

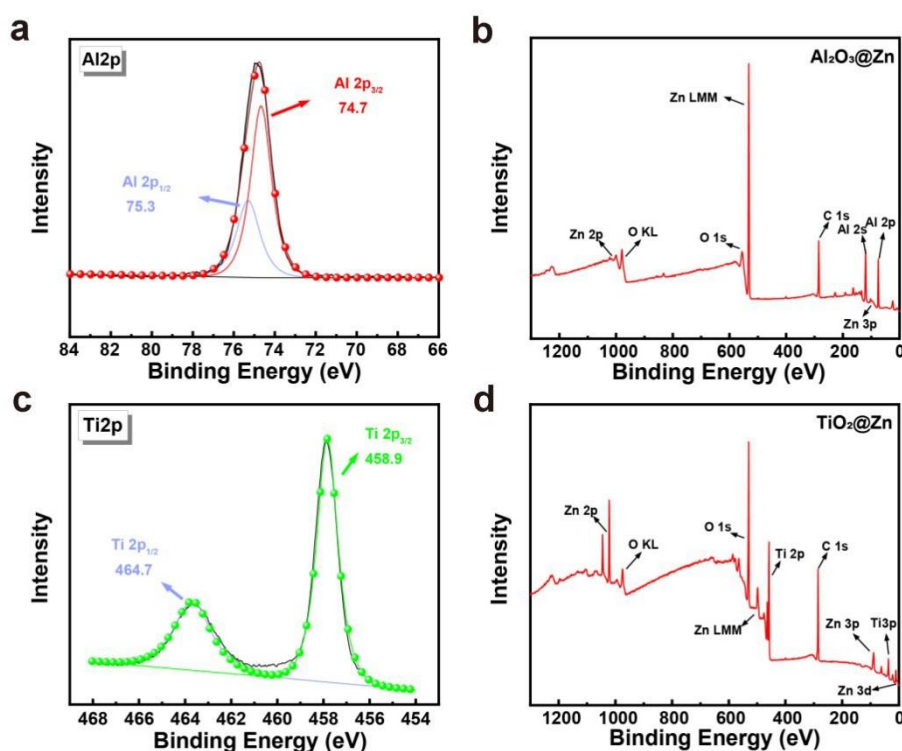


Fig. S1. XPS spectrum of a) Al 2p, b) full surveys before cycle for $\text{Al}_2\text{O}_3@\text{Zn}$ and c) Ti 2p, d) full surveys before cycle for $\text{TiO}_2@\text{Zn}$.

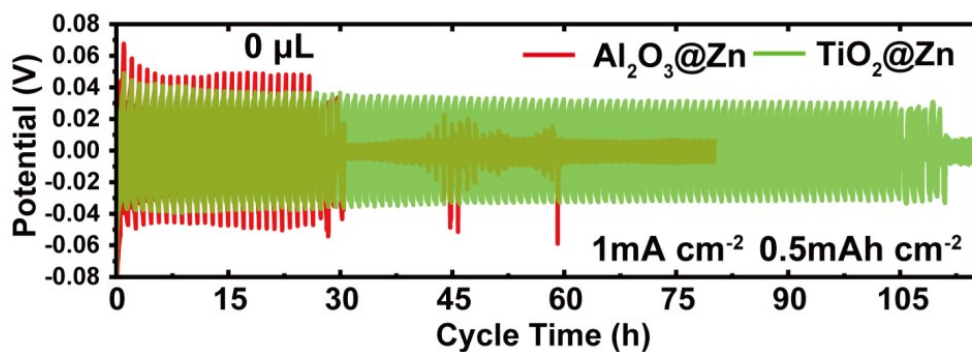


Fig. S2. Long-term symmetric tests of a) $\text{Al}_2\text{O}_3@\text{Zn}$, $\text{TiO}_2@\text{Zn}$ without inducing sulfuric acid at a current density of 1 mA cm^{-2} .

