3D Nanoflower-liked and Core-Shell Structured MCo₂O₄@MCo₂S₄@Polypyrrole (M = Cu,

Mn) Composites as Supercapacitors Electrode Materials with Ultrahigh Specific Capacitances

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KEYWORDS: MCo₂O₄@MCo₂S₄@Polypyrrole (M=Cu, Mn); 3D Self-supported electrode; Nanoflower structure; Core-Shell structure; Ultrahigh Specific Capacitance; Supercapacitors In addition, the specific capacitances of the as-prepared samples were calculated by Equation S1:

$$C_A = \frac{I \int V \Delta t}{s V^2} \tag{S1}$$

Materials	Current density (A g ⁻¹)	$C_s (F g^{-1})$
CuC/NF	1	1098.7
CuC@CuS/NF	1	1513.88
CuC@CuS@PPy-8/NF	1	1750.44
CuC@CuS@PPy-16/NF	1	2978.1
CuC@CuS@PPy-24/NF	1	2479.3
MnC/NF	1	1145.4
MnC@MnS/NF	1	3186.8
MnC@MnS@PPy-8/NF	1	4278.2
MnC@MnS@PPy-16/NF	1	4713.4
MnC@MnS@PPy-24/NF	1	4003.5

Table S1 The $\rm C_s$ values of all as-prepared samples at 1 A g⁻¹.



Figure S1 Optical photographs of (a) $MnCo_2O_4/NF$ and (c) $CuCo_2O_4/NF$ (the black one), (b) $MnCo_2O_4@MnCo_2S_4/NF$ (the green one) and (d) $CuCo_2O_4@CuCo_2S_4/NF$ (the pink one).



Figure S2 SEM images of (a) CuC@CuS@PPy-8, (b) CuC@CuS@PPy-24, (c) MnC@MnS@PPy-

8 and (d) MnC@MnS@PPy-24 at different magnifications.



Figure S3 EDS mapping patterns (a-d) and EDS quantitative analysis spectra (e, f) of CuCo₂O₄/NF.



Figure S4 EDS mapping patterns (a-e) and EDS quantitative analysis spectra (f) of $CuCo_2O_4@CuCo_2S_4/NF$.



Figure S5 EDS mapping patterns (a-d) and EDS quantitative analysis spectra (e, f) of MnCo₂O₄/NF.



Figure S6 EDS mapping patterns (a-e) and EDS quantitative analysis spectra (e) of $MnCo_2O_4@MnCo_2S_4/NF$.



Figure S7 The XRD patterns of MnC/NF and CuC/NF.



Figure S8 XPS survey spectrums of (a) $CuCo_2O_4@CuCo_2S_4@PPy-16/NF$ and (b) $MnCo_2O_4@MnCo_2S_4@PPy-16/NF$.



Figure S9 (a), (d), (g), (j) and (m) GCD curves of as-prepared samples at various current densities. (b), (e), (h), (k) and (n) CV curves of as-prepared samples at different scan rates. (c), (f), (i), (l) and (o) Nyquist plots of as-prepared samples.



Figure S10 (a), (d), (g), (j) and (m) GCD curves of as-prepared samples at various current densities. (b), (e), (h), (k) and (n) CV curves of as-prepared samples at different scan rates. (c), (f), (i), (l) and (o) Nyquist plots of as-prepared samples.



Figure S11 CV curves (a) of PPy-16/NF electrode at different scanning speeds under the potential windows of 0-0.5 V, GCD curves (b) of PPy-16/NF electrode at various current densities within 0-0.5 V and Nyquist plots (c) of PPy-16/NF electrode.



Figure S12 Areal capacitance curves of all prepared electrode materials at a low current density of 1 A g⁻¹.



Figure S13 CV curves (a) of AC electrode at different scanning speeds under the potential windows of -1.0-0 V and GCD curves (b) of AC electrode at various current densities within -1.0-0 V.



Figure S14 CV curves (a, c) and GCD curves (b, d) of MC@MS@PPy-16/NF//AC ASCs device

(M=Cu, Mn) at different potential windows from 0-1.0 V to 0-1.6V.



Figure S15 (a, b) SEM images of CuC@CuS@PPy-16/NF electrode and (c, d) MnC@MnS@PPy-

16/NF electrode at different magnifications after 10000 GCD cycles.