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Supporting Information

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Zn^{2+} Pre-Intercalation Stabilizes the Tunnel Structure of MnO_2 Nanowires and Enables Zinc-Ion Hybrid Supercapacitor of Battery-Level Energy Density

Qiang Chen, Jialun Jin, Zongkui Kou, Cong Liao, Ziang Liu, Liang Zhou, John Wang,* and Liqiang Mai*

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Zn^{2+} Pre-Intercalation Stabilizes the Tunnel Structure of MnO_2 Nanowires and Enables Zinc Ion Hybrid Supercapacitor of Battery-Level Energy Density

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Calculations:

The areal capacitances (C_a) of electrodes were measured by galvanostatic discharge method using the following equation:

$$C_a = \frac{I \times \Delta t}{\Delta V \cdot S} \qquad (1)$$

where I (mA) is the constant discharging current, Δt (s) is the discharging time, and S (cm^2) is the area of electrodes.

The areal energy density (E_a, μWh cm^{-2}) and power density (P_a, mW cm^{-2}) of the Zn-HSCs were obtained from the following equations:

$$E_a = \frac{1}{2} \times C_a \times \frac{(\Delta V)^2}{3600} \times 10^6 \qquad (2)$$

$$P_a = \frac{E_a}{\Delta t} \times 3600 \times 10^{-3} \qquad (3)$$

where ΔV is the discharging voltage range (2.0 V), and Δt is the discharge time (s).

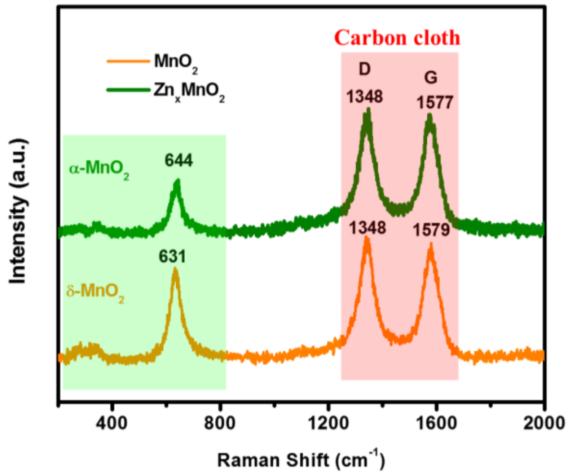

Figure S1. Raman spectra of the MnO_2 nanosheets and Zn_xMnO_2 nanowires.

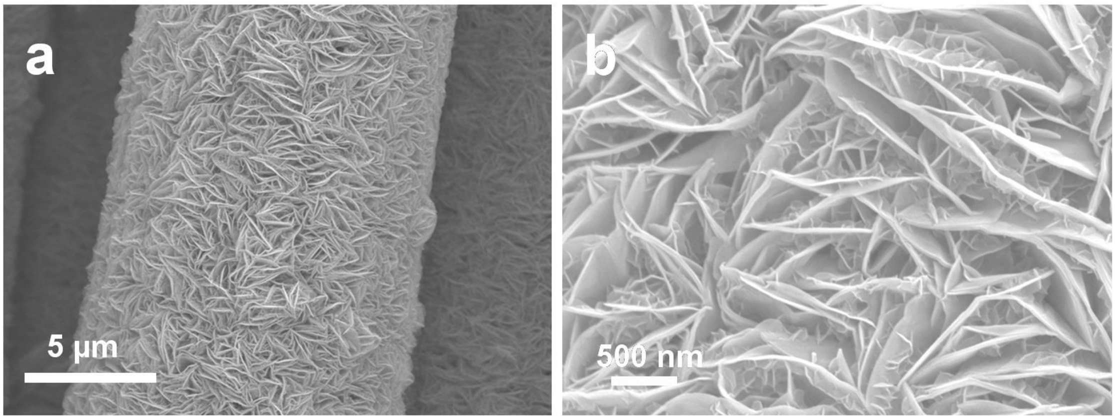

Figure S2. SEM images of the MnO_2 nanosheet at different magnification.

Table S1. Comparison of the material thickness and mass loading of Zn_xMnO_2 to several recently reported supercapacitors and batteries.