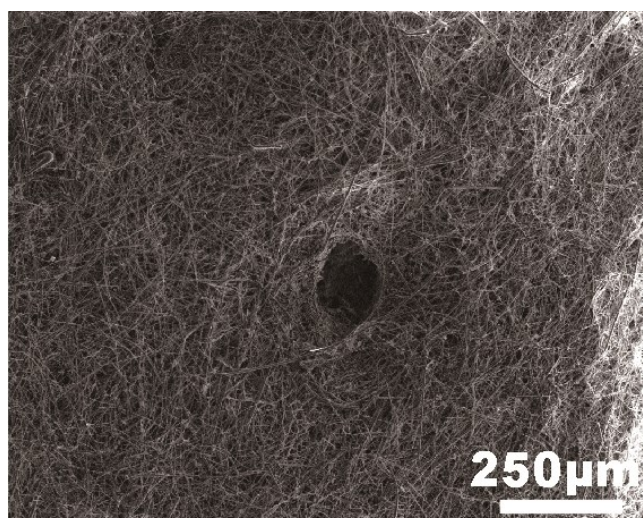


Fig. S3. The SEM image of glass fiber with an obvious pore structure penetrated by dendrite in $\text{Fe}_2\text{O}_3@\text{Zn}-0 \mu\text{L}$.

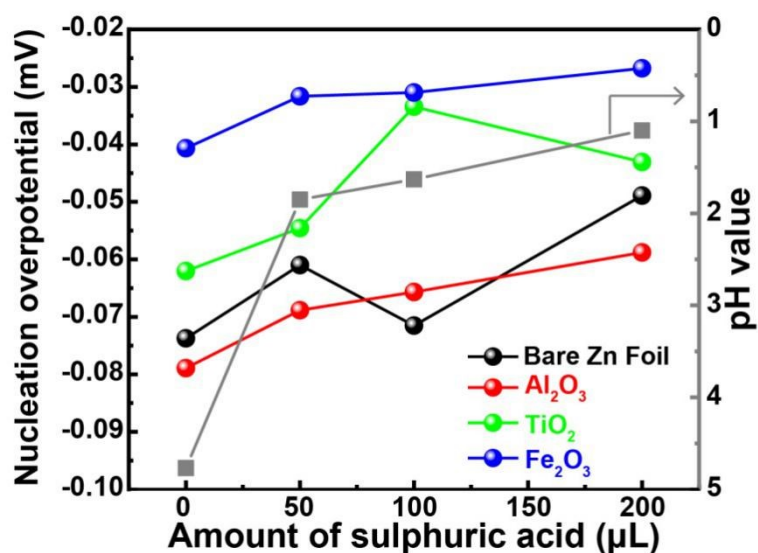


Fig. S4. The overpotentials of bare Zn foil and ALD@Zn with different electrolytes and corresponding pH value of different electrolytes. The pH values of electrolytes are 4.77, 1.85, 1.63 and 1.10 under 0, 50, 100 and 200 μL , respectively.

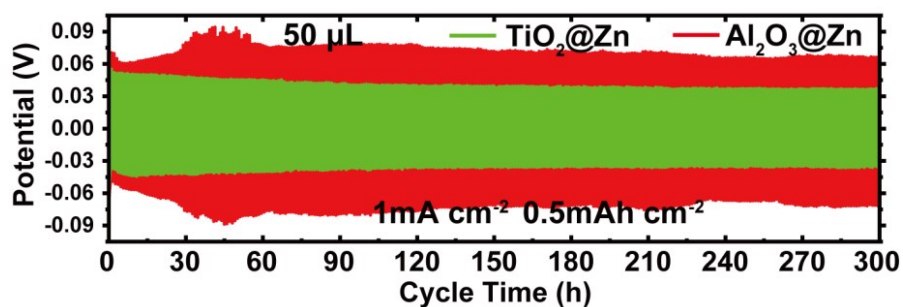


Fig. S5. Long-term symmetric tests of a) $\text{Al}_2\text{O}_3@\text{Zn}$, $\text{TiO}_2@\text{Zn}$ within 50 μL sulfuric acid at a current density of 1 mA cm^{-2} .

