

## Supporting information

### Surface Electroactive Sites of Tungstated Zirconia Catalysts for Vanadium Redox Flow Batteries

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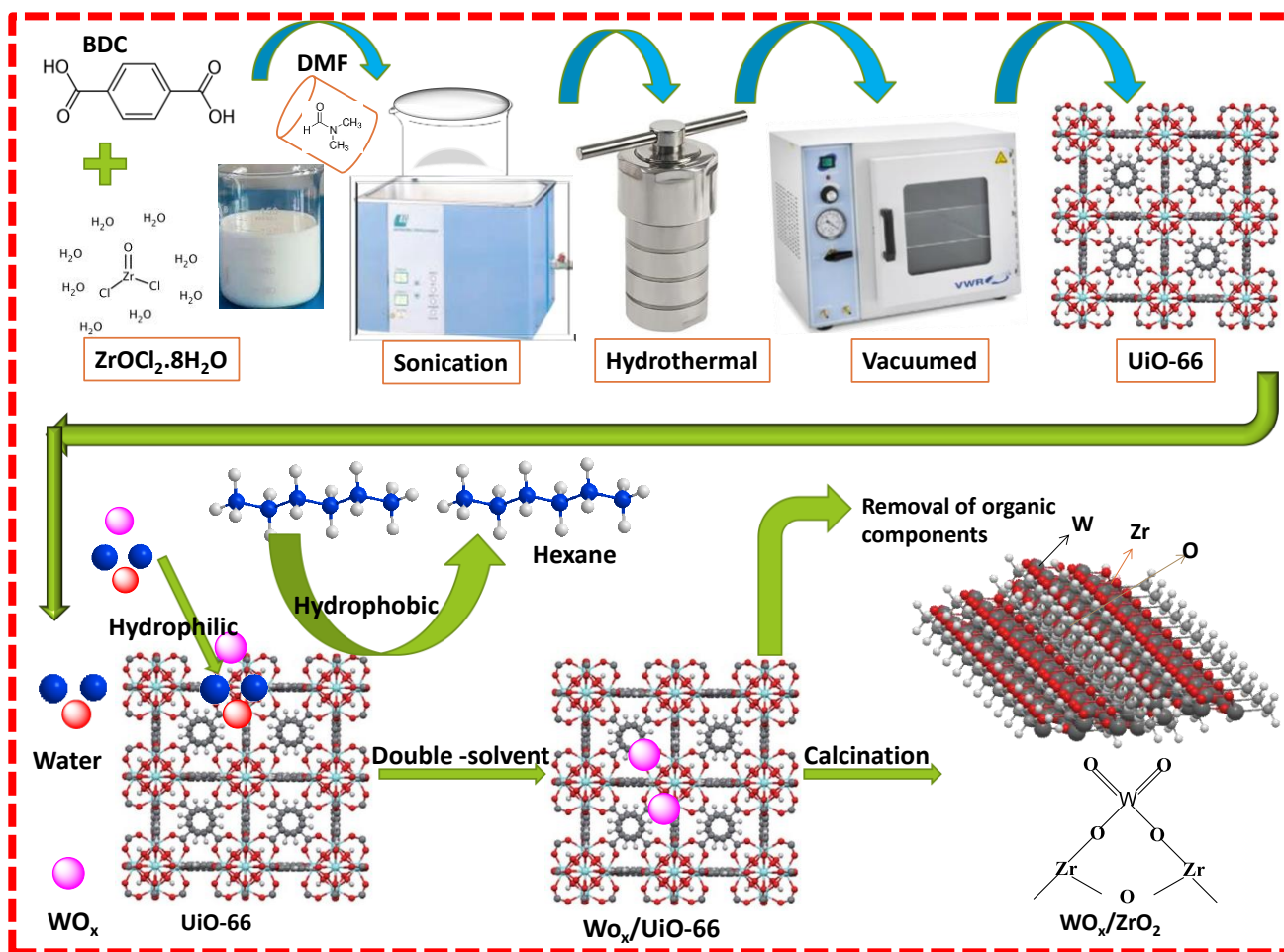
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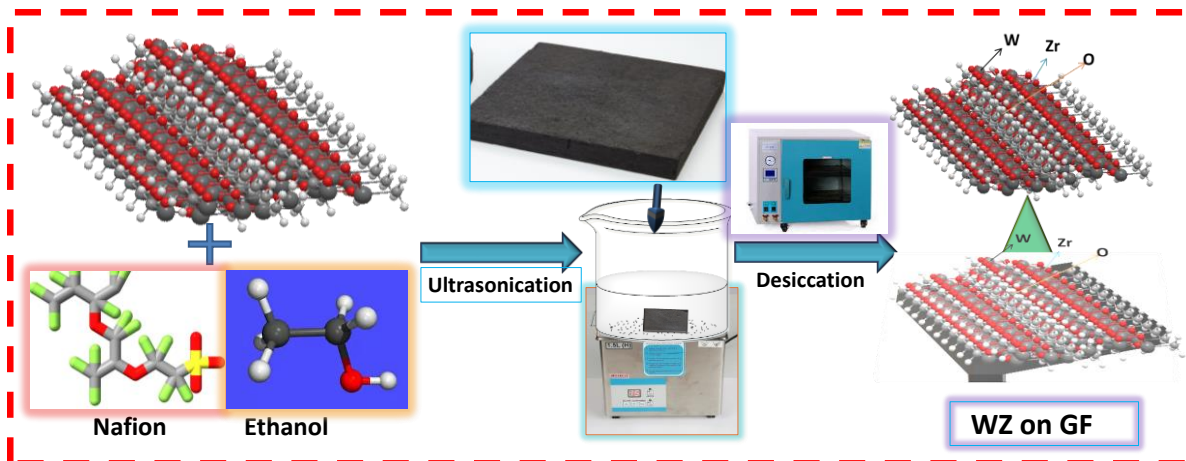
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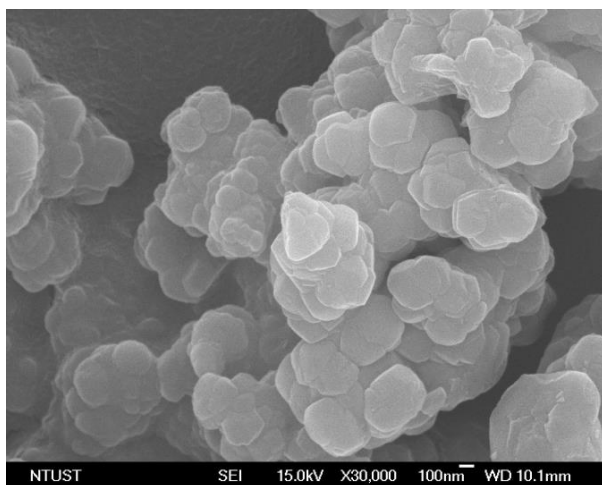


