

## Supporting Information

### **In-situ polymerized synthesis of MnO nanoparticles anchored on N, S co-doped carbon as efficient cathodes for quasi-solid-state zinc ion battery**

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## **Experimental Section:**

All involved chemicals were purchased from Sigma-Aldrich Reagent Co. The reagents and solvents were of analytical grade and used without any extra purification.

### **Preparation of MnO@NSC hybrids**

Typically, 14.7 g (1 M)  $(\text{CH}_3\text{COO})_2\text{Mn}\cdot 4\text{H}_2\text{O}$ , 6 g AM monomer, 36 mg  $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2$  cross-linker and 90 mg  $\text{K}_2\text{S}_2\text{O}_8$  initiator were dispersed into 60 mL deionized water and stirred for 0.5 h at 40 °C to adequately dissolve. Next, the obtained mixture solution was poured into a sealed container glass bottle and heated in an electric oven at 60 °C for 4 h to in situ polymerization, forming uniform PAM-Mn hydrogel. Subsequently, the resulting hydrogel was dried at 60 °C in the oven for 20 h. Finally, the precursor was calcined at 800 °C for 2 h with a heating rate of 5 °C  $\text{min}^{-1}$  in  $\text{N}_2$  flowing to obtain core-shell MnO@NSC nanoparticles.

For comparison study, 7.35 g (0.5 M) and 22.06 g (1.5 M)  $(\text{CH}_3\text{COO})_2\text{Mn}\cdot 4\text{H}_2\text{O}$  were also selected as Mn sources to make MnO@NSC hybrids employing the above method.

### **Materials Characterization:**

The morphology of MnO@NSC samples is investigated by using field emission scanning electron microscopy (FESEM; SU8010, 10 kV) and transmission electron microscopy (TEM, JEM-2100, Japan). Energy-dispersive X-ray spectroscopy (EDS) was used to record elemental distribution. The compositions and structures of MnO@NSC hybrids were analyzed by XRD images (XRD, Bruker, Advance D8A), Raman spectroscopy (Witech. CRM200, 532 nm), and XPS (ESCALAB250Xi) images. The content of C was measured by adopting a TA/SDT650 thermal analyzer at 10 °C  $\text{min}^{-1}$  from 25 to 800 °C under air atmosphere. The specific surface area and the pore-size distribution of MnO@NSC samples is tested by automatic gas adsorption analyzer (Autosorb iQ). The Mn content in electrolyte after the initial CV charge scan was measured by the inductively coupled plasma-optical emission spectrometry (ICP-OES).

### **Electrochemical Performance Testing**

Cyclic voltammetry curves at 0.1, 0.2, 0.4, 0.6 mV s<sup>-1</sup> and electrochemical impedance spectroscopy (100 kHz to 0.1 Hz) were evaluated on electrochemical workstation (CHI 760D). All the galvanostatic charge/discharge tests were conducted on Neware CT-4008 battery test systems (Shenzhen, China) in the potential ranging from 0.8 to 1.9 V (vs. Zn/Zn<sup>2+</sup>). MnO@NSC electrode was prepared by uniformly mixing MnO@NSC active materials, carbon black conductive agents and polytetrafluoroethylene (PTFE) binders via grinding for 20 min to obtain a shiny electrode film, and then such film (area: 1 cm<sup>2</sup>) was pressed onto clean Ti mesh with a pressure of 10 MPa cm<sup>-2</sup> followed by drying in a oven at 100 °C for 16 h. AZIB was assembled by employing Zn foil (thickness: 10 μm) as a anode, MnO@NSC (mass loading: 2-3 mg) a cathode, 2 M ZnSO<sub>4</sub>·7H<sub>2</sub>O + 0.2 M MnSO<sub>4</sub>·H<sub>2</sub>O as an electrolyte and glass fiber separator (GF/D, Whatman) as a separator. The quasi-solid-state ZIB was further assembled by using PAM-based hydrogel instead of the above liquid electrolyte and glass fiber separator. The synthetic methods of hydrogel are as follows: 28.75 g of ZnSO<sub>4</sub>·7H<sub>2</sub>O, 1.69 g of MnSO<sub>4</sub>·H<sub>2</sub>O, 5 g AM monomer, 15 mg C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> cross-linker and 75 mg K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> initiator were dissolved into 50 mL deionized water, held at 40 °C to fully dissolve. Then, the homogenous solution was transferred into a mold and maintained at 60 °C for 4 h to get a brownish red PAM-based hydrogel.