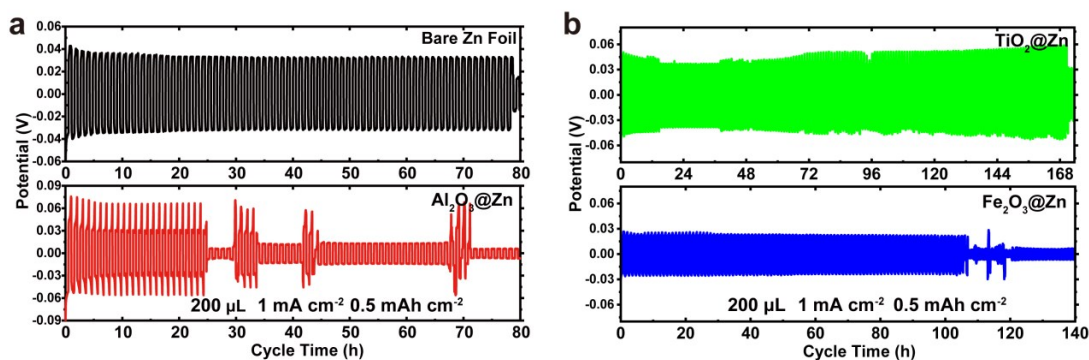


Fig. S6. Long-term symmetric tests of a) bare Zn foil, $\text{Al}_2\text{O}_3@\text{Zn}$, b) $\text{TiO}_2@\text{Zn}$ and $\text{Fe}_2\text{O}_3@\text{Zn}$ with 200 μL at a current density of 1 mA cm^{-2} .

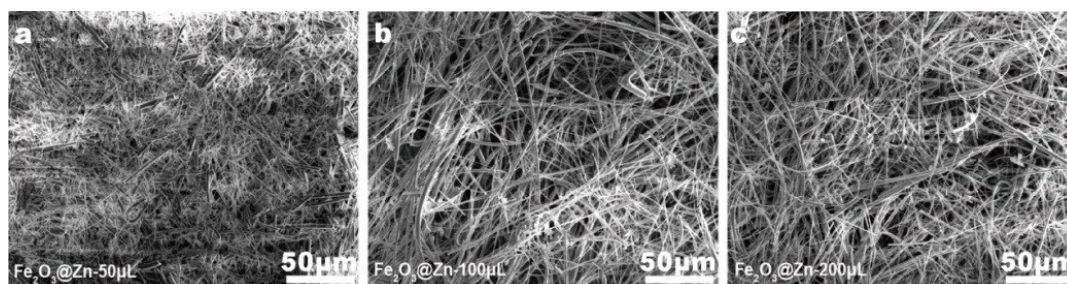


Fig. S7. SEM images of glass fiber after cycle in a) $\text{Fe}_2\text{O}_3@\text{Zn}$ -50 μL , b) $\text{Fe}_2\text{O}_3@\text{Zn}$ -100 μL , c) $\text{Fe}_2\text{O}_3@\text{Zn}$ -200 μL at a current density of 1 mA cm^{-2} .

