Electronic Supplementary Material (ESI) for Industrial Chemistry & Materials.

Copper ions intercalated manganese dioxide self-supporting mesoporous carbon electrode for aqueous zinc-ion batteries

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Supporting information

Synthesis of PEO-*b*-PS diblock copolymer

The PEO-*b*-PS diblock copolymer was obtained by atom transfer radical polymerization (ATRP) method, which consists of a two-step reaction. In the first step, the microinitiator PEO-Br was synthesized through the acyl bromide reaction. 20 g of PEO-5000 was dissolved in 120ml of THF and then 20ml of pyridine was added to obtain a homogeneous solution at 30 ℃. Reduce the temperature down to 0 ℃ with an ice bath, then add 6 g 2-bromoisobutyryl bromide and stir at 30 ℃ for 24 hours. After adding cold ether, the white precipitation of PEO-Br was collected by centrifugation, washed with cold ether, and dried in vacuum at 30 ℃ overnight. In the second step, 5g PEO-Br was dissolved in 35 ml of styrene, 0.15g CuBr was added to stir well, and then the bottle was sealed and ventilated with nitrogen for 1h. The mixture was subsequently immersed in an oil bath at 110 ℃ under stirring. At the same time, add 0.5g PMDETA and react until sticky. Stop the reaction and cool the container to room temperature. After that, add THF to dissolve the sample and filtered through Al_2O_3 column to remove Cu complex. Next, 200 mL of petroleum ether was poured into the solution to precipitate PEO-b-PS block copolymer. The copolymer was then dried in vacuum at 40 ℃.

Synthesis of mesoporous carbon cloth

Dissolve 60mg of PEO-*b*-PS in 8ml of THF, and then quickly add a mixture of water and ethanol solution (24/12 ml) to obtain a light-blue micelle colloid solution,which presents clear Tyndall effect. After stirring for 5 min, 80 mg of dopamine and Carbon clothes (2X2 cm^2) were added. Next, sonicating the solution for 10 min, the reaction was initiated by adjusting the pH to 8 using a certain amount of ammonia hydroxide. After reacting for 12h, the as-made sample were washed repeatedly for three times by using water and ethanol, respectively. Finally, the carbon clothes was calcined at 800 ℃ in N_2 atmosphere.

