

## ESI:

### **Construction of mesoporous Cu-doped Co<sub>9</sub>S<sub>8</sub> rectangular nanotube arrays for high energy density all-solid-state asymmetric supercapacitors**

Wen Lu,<sup>a</sup> Ze Yuan,<sup>a</sup> Chunyang Xu,<sup>a</sup> Jiqiang Ning,<sup>b</sup> Yijun Zhong,<sup>a</sup> Ziyang Zhang<sup>b</sup> and Yong Hu<sup>\*a</sup>

<sup>a</sup>Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Department of Chemistry, Zhejiang Normal University, Jinhua 321004, China.

\*E-mail: [yonghu@zjnu.edu.cn](mailto:yonghu@zjnu.edu.cn); [yonghuzjnu@163.com](mailto:yonghuzjnu@163.com)

<sup>b</sup>Vacuum Interconnected Nanotech Workstation, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China.

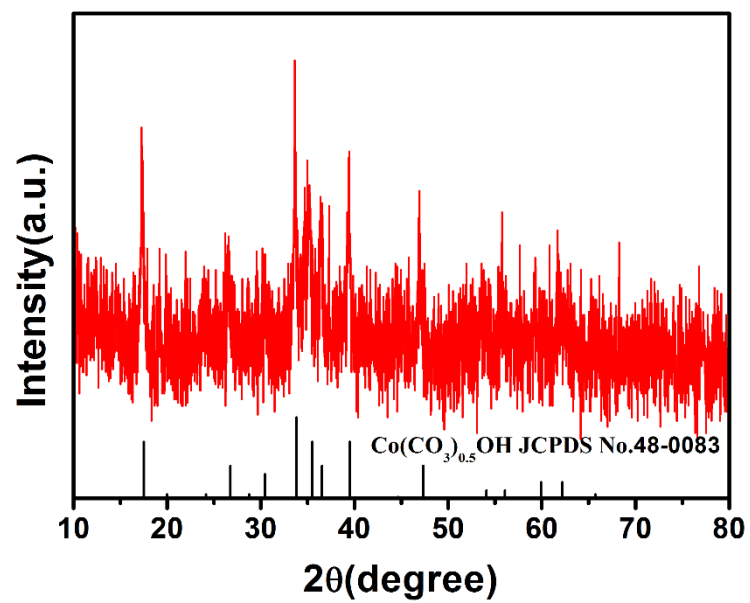


Fig. S1 XRD pattern of the as-prepared Cu-CCO NWAs.

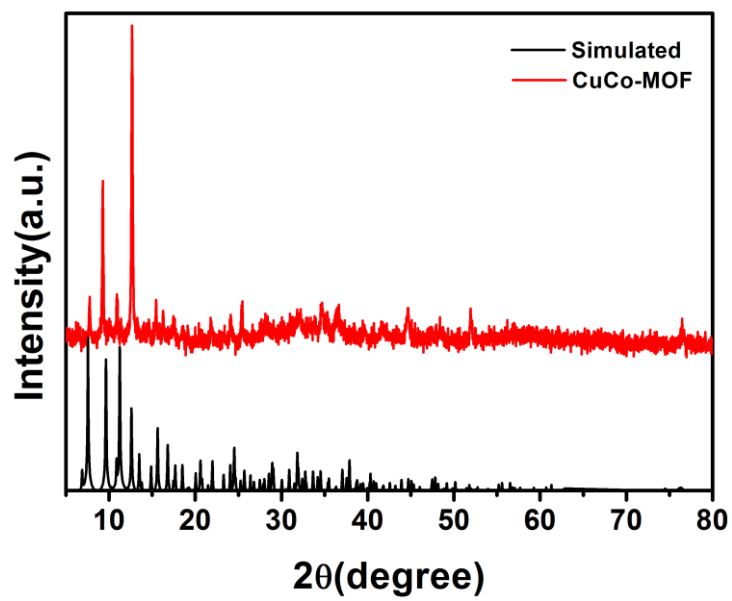
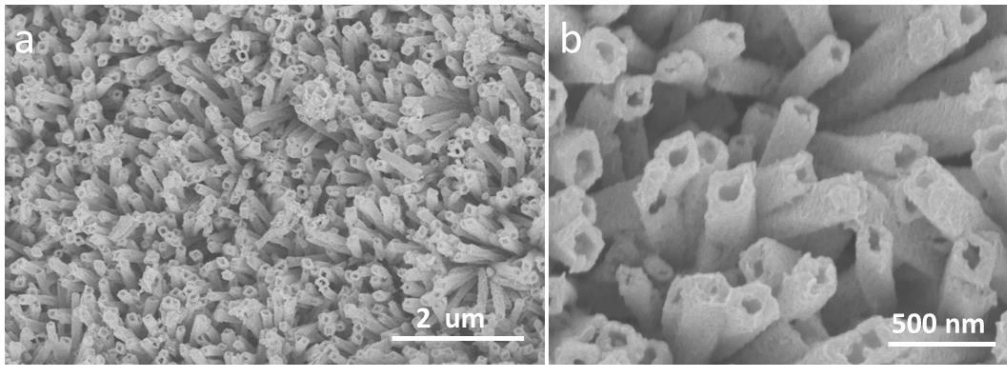
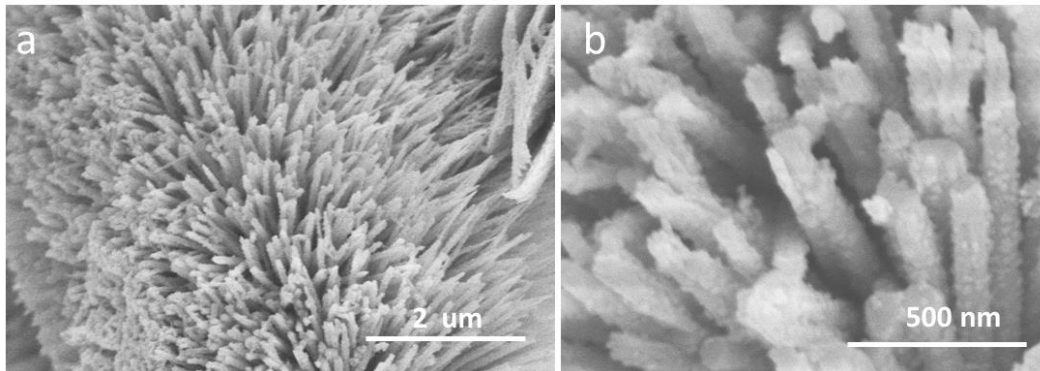