**Scheme S1** Synthetic procedure of the double-solvent method and transformation of  $WO_x/Uio-66$  into tungstated zirconia (WZ) by thermal decomposition.

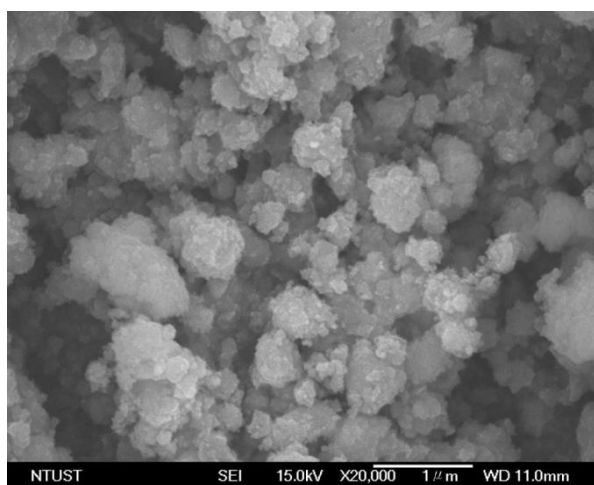


**Scheme S2** Schematic diagram for the preparation of high-entropy oxides on graphite felt.

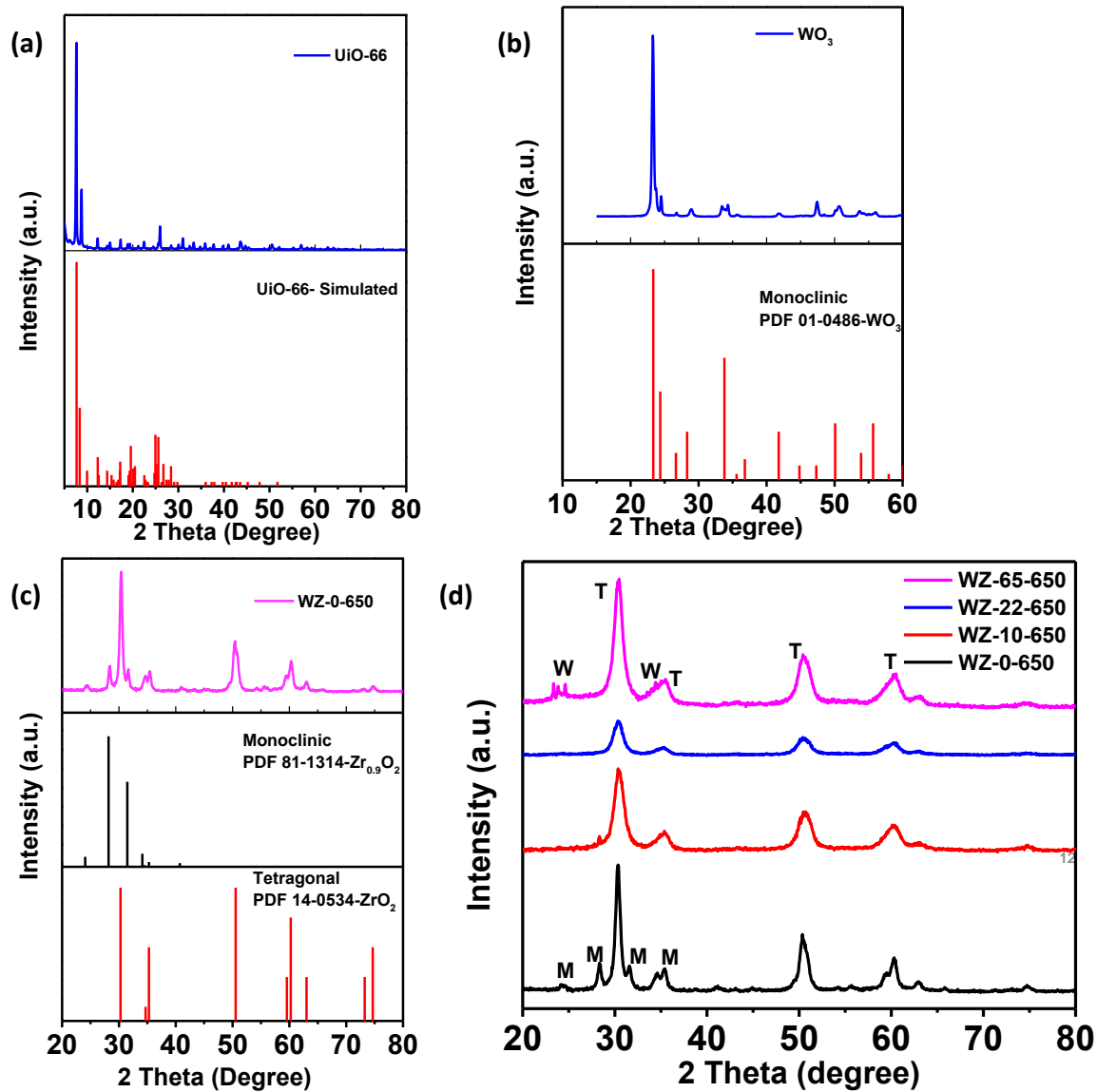
**(a)**



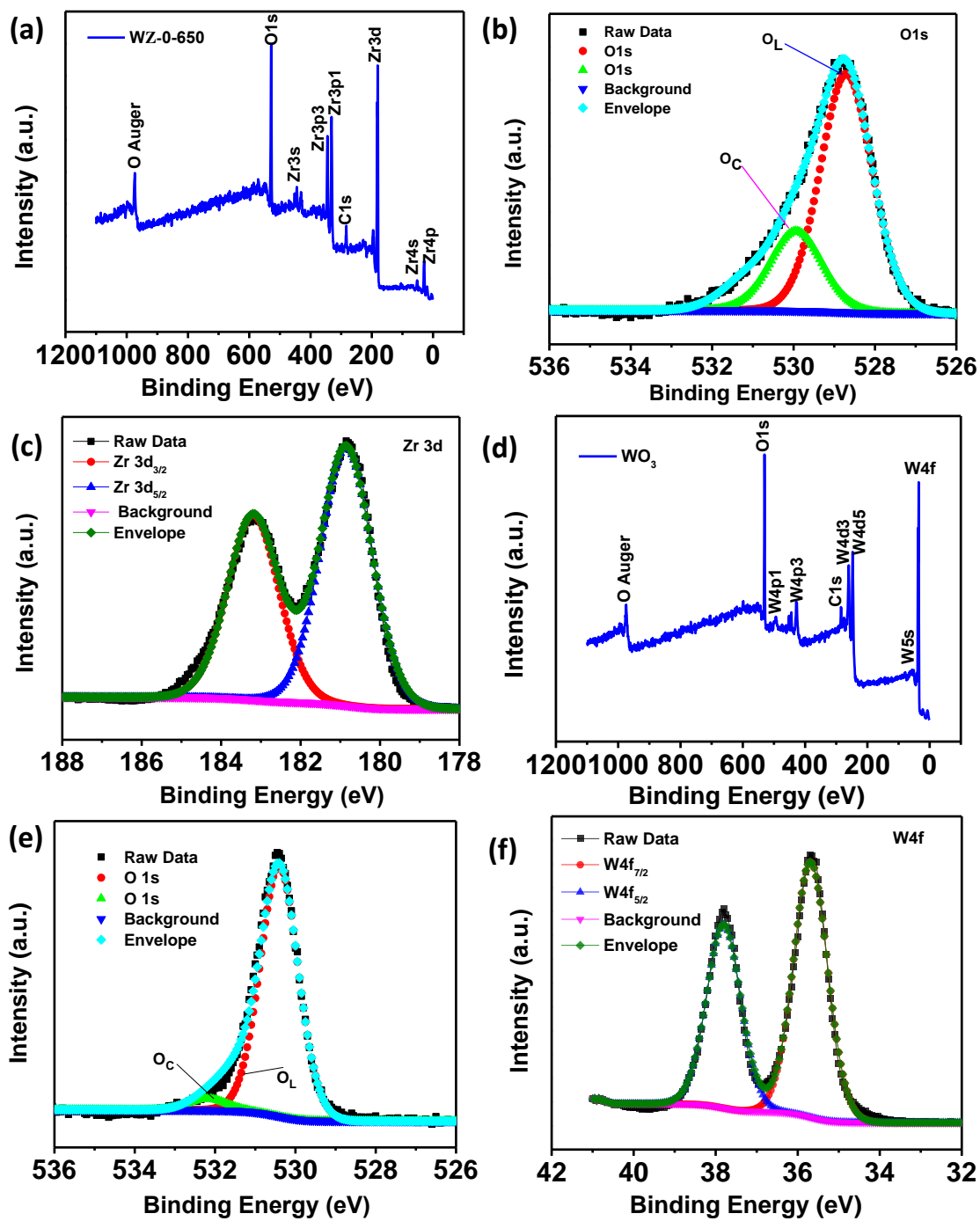
**(b)**



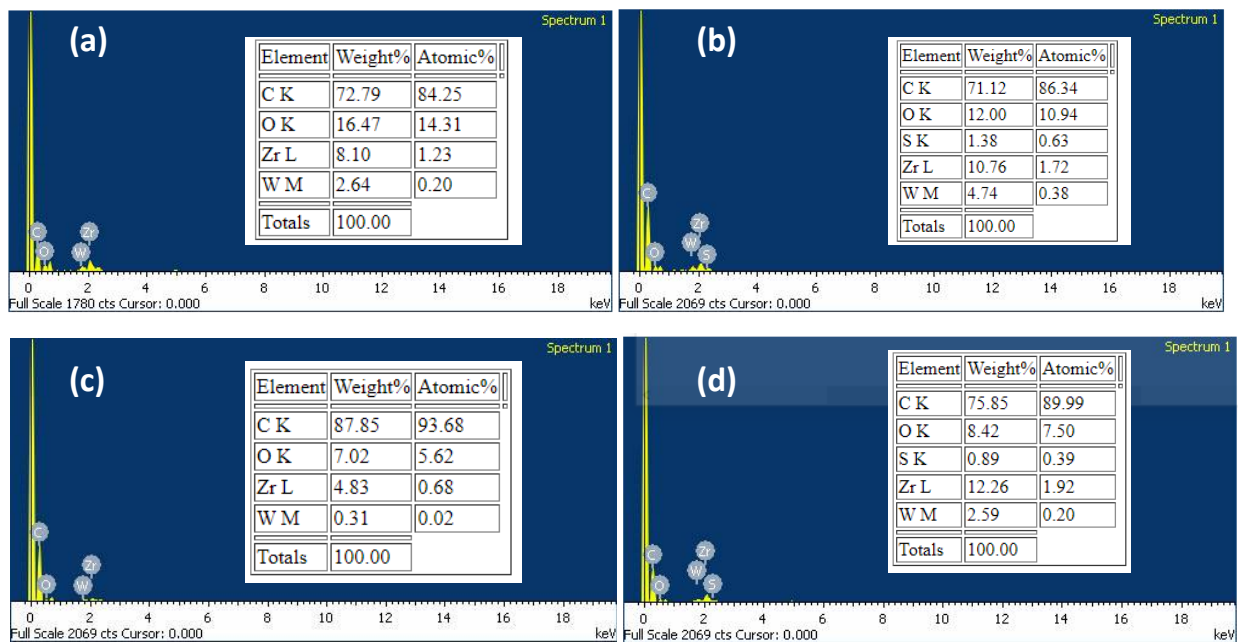
**Figure S1** SEM images of the (a) UiO-66 and (b) WZ-22-650.