Electrode	Substrate	Morphology	Thickness	Mass loading [mg cm^{-2}]	Application area	Reference
Zn_xMnO_2	CC	nanowires	4.2 μm	12	Zn-HSCs	This work
$ZnMn_2O_4$@PEDOT	CC	membrane	2.3 μm	6.2	Zn-ion Batteries	Energy Storage Mater. 2019, 21, 154.
$Na_{0.5}MnO_2$	CC	nanosheet assembled nanowall arrays	N.A.	1-2	Supercapacitors	Adv. Mater. 2017, 29, 1700804.
MnO_2	CC	membrane	N.A.	3.6	Zn-ion Batteries	Adv. Mater. 2017, 1700274
α-MnO_2@δ-MnO_2	CC	nanorod/nanosheets	N.A.	10	Supercapacitors	ACS Nano 2018, 12, 3557
3D-G-δ-MnO_2	Ni foam	nanosheets	3–4 nm	1.7	Li-O_2 Batteries	Adv. Energy Mater. 2014, 1301960
$ZnMn_2O_4$	Ti	mesoscale tubular arrays	150 nm	0.49	Li-ion Batteries	ACS Appl. Mater. Interfaces 2013, 5, 11321
α-MnO_2/C	N.A.	nanorods	N.A.	0.5-2	Li-O_2 Batteries	Energy Environ. Sci., 2013, 6, 519
$Zn_2(OH)VO_4$	NF	nanosheets	5 μm	4.1	Zn-ion Batteries	Adv. Mater. 2018, 1803181
AC	N.A.	micron particles	N.A.	0.7-1.8	Zn-HSCs	Energy Storage Mater. 2018, 13, 96.

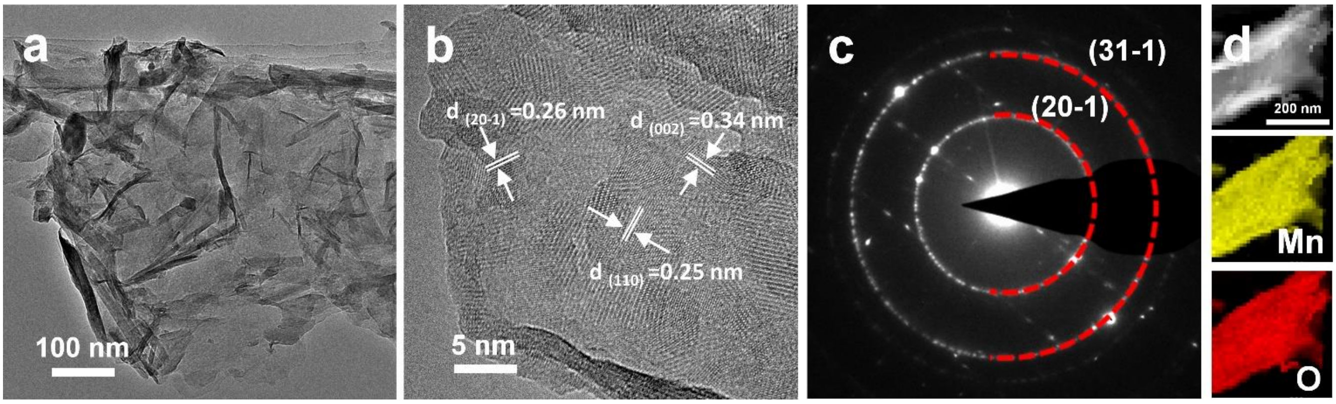

Figure S3. (a) TEM (b) HRTEM (c) SAED and (d) element mapping of the MnO_2 nanosheet.

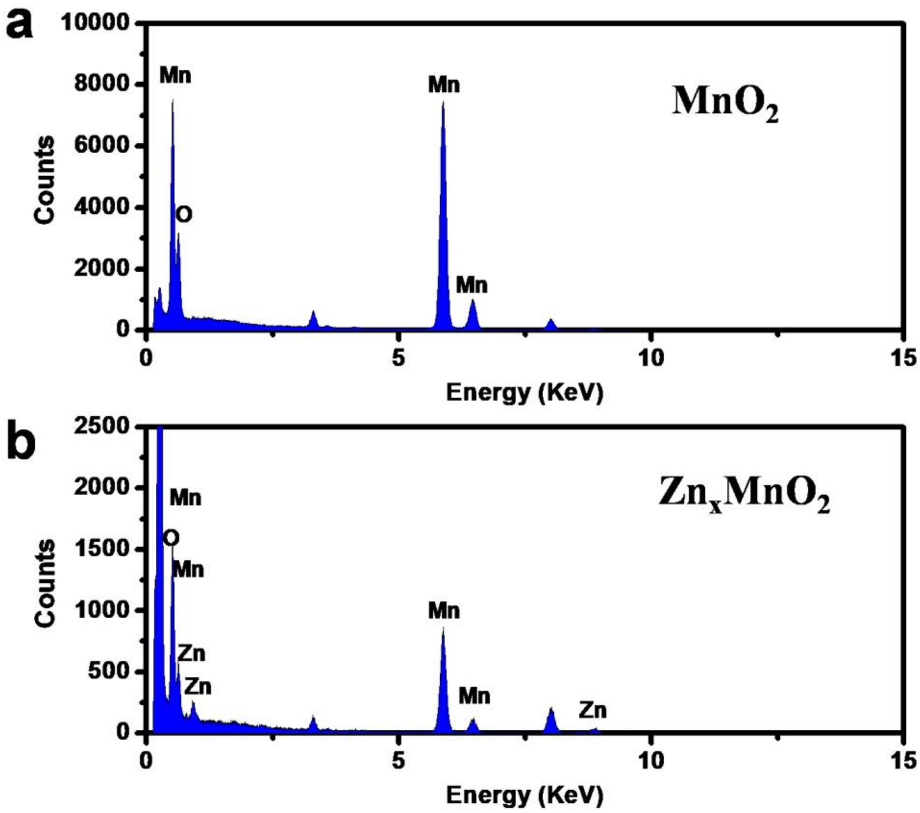

Figure S4. EDS spectraof (a) MnO_2 nanosheets and (b) Zn_xMnO_2 nanowires.