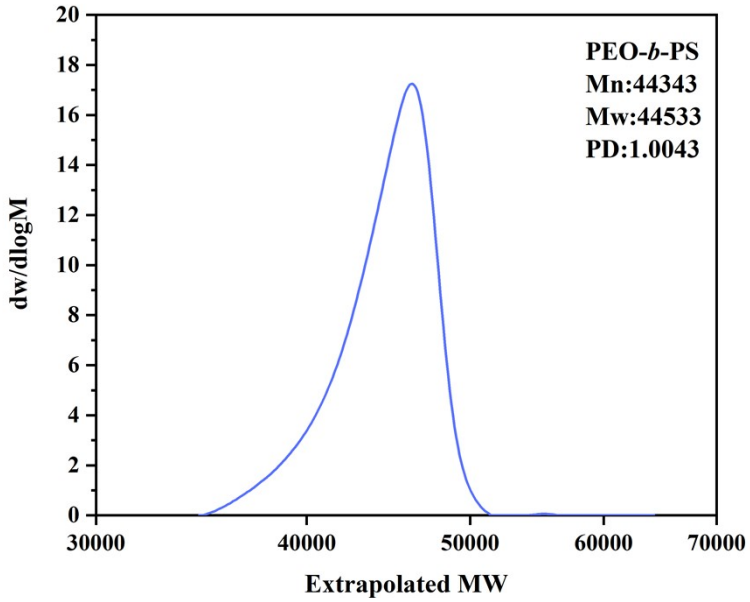

Fig. s1 GPC spectrum of PEO-b-PS

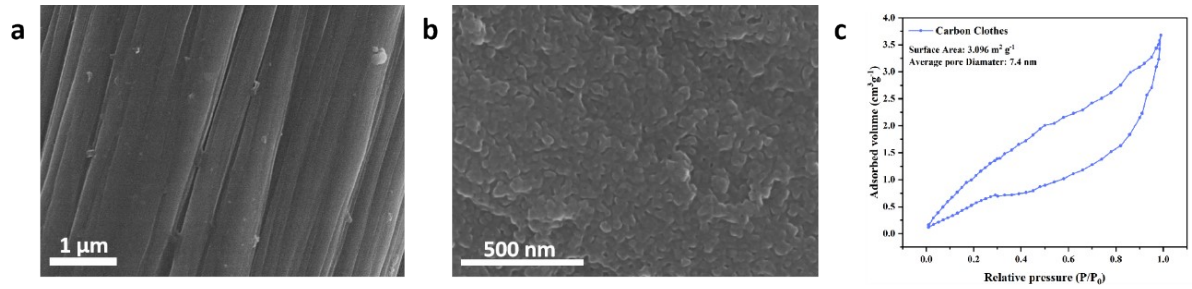

Fig. s2(a) Original carbon cloth scan image, (b) Scanned image of carbon cloth after mesoporous modification, (c) N_2 sorption isothermals and pore size distribution of carbon cloth after mesoporous modification.

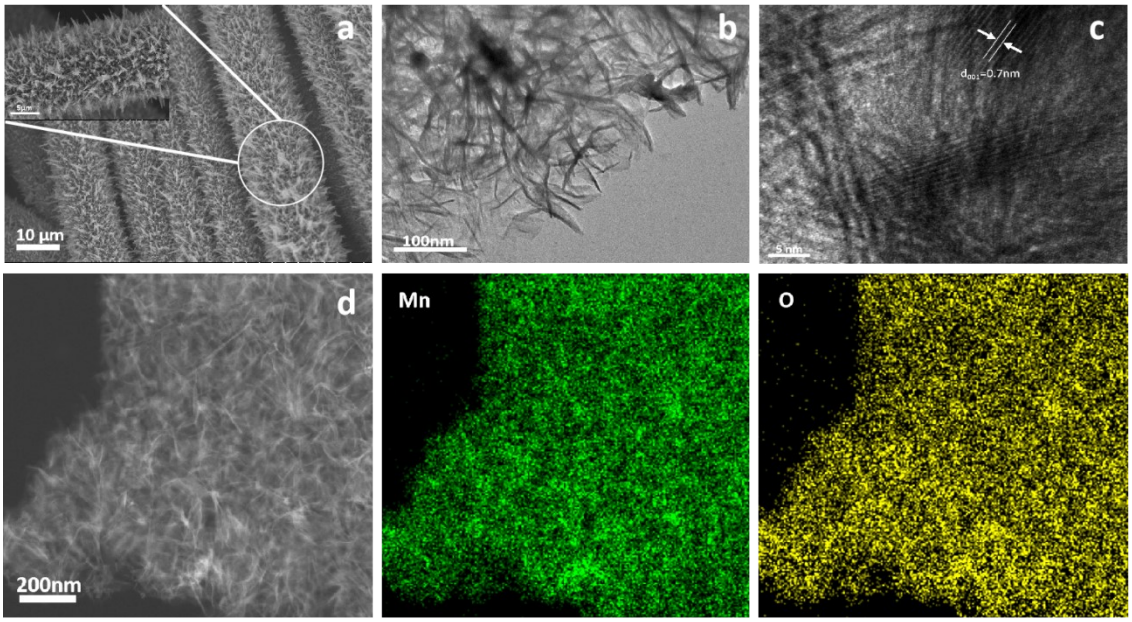

Fig. s3 (a) SEM images, (b) TEM image, (c) HRTEM image, (d) HAADF-STEM image and

corresponding elemental mapping images of Cu-MnO_2.

