

## Supporting Information

### **Facile synthesis of mesoporous Ni<sub>x</sub>Co<sub>9-x</sub>S<sub>8</sub> hollow spheres for high-performance supercapacitor and aqueous Ni/Co-Zn battery**

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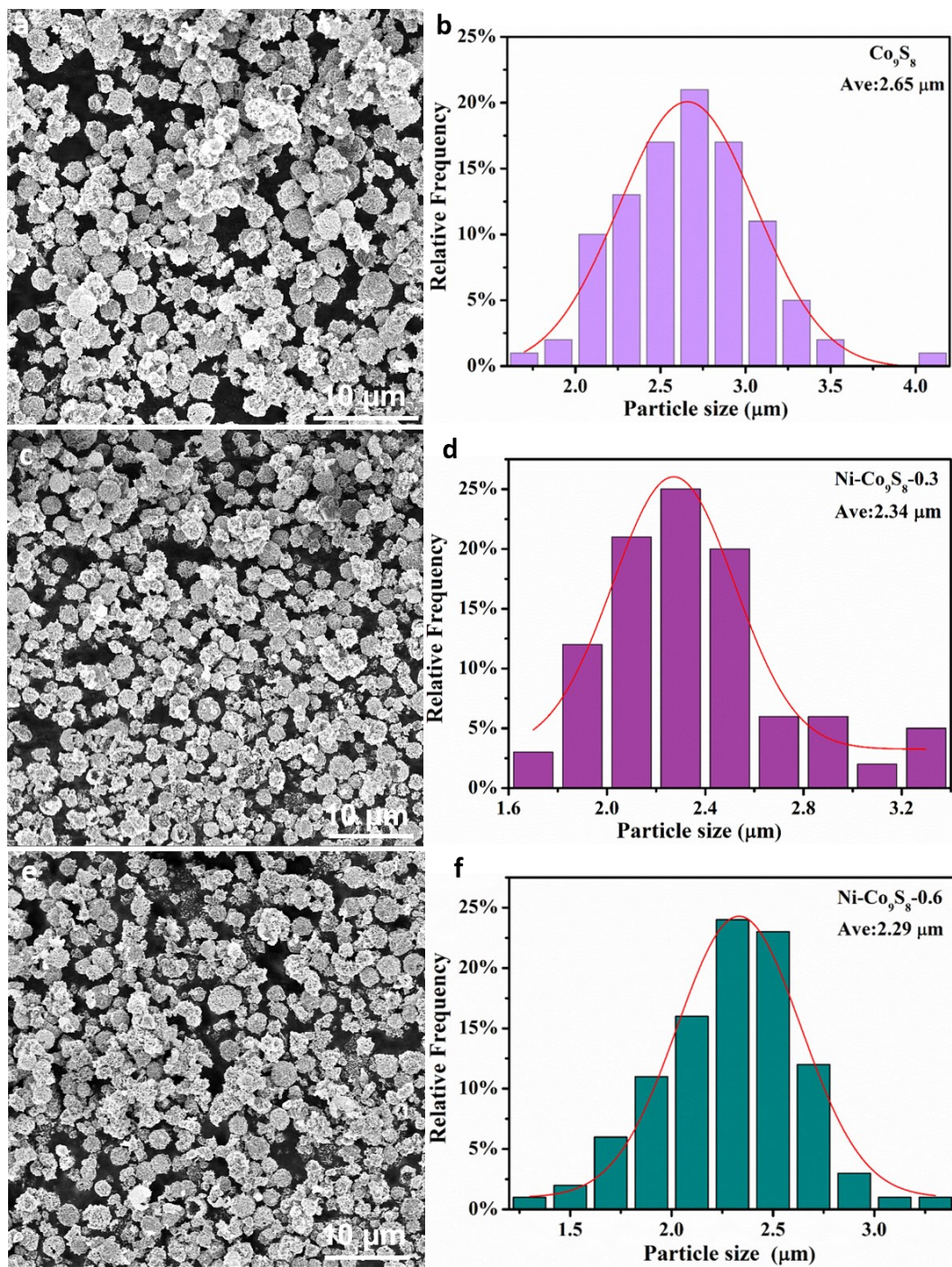


Fig.S1 The SEM images and size distribution of (a-b)  $\text{Co}_9\text{S}_8$ , (c-d)  $\text{Ni-Co}_9\text{S}_8-0.3$ , and (e-f)  $\text{Ni-Co}_9\text{S}_8-0.6$  hollow spheres.