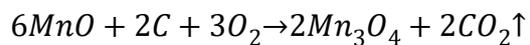
Energy and power densities ( $E$  and  $P$ ) of such AZIB were evaluated based on the calculation formulas of

$$E = \int_0^{\Delta t} IV(t) dt / m$$

$$P = E/\Delta t$$

where  $I$  refers to discharging current (A),  $V(t)$  represents discharging voltage at  $t$  (V),  $dt$  and  $\Delta t$  is time differential and discharging time (s), respectively,  $m$  is mass of MnO

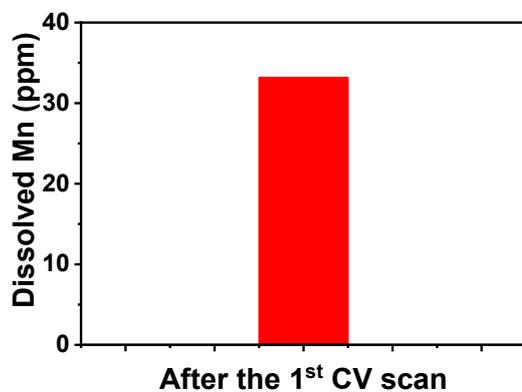
The total MnO content in final sample can be estimated by TGA analysis toward MnO@C. The corresponding reaction equation for MnO@C in air atmospheres is shown below:



According to the mass for annealed products of MnO@C and molar ratio relationships in between  $Mn_3O_4$ , we can calculate the MnO ( $M_1$ ) content in MnO@NSC. The calculation details are listed as follows:

$$\frac{\frac{M_1 \times 0.8044}{228.81} \times 3 \times 70.938}{M_1} = 0.748$$

Therefore, the mass percent concentration of MnO in the MnO@C sample is calculated to be ~74.8%.