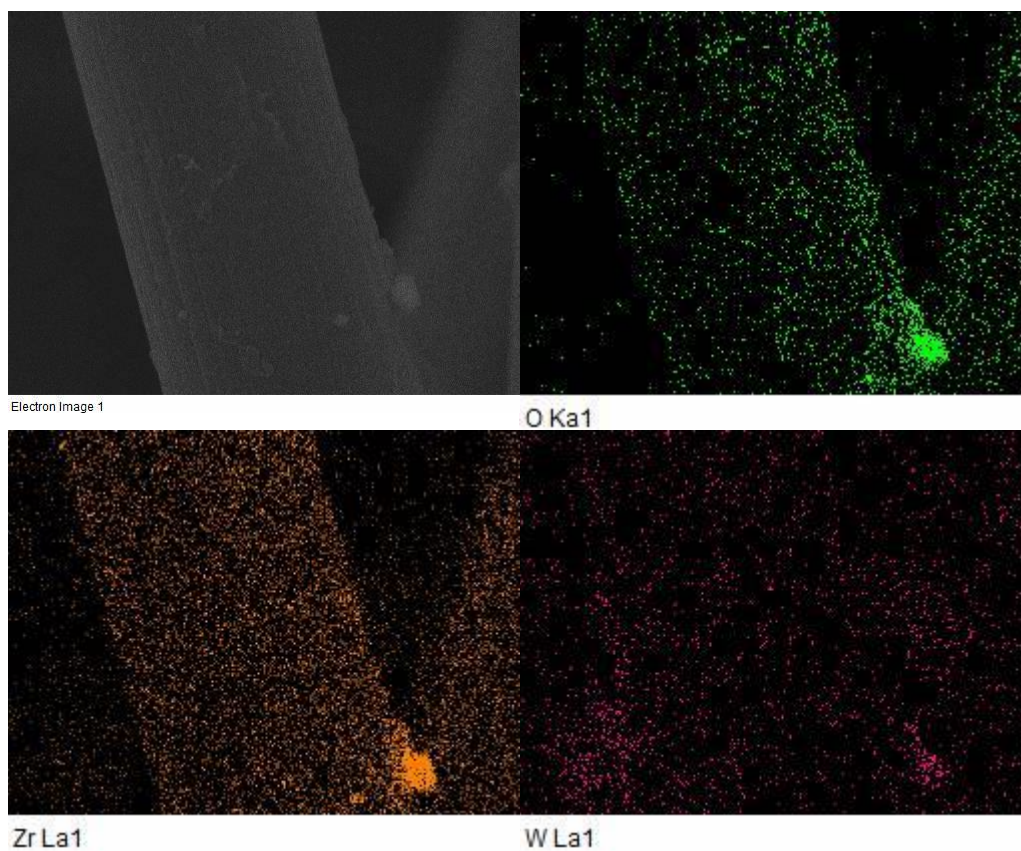
**Figure S2** the XRD pattern of (a) UiO-66, (b) WO<sub>3</sub>, (c) WZ-0-650, and (d) different W contents.



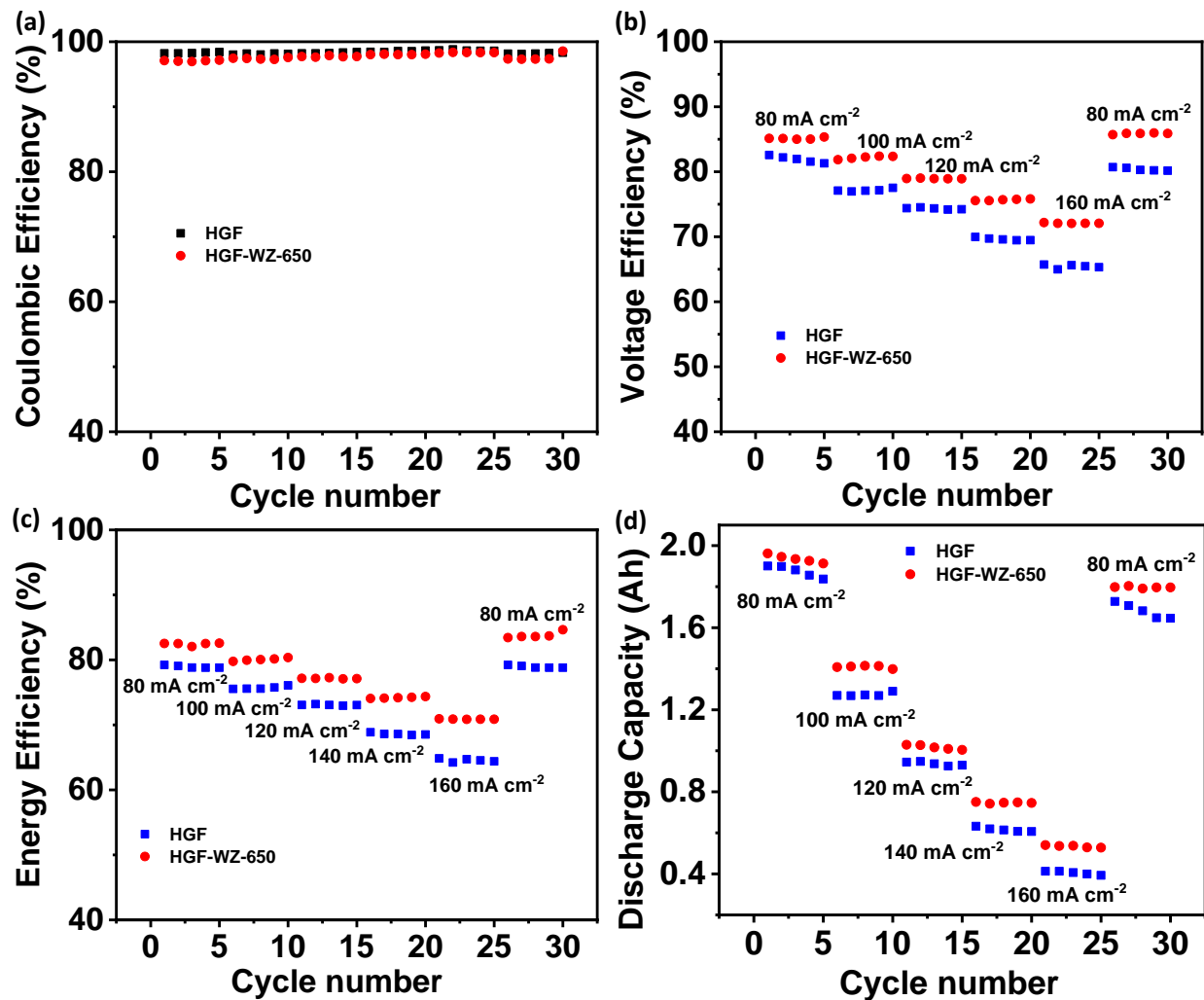
**Figure S3** XPS analysis of the WZ-0-650 and WO<sub>3</sub>: (a) element survey, (b) O1s, (c) Zr3d, (d) element survey, (e) (O1s), and (f) W4f, respectively.