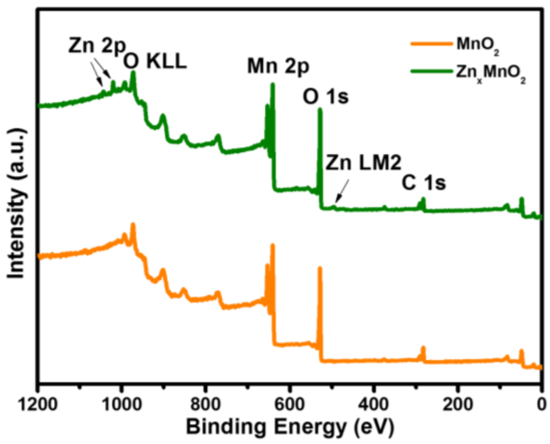

Figure S5. XPS survey spectra of Zn_xMnO_2 nanowires.

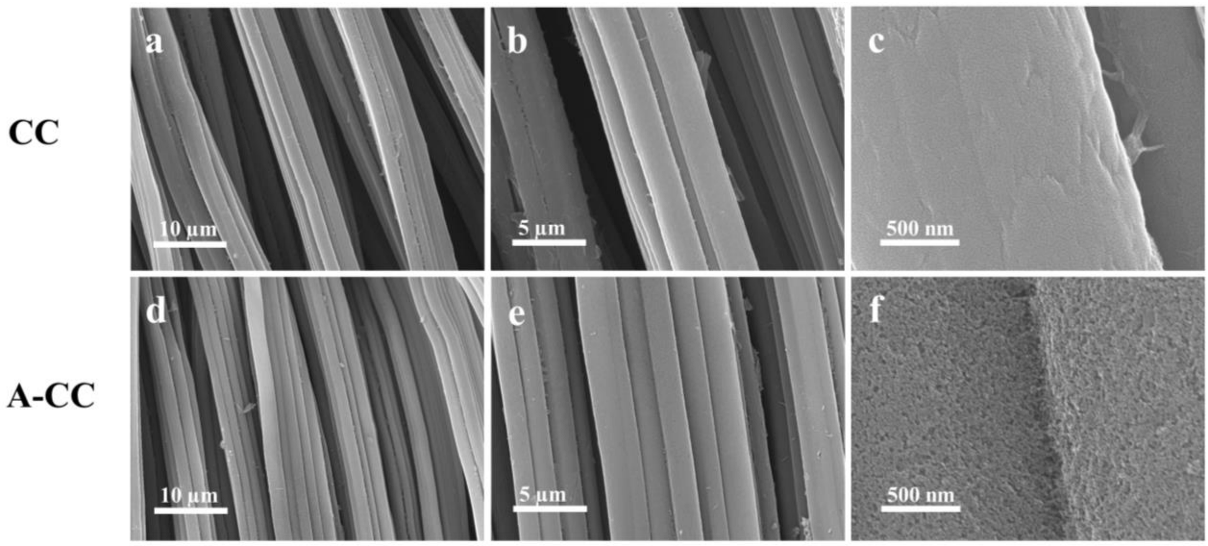

Figure S6. SEM images of CC and ACC at different magnification.

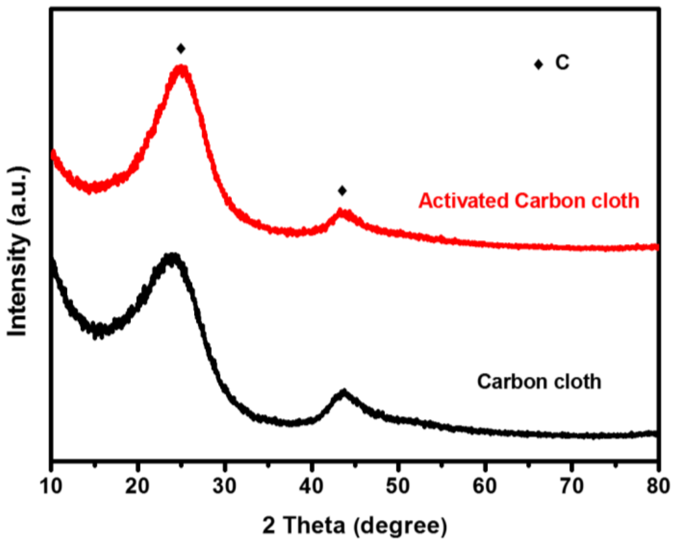

Figure S7. XRD patterns of CC and ACC nanoparticles.