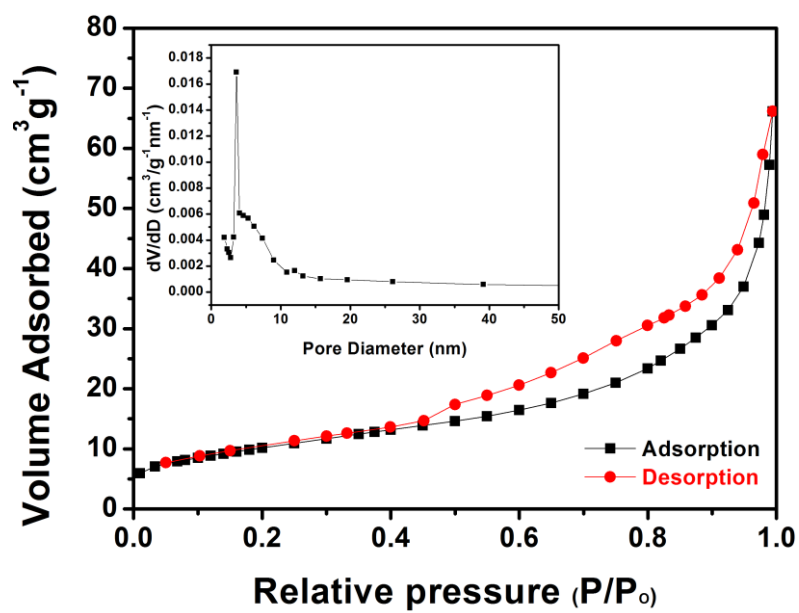
Fig. S2 XRD pattern of the as-prepared CuCo-MOF NRAs.



**Fig. S3** (a, b) SEM images of the as-prepared  $\text{Co}_9\text{S}_8$  rectangular NTAs.



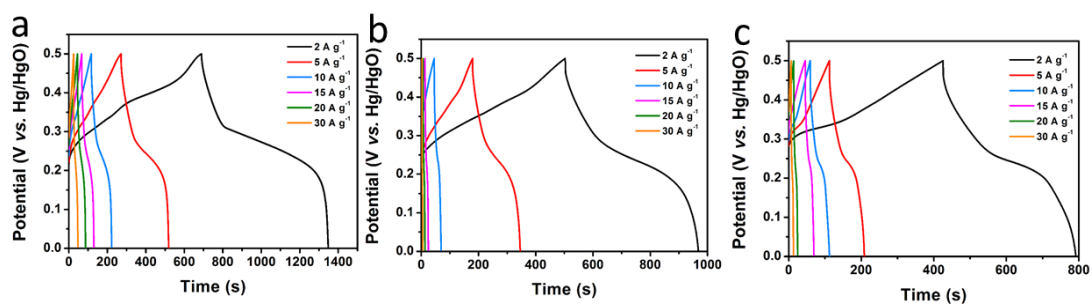
**Fig. S4** (a, b) SEM images of the as-prepared Cu-Co<sub>9</sub>S<sub>8</sub> NRAs.



**Fig. S5** N<sub>2</sub> adsorption-desorption isotherm and pore-size distribution curve of the as-prepared Cu-Co<sub>9</sub>S<sub>8</sub> rectangular NTAs.

