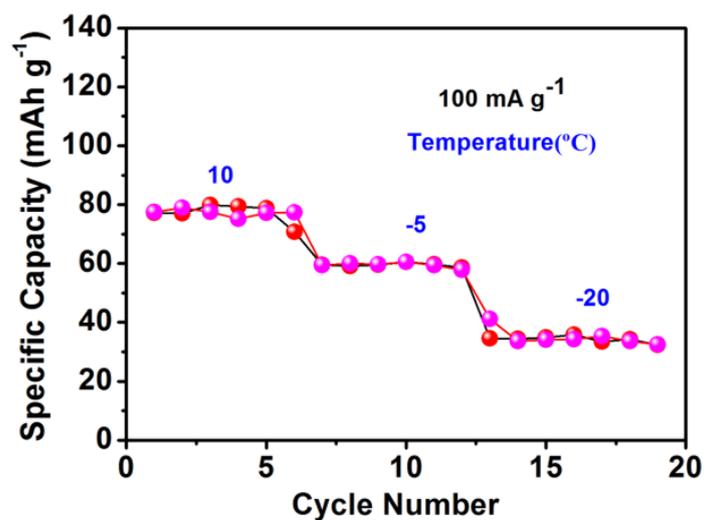


Figure S3. Discharge and charge specific capacity of $\text{H}_2\text{V}_3\text{O}_8$ nanowires at low temperatures between 10 and $-20\text{ }^\circ\text{C}$ at 100 mA g^{-1} .

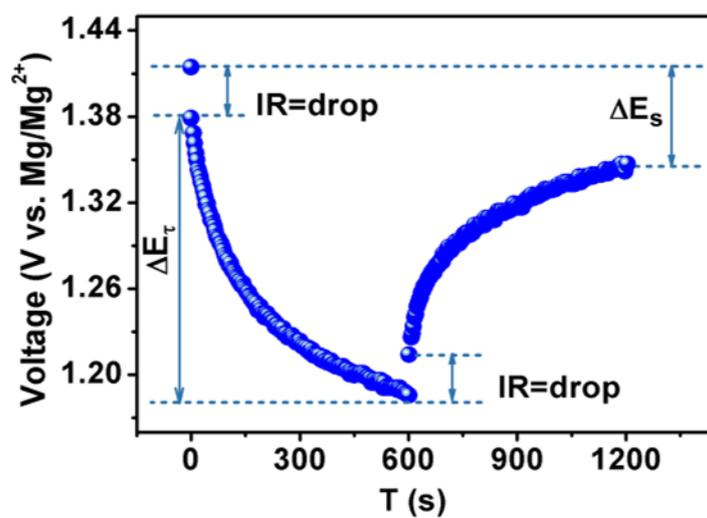


Figure S4. GITT potential feedback curve with time.

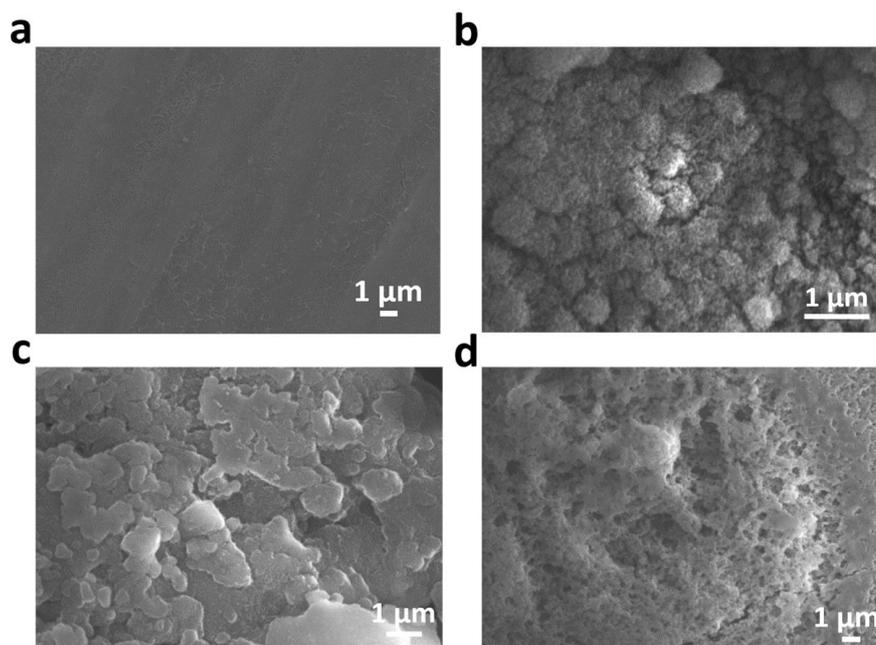


Figure S5. SEM images of Mg anode in fresh (a) and after 30 (b), 50 (c), 100 (d) cycles.