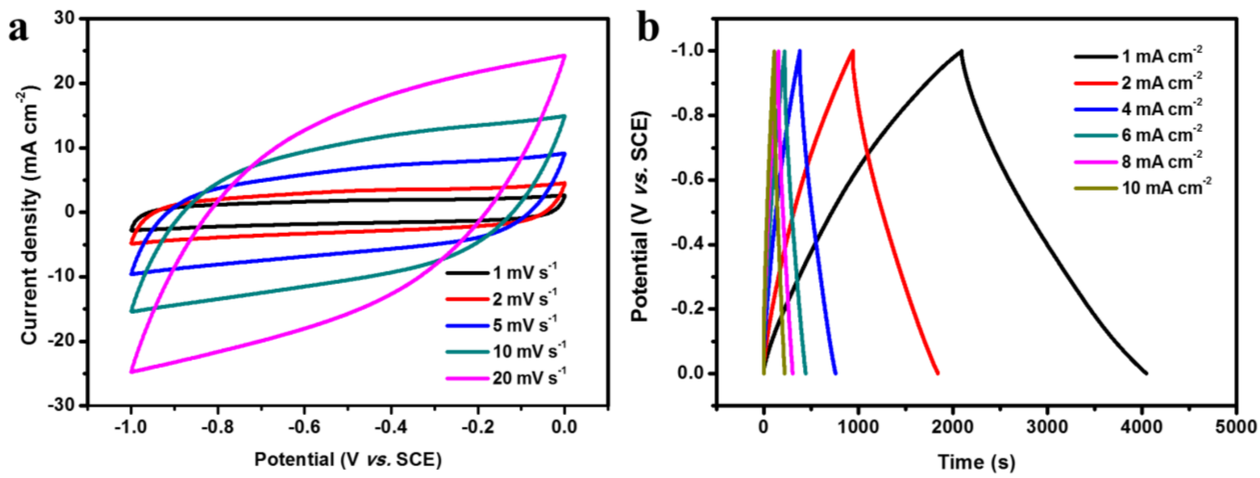

Figure S8. CV curves and GCD curves for ACC nanoparticles.

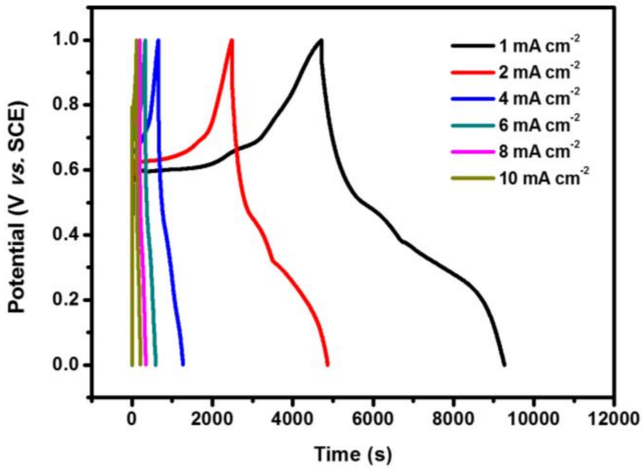

Figure S9. GCD of single electorde at different current density of the Zn_xMnO_2 nanowires.

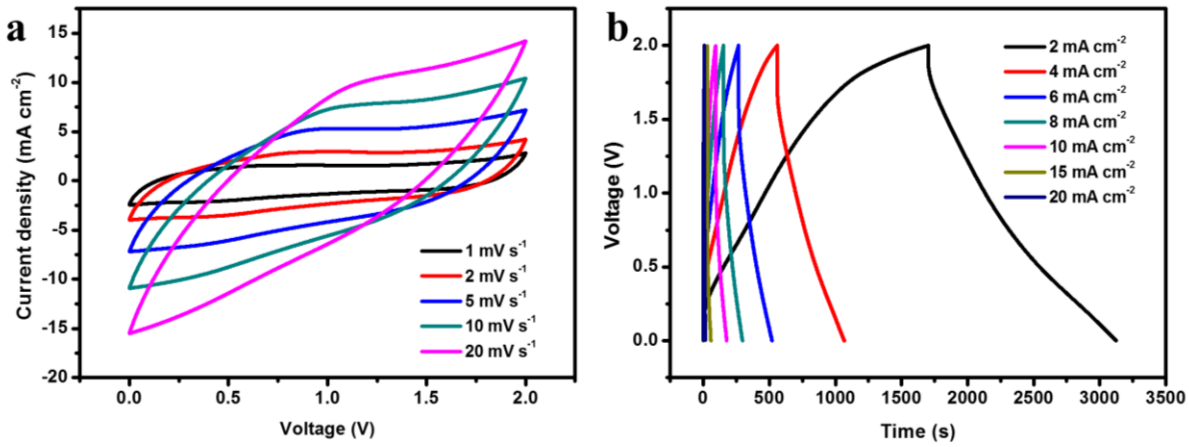

Figure S10. CV curves (a) and GCD (b) curves collected at different scan rate and current density of the MnO_2//ACC HSCs.