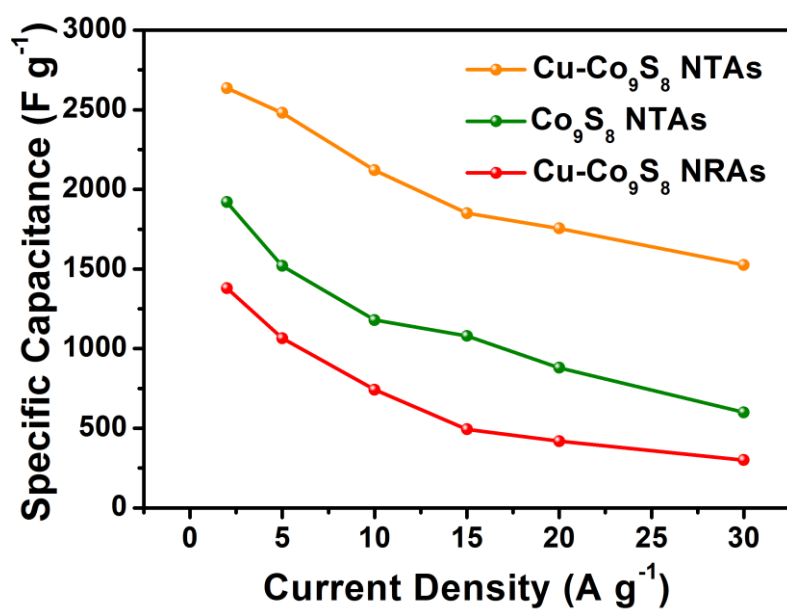
**Table S1.** Elemental contents of the as-prepared Cu-Co<sub>9</sub>S<sub>8</sub> rectangular NTAs estimated from XPS.

Sample	Cu [at.%]	Co [at.%]	S [at.%]
Cu-Co <sub>9</sub> S <sub>8</sub>	2.78	26.7	22.96



**Fig. S6** (a, b, c) GCD curves of the as-prepared Cu-Co<sub>9</sub>S<sub>8</sub> rectangular NTAs, Co<sub>9</sub>S<sub>8</sub> rectangular NTAs and Cu-Co<sub>9</sub>S<sub>8</sub> NRAs at various current densities (from 2 to 30 A g<sup>-1</sup>).

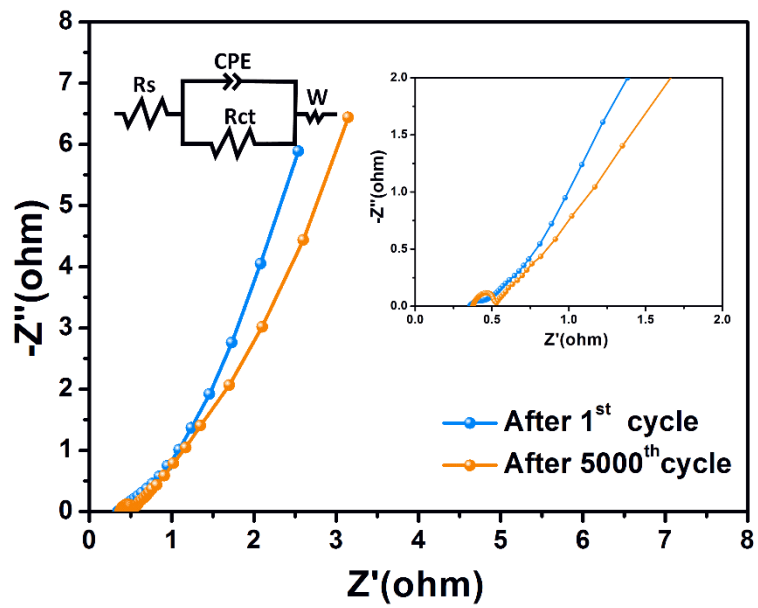




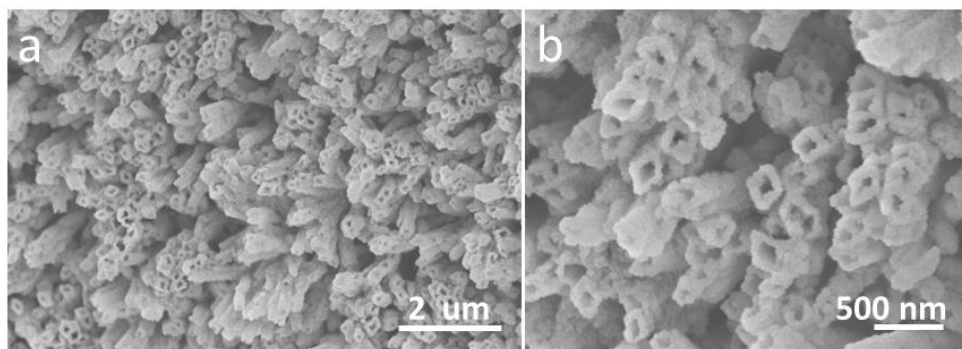
**Fig. S7** Specific capacitances at different current densities of the as-prepared Cu-Co<sub>9</sub>S<sub>8</sub> rectangular NTAs, Co<sub>9</sub>S<sub>8</sub> rectangular NTAs and Cu-Co<sub>9</sub>S<sub>8</sub> NRAs.

