# **Electronic Supplementary Information**

## S, N-Containing Co-MOFs Derived Co<sub>9</sub>S<sub>8</sub>@S,N-Doped Carbon

### Materials as Efficient Oxygen Electrocatalysts and Supercapacitor

### **Electrode Materials**

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Table. S1 Summary of the ORR and OER performances for some other  $Co_9S_8$ -based catalysts reported recently.

Sample	OER Current density of 10 mA cm <sup>-2</sup> at 0.1M KOH	ORR 0.1M KOH		
		potential	n (electron transfer number)	Reference
Co <sub>9</sub> S <sub>8</sub> /NSPC9–45	0.31 V	0.79 V (E <sub>1/2</sub> )	3.94 at 0.3 V	1
Co-C@Co <sub>9</sub> S <sub>8</sub> DSNCs		0.96 V (onset)	3.9 at 0.1-0.4 V	2
N-Co <sub>9</sub> S <sub>8</sub> /G	0.28 V	0.94 V(onset)	3.7 ~3.9 at -0.2-0.8 V	3
Fe <sub>3</sub> O <sub>4</sub> @Co <sub>9</sub> S <sub>8</sub> /rGO	0.47 V			4
Co <sub>9</sub> S <sub>8</sub> @SNCC	0.33 V	0.75 V(E <sub>1/2</sub> ) 0.84 V(onset)	3.99 at 0.2-0.6V	this work

Sample	Capacitance	Electrolyte	Reference
Co <sub>9</sub> S <sub>8</sub> /RGO/Ni <sub>3</sub> S <sub>2</sub>	2611.9 F g <sup>-1</sup> at 3.9 A g <sup>-1</sup>	2 M KOH	5
Co <sub>9</sub> S <sub>8</sub> @Ni(OH) <sub>2</sub> core@shell structure	1620 F g <sup>-1</sup> at 0.5 A g <sup>-1</sup>	2 M KOH	6
C@Co <sub>9</sub> S <sub>8</sub> hollow structures	654 F g <sup>-1</sup> at 2 A g <sup>-1</sup>	2 M KOH	7
Co <sub>9</sub> S <sub>8</sub> /NF	1645 F g <sup>-1</sup> at 3 A g <sup>-1</sup>	2 M KOH	8
$Co_9S_8$ nanotubes	1775 F g <sup>-1</sup> at 4 A g <sup>-1</sup>	2 M KOH	9
Co <sub>9</sub> S <sub>8</sub> @SNCC	429 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	6M KOH	this work

Table. S2 Summary of the capacitances of some other  $\text{Co}_9\text{S}_8$ -based composites reported recently.



Fig. S1 SEM image of the Co<sub>9</sub>S<sub>8</sub>@SNCB



Fig. S2 (a) Koutecky-Levich plots derived from the RDE data of  $Co_9S_8@SNCC$ , (c) electron transfer number of  $Co_9S_8@SNCC$  at 0.2 V~0.6 V.



Fig. S3 (a) LSV curves of Pt/C at various rotation rates; (b) Corresponding Koutecky–Levich plots derived from the RDE data; inset of electron transfer number of Pt/C at  $0.2 \text{ V} \sim 0.6 \text{ V}$ .



**Fig. S4** (a) LSV curves of  $Co_9S_8$ @SNCB at various rotation rates; (b) Corresponding Koutecky–Levich plots derived from the RDE data; inset of electron transfer number of  $Co_9S_8$ @SNCB at 0.2 V~0.6 V.



**Fig. S5** XRD pattern of the  $Co_9S_8@SNCC$  composite after electrochemical test at 0.1 KOH, 250 cycles for cyclic voltammetry at a scan rate of 50 mV s<sup>-1</sup>, illustrated that the  $Co_9S_8$  is very stability during this electrochemical test. The  $Co_9S_8@SNCC$  was coated on the graphitic carbon paper as an electrode for electrochemical test.



Fig. S6 LSV curves of electrocatalysts of  $Co_9S_8$  SNCC, SNCC for (a) ORR and (b) OER measurements.



**Fig. S7** (a) Cyclic voltammogram curves at various scan rates ranging from 5 mV s<sup>-1</sup> to 100 mV s<sup>-1</sup> and (b) charge-discharge curves measured at different current densities of  $Co_9S_8@SNCC$ .



**Fig. S8** (a) Cyclic voltammogram curves at various scan rates ranging from 5 mV s<sup>-1</sup> to 100 mV s<sup>-1</sup> and (b) charge-discharge curves measured at different current densities of  $Co_9S_8@SNCB$ 



Fig. S9 Nyquist plots of  $Co_9S_8$  (BNCB and  $Co_9S_8$  (BNCC electrode materials for supercapacitors

#### **References:**

- 1 Zhong H.-x.; Li K.; Zhang Q.; Wang J.; Meng F.-l.; Wu Z.-j.; Yan J.-m.; Zhang X.-b., *NPG Asia Mater.* **2016**, *8*, e308.
- 2 Hu H.; Han L.; Yu M.; Wang Z.; Lou X. W., Energy Environ. Sci. 2016, 9, 107-111.
- 3 Dou S.; Tao L.; Huo J.; Wang S.; Dai L., *Energy Environ. Sci* **2016**, *9*, 1320-1326.
- 4 Yang J.; Zhu G.; Liu Y.; Xia J.; Ji Z.; Shen X.; Wu S., *Adv. Funct. Mater.* **2016**, *26*, 4712-4721.
- 5 Zhang Z.; Wang Q.; Zhao C.; Min S.; Qian X., ACS Appl. Mater. Interf. 2015, 7, 4861-4868.
- 6 Wen J.; Li S.; Li B.; Song Z.; Wang H.; Xiong R.; Fang G., *J. Power Sources* **2015**, *284*, 279-286.
- 7 Wu T.; Ma X.; Zhu T., Mater. Lett. 2016, 183, 290-295.
- 8 Li H.; Gao Y.; Shao Y.; Su Y.; Wang X., Nano. Lett **2015**, *15*, 6689-6695.
- 9 Pu J.; Wang Z.; Wu K.; Yu N.; Sheng E., Phys. Chem. Chem. Phys. 2014, 16, 785-791.