Supporting information

Double Metal Ions Synergistic Effect in Hierarchical Multiple Sulfide Microflowers for Enhanced in Supercapacitor Performance

Yang Gao,[†] *Liwei Mi,*[*,‡ §,] *Wutao Wei,*[‡] *Shizhong Cui,*[‡] *Zhi Zheng,*[§]*Hongwei Hou*[†] *and Weihua Chen*[*,†]

[†] College of Chemistry and Molecular Engineering, Zhengzhou University, Henan 450001, P. R. China,

[‡] Center for Advanced Materials Research, Zhongyuan University of Technology, Henan 450007, P. R. China, and [§]Key Laboratory for Micro-Nano Energy Storage and Conversion Materials of Henan Province, Institute of Surface Micro and Nano Materials, Xuchang University, Henan 461000, P. R. China.

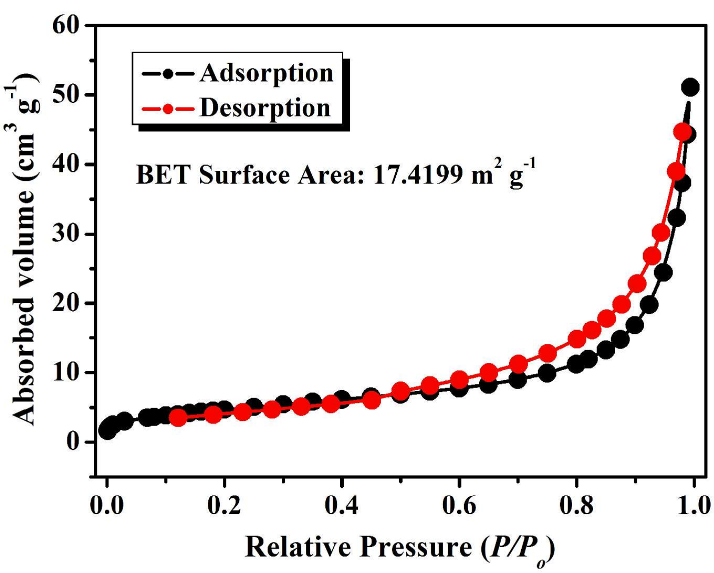

Figure S1. Nitrogen adsorption–desorption isotherms of $CoS_{1.097}$.

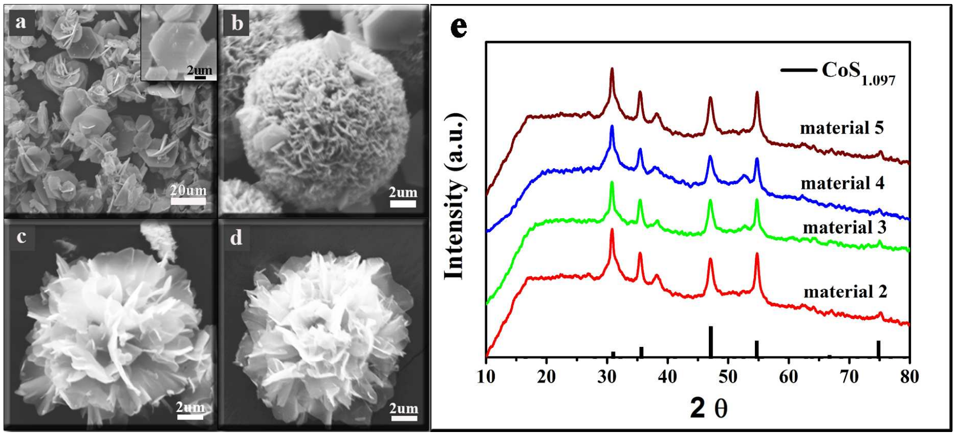

Figure S2. The SEM images of $CoS_{1.097}$ which were prepared in (a) 0 mL CH_3COOH, (b) 0.25 mL CH_3COOH, (c) 0.75 mL CH_3COOH, (d) 1.25 mL CH_3COOH at 160 °C for 24 h, respectively. (e) XRD patterns of $CoS_{1.097}$ with different amount of CH_3COOH.

