Supporting Information

$BiVO_4/V_2O_5$ Heterostructures for Durable and Highly Reversible Calcium- and Zinc- Ion Batteries

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Scheme S1 Synthesis process of the $BiVO_4/V_2O_5$ heterostructures.

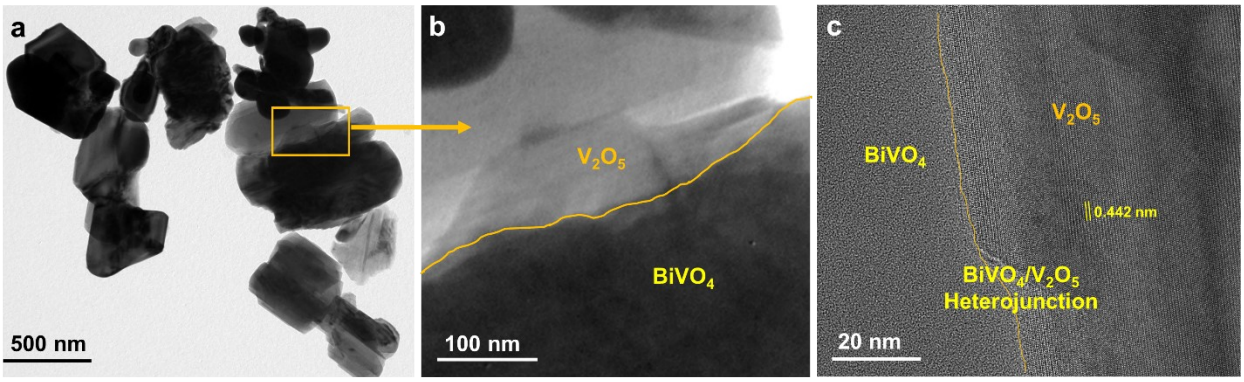

Figure S1: High Resolution TEM images of lattice fringes confirming the heterostructure formation of BVO/VO.

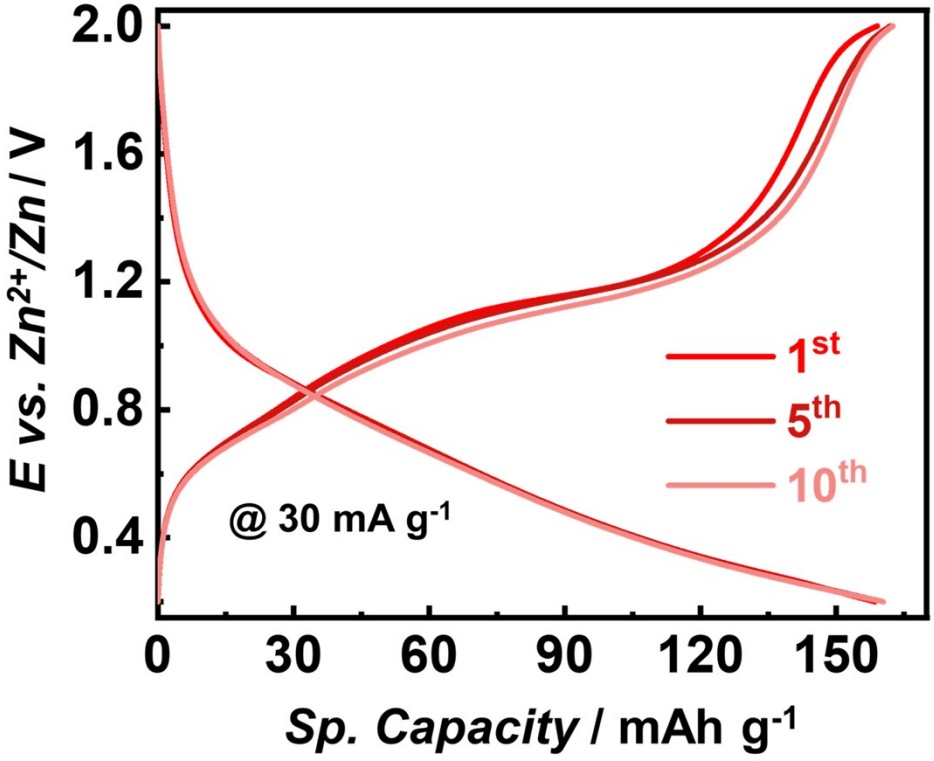

Figure S2: GCD plots of the ZIB (BVO/VO/CNTs/Zn^{2+}/Zn-AC) at intermittent stages of cycling at j = 30 mA g^{-1}.

