Supporting Information

Superior Performance Asymmetric Supercapacitors Based on $ZnCo_2O_4$@MnO_2 Core-shell Electrode

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Experimental Section:

Synthesis of 3D porous spinous α-Fe_2O_3 on soft thin Fe substrate

In a typical procedure, a Fe foil (1 cm × 1 cm) was cleaned from a consecutive ultrasonication in acetone, ethanol, distilled water. 5 mL Oleic,2 mL HCl (36%-38%) and 10 mL Ethanol were added and formed solution ,After that the prepared Fe foil being immersed in solution in a 60 mL autoclave. Meanwhile the autoclave was sealed and maintained at 60℃ for 4h, and then cooled naturally to room temperature. The Fe substrate attached with brown things was washed with water and ethanol for several times before characterization. Finally as-synthesized materials were subsequent annealing at 400 °C in air.

Calculation methods:

The discharge specific capacitance (C_{sp}) or areal capacitance(C_a) in the three-electrode was calculated from the discharge curves using the following equation:[1,2]

$$\mathbf{C_{sp}} = \mathbf{It}/\mathbf{m\Delta V} \qquad \mathbf{C_a} = \mathbf{It}/\mathbf{S\Delta V}$$

where **I** (A) is the discharge current, **t** (s) is the discharge time, **ΔV** (V) is the voltage interval of the discharge, and **m** (g) is the active material mass of the electrode. **S** is the geometrical area of the electrode.

The energy density and power density are calculated according to the following equations respectively:[3,4]

$$\mathbf{E} = 0.5\mathbf{C}\Delta\mathbf{V}^2 \qquad \mathbf{P} = \frac{\mathbf{E}}{\mathbf{t}}$$

Where **C** ($F\ g^{-1}$) is the specific capacitance, **E** ($Wh\ kg^{-1}$) is the energy density, **P** ($W\ kg^{-1}$) is the power density, **I** (A) is the discharge current, **t** (s) is the discharge time, and **ΔV** (V) is the potential window of discharge.

For supercapacitors, the charge balance between the two electrodes will follow the relationship $\mathbf{q^+ = q^-}$, where q^+ means the charges stored at the positive electrode,q^-means the charges stored at the negative electrode. The charge stored by each electrode usually depends on the specific capacitance (**C**), the potential window for the charge/discharge process (**ΔE**), and the mass of the electrode (**m**) following Equation: $\mathbf{q = C \times \Delta E \times m}$.The mass ratio between the positive and negative electrodes needs to follow: [5]

$$\frac{\mathbf{m_+}}{\mathbf{m_-}} = \frac{\mathbf{C_-} \times \Delta\mathbf{E_-}}{\mathbf{C_+} \times \Delta\mathbf{E_+}}$$

Therefore, the optimal mass ratio between such two electrodes can be determined by the specific capacitance values and potential windows. The $ZnCo_2O_4@MnO_2$ to α-Fe_2O_3 mass ratio was adjusted to be 0.92:1. So the total mass of the two active electrode materials is 2.5 mg cm^{-2}.

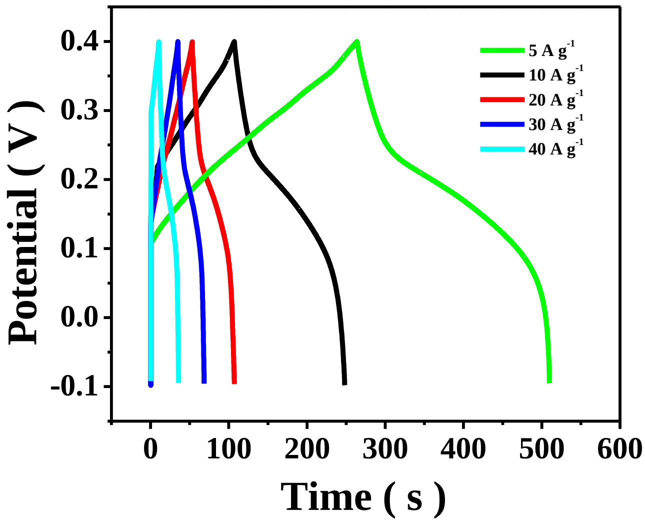

Figure S1 Electrochemical characterizations of the hierarchical $ZnCo_2O_4@MnO_2$ core-shell NTs arrays grown on Ni foam:charge-discharge voltage profiles at different current densities.