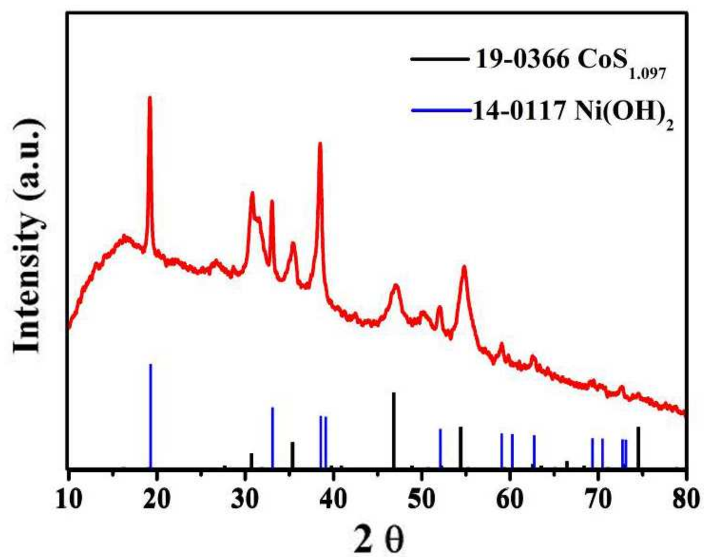

Figure S3. XRD patterns of materials prepared through cation exchange reaction between $CoS_{1.097}$ and Ni^{2+} with Co/Ni moral ratio 1:2 for 3h.

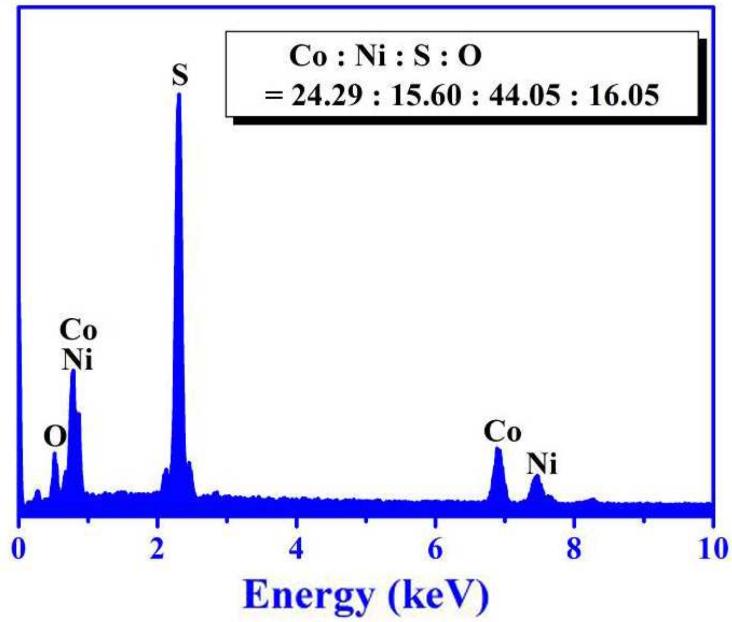

Figure S4. EDX patterns of materials prepared through cation exchange reaction between $CoS_{1.097}$ and Ni^{2+} with Co/Ni moral ratio 1:2 for 3h

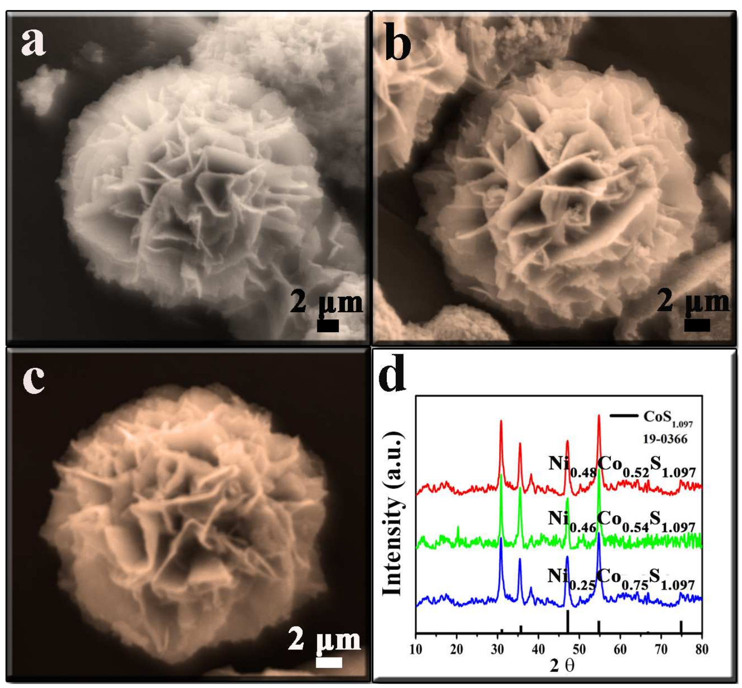

Figure S5. SEM images of (a) $Ni_{0.25}Co_{0.75}S_{1.097}$, (b) $Ni_{0.46}Co_{0.54}S_{1.097}$, (c) $Ni_{0.48}Co_{0.52}S_{1.097}$; XRD patterns of materials $Ni_xCo_{1-x}S_{1.097}$ (x=0.25, 0.46, 0.48).