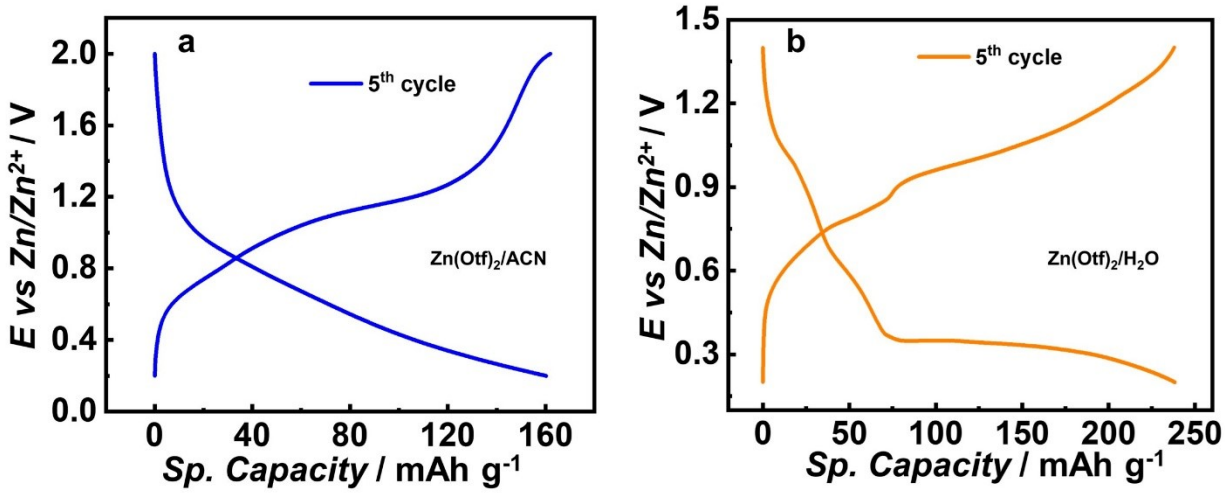

Figure S3: GCD curves of BVO/VO in a) Acetonitrile and b) water-based electrolytes.