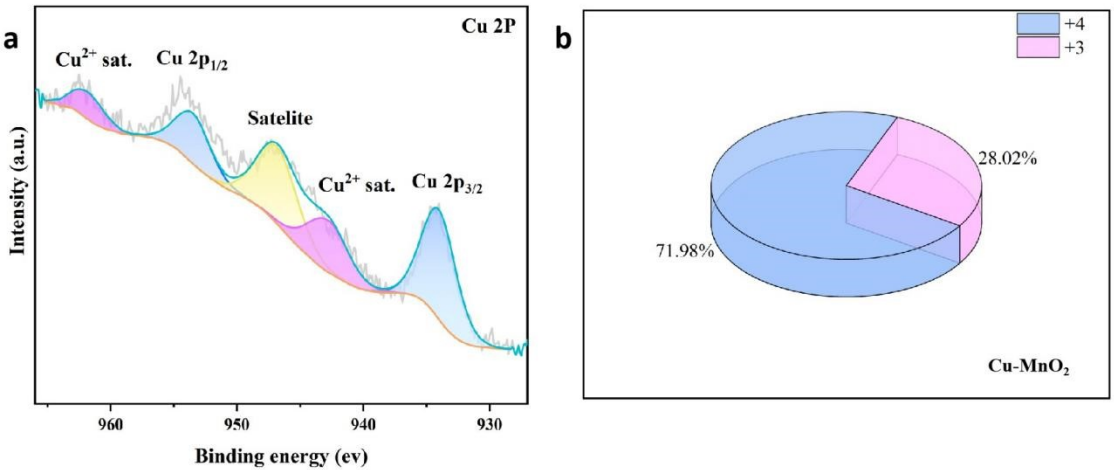

Fig. s4 (a) Cu 2p XPS spectrum, (b) Valence distribution of Mn in Cu-MnO_2

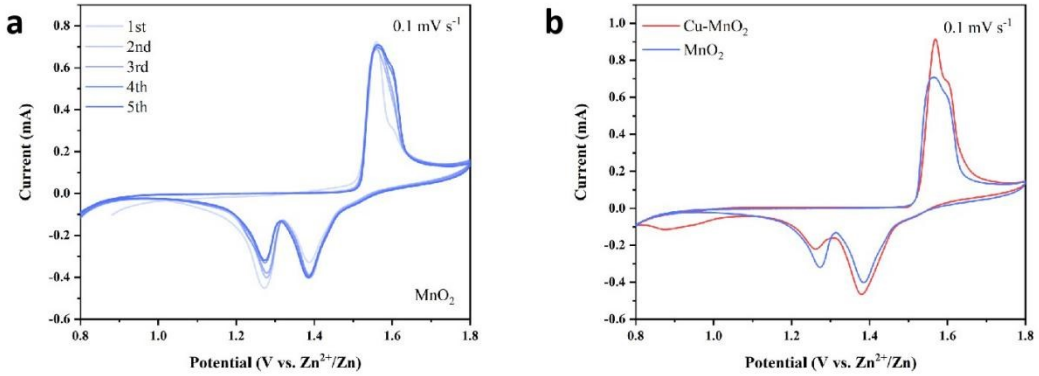

Fig. s5 (a) CV curves at a scan rate of 0.1 mV s^{-1}, (b) CV curve comparison at scan rate of 0.1 mV s^{-1}