**Table S2.** Electrochemical performances of the different Co-based electrode materials.

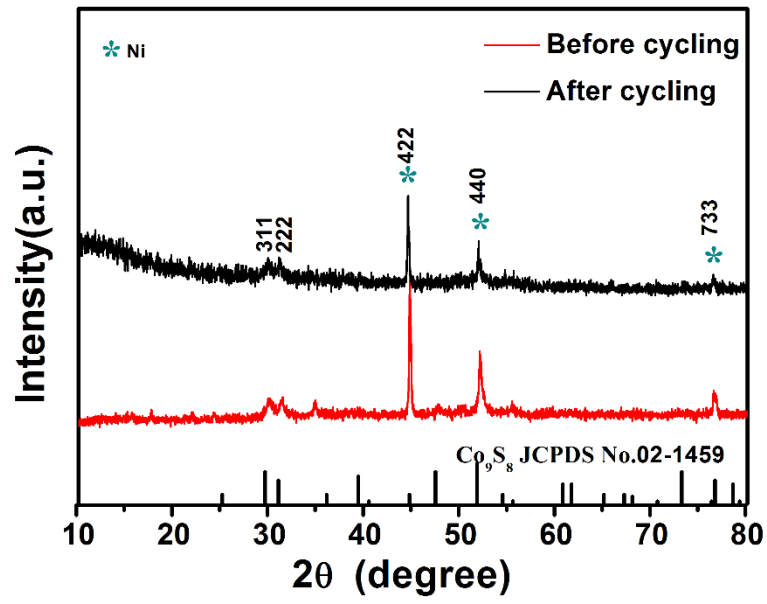
Electrode Materials	Areal Capacitance/ capacity (F cm <sup>2</sup> /mA h cm <sup>2</sup> )	Specific capacitance/ capacity (F g <sup>-1</sup> /mA h g <sup>-1</sup> )	Electrolyte	Stability (Cycles)	References
Cu-Co <sub>9</sub> S <sub>8</sub> NTAs	4.1 F cm <sup>-2</sup> / 0.57 mA h cm <sup>-2</sup>	2636 F g <sup>-1</sup> / 366 mA h g <sup>-1</sup>	6 M KOH	92% (5000)	This work
Co <sub>9</sub> S <sub>8</sub> /MnS@N-C @MoS <sub>2</sub>	-	1938 F g <sup>-1</sup> / 306 mA h g <sup>-1</sup>	2 M KOH	86.9% (10000)	1
Multi shelled CoO @Co <sub>9</sub> S <sub>8</sub>	-	1100 F g <sup>-1</sup>	2 M KOH	83.7% (15000)	2
Co <sub>9</sub> S <sub>8</sub> @Ni(OH) <sub>2</sub>	-	149.4 mA h g <sup>-1</sup>	6 M KOH	97.3% (5000)	3
CoS hollow cubes	-	980 F g <sup>-1</sup>	2 M KOH	88% (10000)	4
CC/H-Ni@Al-Co-S	-	1830 F g <sup>-1</sup>	2 M KOH	90.6% (10000)	5
Co <sub>9</sub> S <sub>8</sub> @C	-	1877 F g <sup>-1</sup>	2 M KOH	90% (10000)	6
Co <sub>9</sub> S <sub>8</sub> /NS-C-1.5 h	-	734 F g <sup>-1</sup>	6 M KOH	99.8% (14000)	7
MCO-NW@CS	-	1607.4 F g <sup>-1</sup>	2 M KOH	91.5% (6000)	8
Co <sub>9</sub> S <sub>8</sub> -NSA/NF	-	1098.8 F g <sup>-1</sup>	1 M KOH	87.4% (1000)	9
CuCo <sub>2</sub> S <sub>4</sub> -HNN	-	2163 F g <sup>-1</sup>	3 M KOH	98.7% (6000)	10
FeCo <sub>2</sub> S <sub>4</sub> -NiCo <sub>2</sub> S <sub>4</sub>	3.5 F cm <sup>-2</sup>	1519 F g <sup>-1</sup>	3 M KOH	77% (3000)	11
Co <sub>0.67</sub> Ni <sub>0.33</sub> DHs/ NiCo <sub>2</sub> O <sub>4</sub> /CFP	1.64 F cm <sup>-2</sup>	-	1 M KOH	90% (2000)	12
36-CSC	2.35 F cm <sup>-2</sup>	-	3 M KOH	92% (2000)	13
HO-CuCo <sub>2</sub> O <sub>4</sub>	0.6 F cm <sup>-2</sup>	1210 F g <sup>-1</sup>	6 M KOH	93.5% (4000)	14
NiCo <sub>2</sub> O <sub>4</sub> Nanosheets	3.51 F cm <sup>-2</sup>	-	2 M KOH	93.3% (3000)	15
NiCo <sub>2</sub> O <sub>4</sub> Nanowire	3.12 F cm <sup>-2</sup>	-	2 M KOH	89.4% (2000)	16
ZnCo <sub>2</sub> O <sub>4</sub> @ Ni <sub>x</sub> Co <sub>2-x</sub> (OH) <sub>6x</sub>	419.1 μA h cm <sup>-2</sup>	-	2 M KOH	85.6% (2000)	17
CoSe <sub>2</sub>	332 mF cm <sup>-2</sup>	-	1 M Na <sub>2</sub> SO <sub>4</sub>	95.4% (5000)	18
FeCo <sub>2</sub> O <sub>4</sub> tube	1.88 F cm <sup>-2</sup>	1254 F g <sup>-1</sup>	3 M KOH	91% (5000)	19