Table S2. Comparison of the capacity performance and energy density of Zn_xMnO_2//ACC to several recently reported supercapacitors and batteries.

Cathode	Anode	Current density) [mA cm^{-2}]	CP areal capacitance [mF cm^{-2}]	Voltage Window [V]	Energy density [μWh cm^{-2}]	Electrolyte	Reference
Zn_xMnO_2 [a)]	ACC [a)]	2	1745.8	0 – 2.0	969.9	2.0 M $ZnSO_4$ + 0.4 M $MnSO_4$	This work
Zn_xMnO_2 [a)]	ACC [a)]	1	1446.6	0 – 2.0	803.6	PVA /$ZnCl_2$-$MnSO_4$ gel	This work
AC [a)]	Zn foil [a)]	0.16	1297	0.5 - 1.5	115.4	2.0 M $ZnSO_4$	Adv. Mater. 2019, 31, 1806005
Carbon nanotube [a)]	Zn nanoflakes [a)]	1	83.2	0.2 - 1.8	29.6	1.0 M $ZnSO_4$	Energy Environ. Sci. 2018, 11, 3367.
G@PANI [a)]	Zn foil [a)]	0.2	874	0 – 0.8	410	2.0 M $ZnSO_4$	Nanoscale 2018, 10, 13083.
AC [a)]	Zn foil [a)]	0.08	217.8	0.2 - 1.8	67.2	2.0 M $ZnSO_4$	Energy Storage Mater. 2018, 13, 96.
GaN/MnO_2/ MnON [b)]	G/M/M [b)]	0.1	1915.5	0 - 1.0	61	6.0 M KOH	J. Mater. Chem. A 2018, 6, 13215.
CoHCF [b)]	AC [b)]	4.5	351	0 – 2.0	191.25	0.5 M Na_2SO_4	Nano Energy 2017, 39, 647.
$Ni_{0.25}Mn_{0.75}O$ @C [c)]	AC [c)]	1	146	0 – 2.4	N. A	1.0 M LiCl	Adv. Mater. 2017, 29,1703463.

$Ni_{0.25}Mn_{0.75}O$ @C [c)]	AC [c)]	1	114.8	0 – 2.4	N. A	1.0 M LiCl/PVA gel	Adv. Mater. 2017, 29,1703463
$V_2O_5\cdot nH_2O$[d)]	Graphene [d)]	0.75	N. A	N. A	360	3.0 M $Zn(CF_3SO_3)_2$	Adv. Mater. 2018, 30, 1703725.
$NaV_3O_8\cdot 1.5H_2O$ [d)]	Zn foil [d)]	0.2	N. A	N. A	600	1.0 M $ZnSO_4$ + 1.0 M $NaSO_4$	Nat. Commun. 2018, 9, 1656
$ZnMn_2O_4$ [d)]	Zn foil [d)]	0.1	N. A	N. A	404	3.0 M $Zn(CF_3SO_3)_2$	J. Am. Chem. Soc. 2016, 138, 12894.
ZnHCF@MnO_2 [d)]	Zn foil [d)]	0.12	N. A	N. A	178.8	0.5 M $ZnSO_4$/PVA gel	J. Mater. Chem. A 2017, 5, 23628.
$Zn_2V_2O_7$ [d)]	Zn foil [d)]	0.175	N. A	N. A	581	1.0 M $ZnSO_4$	J. Mater. Chem. A 2018, 6, 3850.

[a)] Zn-HSCs; [b)] HSCs; [c)] Li-ion HSCs [d)] Zn-ion batteries

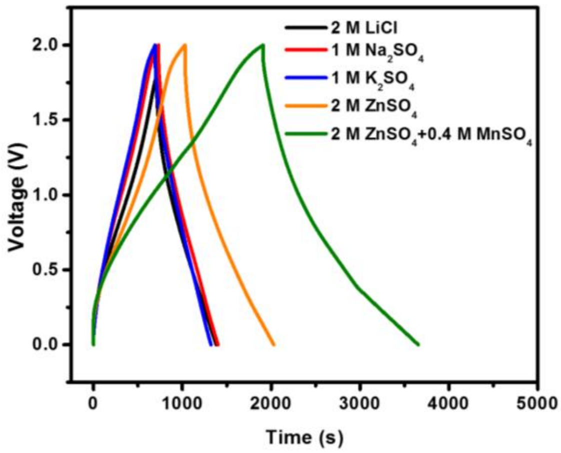

Figure S11. GCD curves of the Zn_xMnO_2//ACC HSCs in different electrolyte.