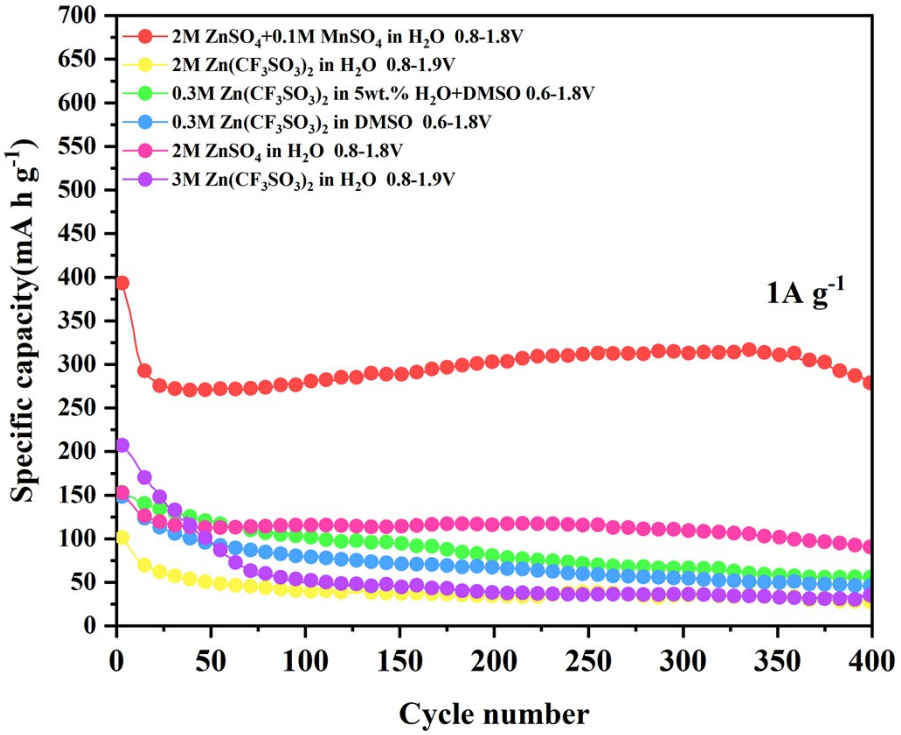

Fig. s6 Electrochemical properties of Cu-MnO_2 in different electrolytes

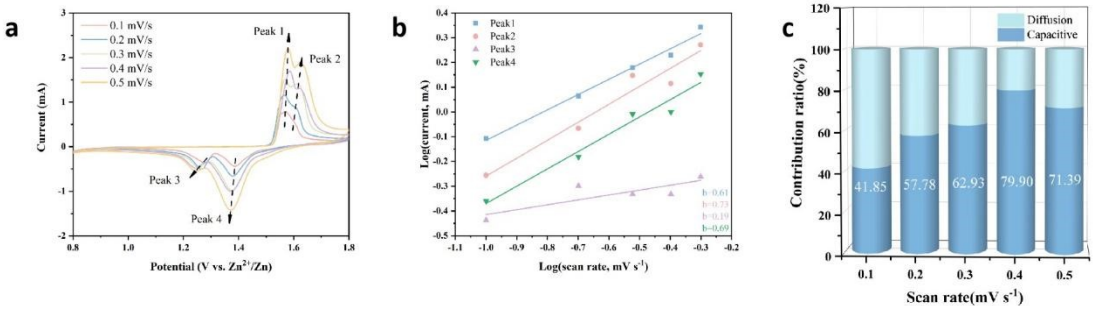

Fig. s7 (a) CV curves at different scan rates, (b) The relationship curves of log i versus log v plots according to the CV data at selected oxidation/ reduction states, (c) Capacitive-controlled ratio at various scan rates of δ-MnO_2

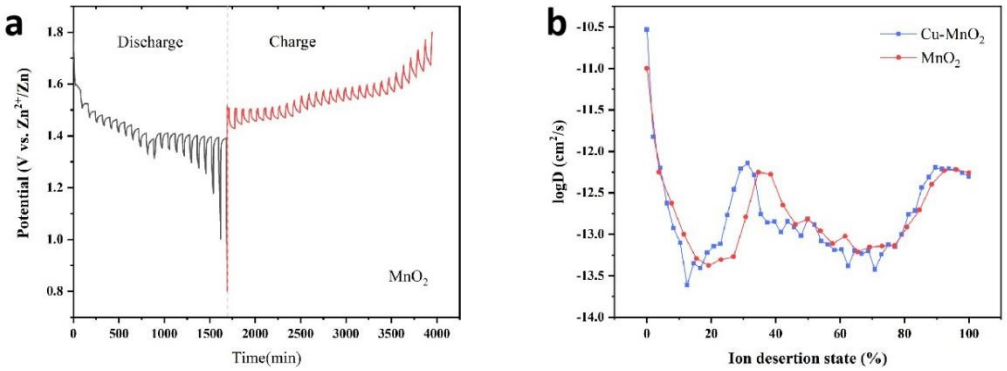

Fig. s8 GITT curves of δ-MnO_2, (e) Diffusion energy barrier values of Cu-MnO_2 and δ-MnO_2 at charge