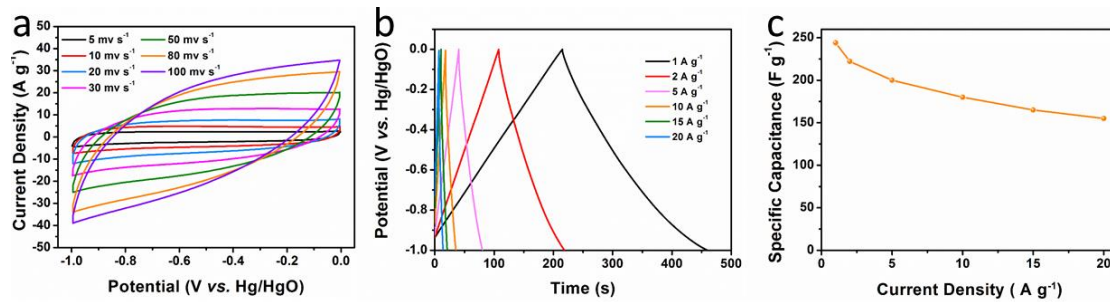
**Fig. S8** EIS of the as-prepared Cu-Co<sub>9</sub>S<sub>8</sub> rectangular NTAs electrode in three-electrode configuration (after 1<sup>st</sup> and 5000<sup>th</sup> cycling test).



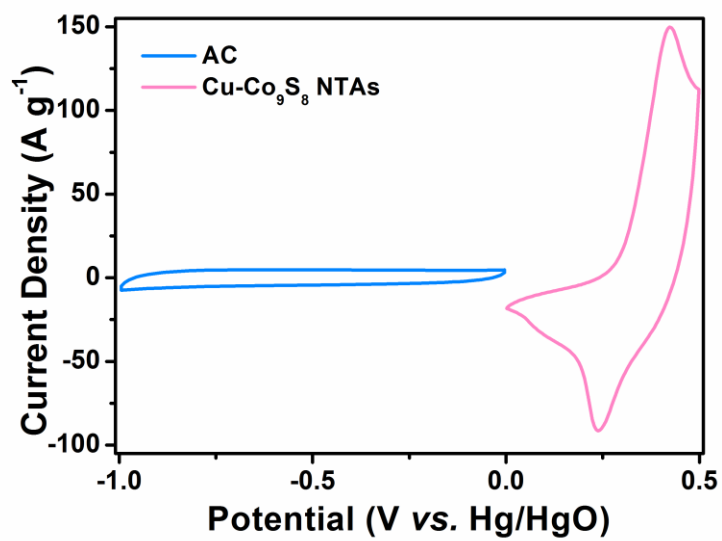
**Fig. S9** (a, b) SEM images of the as-prepared Cu-Co<sub>9</sub>S<sub>8</sub> rectangular NTAs after 5000 cycles test.