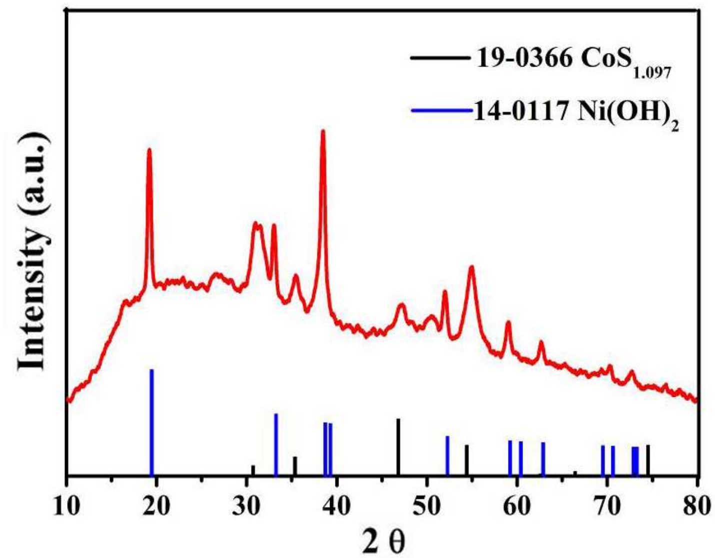

Figure S6. XRD patterns of materials prepared through cation exchange reaction between $CoS_{1.097}$ and Ni^{2+} with Co/Ni moral ratio 1:5 for 1h.

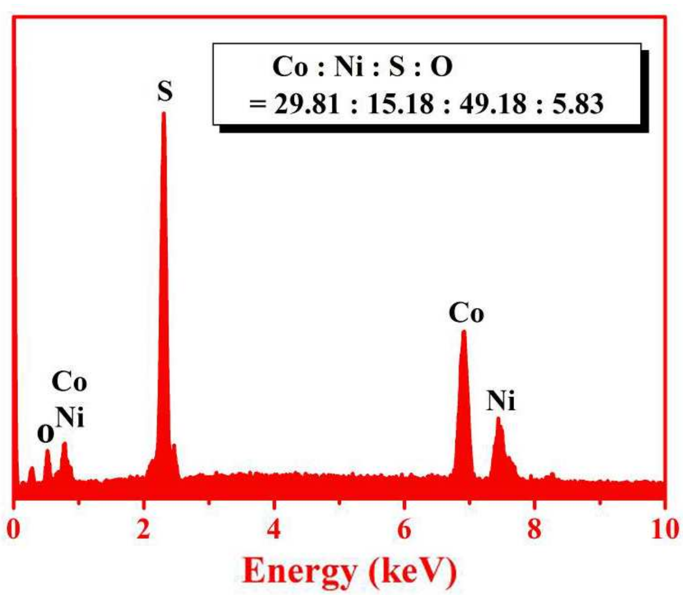

Figure S7. EDX patterns of materials prepared through cation exchange reaction between $CoS_{1.097}$ and Ni^{2+} with Co/Ni moral ratio 1:5 for 1h

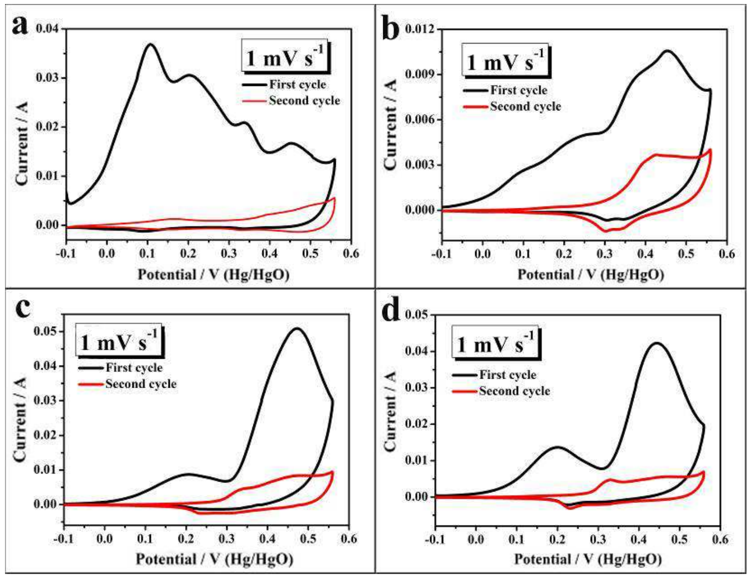

Figure S8. CV curves of (a) $CoS_{1.097}$, (b) $Ni_{0.48}Co_{0.52}S_{1.097}$, (C) $CoS_{1.097}$-rGO, (d) $Ni_{0.48}Co_{0.52}S_{1.097}$-rGO at scan rate of 1 mV s^{-1}.