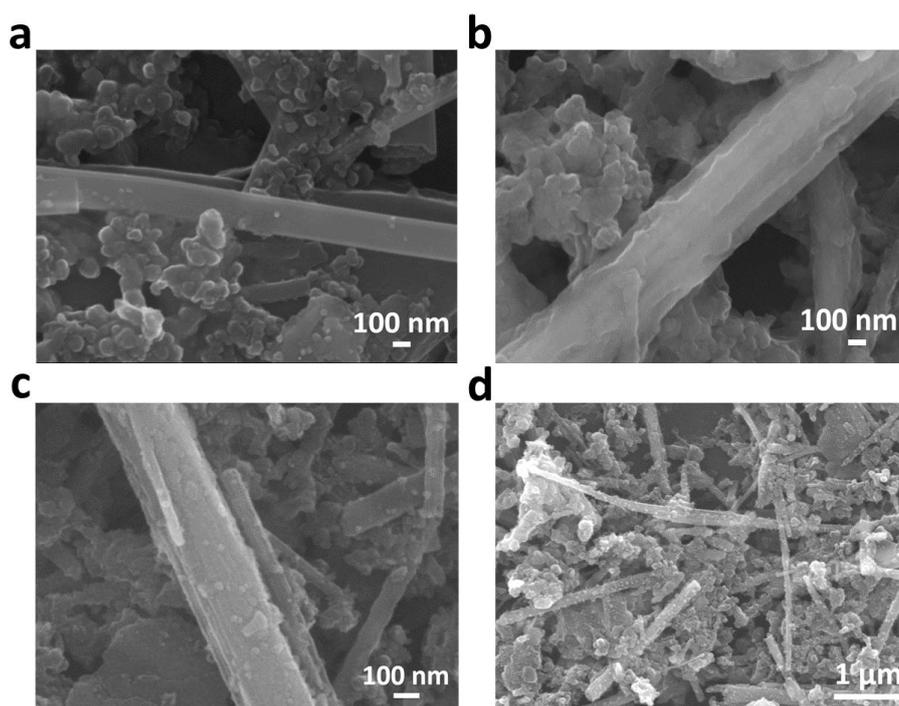


Figure S6. SEM images of $\text{H}_2\text{V}_3\text{O}_8$ nanowires in fresh (a) and after 30 (b), 50 (c), 100 (d) cycles.

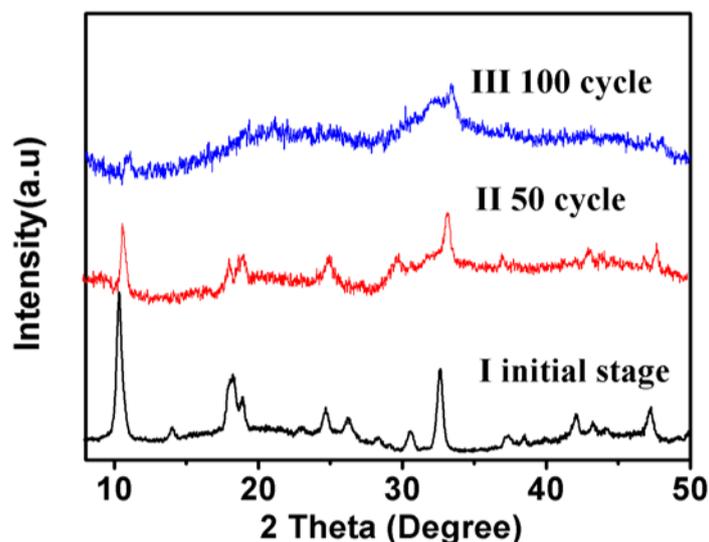


Figure S7. XRD patterns of $\text{H}_2\text{V}_3\text{O}_8$ nanowires in initial stage and after 50, 100 cycles.

$$D^{GITT} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau} \right)^2$$

Scheme 1. τ is the constant current pulse time, m_B is mass of active materials, V_M refers to molar volume of $\text{H}_2\text{V}_3\text{O}_8$, M_B is the molar mass of $\text{H}_2\text{V}_3\text{O}_8$, S is the electrode–electrolyte interface, ΔE_S is the voltage difference during the open circuit time, and ΔE_τ is the total change of battery voltage during a constant current pulse without the IR drop.

References

1. An, Q.; Sheng, J.; Xu, X.; Wei, Q.; Zhu, Y.; Han, C.; Niu, C.; Mai, L. Ultralong $\text{H}_2\text{V}_3\text{O}_8$ nanowire bundles as a promising cathode for lithium batteries. *New. J. Chem.* **2014**, *38*, 2075-2080.
2. Mizrahi, O.; Amir, N.; Pollak, E.; Chusid, O.; Marks, V.; Gottlieb, H.; Larush, L.; Zinigrad, E.; Aurbach, D. Electrolyte Solutions with a Wide Electrochemical Window for Rechargeable Magnesium Batteries. *J. Electrochem. Soc.* **2008**, *155*, A103-A109.
3. Gershinsky, G.; Yoo, H. D.; Gofer, Y.; Aurbach, D. Electrochemical and Spectroscopic Analysis of Mg^{2+} Intercalation into Thin Film Electrodes of Layered Oxides: V_2O_5 and MoO_3 . *Langmuir*, **2013**, *29*, 10964-10972.