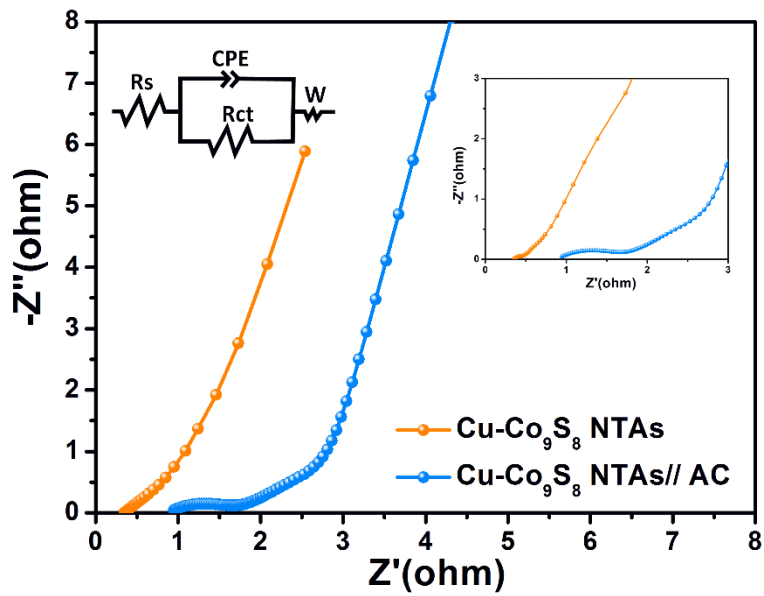
**Fig. S10** XRD pattern of the as-prepared Cu-Co<sub>9</sub>S<sub>8</sub> rectangular NTAs before and after cycling test.