**Figure S4** the EDS images of HGF-WZ-22-650 electrode, (a) before CV, (b) after CV, (c) before charge-discharge, and (d) after charge-discharge.

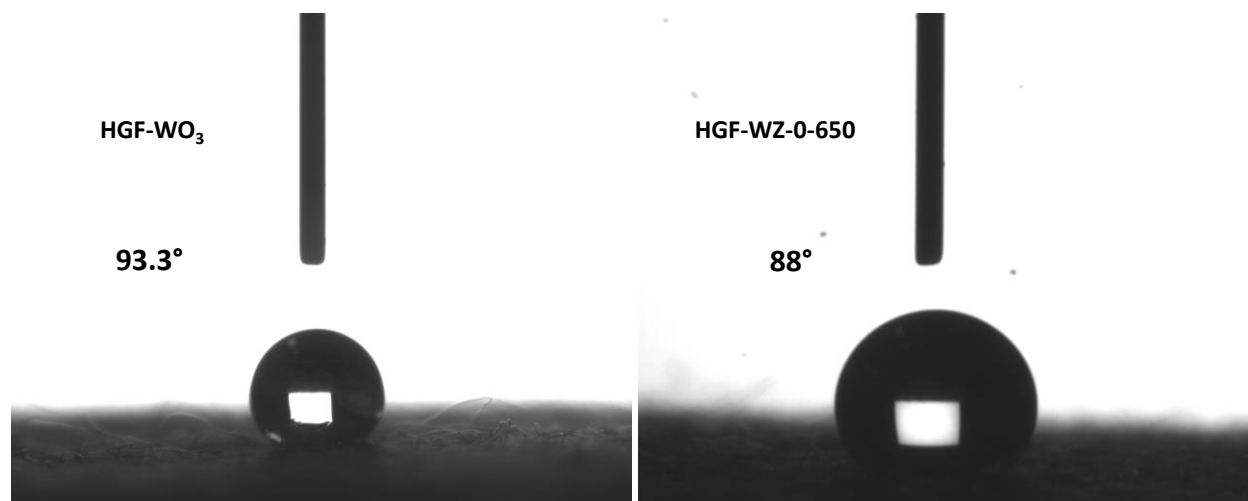


**Figure S5** SEM elemental mapping of the HGF-WZ-22-650 electrode after 100 charge-discharge cycles.

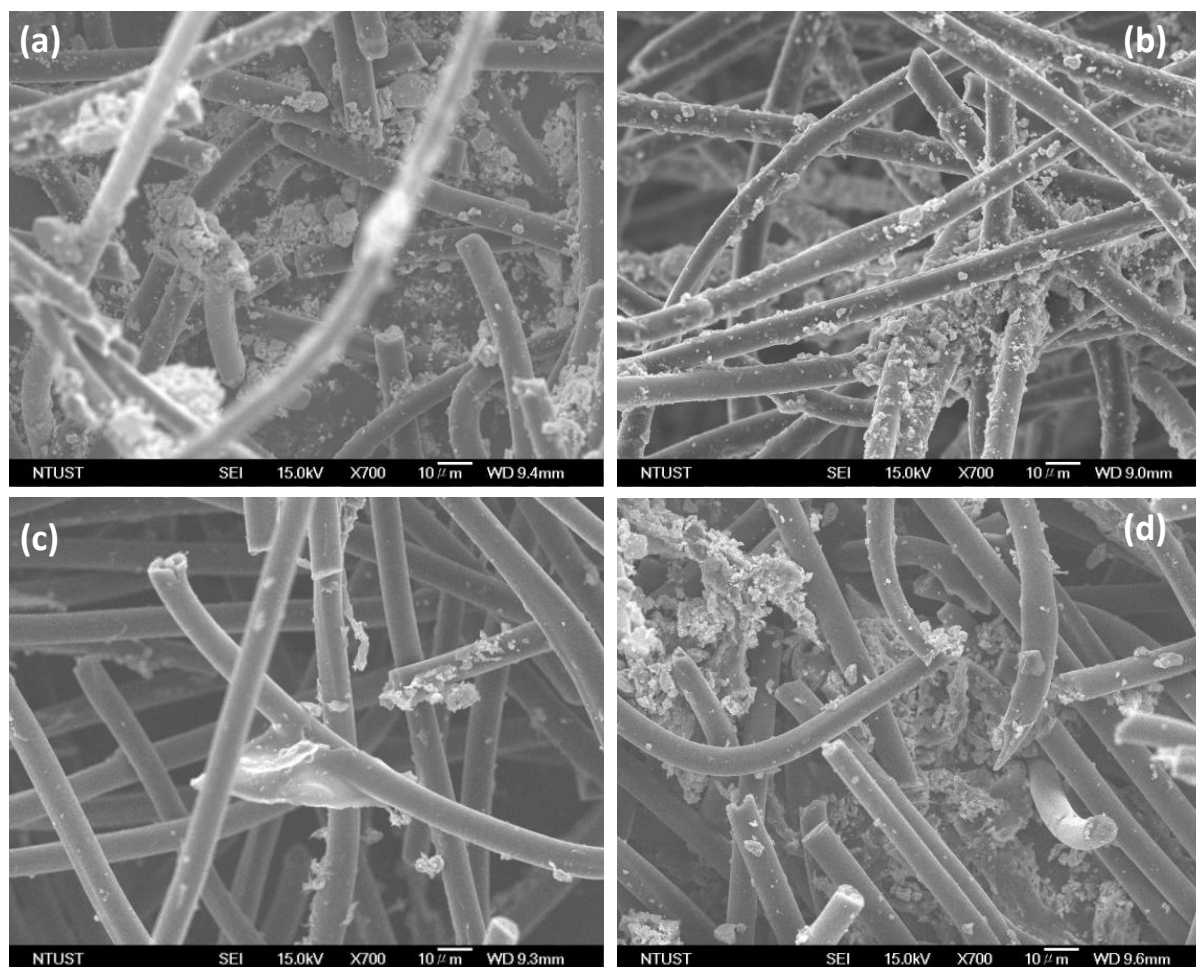


**Figure S6** (a) The CE, (b) VE, (c) EE, and (d) discharge capacity of the HGF and HGF-WZ-22-650 electrodes with cycle numbers at different current densities of 80 to 160 mA cm<sup>-2</sup>.





**Figure S7** The photographs of the contact angle measurements in (a) HGF-WO<sub>3</sub> and (b) HGF-WZ-0-650 electrodes.



**Figure S8** The SEM images (a) before CV, (b) after CV, (c) before charge/discharge, and (d) after charge/discharge of the HGF-WZ-22-650 electrode.

**Table S1.** Comparison of the CE, VE, and EE of the HGF-WZ-22-650 material with previously reported metal/metal oxide materials for VRFBs Application.

Material	Electrolyte	Current density (mA cm <sup>-2</sup> )	CE (%)	VE (%)	EE (%)	Ref.
HGF-WZ-22-650	1.6 M VOSO <sub>4</sub> + 4.6 M H <sub>2</sub> SO <sub>4</sub>	80	95.65	87.76	83.94	This
		160	97.52	76.76	74.86	Work