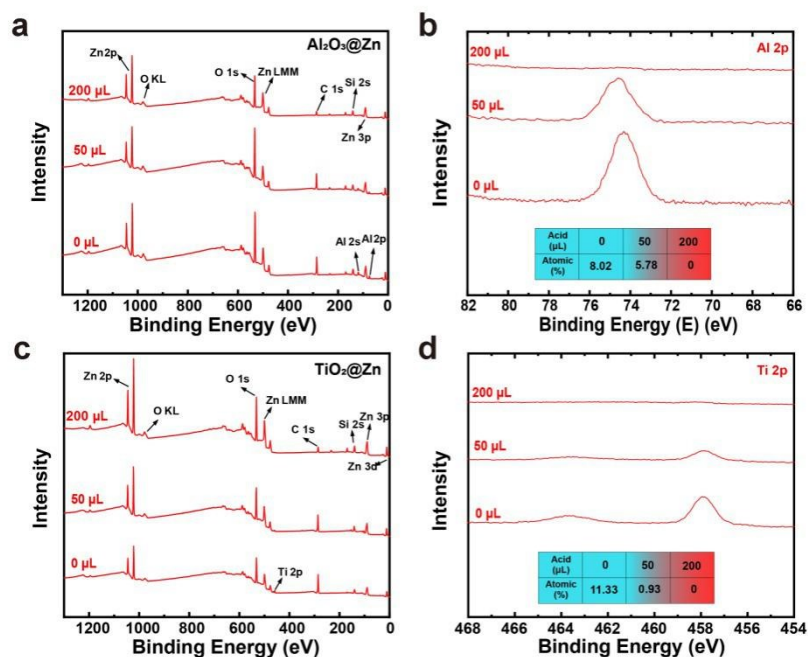


Fig. S8. XPS spectrum of a) surveys after cycling in 0, 50 and 200 μL and corresponding b) Al 2p on $\text{Al}_2\text{O}_3@\text{Zn}$; XPS spectrum of c) surveys after cycling in 0 and 50 and 200 μL and corresponding d) Ti 2p on $\text{TiO}_2@\text{Zn}$. The insets show Al 2p and Ti 2p peak table, respectively.

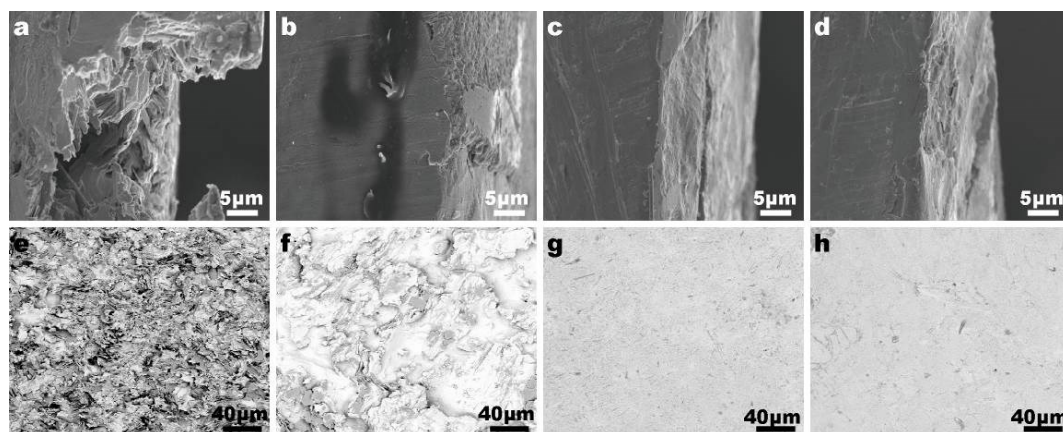


Fig. S9. Cross-sectional SEM images of a) bare Zn foil, b) $\text{Al}_2\text{O}_3@\text{Zn}$, c) $\text{TiO}_2@\text{Zn}$ and d) $\text{Fe}_2\text{O}_3@\text{Zn}$ after cycling at a current density of 0.1 mA cm^{-2} . SEM images of e) bare Zn foil, f) $\text{Al}_2\text{O}_3@\text{Zn}$, g) $\text{TiO}_2@\text{Zn}$ and h) $\text{Fe}_2\text{O}_3@\text{Zn}$ after cycling at a current density of 10 mA cm^{-2} .

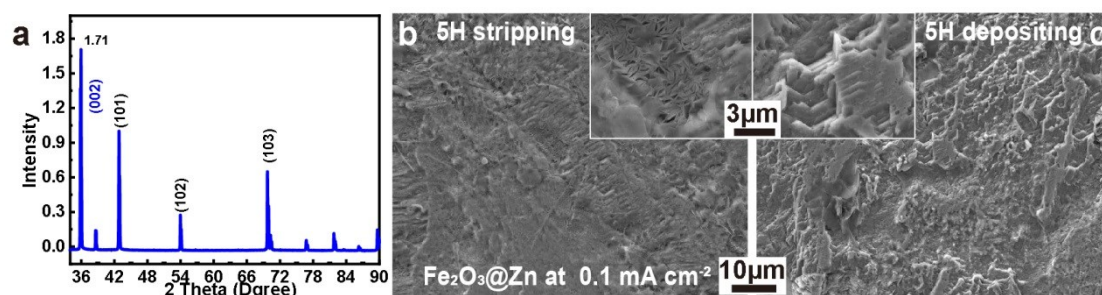


Fig. S10. a) XRD pattern of $\text{Fe}_2\text{O}_3@\text{Zn}$ after 5 hours stripping at a current density of 0.1 mA cm^{-2} and corresponding b) SEM image. c) The texture on $\text{Fe}_2\text{O}_3@\text{Zn}$ after 5 hours depositing at the same current.