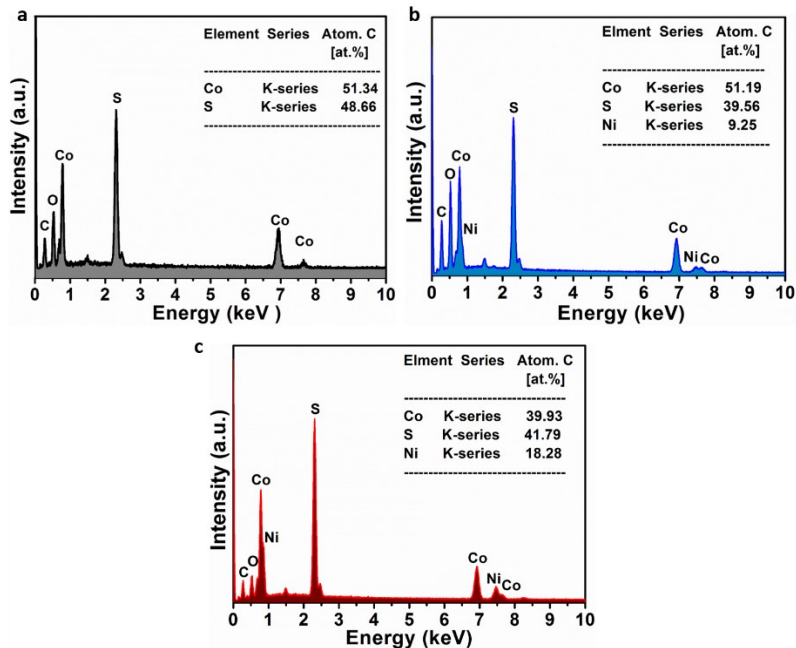


Fig.S2 EDS of (a)  $\text{Co}_9\text{S}_8$ , (b)  $\text{Ni-Co}_9\text{S}_8\text{-0.3}$ , and (c)  $\text{Ni-Co}_9\text{S}_8\text{-0.6}$  hollow spheres.

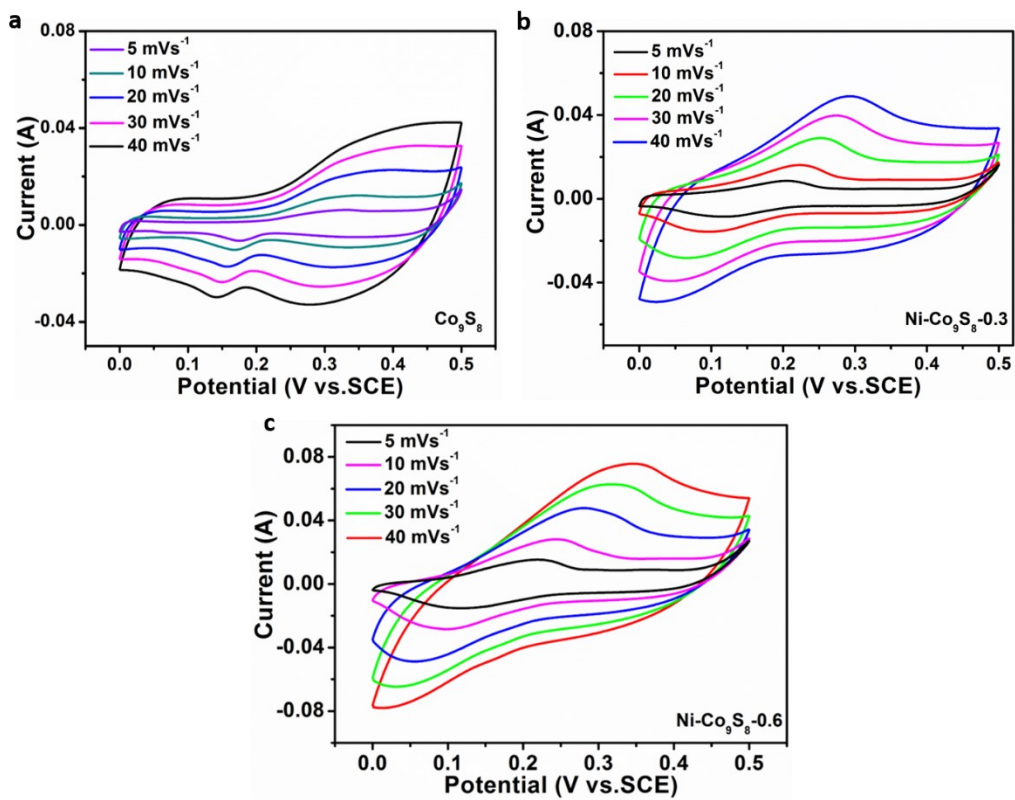


Fig.S3 CV curves of (a)  $\text{Co}_9\text{S}_8$ , (b)  $\text{Ni-Co}_9\text{S}_8\text{-0.3}$ , and (c)  $\text{Ni-Co}_9\text{S}_8\text{-0.6}$  hollow spheres.