**Fig. S11** (a) CV curves, (b) GCD curves, (c) Specific capacitance of the commercial AC.

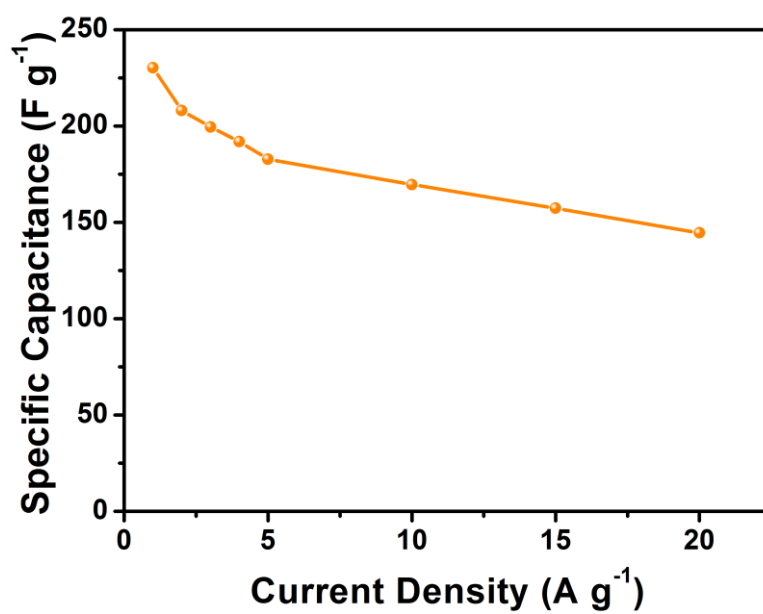


**Fig. S12** CV curves of the commercial AC and the as-prepared Cu-Co<sub>9</sub>S<sub>8</sub> rectangular NTAs.



**Fig. S13** EIS of the as-prepared Cu-Co<sub>9</sub>S<sub>8</sub> and Cu-Co<sub>9</sub>S<sub>8</sub>//AC ASC device.

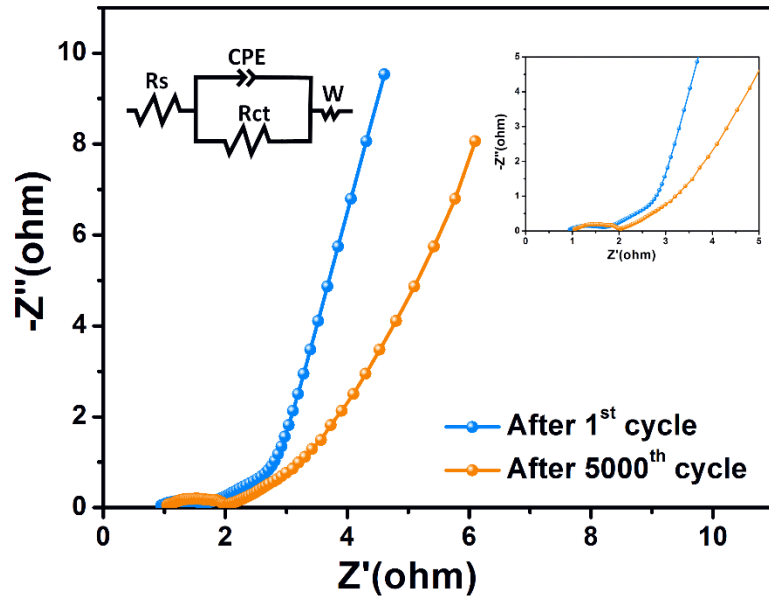




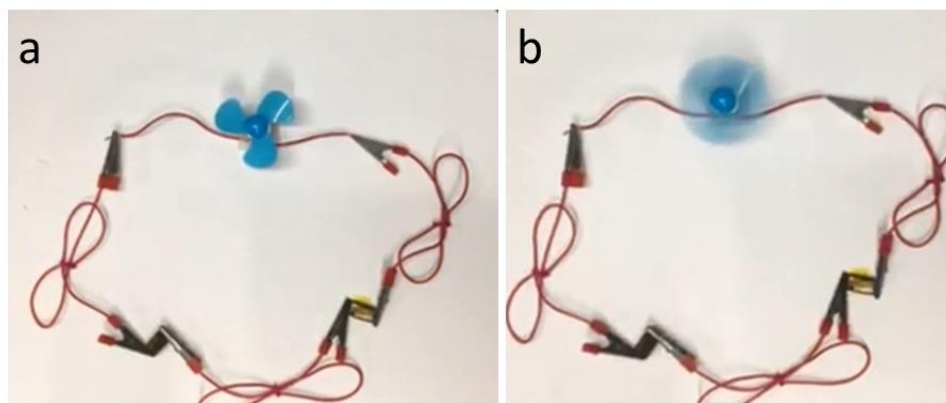
**Fig. S14** Specific capacitance of the as-prepared Cu-Co<sub>9</sub>S<sub>8</sub> rectangular NTAs at different current densities.

**Table S3.** ASC device properties comparison with the reported literature.

Electrode Materials	Areal Capacitance/capacity (F cm <sup>-2</sup> /mA h cm <sup>-2</sup> )	Specific capacitance (F g <sup>-1</sup> )	Electrolyte	Stability (Cycles)	References
Cu-Co <sub>9</sub> S <sub>8</sub> NTAs//AC	2.42 F cm <sup>-2</sup>	230	PVA/KOH	96.2% (5000)	This work
CoO/Co <sub>9</sub> S <sub>8</sub> //AC	-	73	2 M KOH	95.27% (5000)	2
CC/H-Ni@Al-Co-S//graphene/CNT	-	159	PVA/KOH	90.6% (10000)	5
Co <sub>9</sub> S <sub>8</sub> @C//AC	-	166	2 M KOH	86% (10000)	6
CuCo <sub>2</sub> O <sub>4</sub> /MnCo <sub>2</sub> O <sub>4</sub> //graphene/NF	-	118.4	2 M KOH	88.4% (10000)	21
Co <sub>9</sub> S <sub>8</sub> -NSA//AC	-	52.7	1 M KOH	84.4% (1000)	9
CuCo <sub>2</sub> S <sub>4</sub> -HNN//AC	-	124	3 M KOH	94.1% (6000)	10
NiCo <sub>2</sub> O <sub>4</sub> //FeSe <sub>2</sub>	-	71.7	2 M KOH	90% (1000)	20
Co <sub>9</sub> S <sub>8</sub> /NS-C-1.5 h//AC	-	75.59	6 M KOH	99.5% (2000)	7
MnCo <sub>2</sub> O <sub>4</sub> @Ni(OH) <sub>2</sub> //AC	-	141	2 M KOH	90% (2500)	22
H-NiCoSe <sub>2</sub> //AC	-	112	6 M KOH	82.3% (5200)	23
Co <sub>3</sub> O <sub>4</sub> @NiCo <sub>2</sub> O <sub>4</sub> //AC	1343.7 mF cm <sup>-2</sup>	-	PVA/KOH	98.5% (5000)	24
Co <sub>3</sub> O <sub>4</sub> @C@Ni <sub>3</sub> S <sub>2</sub> //AC	0.52 F cm <sup>-2</sup>	-	PVA/KOH	91.43% (10000)	25
NiCo <sub>2</sub> O <sub>4</sub> @Co <sub>0.33</sub> Ni <sub>0.67</sub> (OH) <sub>2</sub> //CMK-3-ASC	887.5 mF cm <sup>-2</sup>	-	1 M KOH	82% (3000)	26
Co(OH) <sub>2</sub> @CW//CW	2.2 F cm <sup>-2</sup>	-	PVA/KOH	85% (10000)	27
NiCo <sub>2</sub> S <sub>4</sub> //C	341 mF cm <sup>-2</sup>	-	6 M KOH	-	28
Cu <sub>3</sub> N@CoFe-LDH//AC	1190 mF cm <sup>-2</sup>	-	2 M KOH	92.6% (10000)	29
MnO <sub>2</sub> FeCo <sub>2</sub> O <sub>4</sub> //AC	2.52 F cm <sup>-2</sup>	-	PVA/KOH	94% (1500)	30



**Fig. S15** EIS of the as-prepared ASC device (after 1st and 5000th cycling test).



**Fig. S16** (a, b) The photographic images of an electric motor fan driven by two Cu-Co<sub>9</sub>S<sub>8</sub> NTAs//AC ASCs in series.