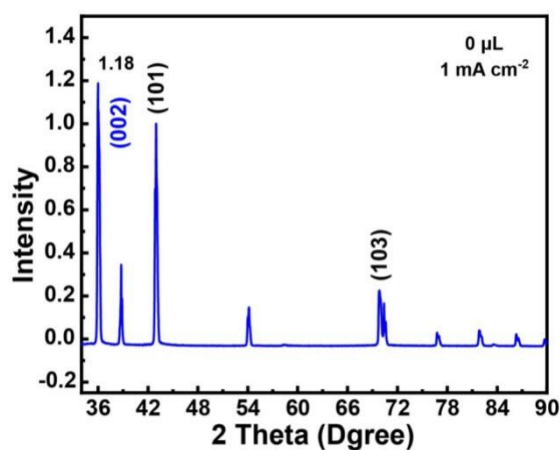


Fig. S11. XRD patterns of $\text{Fe}_2\text{O}_3@\text{Zn}$ after depositing without inducing H^+ in the electrolyte.

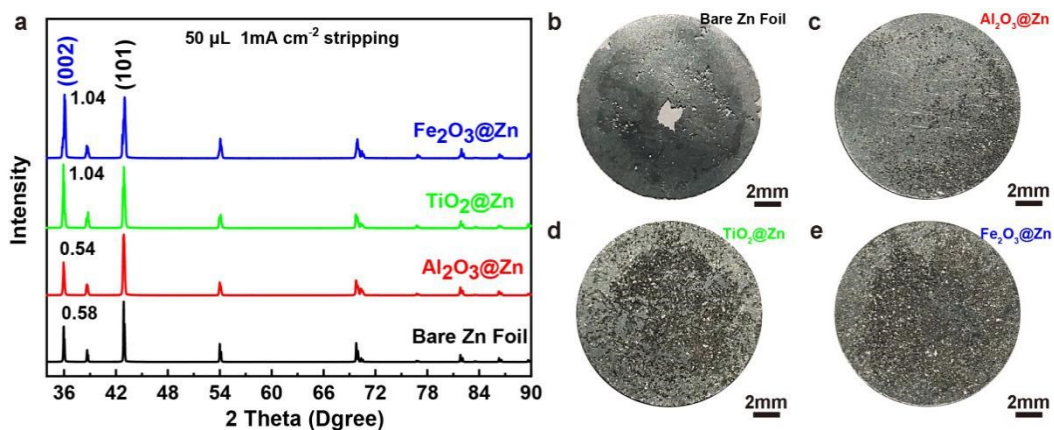


Fig. S12. a) XRD patterns of Zn after stripping and corresponding optical images of b) bare Zn foil, c) $\text{Al}_2\text{O}_3@\text{Zn}$, d) $\text{TiO}_2@\text{Zn}$ and e) $\text{Fe}_2\text{O}_3@\text{Zn}$ at a current density of 1 mA cm^{-2} .

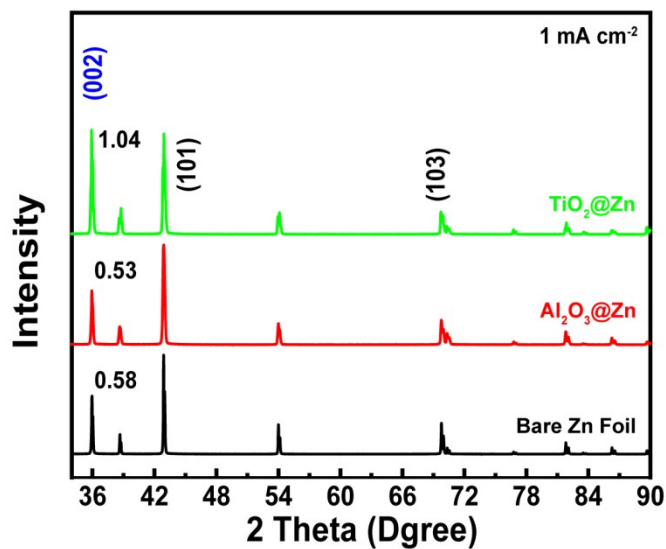


Fig. S13. XRD patterns of bare Zn foil, $\text{Al}_2\text{O}_3@\text{Zn}$, $\text{TiO}_2@\text{Zn}$ after depositing.