BiVO <sub>4</sub> -GF	1.6 M VOSO <sub>4</sub> + 4.6 M H <sub>2</sub> SO <sub>4</sub>	100	97.23	77.57	75.42	<sup>1</sup>
SnO <sub>2</sub> -P-GF	0.8 M VOSO <sub>4</sub> + 3 M H <sub>2</sub> SO <sub>4</sub>	150	96.11	69.20	71.90	<sup>2</sup>
Ti/IrO <sub>2</sub> : Ta <sub>2</sub> O <sub>5</sub>	1.7 M VOSO <sub>4</sub> + 4 M H <sub>2</sub> SO <sub>4</sub>	40	90	91	81.0	<sup>3</sup>
Mn <sub>3</sub> O <sub>4</sub> /CF	2 M VOSO <sub>4</sub> + 2.5 M H <sub>2</sub> SO <sub>4</sub>	40	83.5	91.0	76.0	<sup>4</sup>
CeO <sub>2</sub> /GF	2 M VOSO <sub>4</sub> + 2 M H <sub>2</sub> SO <sub>4</sub>	100	87.9	84.2	74.0	<sup>5</sup>
Nb-doped h-WO <sub>3</sub> NWs/GF	1.6 M VOSO <sub>4</sub> + 2.5 M H <sub>2</sub> SO <sub>4</sub>	80	93.16	83.83	78.10	<sup>6</sup>
WO <sub>3</sub> /GF	1 M VOSO <sub>4</sub> + 3 M H <sub>2</sub> SO <sub>4</sub>	100	99.7	72.2	72	<sup>7</sup>
PbO <sub>2</sub> /GF	0.5 M VOSO <sub>4</sub> + 3 M H <sub>2</sub> SO <sub>4</sub>	80	99.7	78.3	78.1	<sup>8</sup>
H-CeO <sub>2</sub> NWs-GF	1.6 M VOSO <sub>4</sub> + 2.5 M H <sub>2</sub> SO <sub>4</sub>	80	93.6	81.7	76.84	<sup>9</sup>
TNO-GF	1.6 M VOSO <sub>4</sub> + 2.5 M H <sub>2</sub> SO <sub>4</sub>	100	95.52	82.77	79.06	<sup>10</sup>

