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Electronic Supplementary Information

Binary Metal Organic Frameworks Derived Hierarchical Hollow Ni₃S₂/Co₉S₈/N-

doped Carbon Composite with Superior Sodium Storage Performance

Xinye Liu^a[†], Feng Zou^a[†], Kewei Liu^a, Zhe Qiang^b, Clinton J. Taubert^a, Putu

Ustriyanaa^a, Bryan D. Vogt^b and Yu Zhu*a

^a Department of Polymer Science, University of Akron, Akron, Ohio 44325, United

States

^b Department of Polymer Engineering, University of Akron, Akron, OH, 44325,

United States

*Address correspondence to: Yu Zhu (yu.zhu@uakron.edu)

[†] These authors contribute equally to this work



Figure S1. ICP test results for Ni and Co elements. The sample was prepared by dissolving 50 mg MOF precursor in 500 ml 4 wt% HNO₃ (100 ppm).



Figure S2. XRD pattern of Ni-Co-MOF.



Figure S3. TGA of Ni-Co-MOF under N_2 with a temperature ramp rate of 5 °C/min.

```
DATE 08 02 17 TIME 11 15 58 OPERATOR ID QUICK
RUN 1 ID MSNC1 WEIGHT 1.974
                              SIGNALS
                              ZR 8451
   CARBON 19.24% NR 9485
HYDROGEN .41% CR 15420
NITROGEN 9.19% HR 15906
    BLANKS 6 133 23
    KFACTORS 15.614 43.562 5.572
    OXFILL COMB BOOST1 BOOST2
     3 10 1 0
FILL TIME 22 SECONDS
DATE 08 02 17 TIME 11 20 56 OPERATOR ID QUICK
RUN 2 ID MSNC2 WEIGHT 1.610
                              SIGNALS
                              ZR 8449
   CARBON 19.34%
HYDROGEN .37%
NITROGEN 9.31%
                              NR 9307
                              CR 14174
                             HR 14567
   BLANKS 6 133 23
   KFACTORS 15.614 43.562 5.572
   OXFILL COMB BOOST1 BOOST2
     3 10 1 0
FILL TIME 22 SECONDS
```

Figure S4. CHN analysis results for the Ni₃S₂/Co₉S₈/N-doped carbon composite



Figure S5. TGA of $Ni_3S_2/Co_9S_8/N$ -doped carbon composite under air with a temperature ramp rate of 5 °C/min.



Figure S6. Nitrogen adsorption-desorption isotherm of the $Ni_3S_2/Co_9S_8/N$ -doped carbon composite (BET surface area: 41.5 m²g⁻¹)

Calculation of crystal sizes based on the Scherrer equation

$$D = \frac{K\lambda}{\beta\cos\theta}$$

D: grain size
K: shape factor, (0.9)
λ: X-ray wavelength (nm)
β: full width at half the maximum intensity (FWHM)
θ: Bragg angle

The XRD pattern is shown in Figure 2b. The X-ray wavelength is 1.541 Å. Peak (1-10) of Ni_3S_2 (2 θ =31.245°) and peak (440) of Co_9S_8 (2 θ =52.104°) are used for calculation. The FWHMs are 0.232° and 0.269°, respectively.

For calculation, the FWHMs were converted into radian. The value of β for Ni₃S₂ and Co₉S₈ are 0.0040 and 0.0047, respectively.

Based on the Scherrer equation

 $\begin{array}{c} 0.9 * 0.154 \\ D(Ni_3S_2) = \overline{0.0040 cos~(15.625)} \ nm = 35.5 \ nm \\ \hline 0.9 * 0.154 \\ D(Co_9S_8) = \overline{0.0047 cos~(26.052)} \ nm = 32.4 \ nm \end{array}$

Table S1 Sodium storage performance comparison between our work and previous results.

Reference	Active Materials	Current	Capacity	Cycles	Retention
		Density	(mAh/g)		
		(A/g)			
Wang et al. ¹	NiS ₂ -GNS	0.08	314	200	77%
		1.6	168		

Shang et al. ²		0.6	280	30	88%		
0.000	N ₁₃ S ₂ -PEDOT	1.2	310				
Pan et al. ³	NiS-20rGO	Charge	160	10	88%		
		0.2					
		Discharge					
		0.05					
Song et al. ⁴	Rod-like	0.05	315.3	100	90.6%		
	Ni S /Ni	0.8	230				
	¹ ¹ ³ ³ ² ¹ ¹ ¹						
Kim et al. ⁵	Ni ₃ S ₂	0.05	342	16	81%		
Qin et al. ⁶	NiS-rGO	0.1	391.6	50	77.1%		
		1	346				
Zhang et al. ⁷	$\overline{\text{Core-shell Co}_{x}S_{y}}$	0.5	300	50	77%		
Du et al. 8	Co2S4-PNS/GS	0.5	329	50	71		
	00304 1110/00	2	307	50	/ 1		
Zhou et al ⁹	Co ₃ S ₄ @PANI	0.2	252.5	100	44%		
Zhou et ul.		2	189.3	100			
Ko et al. ¹⁰	Co ₉ S ₈ @carbon	0.5	404	50	80%		
		1.5	326				
Zhang et al. ¹¹	CuO/Cu ₂ O	0.05	415	50	/		
	_	1	217.3				
Feng et al. ¹²	NiO/Ni/Graphene	1	248	190	60%		
_	_	2	207				
This work	Ni ₃ S ₂ /Co ₉ S ₈ /N-	0.1	419.9	100	98.6%		
	doped carbon	2	323.2				
	composite						
* GNS: graphene nanosheets; PEDOT: poly(3,4-ethylenedioxythiophene); rGO:							
reduced graphene oxide; Co ₃ S ₄ -PNS/GS: Co ₃ S ₄ porous nanosheets/graphene sheets;							
PANI: polyaniline							

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