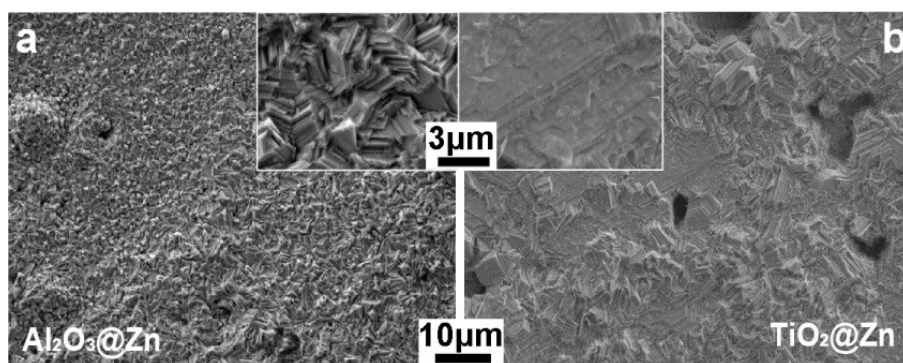


Fig. S14. SEM images of a) $\text{Al}_2\text{O}_3@\text{Zn}$ and b) $\text{TiO}_2@\text{Zn}$ after 5 hours depositing progress at a current density of 1 mA cm^{-2} .

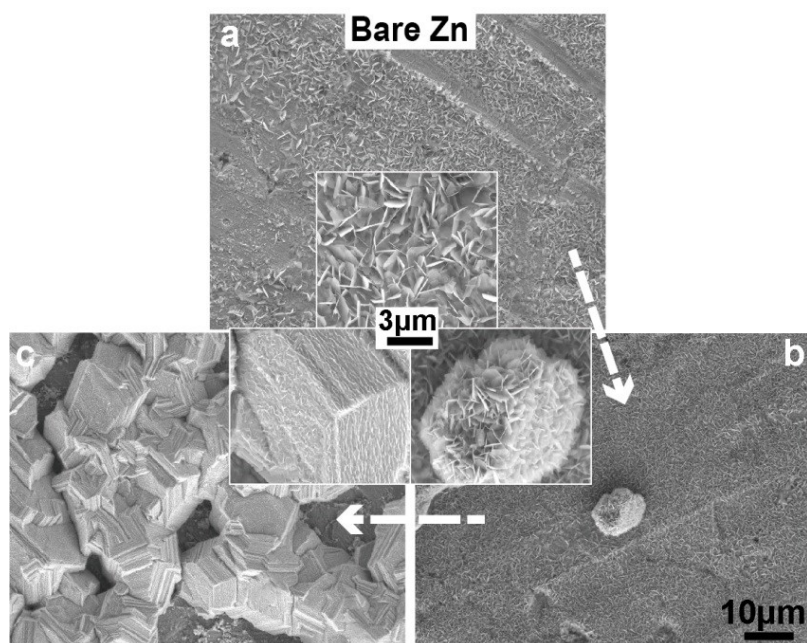


Fig. S15. a-c) SEM images of the growth evolution morphologies of favourable (101) orientation on bare Zn foil during depositing progress.

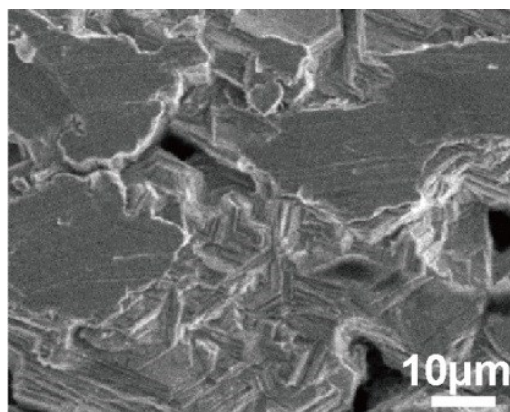


Fig. S16. SEM image of Fe₂O₃@Zn after depositing at a current density of 10 mA cm⁻².