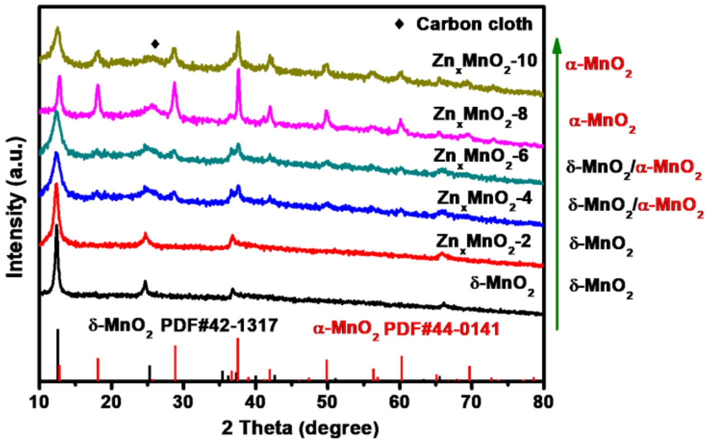

Figure S12. XRD patterns of the Zn_xMnO_2 samples prepared with different $Zn(NO_3)_2$ feeding amount.

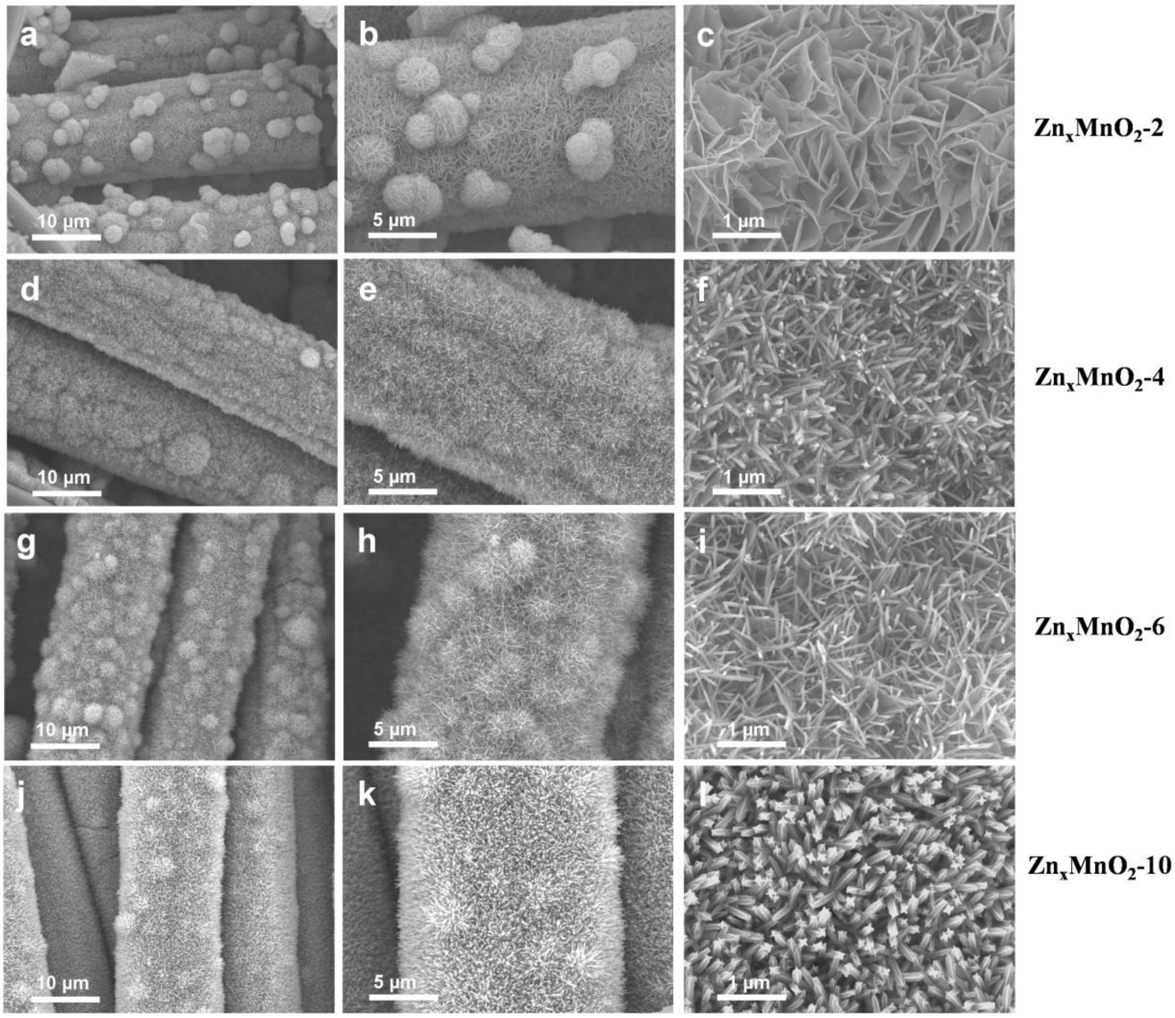

Figure S13. SEM images of Zn_xMnO_2 samples with different $Zn(NO_3)_2$ feeding amount: (a, b, c) 2 mmol, (d, e, f) 4 mmol, (g, h, i) 6 mmol, and (j, k, l) 10 mmol.