## References

- (1) Kabtamu, D. M.; Li, Y.-Z.; Bayeh, A. W.; Ou, Y.-T.; Huang, Z.-J.; Chiang, T.-C.; Huang, H.-C.; Wang, C.-H. BiVO<sub>4</sub>-Decorated Graphite Felt as Highly Efficient Negative Electrode for All-Vanadium Redox Flow Batteries. *ACS Applied Energy Materials* **2023**, *6* (6), 3301-3311.
- (2) Feng, X.; Zhang, Z.; Zhang, T.; Xue, J.; Han, C.; Dai, L.; Wang, L.; He, Z. Enhanced Catalysis of P-doped SnO<sub>2</sub> for the V<sup>2+</sup>/V<sup>3+</sup> Redox Reaction in Vanadium Redox Flow Battery. *Frontiers in Chemistry* **2021**, *9*, 688634.
- (3) Raghu, S. C.; Ulaganathan, M.; Lim, T. M.; Kazacos, M. S. Electrochemical behaviour of titanium/iridium (IV) oxide: Tantalum pentoxide and graphite for application in vanadium redox flow battery. *Journal of power sources* **2013**, *238*, 103-108.
- (4) Kim, K. J.; Park, M.-S.; Kim, J.-H.; Hwang, U.; Lee, N. J.; Jeong, G.; Kim, Y.-J. Novel catalytic effects of Mn<sub>3</sub>O<sub>4</sub> for all vanadium redox flow batteries. *Chemical Communications* **2012**, *48* (44), 5455-5457.
- (5) Zhou, H.; Xi, J.; Li, Z.; Zhang, Z.; Yu, L.; Liu, L.; Qiu, X.; Chen, L. CeO<sub>2</sub> decorated graphite felt as a high-performance electrode for vanadium redox flow batteries. *Rsc Advances* **2014**, *4* (106), 61912-61918.
- (6) Kabtamu, D. M.; Chen, J.-Y.; Chang, Y.-C.; Wang, C.-H. Electrocatalytic activity of Nb-doped hexagonal WO<sub>3</sub> nanowire-modified graphite felt as a positive electrode for vanadium redox flow batteries. *Journal of Materials Chemistry A* **2016**, *4* (29), 11472-11480.
- (7) Shen, Y.; Xu, H.; Xu, P.; Wu, X.; Dong, Y.; Lu, L. Electrochemical catalytic activity of tungsten trioxide-modified graphite felt toward VO<sub>2</sub><sup>+</sup>/VO<sub>2</sub><sup>+</sup> redox reaction. *Electrochimica Acta* **2014**, *132*, 37-41.
- (8) Wu, X.; Xu, H.; Lu, L.; Zhao, H.; Fu, J.; Shen, Y.; Xu, P.; Dong, Y. PbO<sub>2</sub>-modified graphite felt as the positive electrode for an all-vanadium redox flow battery. *Journal of Power Sources* **2014**, *250*, 274-278.
- (9) Bayeh, A. W.; Lin, G.-Y.; Chang, Y.-C.; Kabtamu, D. M.; Chen, G.-C.; Chen, H.-Y.; Wang, K.-C.; Wang, Y.-M.; Chiang, T.-C.; Huang, H.-C. Oxygen-vacancy-rich cubic CeO<sub>2</sub> nanowires as catalysts for vanadium redox flow batteries. *ACS Sustainable Chemistry & Engineering* **2020**, *8* (45), 16757-16765.

(10) Kabtamu, D. M.; Bayeh, A. W.; Chiang, T.-C.; Chang, Y.-C.; Lin, G.-Y.; Wondimu, T. H.; Su, S.-K.; Wang, C.-H. TiNb<sub>2</sub>O<sub>7</sub> nanoparticle-decorated graphite felt as a high-performance electrode for vanadium redox flow batteries. *Applied Surface Science* **2018**, *462*, 73-80.