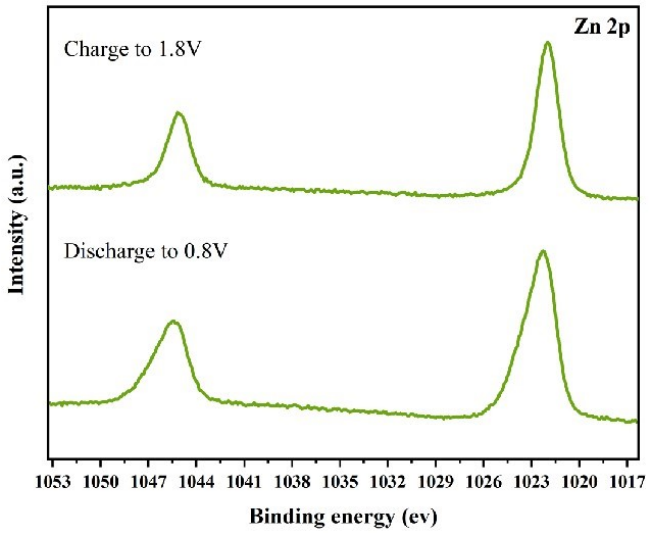

Fig. s9 Zn 2p XPS spectrum of different charging and discharging stages

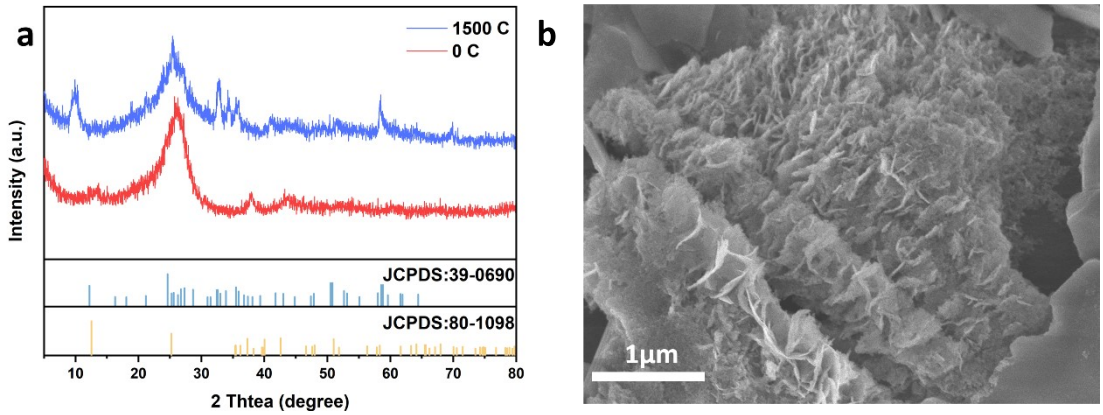

Fig. s10 (a) XRD curves, (b) SEM image after 1500 C

Table.s1 Electrochemical performances fo recently reported cathodes for ZIBs.