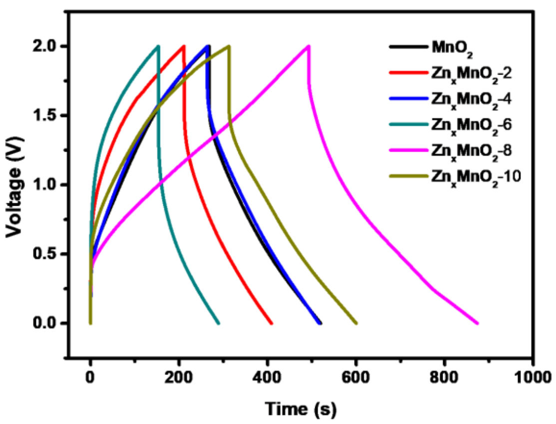

Figure S14. GCD curves of the Zn_xMnO_2 samples prepared with different $Zn(NO_3)_2$ feeding amount.

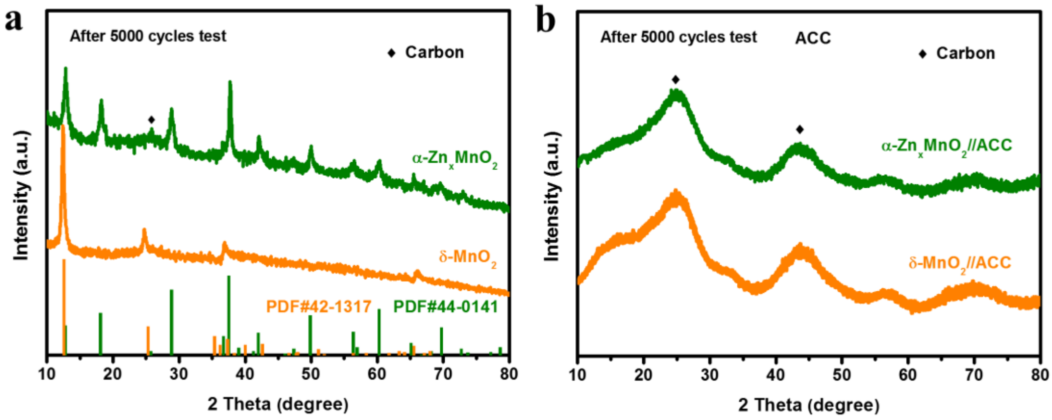

Figure S15. XRD patterns of the Zn_xMnO_2, MnO_2 and ACC after cycle testing.

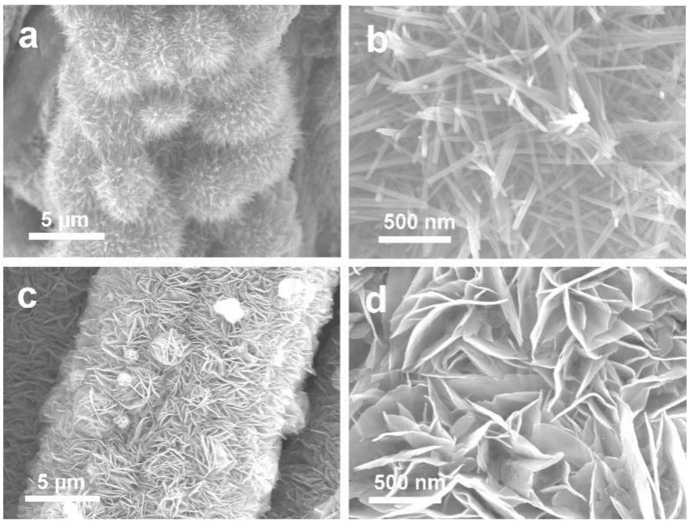

Figure S16. SEM images of (a, b) Zn_xMnO_2 nanowires and (c, d) MnO_2 nanosheets after 5000 cycles testing.

