Supporting Information

Flower-like W/WO₃ as Novel Cathode for Aqueous Zinc-Ion Batteries

Korkrit Songmueang¹,²†, Dongdong Zhang²,³†, Jin Cao²,³, Xinyu Zhang⁴*, Soorathep Kheawhom⁵,⁶, Chakrit Sriprachuabwong⁷, Adisorn Tuantranont⁷, Panyawat Wangyao¹*, Jiaqian Qin²,⁶*

¹ Metallurgical Engineering Department, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand
² Metallurgy and Materials Science Research Institute, Chulalongkorn University, Bangkok, 10330, Thailand
³ International Graduate Program of Nanoscience & Technology, Chulalongkorn University, Bangkok, 10330, Thailand
⁴ State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, P. R. China
⁵ Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
⁶ Research Unit of Advanced Materials for Energy Storage, Chulalongkorn University, Bangkok 10330, Thailand
⁷ Graphene and Printed Electronics for Dual-Use Applications Research Division (GPERD), Nation Security and Dual-Use Technology Center (NSD), National Science and Technology Development Agency (NSTDA), 111 Thailand Science Park, Phathum Thani 12120, Thailand

† These authors contributed equally to this work.
* Corresponding author e-mail: xyzhang@ysu.edu.cn, Panyawat.W@chula.ac.th, Jiaqian.q@chula.ac.th

Phone: +66 (0) 2218 1834, Fax: +66 (0) 2611 7586
Experimental

Preparation of flower-like W/WO$_3$

The fabrication of flower-like W/WO$_3$ only includes a heat treatment process for pure tungsten powder (Xianglu Tungsten Co. Ltd., China). Typically, 1 g tungsten powder was directly calcined in muffle furnace to 550 °C with a heating rate of 5 °C min$^{-1}$ and then hold for 1 h. WO$_3$ was synthesized by heating tungsten powder in muffle furnace at 700 °C with a heating rate of 5 °C min$^{-1}$ and then hold for 1 h.

Characterization

The morphology of as-prepared materials was observed via scanning electron microscopy (SEM, Hitachi S4800) and the transmission electron microscopy (TEM, JEM-1400). And the phase structures and chemical composition of materials were investigated by X-ray diffraction (XRD, Rigaku D) and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB).

Electrochemical performance

The electrochemical performance of the as-prepared materials was investigated by assembling the coin cells (CR2032) with zinc foil anode. And the cathodes were prepared via mixing the materials, conductive carbon and PVDF at the mass ratio of 8:1:1, and then coating the slurry on graphite paper. The average mass loading of the active materials was about 1.1 mg cm$^{-2}$. After drying under vacuum at 80 °Cs for 12 h, cutting into round electrode pieces with a diameter of 14 mm. The 2 M ZnSO$_4$ solution was served as electrolyte. The galvanostatic charge/discharge (GCD) measurement was performed to identify the rate performance and cycling stability (BTS, CT-4008,
Neware, China) with a potential range of 0.1-1.2 V. The cyclic voltammetry (CV) profiles and electrochemical impedance spectroscopy (EIS) (0.01 Hz to 10 kHz) of the materials were recorded on a CHI 660E workstation (China).

**Details of the Calculation**

**Capacitance Contribution**

According to the reported literatures,[1-2] the measure current \(i\) and scan rate \(v\) in CV curves have relationships with equation:

\[
i = av^b
\]

\[
\lg(i) = blg(v) + lg(a)
\]

where \(i\) represents peak current, \(a\) denotes constant, \(v\) is the scan rate and \(b\) is equaled to the slope of the \(\lg(v)\)-\(\lg(i)\) plots. If \(b\) approximately equals to 0.5, suggesting the diffusion process is dominant, while a capacitive behavior will dominate when \(b\) is about 1. [3]

The capacitance contribution can be further measured according to equations (3) and (4):

\[
i(v) = k_1v + k_2v^{1/2}
\]

\[
\frac{i(v)}{v^{1/2}} = k_1v^{1/2} + k_2
\]

Where the capacitive contribution can be divided into capacitive (measured with \(k_1\)) and diffusion-controlled (measured with \(k_2\)). By determining values of both \(k_1\) and \(k_2\), we can distinguish the fraction of the current from surface capacitance and diffusion limited. [4]
**Zn\(^{2+}\) Diffusion Coefficient**

The diffusion coefficient of Zn\(^{2+}\) was measured by using GITT and calculated based on the following equation: \(^{5-7}\)

\[
D = \frac{4L^2 \Delta E_S^2}{\pi \tau (\Delta E_t)^2}
\]

(5)

Where \(t\) and \(\tau\) represent the duration of current pulse (s) and relaxation time (s), respectively. \(L\) corresponds to Zn\(^{2+}\) diffusion length, which is equal to thickness of electrode. \(\Delta E_S\) and \(\Delta E_t\) are the steady-state voltage change (V) by the current pulse and voltage change (V) during the constant current pulse (eliminating the voltage changes after relaxation time).

**Energy Density and Power Density**

For coin cell, the energy density and power density were obtained by the following equations (6) (7):

\[
E = \int_0^{\Delta t} \frac{V \times i}{m} dt
\]

(6)

\[
P = \frac{E}{1000 \times \Delta t}
\]

(7)

where \(E\) (Wh kg\(^{-1}\)) is the energy density, \(P\) is the power density (kW kg\(^{-1}\)), \(V\) (V), \(i\) (mA), \(m\) (g) and \(\Delta t\) (h) represent the working potential, discharging current, the mass loading of the cathode and the discharging time, respectively.
Figure S1 Quantitative analysis of the W/WO$_3$. 
Figure S2 (a) (b) (c) SEM images of pure W.
Figure S3 EDS result of W/WO$_3$. 
Figure S4 XPS survey of W/WO$_3$. 
Figure S5 SEM image of W/WO$_3$ after cycling.
References