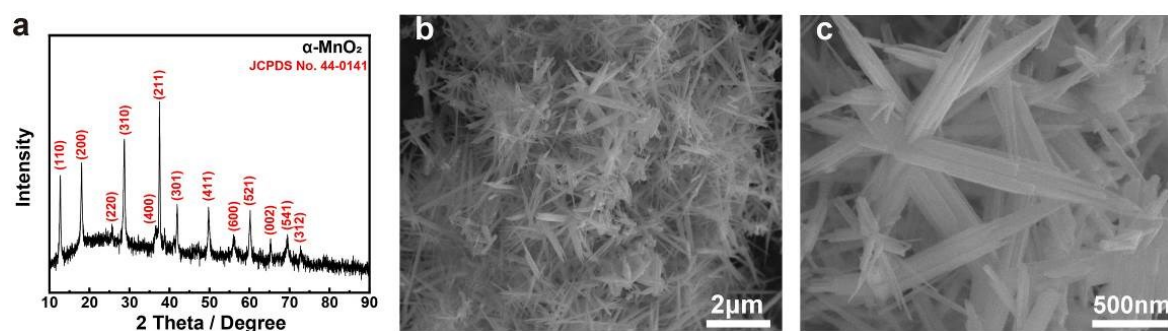


Figure S17. a) XRD pattern and b-c) SEM images of nanorod α-MnO₂.

Table S1. Summary comparison of electrochemical performance of Zn-MnO₂ batteries.

Cathod	Anode	Electrolyte	Capacity after fully activate (mAh g ⁻¹)	Cycle number	Capacity after cycle (mAh g ⁻¹)	Current density (A g ⁻¹)	Reference
α -MnO ₂	Fe ₂ O ₃ @Zn	3 M ZnSO ₄ + 0.1 M MnSO ₄ + H ₂ SO ₂	280	1000	244.3	1	This work
α -MnO ₂	TiO ₂ @Zn	3 M ZnSO ₄ + 0.1 M MnSO ₄ + H ₂ SO ₂	227.8	1000	192.6	1	This work
α -MnO ₂	Al ₂ O ₃ @Zn	3 M ZnSO ₄ + 0.1 M MnSO ₄ + H ₂ SO ₂	148.1	1000	147.2	1	This work
α -MnO ₂	Zn@ZnO-3D	2 M ZnSO ₄ + 0.1 M MnSO ₄	226.5	500	212	0.5	1
δ -MnO ₂	Al ₂ O ₃ @Zn	3 M Zn(SO ₃ CF ₃) ₂ + 0.1 M Mn(SO ₃ CF ₃) ₂	177.2	1000	158.4	1	2
α -MnO ₂	TiO ₂ @Zn	3 M Zn(SO ₃ CF ₃) ₂ + 0.1 M Mn(SO ₃ CF ₃) ₂	<200	1000	134	1	3
CNT/MnO ₂	nano-CaCO ₃ -coated Zn	3 M ZnSO ₄ + 0.1 M MnSO ₄	236	1000	177	1	4
CNT/MnO ₂	Zn@ZnP	2 M ZnSO ₄ + 0.1 M MnSO ₄	<200	1000	154.4	1	5
δ -MnO ₂	PPy-coated Zn	2 M ZnSO ₄ + 0.1 M MnSO ₄	≈200	200	≈175	1	6
MnO ₂ NW	MOF-based Zn	2 M ZnSO ₄ + 0.1 M MnSO ₄	≈60	5000	≈50	0.308	7
α -MnO ₂	3D Zn@Cu	2 M ZnSO ₄ + 0.5 M MnSO ₄	≈250	300	173	0.4	8
β -MnO ₂	Zn@Cu foam	2 M ZnSO ₄ + 0.1 M MnSO ₄	≈210	600	173.8	1	9

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