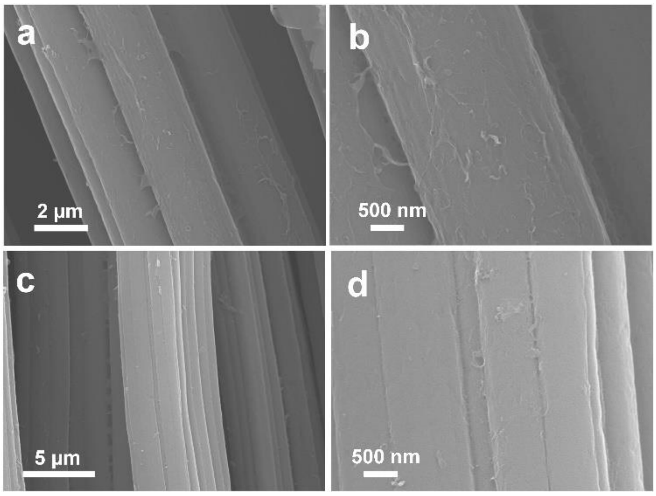

Figure S17. SEM images of the corresponding ACC. (a, b)Zn_xMnO_2//ACC and (c, d) MnO_2//ACC HSCsafter 5000 cycles testing.

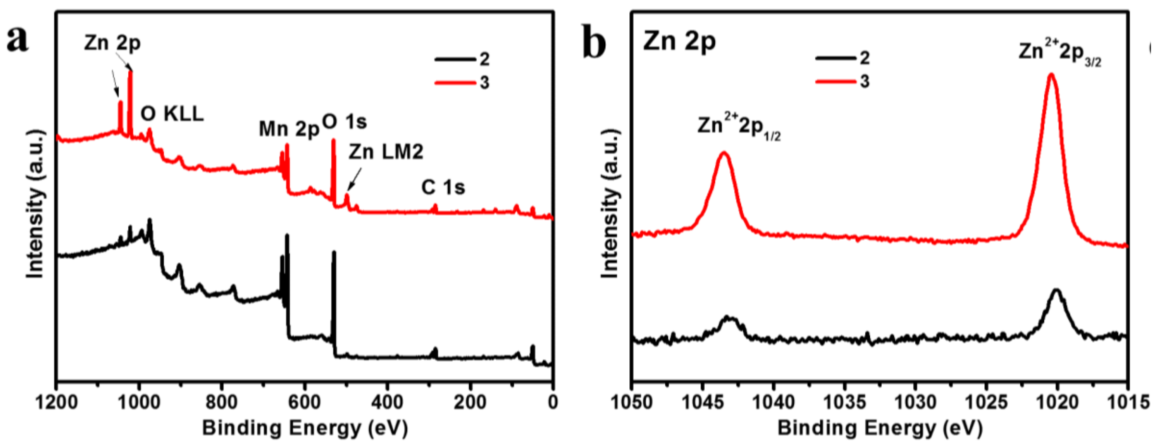

Figure S18. (a) XPS survey and (b) Zn 2p spectra of different point, corresponding to point 2 and 3 in Figure 5d.

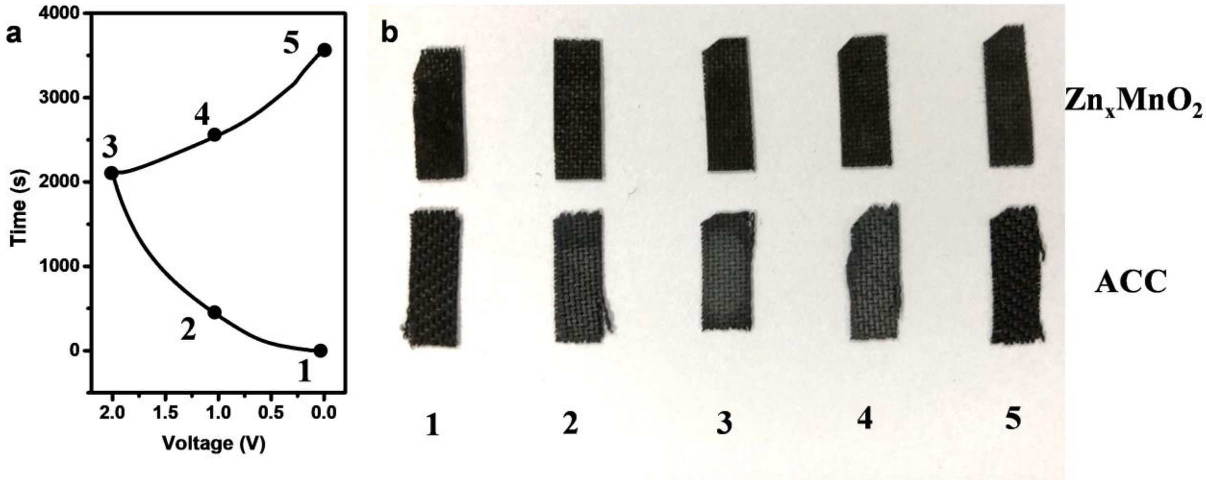

Figure S19. (a) GCD curves of the Zn_xMnO_2//ACC HSCs at 2 mA cm^{-2}. (b) Digital photo of the Zn_xMnO_2 nanowires and ACC nanoparticles at different point during the GCD.