**Fig. S1** Content of  $Mn^{2+}$  in 2 M  $ZnSO_4$  electrolytes after the initial CV charge scan

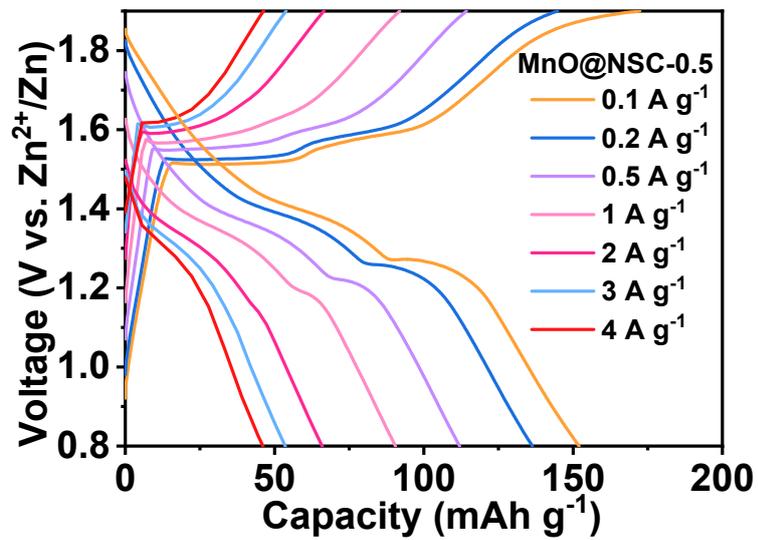


Fig. S2 GCD curves of MnO@NSC-0.5

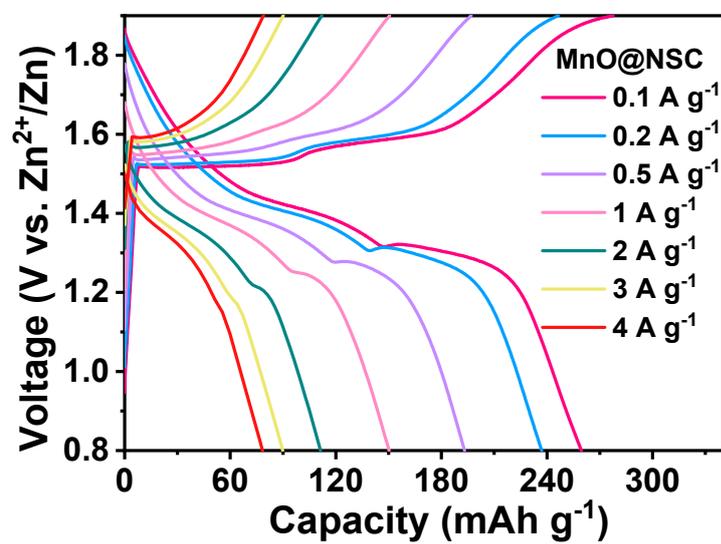


Fig. S3 GCD curves of MnO@NSC

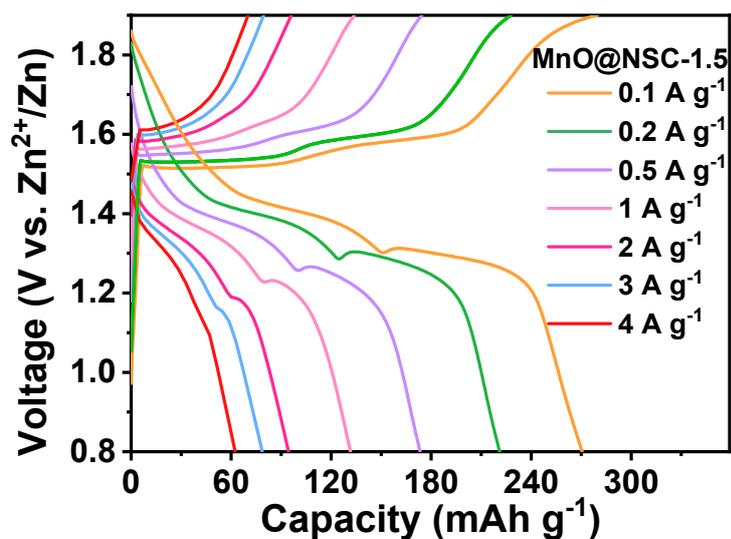


Fig. S4 GCD curves of MnO@NSC-1.5

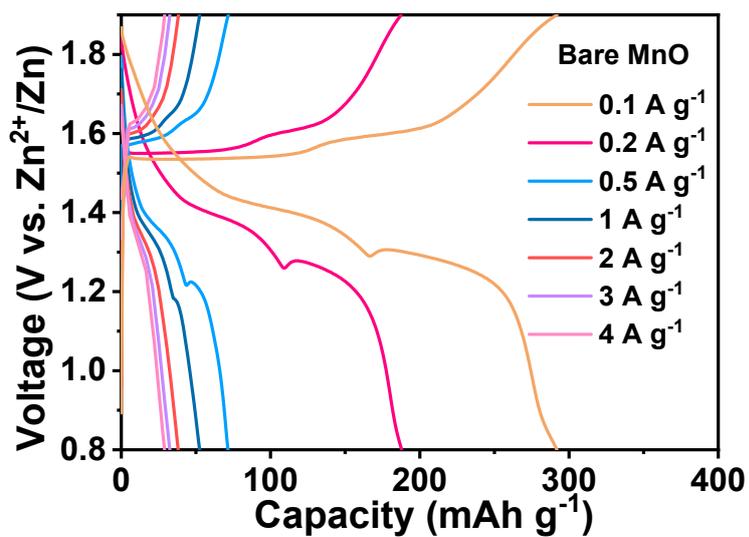


Fig. S5 GCD curves of bare MnO

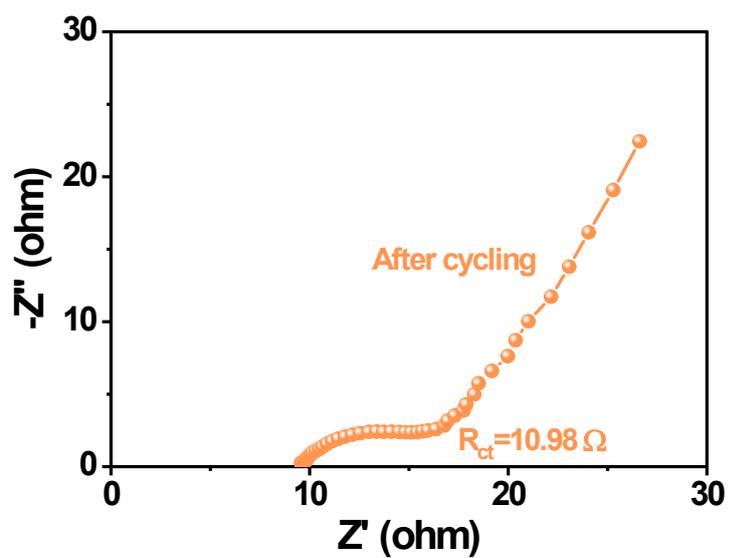


Fig. S6 Nyquist plot of cycled MnO@NSC electrode

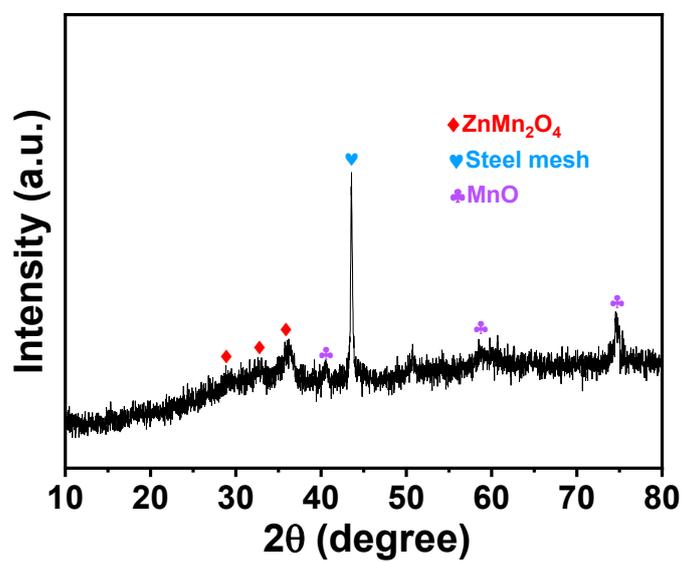


Fig. S7 XRD pattern of the cycled cathode

**Table S1** Cyclic performance comparison

Electrode	Remained Capacity (mAh g <sup>-1</sup> )	Mass loading (mg cm <sup>-2</sup> )	Ref.
MnO@NSC	139.75 at 2 A g <sup>-1</sup> after 5000 cycles	3	This work
$\alpha$ -Mn <sub>2</sub> O <sub>3</sub>	82.2 at 2 A g <sup>-1</sup> after 1000 cycles	-	[1]
CoMn-PBA	57.3 at 1 A g <sup>-1</sup> after 1000 cycles	-	[2]
N-VO-MnO <sub>1-x</sub>	135 at 0.5 A g <sup>-1</sup> after 600 cycles	1	[3]