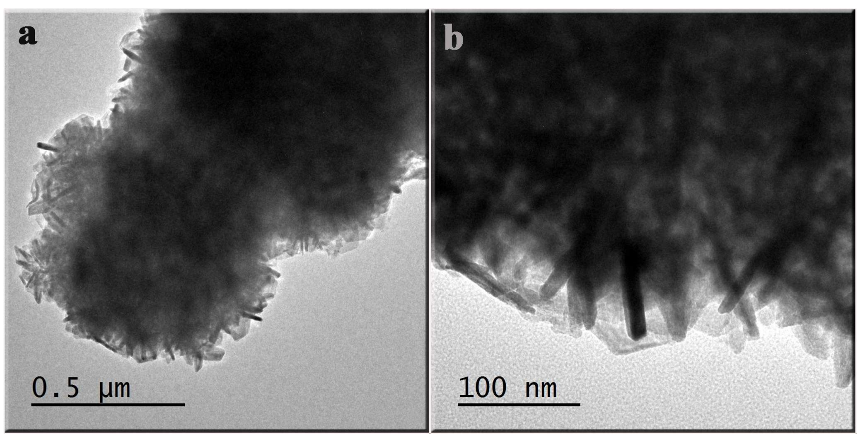

Figure S9. (a, b) TEM images of $Ni_{0.48}Co_{0.52}S_{1.097}$-rGO electrode materials.

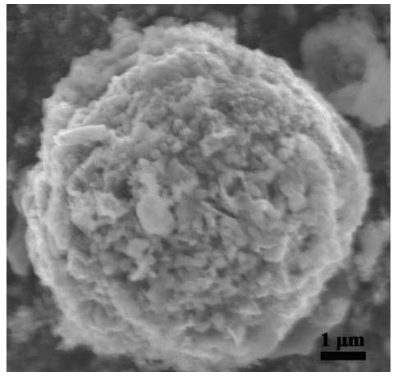

Figure S10. SEM image $Ni_{0.43}Co_{0.57}S_{1.097}$ after 1000 cycles CV test with a scan rate of 5 mV s^{-1}.

The SEM image of $Ni_{0.43}Co_{0.57}S_{1.097}$ material after 1000cycles CV test is shown in Figure S10. Comparing the morphologies of $Ni_xCo_{1-x}S_{1.097}$ composite as-deposited (Figure 2a to d) with charged/discharged (Figure S10), it can be deduced that in the charge /discharge processes the microflower transform to microsphere with rough surface structures, the morphology of the electrode material can be largely remained which may be responsible for the phase transformation reaction from $Ni_xCo_{1-x}S_{1.097}$ to $Ni(OH)_2$ (or $Co(OH)_2$).

The $CoS_{1.097}$, $Ni_{0.22}Co_{0.78}S_{1.097}$, $Ni_{0.46}Co_{0.54}S_{1.097}$, and $Ni_{0.48}Co_{0.52}S_{1.097}$ electrodes exhibited a remarkable specific capacitance of 186.0, 551.6, 768.6, and 867 F g^{-1} at current densities of 0.5 A g^{-1}, respectively. The rGO modified electrodes exhibit much higher specific capacitance of 425, 830, 1102, 1152 F g^{-1} The specific capacitance of hybrids materials are based on the mass of $Ni_xCo_{1-x}S_{1.097}$ (x=0, 0.22, 0.46, 0.48). Studies have shown that graphene as electrodes for supercapacitors posses a specific capacitance of 135 F g^{-1} at current density of 10 mA g^{-1} in aqueous.[1] So graphene will exhibit much lower specific capacitance as the current density increased to 0.5 A g^{-1}. Therefore, the value of specific capacitance of 5% rGO is very small that we can ignore.

The mass loading per unit area of active materials $Ni_xCo_{1-x}S_{1.097}$ in this communication:

materials	**$CoS_{1.097}$**	**$Ni_{0.10}Co_{0.90}S_{1.097}$**	**$Ni_{0.22}Co_{0.78}S_{1.097}$**
m (g/cm^2)	0.0045	0.0047	0.0040
materials	**$Ni_{0.43}Co_{0.57}S_{1.097}$**	**$Ni_{0.46}Co_{0.54}S_{1.097}$**	**$Ni_{0.48}Co_{0.52}S_{1.097}$**
m (g/cm^2)	0.0045	0.0043	0.0045
materials	**$CoS_{1.097}$-rGO**	**$Ni_{0.22}Co_{0.78}S_{1.097}$-rGO**	**$Ni_{0.48}Co_{0.52}S_{1.097}$-rGO**
m (g/cm^2)	0.0042	0.0040	0.0041

1 M. D. Stoller, S. Park, Y. J.An, Zhu, R. S. Ruoff, *Nano Lett*., 2008, **8**, 3498–3502.