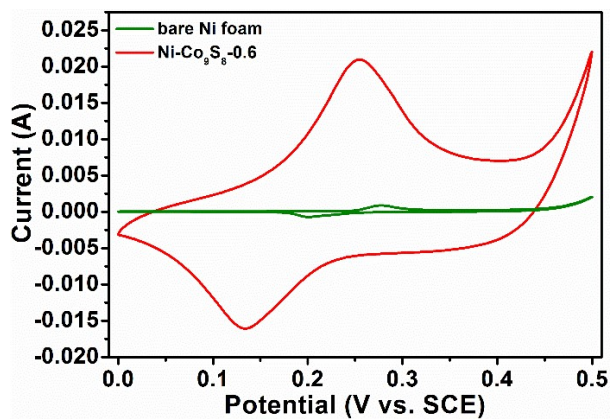


Fig.S4 The comparison of CV curves of bare Ni foam and Ni-Co<sub>9</sub>S<sub>8</sub>-0.6 hollow spheres at the scan rate of 5 mV s<sup>-1</sup>.

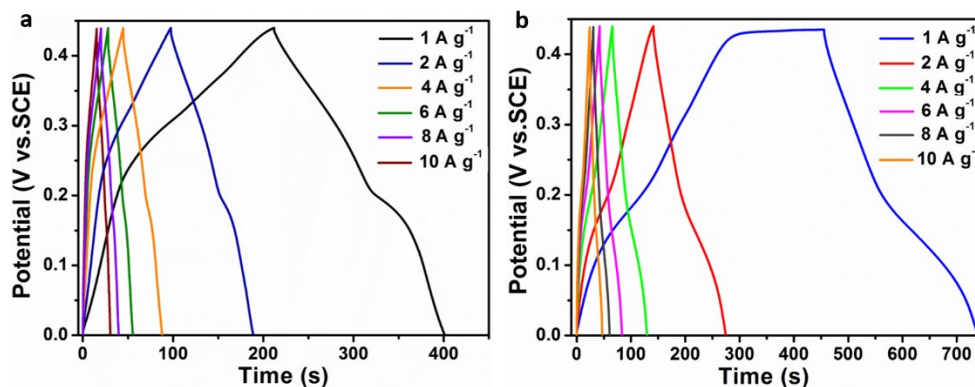


Fig.S5 GCD curves of (a) Co<sub>9</sub>S<sub>8</sub> and (b) Ni-Co<sub>9</sub>S<sub>8</sub>-0.3 electrodes.

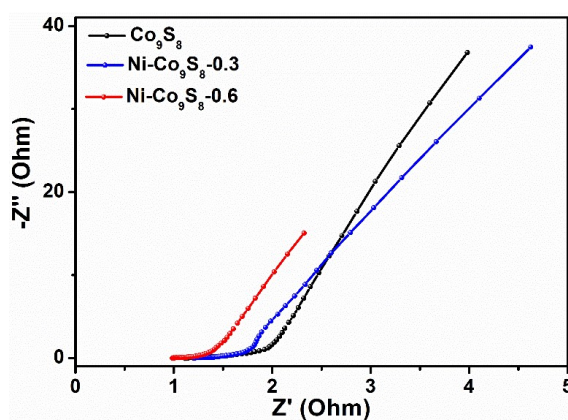


Fig.S6 The Nyquist plots of Co<sub>9</sub>S<sub>8</sub>, Ni-Co<sub>9</sub>S<sub>8</sub>-0.3, and Ni-Co<sub>9</sub>S<sub>8</sub>-0.6 hollow spheres.

Table S1 The peak area ratio of  $\text{Co}^{3+}/\text{Co}^{2+}$  and  $\text{Ni}^{3+}/\text{Ni}^{2+}$  in  $\text{Ni}_x\text{Co}_{9-x}\text{S}_8$  series microspheres.

Sample	$\text{Co}^{3+}/\text{Co}^{2+}$	$\text{Ni}^{3+}/\text{Ni}^{2+}$
$\text{Co}_9\text{S}_8$	0.3248	0
$\text{Ni-Co}_9\text{S}_8\text{-30}$	0.3127	1.8803
$\text{Ni-Co}_9\text{S}_8\text{-60}$	0.3529	2.3823

Table S2 Comparison of the performance of the  $\text{Ni}_x\text{Co}_{9-x}\text{S}_8$  mesoporous hollow microspheres electrode with other reported Co-based and sulfides electrode.