MnO	10.5 at 0.5 A g <sup>-1</sup> after 600 cycles	1	[4]
MgMn <sub>2</sub> O <sub>4</sub>	96.8 at 0.5 A g <sup>-1</sup> after 500 cycles	-	[5]
MnO@NGS	112.3 at 0.5 A g <sup>-1</sup> after 300 cycles	-	[6]
Mn <sub>3</sub> O <sub>4</sub>	124 at 0.5 A g <sup>-1</sup> after 300 cycles	-	[7]
ZnMn <sub>2</sub> O <sub>4</sub> /C	84.6 at 0.5 A g <sup>-1</sup> after 500 cycles	2	[8]
MnO@C	102.9 at 1.5 A g <sup>-1</sup> after 1200 cycles	1.2	[9]
Cu-MnO <sub>2</sub>	111 at 5 A g <sup>-1</sup> after 700 cycles	1.5	[10]
MnO	103 at 1 A g <sup>-1</sup> after 1000 cycles	1.5	[11]
V <sub>2</sub> O <sub>5</sub>	36 at 10 A g <sup>-1</sup> after 1000 cycles	2.8	[12]
Zn <sub>x</sub> MnO <sub>2</sub> /CNT	101 at 3 A g <sup>-1</sup> after 2000 cycles	1	[13]
s			
MnO@N-C	95.3 at 0.5 A g <sup>-1</sup> after 200cycles	2	[14]
MnO <sub>2</sub>	131 at 0.5 A g <sup>-1</sup> after 400 cycles	2	[15]
MnO@C	56.5 at 2 A g <sup>-1</sup> after 1000 cycles	1	[16]

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