## References

- 1 S. Kandula, K. R. Shrestha, N. H. Kim and J. H. Lee, *Small*, 2018, **14**, 1800291.
- 2 Y. Wang, T. Zhu, Y. Zhang, X. Kong, S. Liang, G. Cao and A. Pan, *J. Mater. Chem. A*, 2017, **5**, 18448.
- 3 F. Zhu, M. Yan, Y. Liu, H. Shen, Y. Lei and W. Shi, *J. Mater. Chem. A*, 2017, **5**, 22782.
- 4 H. Hu, B. Y. Guan and X. W. Lou, *Chem*, 2016, **1**, 102.
- 5 J. Huang, J. Wei, Y. Xiao, Y. Xu, Y. Xiao, Y. Wang, L. Tan, K. Yuan and Y. Chen, *ACS Nano*, 2018, **12**, 3030.
- 6 S. Sun, J. Luo, Y. Qian, Y. Jin, Y. Liu, Y. Qiu, X. Li, C. Fang, J. Han and Y. Huang, *Adv. Energy Mater.*, 2018, **8**, 1801080.
- 7 S. Zhang, D. Li, S. Chen, X. Yang, X. Zhao, Q. Zhao, S. Komarneni and D. Yang, *J. Mater. Chem. A*, 2017, **5**, 12453.
- 8 G. Liu, B. Wang, T. Liu, L. Wang, H. Luo, T. Gao, F. Wang, A. Liu and D. Wang, *J. Mater. Chem. A*, 2018, **6**, 1822.
- 9 X. Han, K. Tao, D. Wang and L. Han, *Nanoscale*, 2018, **10**, 2735.
- 10 S. E. Moosavifard, S. Fani and M. Rahmanian, *Chem. Commun.*, 2016, **52**, 4517.
- 11 J. Zhu, S. Tang, J. Wu, X. Shi, B. Zhu and X. Meng, *Adv. Energy Mater.*, 2017, **7**, 1601234.
- 12 L. Huang, D. Chen, Y. Ding, S. Feng, Z. L. Wang and M. Liu, *Nano Lett.*, 2013, **13**, 3135.
- 13 J. Xu, Q. Wang, X. Wang, Q. Xiang, B. Liang, D. Chen and G. Shen, *ACS Nano*, 2013, **7**, 5453.
- 14 A. Pendashteh, S. E. Moosavifard, M. S. Rahmanifar, Y. Wang, M. F. El-Kady, R. B. Kaner and M. F. Mousavi, *Chem. Mater.*, 2015, **27**, 3919.
- 15 G. Zhang and X. W. Lou, *Adv. Mater.*, 2013, **25**, 976.
- 16 G. Q. Zhang, H. B. Wu, H. E. Hoster, M. B. Chan-Park and X. W. Lou, *Energy Environ. Sci.*, 2012, **5**, 9453.
- 17 W. Fu, Y. Wang, W. Han, Z. Zhang, H. Zha and E. Xie, *J. Mater. Chem. A*, 2016, **4**, 173.
- 18 N. Yu, M. Q. Zhu and D. Chen, *J. Mater. Chem. A*, 2015, **3**, 7910.
- 19 B. Zhu, S. Tang, S. Vongehr, H. Xie, J. Zhu and X. Meng, *Chem. Commun.*, 2016, **52**, 2624.
- 20 C. Ji, F. Liu, L. Xu and S. Yang, *J. Mater. Chem. A*, 2017, **5**, 5568.

- 21 S. Liu, K. San Hui, K. N. Hui, J. M. Yun and K. H. Kim, *J. Mater. Chem. A*, 2016, **4**, 8061.
- 22 Y. Zhao, L. Hu, S. Zhao and L. Wu, *Adv. Funct. Mater.*, 2016, **26**, 4085.
- 23 L. Hou, Y. Shi, C. Wu, Y. Zhang, Y. Ma, X. Sun, J. Sun, X. Zhang and C. Yuan, *Adv. Funct. Mater.*, 2018, **28**, 1705921.
- 24 Y. Lu, L. Li, D. Chen and G. Shen, *J. Mater. Chem. A*, 2017, **5**, 24981.
- 25 D. Kong, C. Cheng, Y. Wang, J. I. Wong, Y. Yang and H. Y. Yang, *J. Mater. Chem. A*, 2015, **3**, 16150.
- 26 K. Xu, R. Zou, W. Li, Q. Liu, X. Liu, L. An and J. Hu, *J. Mater. Chem. A*, 2014, **2**, 10090.
- 27 Y. Wang, X. Lin, T. Liu, H. Chen, S. Chen, Z. Jiang, J. Liu, J. Huang and M. Liu, *Adv. Funct. Mater.*, 2018, **28**, 1806207.
- 28 W. Kong, C. Lu, W. Zhang, J. Pu and Z. Wang, *J. Mater. Chem. A*, 2015, **3**, 12452.
- 29 X. Zhou, X. Li, D. Chen, D. Zhao and X. Huang, *J. Mater. Chem. A*, 2018, **6**, 24603.
- 30 B. Zhu, S. Tang, S. Vongehr, H. Xie and X. Meng, *ACS Appl. Mater. Inter.* 2016, **8**, 4762.