Cathode	Specific capacity	Cycling stability	electrolyte	Ref.
Cu-MnO_2	280 mAh g^{-1} (1 A g^{-1})	200.4 mAh g^{-1} at 5 A g^{-1} with 57% capacity retention after 1500 cycles	2.0 M $ZnSO_4$ + 0.1 M $MnSO_4$	This work
δ–$K_{0.32}MnO_2 \cdot 0.15 H_2O$	373 mAh g^{-1} (0.03 A g^{-1}) 218 mAh g^{-1} (1.54 A g^{-1})	173 mAh g^{-1} at 3 A g^{-1} with 35% capacity retention after 2000cycles	2.4 M $Zn(CF_3SO_3)_2$ + 0.1 M Mn $(C_2F_6S_2O_4N)_2$	1
$MnBi_2Te_4$	264.8 mAh g^{-1} (0.4 A g^{-1})	90 mAh g^{-1} at 4 A g^{-1} with 79.9% capacity retention after 1000 cycles	PAM/$ZnSO_4$ hydrogel electrolyte	2
Mn@FeHCF	166.3 mAh g^{-1} (0.1 A g^{-1})	117 mAh g^{-1} at 4 A g^{-1} with 72.4% capacity retention after4800 cycles	1 M $CF_3(CF_2)_3SO_3K$ + 0.1 M $(Zn(CF_3SO_3)_2$	3
MnSe@rGO	290 mAh g^{-1} (0.03 A g^{-1})	178 mAh g^{-1} at 1.5 A g^{-1} with 88.2% capacity retention after1000 cycles	2.0 M $ZnSO_4$ + 0.1 M $MnSO_4$	4
Zn 0.5Mn2O4	299.7 mAh g^{-1} (0.03 A g^{-1})	135.5 mAh g^{-1} at 3.08 A g^{-1} with 90% capacity retention after 1000 cycles	3 M ZnSO4 + 0.2 M $MnSO_4$	5
MON-coated MnO_2	273 mAh g^{-1} (0.2 A g^{-1})	82 mAh g-1 at 10 A g-1 with 85.9% capacity retention after 1000 cycles	2 M $ZnSO_4$ + 0.2 M $MnSO_4$	6
VO-OH	291 mAh g^{-1} (1 A g^{-1})	213 mAh g-1 at 5 A g-1 with 96% capacity retention after 2000 cycles	3 M $Zn(CF_3SO_3)_2$	7
Cu-BTA-H	105 mAh g^{-1} (1 A g^{-1})	106.1 mAh g-1 at 2 A g-1 with 68.5% capacity retention after 500 cycles	2.5 M $ZnSO_4$	8
δ -MnO_2	123 mAh g^{-1} (0.0123 A g^{-1})	60 mAh g-1 at 0.0123 A g-1 with 50% capacity retention after 125 cycles	0.5 M AN–$Zn(TFSI)_2$	9
α -MnO_2	80 mAh g-1 (0.05 A g-1)	50 mAh g^{-1} at 0.1 A g-1 with 80% capacity retention after 2050 cycles	0.1 M $Zn(OTf)_2$ in DMSO	10
δ -MnO_2	112 mAh g-1 (0.1 A g-1)	50 mAh g-1 at 0.5 A g-1 with 94.4% capacity retention after 1000 cycles	Zn-NMF+0.1 M MnCl2	11
α -MnO_2/CNT	275 mAh g-1	100 mAh g-1 at 2.7 A g-1 with 97% capacity	PAM-HFP	12

	(0.0616 A g-1)	retention after 1000 cycles		
δ -MnO_2	144 mAh g-1 (0.5 A g-1)	105mAh g-1 at 2.7 A g-1 with 97.14% capacity retention after 1000 cycles	Mn-DMF	13
Bi- α -MnO_2	250 mAh g-1 (1 A g-1)	at 1 A g-1 with 90.9% capacity retention after 2000 cycles	2 M ZnSO4 + 0.1 M MnSO4	14
MnBirMO	250 mAh g-1 (0.3 A g-1)	103mAh g-1 at 3 A g-1 with 97% capacity retention after 8000 cycles	2 M ZnSO4	15
PANI-MnO_2	280 mAh g-1 (0.2 A g-1)		2 M ZnSO4 + 0.1 M MnSO4	16
C@PODA/MnO2	192 mAh g-1 (0.5 A g-1)	137mAh g-1 at 2 A g-1 with 89.3% capacity retention after 2000 cycles	2 M ZnSO4 + 0.1 M MnSO4	17

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