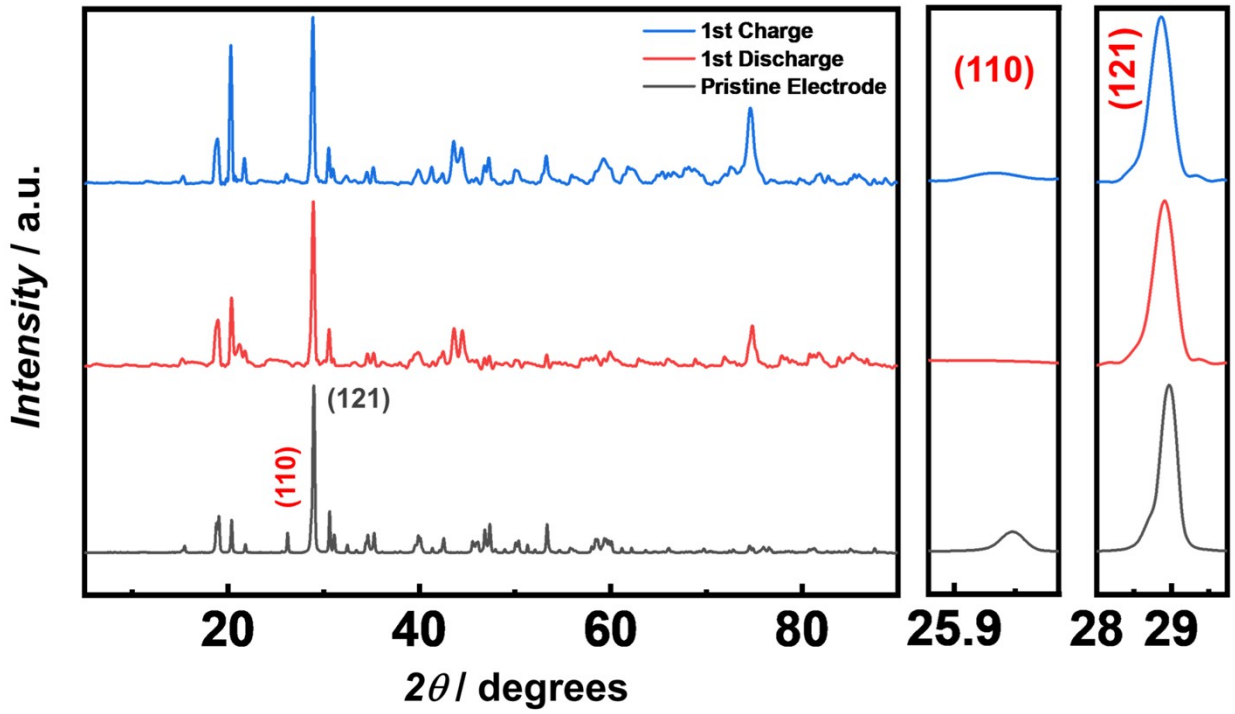

Figure S4: The Ex-situ XRD patterns of BVO/VO electrodes in pristine, 1st discharge and first charge states.

