Supplementary Information

In Situ N-doped Carbon Modified (Co_{0.5}Ni_{0.5})₉S₈ Solid-solution

Hollow Spheres as High-capacity Anode for Sodium-Ion Battery

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^c College of Chemistry and Molecular Sciences, Hubei International Scientific and Technological Cooperation Base of Sustainable Resource and Energy, Wuhan University, Wuhan 430072, PR China Carbon content analysis:

Take $(Co_{0.5}Ni_{0.5})_9S_8/N-C$ as an example, we assume the mole ratio of C: Co = n. Thus, based on the ICP result, the mole ratio of Co: Ni: C is 1 : 0.83 : n. During the TGA test, the corresponding oxidation reactions is as follows.

$$(Co_{0.5}Ni_{0.5})_9S_8/N-C+O_2 \rightarrow Co_3O_4 + NiO + CO_2$$

58.9 + 58.6 × 0.83 + 56.9 + 12n 80.3 74.7 × 0.83

From this reaction, the weight loss ratio after calcination in O_2 atmosphere is as follows.

$$\frac{58.9 + 58.6 \times 0.83 + 56.9 + 12n - 80.3 - 74.7 \times 0.83}{58.9 + 58.6 \times 0.83 + 56.9 + 12n}$$

Based on the weight loss of 24.78% measured from TGA, an equation can be given:

$$\frac{58.9 + 58.6 \times 0.83 + 56.9 + 12n - 80.3 - 74.7 \times 0.83}{58.9 + 58.6 \times 0.83 + 56.9 + 12n} = 24.78\%$$

$$n \approx 2.1$$

So the carbon content in $(Co_{0.5}Ni_{0.5})_9S_8/N-C$ is determined to be 13.5%.



Fig. S1 Schematic crystal structure of cubic Co_9S_8 phase.



Fig. S2 XRD patterns for (A) $(Co_{1-x}Ni_x)_9S_8$ -NiS/N-C, (B) Ni₃S₂/N-C; (C) TGA curves of $(Co_{1-x}Ni_x)_9S_8$ -NiS/N-C and Ni₃S₂/N-C and (D) N₂ adsorption-desorption isotherms curves of $(Co_{0.5}Ni_{0.5})_9S_8$ /N-C.

Table S1 Quantitative analysis of the Ni/Co ratio in $(Co_{1-x}Ni_x)_9S_8/N-C$ and $(Co_{1-x}Ni_x)_9S_8-N-C$

NiS/N-C samples by ICP

Samples	Molar ratio of Ni/Co
(Co _{0.67} Ni _{0.33}) ₉ S ₈ /N-C	0.48
(Co _{0.5} Ni _{0.5}) ₉ S ₈ /N-C	0.83
(Co _{1-x} Ni _x) ₉ S ₈ -NiS/N-C	1.77



Fig. S3 SEM images of (A) Co-MOF, (B) Ni-Co-MOF-0.5, (C) Ni-Co-MOF-1, (D) Ni-Co-

MOF-2, (E) Ni-MOF.



Fig. S4 SEM images of (A, E) Co₉S₈/N-C, (B, F) (Co_{0.67}Ni_{0.33})₉S₈/N-C, (C, G) (Co_{1-x}Ni_x)₉S₈-NiS/N-C, (D, H) Ni₃S₂/N-C.



Fig. S5 HRTEM images of $(Co_{0.5}Ni_{0.5})_9S_8/N-C$.



Fig. S6 Full XPS spectra for (A) Co₉S₈/N-C, (B) (Co_{0.67}Ni_{0.33})₉S₈/N-C and (C) (Co_{1-x}Ni_x)₉S₈-

NiS/N-C.



Fig. S7 XPS spectra of $(Co_{1-x}Ni_x)_9S_8/N-C$ and $(Co_{1-x}Ni_x)_9S_8-NiS/N-C$ for Ni $2p_{3/2}$, Co $2p_{3/2}$ and S $2p_{3/2}$ regions.



Fig. S8 SEM images of the $(Co_{0.5}Ni_{0.5})_9S_8/N$ -C electrode after 50 cycles.



Fig. S9 (A) Charge-discharge curves and (B) cycling performance of $(Co_{0.5}Ni_{0.5})_9S_8/N-C//NVP@C$ full cell at 0.5 A g⁻¹ after 0.05 A g⁻¹ in the initial cycle; (C) LED lights powered by the full cell.