Materials	Morphology	Electrolyte (KOH)	Specific capacity ( $\text{F g}^{-1}$ )	Rate capability	Capacity retention (%)	Ref
$\text{Co}_9\text{S}_8@\text{N-C@MoS}_2$	core-shell structured nanocubes	3 M	410.0 ( $10 \text{ A g}^{-1}$ )	79.8% ( $0.5\text{-}10 \text{ A g}^{-1}$ )	101.7% ( $20000, 10 \text{ A g}^{-1}$ )	ACS Appl. Energy Mater. 2018, 1, 3513–3520
rGO/ $\text{Co}_9\text{S}_8$	hollow particles	1 M	575.9 ( $2 \text{ A g}^{-1}$ )	77.7% ( $2\text{-}10 \text{ A g}^{-1}$ )	92% ( $9000, 4 \text{ A g}^{-1}$ )	Chin. Chem. Lett. 2018, 29, 612–615
NiCo-MOF NSHS	nanosheet-assembled hollow spheres	3 M	1126.7 ( $0.5 \text{ A g}^{-1}$ )	65% ( $0.5\text{-}10 \text{ A g}^{-1}$ )	93% ( $3000, 10 \text{ A g}^{-1}$ )	Inorg. Chem. 2020, 59, 11385–11395
$\text{Co}_9\text{S}_8\text{-X@CN}$	octahedral nanoparticles / carbon matrix	6 M	471.1 ( $0.5 \text{ A g}^{-1}$ )	59.0% ( $0.5\text{-}10 \text{ A g}^{-1}$ )	79.2% ( $1000, 10 \text{ A g}^{-1}$ )	Chem Asian J. 2021, 16, 1-8
$\text{Co}_9\text{S}_8/\text{GPs}$	nanotube arrays / graphene paper	2 M	653 ( $0.5 \text{ A g}^{-1}$ )	71.8% ( $0.5\text{-}10 \text{ A g}^{-1}$ )	91.8% ( $2500, 10 \text{ A g}^{-1}$ )	Chem. Eur. J. 2018, 24, 2339–2343
$\text{NiS@CoS}$	core-shell		1210 ( $1 \text{ A g}^{-1}$ )	82% ( $1\text{-}10 \text{ A g}^{-1}$ )	80.94% ( $2000, 10 \text{ A g}^{-1}$ )	Adv. Mater. Interfaces 2019, 7, 1901618
$\text{Co}_9\text{S}_8@\text{C}$	hollow microspheres	1 M	514 ( $1 \text{ A g}^{-1}$ )	77% ( $1\text{-}16 \text{ A g}^{-1}$ )	88% ( $1000, 8 \text{ A g}^{-1}$ )	ChemElectro Chem, 2018, 2, 137-143
P-CoS <sub>1.097-6</sub>	dandelion-like		536 $\text{C g}^{-1}$ ( $5 \text{ A g}^{-1}$ )	94% ( $5\text{-}20 \text{ A g}^{-1}$ )	97% ( $5000, 10 \text{ A g}^{-1}$ )	J. Electroanal. Chem. 2021, 889, 115231

CoS <sub>2</sub> HNs	nanocuboids	3 M	703.3 ± 0.5 (0.5 A g <sup>-1</sup> )	72.5% (0.5- 10 A g <sup>-1</sup> )	---	J. Colloid Interface Sci. 2021, 599, 577–585
CoS <sub>x</sub> /C	Hierarchical hollow nanocages	1 M	618 (2 A g <sup>-1</sup> )	83.6% (2-50 A g <sup>-1</sup> )	ca.100% (10000, 4 A g <sup>-1</sup> )	RSC Adv., 2019, 9, 11253
Co-S-P	Nanoflowers	6 M	969.5 (1 A g <sup>-1</sup> )	79.9% (1- 20A g <sup>-1</sup> )	105% (30 000, 10 A g <sup>-1</sup> )	ACS Sustain. Chem. Eng., 2019, 7, 11448 –11454
Ni-Co <sub>9</sub> S <sub>8</sub> - 0.6	Mesoporous hollow microspheres	2 M	1300 (1 A g <sup>-1</sup> )	80.6% (1- 10A g <sup>-1</sup> )	74.5% (5000 , 4 A g <sup>-1</sup> )	This work