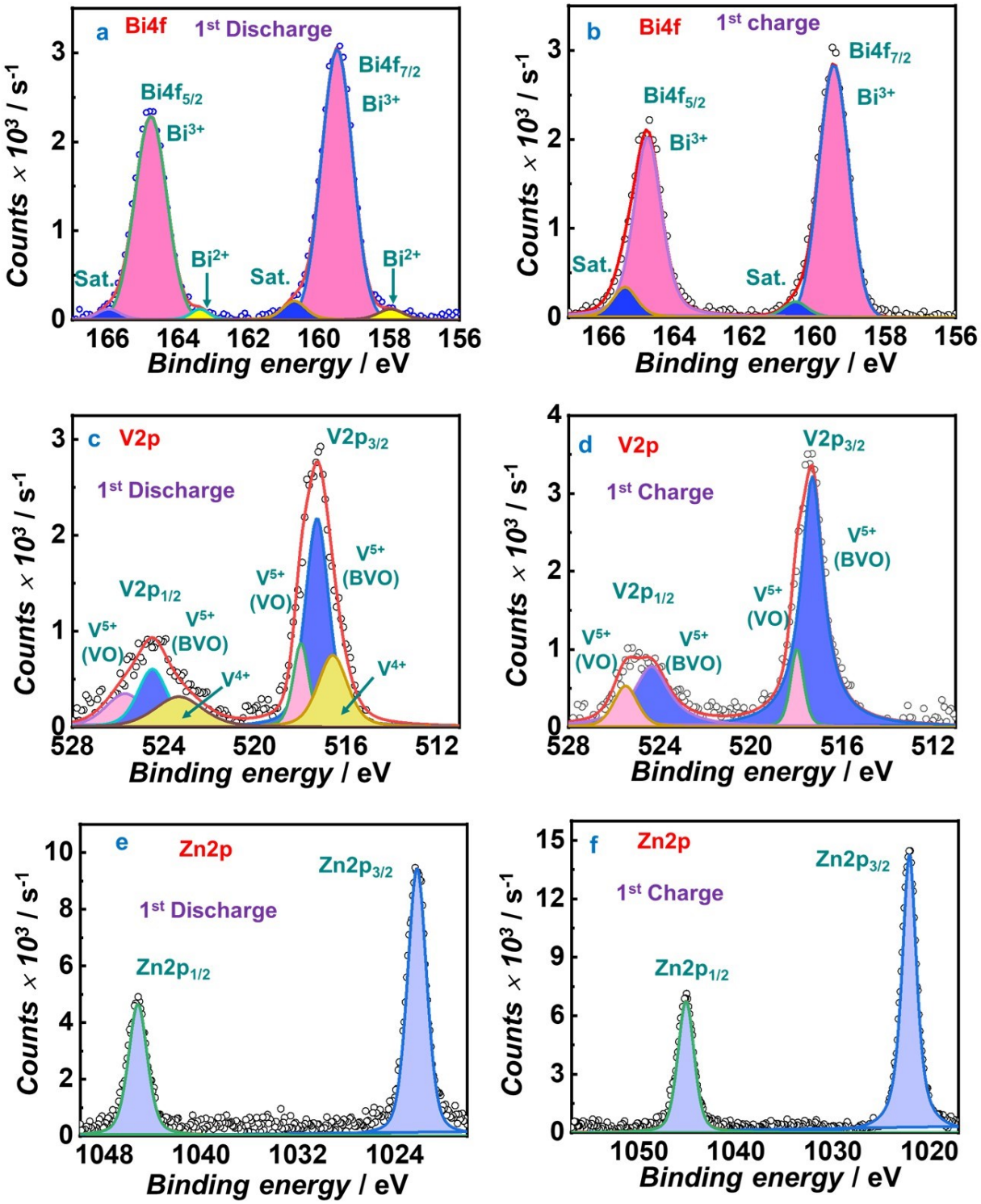

Figure S5: Ex-situ XPS spectra of BVO/VO electrodes in first discharged and charged states.

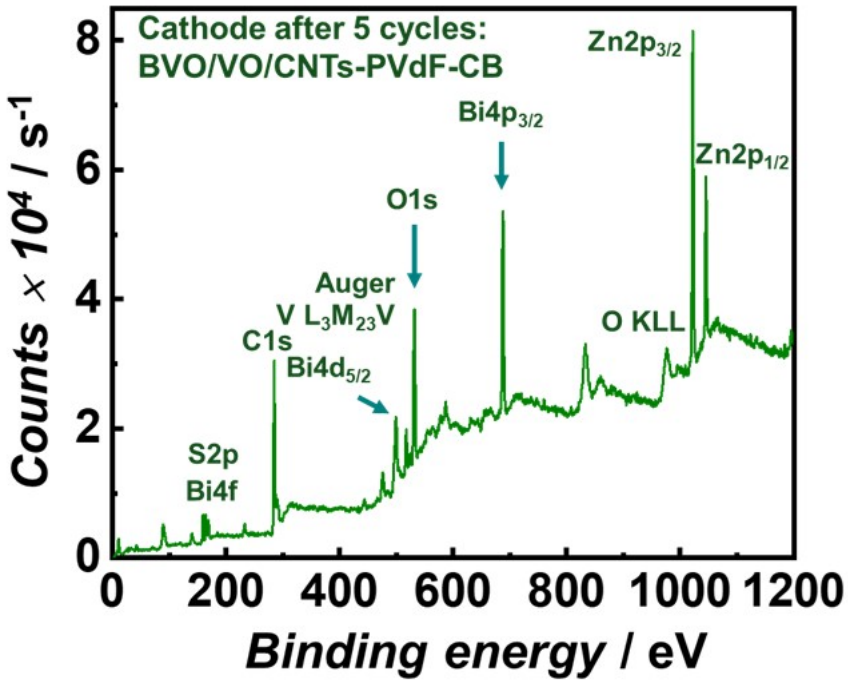

Figure S6: XPS survey spectrum of cathode after 5 cycles.