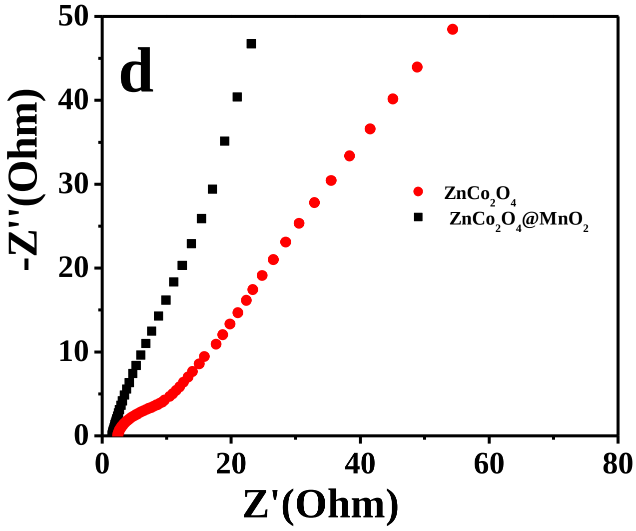

Figure S2 Impedance Nyquist plots of the $ZnCo_2O_4$ NW arrays and the hierarchical $ZnCo_2O_4@MnO_2$ core-shell NTs arrays grown on Ni foam at open circuit potential.

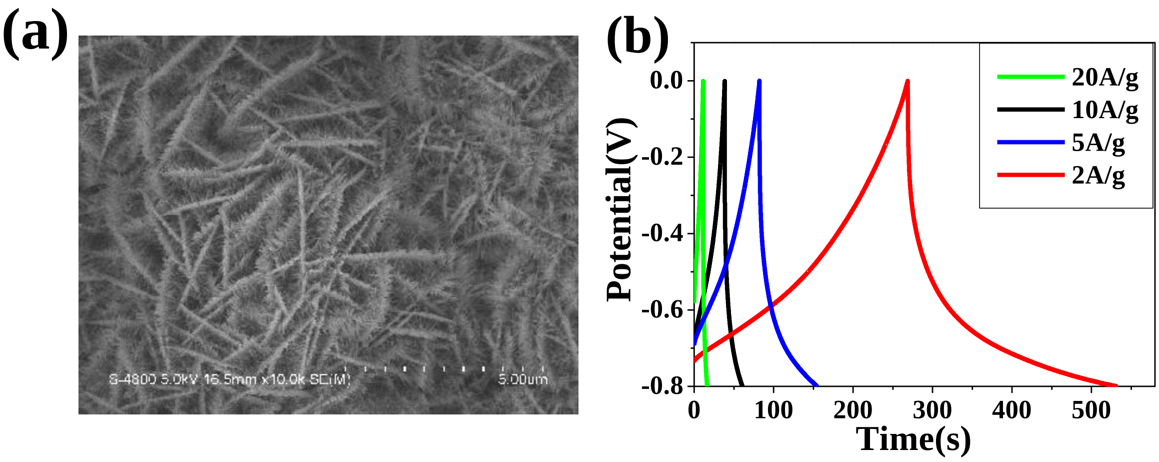

Figure S3 (a) Typical FESEM images of the 3D porous α-Fe_2O_3; (b) Galvanostatic charging/discharging curves of the 3D porous α-Fe_2O at different current densities.

Table 1 Summarization of the supercapacitor performance of different electrode material.

Electrode material	Current density	Specifc capacitance	Reference
$ZnCo_2O_4$@MnO_2 NTs	12 mA cm^{-2}	2.32 F cm^{-2}	This our work
Co_3O_4-MnO_2 NW/nanosheet	12 mA cm^{-2}	0.56 F cm^{-2}	Ref. 6
MnO_2-NiO NWs	12 mA cm^{-2}	0.35 F cm^{-2}	Ref. 7
Co_3O_4-NiO NWs	12 mA cm^{-2}	1.35 F cm^{-2}	Ref. 8
$ZnCo_2O_4$ NWs	12 mA cm^{-2}	0.866 F cm^{-2}	Ref. 9

Reference:

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