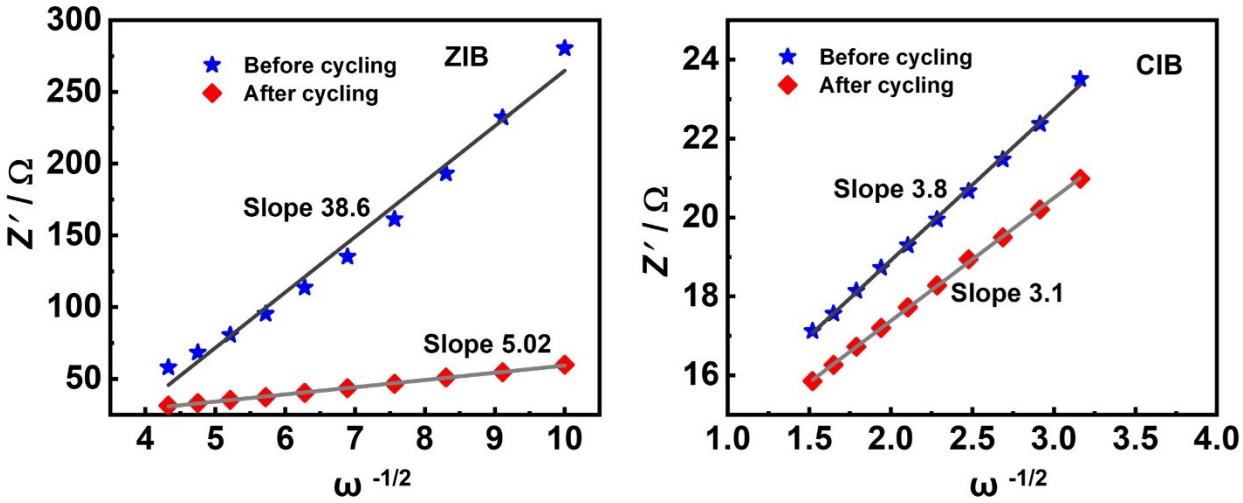

Figure S7 Change of the real part of the impedance Z′ versus the inverse square root of frequency $\omega^{-1/2}$ (in the low-frequency region).

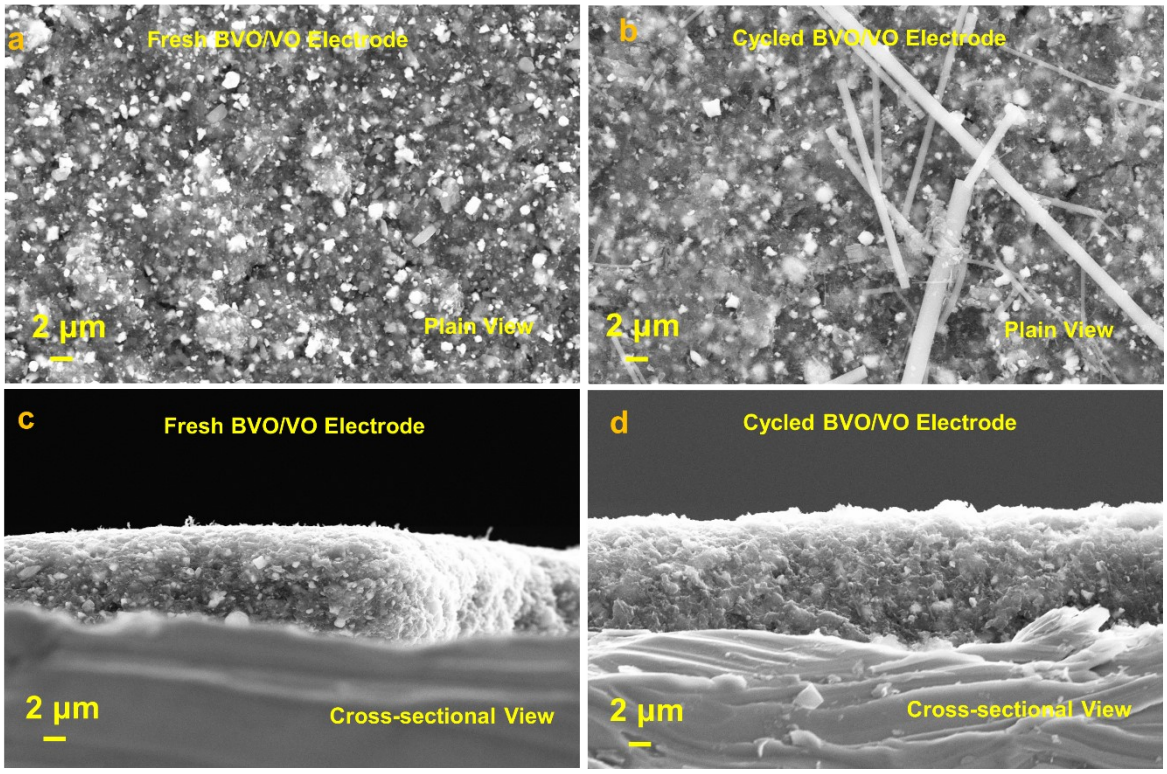

Figure S8: FE-SEM images of fresh and cycled BVO/VO electrodes of Calcium ion batteries.

Table S1 Comparison for D_{Zn} of various cathode materials in ZIBs.

Cathode	D_{Zn}^{2+} (cm^2 s^{-1})	Reference
$BiVO_4/V_2O_5$ Heterostructures	~10^{-10}	*[this work]*
Mn_3O_4 nanoflowers	10^{-12}	**1**
$ZnMn_2O_4$	1.0×10^{-11}	**2**
VO_2	10^{-11}	**3**
$H_2V_3O_8$	5×10^{-11} to 1.5×10^{-10}	**4**
$K_2V_8O_{21}$	1.99×10^{-11} to 2.33×10^{-10}	**2**
$K_2V_6O_{16}{\cdot}1.57H_2O$	6.75×10^{-12} to 2.10×10^{-11}	**2**
$K_{0.25}V_2O_5$	1.015×10^{-11} to 1.14×10^{-10}	**2**
KV_3O_8	4.96×10^{-12} to 3.75×10^{-11}	**2**

Table S2 EIS fitting parameters of ZIB in the [R(RC)W] circuit.

ZIB	Rs (Ω cm^2)	R_{ct} (Ω cm^2)	C_{dl} (mF cm^{-2})	Y_o (S $s^{0.5}$ cm^{-2})
Before cycling	2.6	1.5	6.9	0.018
After cycling	2.7	19.5	0.01	0.14

Table S3 EIS fitting parameters of CIB in the [R(RC)W] circuit.

CIB	Rs (Ω cm^2)	R_{ct} (Ω cm^2)	C_{dl} (mF cm^{-2})	Y_o (S $s^{0.5}$ cm^{-2})
Before cycling	6.6	5.0	31.1	0.186
After cycling	7.8	6.0	25.6	0.228

References

(1) Zhu, C.; Fang, G.; Zhou, J.; Guo, J.; Wang, Z.; Wang, C.; Li, J.; Tang, Y.; Liang, S. Binder-Free Stainless Steel@Mn_3O_4 Nanoflower Composite: A High-Activity Aqueous Zinc-Ion Battery Cathode with High-Capacity and Long-Cycle-Life. *J. Mater. Chem. A* **2018**, *6* (20), 9677–9683. https://doi.org/10.1039/C8TA01198B.

(2) Zhang, N.; Cheng, F.; Liu, Y.; Zhao, Q.; Lei, K.; Chen, C.; Liu, X.; Chen, J. Cation-Deficient Spinel ZnMn2O4 Cathode in $Zn(CF_3SO_3)_2$ Electrolyte for Rechargeable Aqueous Zn-Ion Battery. *J. Am. Chem. Soc.* **2016**, *138* (39), 12894–12901. https://doi.org/10.1021/jacs.6b05958.

(3) Ding, J.; Du, Z.; Gu, L.; Li, B.; Wang, L.; Wang, S.; Gong, Y.; Yang, S. Ultrafast Zn^{2+} Intercalation and Deintercalation in Vanadium Dioxide. *Adv. Mater.* **2018**, *30* (26), 1800762. https://doi.org/10.1002/adma.201800762.

(4) He, P.; Quan, Y.; Xu, X.; Yan, M.; Yang, W.; An, Q.; He, L.; Mai, L. High-Performance Aqueous Zinc–Ion Battery Based on Layered $H_2V_3O_8$ Nanowire Cathode. *Small* **2017**, *13* (47), 1702551. https://doi.org/10.1002/smll.201702551.