

Electronic Supplementary Information

Two-dimensional CoNi nanoparticles@S,N-doped carbon composites derived from S, N-containing Co/Ni MOFs for high performance supercapacitors

Mingyu Tong,^{‡a,b} Shengwen Liu,^{‡a} Xian Zhang,^{a,b} Tianxing Wu,^a Haimin Zhang,^{*a} Guozhong Wang,^a
Yunxia Zhang,^a Xiaoguang Zhu,^a and Huijun Zhao^{*a,c}

^a Key Laboratory of Materials Physics, Centre for Environmental and Energy Nanomaterials, Anhui Key Laboratory of Nanomaterials and Nanotechnology, CAS Center for Excellence in Nanoscience, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China.
E-mail: zhanghm@issp.ac.cn, h.zhao@griffith.edu.au

^b University of Science and Technology of China, Hefei 230026, China

^c Centre for Clean Environment and Energy, Griffith University, Gold Coast Campus, QLD 4222, Australia.

[‡]These authors contributed equally to this work.

Table S1 Performance comparison of Co/Ni based electrode materials for supercapacitors.

Num.	Materials	Specific capacitance $F g^{-1}$ (conditions)	Electrolyte	Capacitance retention (cycles)	References
a	Ni-Co alloy NPs in 3D porous graphitic carbon	1091 (1 A g^{-1})	6 M KOH	95% (1500)	1
b	Co-rich Ni-Co oxides	473 (1.67 A g^{-1})	6 M KOH	none	2
c	Ni/Co-based MOFs	1049 (1 A g^{-1})	6 M KOH	97.4% (5000)	3
d	Ni-MOF/CNT	1765 (0.5 A g^{-1})	6 M KOH	95% (5000)	4
e	Zn-doped MOFs	1620 (0.25 A g^{-1})	6 M KOH	91% (3000)	5
f	MOF derived 2D $CoS_{1.097}/N$ -doped Carbon	360.1 (1.5A g^{-1})	2 M KOH	90% (2000)	6
g	MOF derived CoS hollow structure	980 (1A g^{-1})	2 MKOH	88% (10000)	7
h	MOF derived $Ni_xCo_{1-x}(OH)_2$ microspheres	1235.9 (0.5A g^{-1})	6 M KOH	73% (10000)	8
i	MOF derived $CoNi@SNC$	1970(1A g^{-1})	6 M KOH	95.1% (3000)	Our work

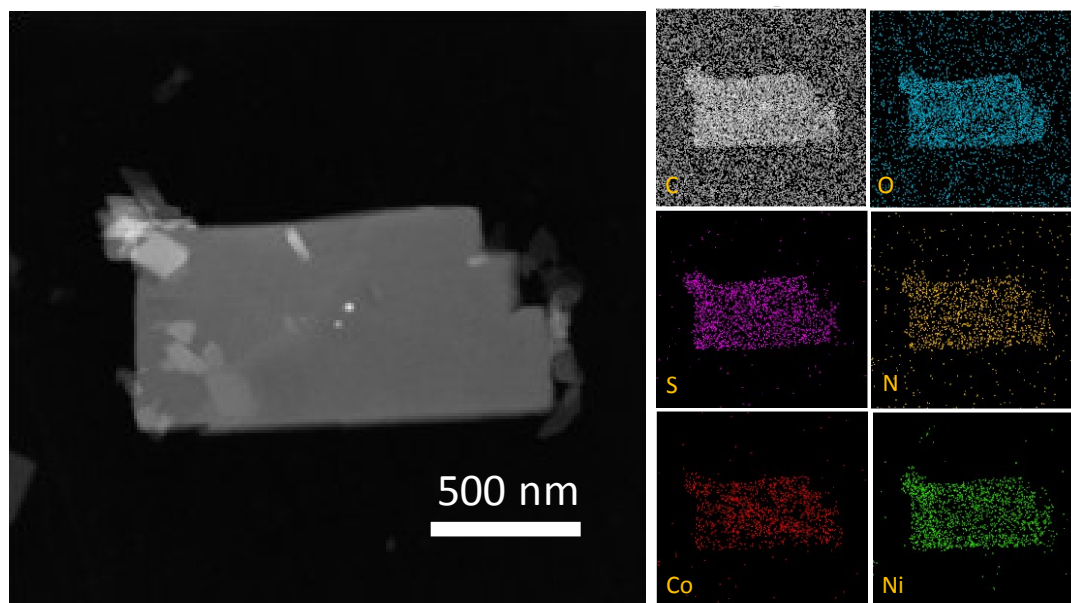


Fig. S1 (a) TEM image of the synthesized Co/Ni MOFs and corresponding element mapping images of C, O, S, N, Co and Ni elements.

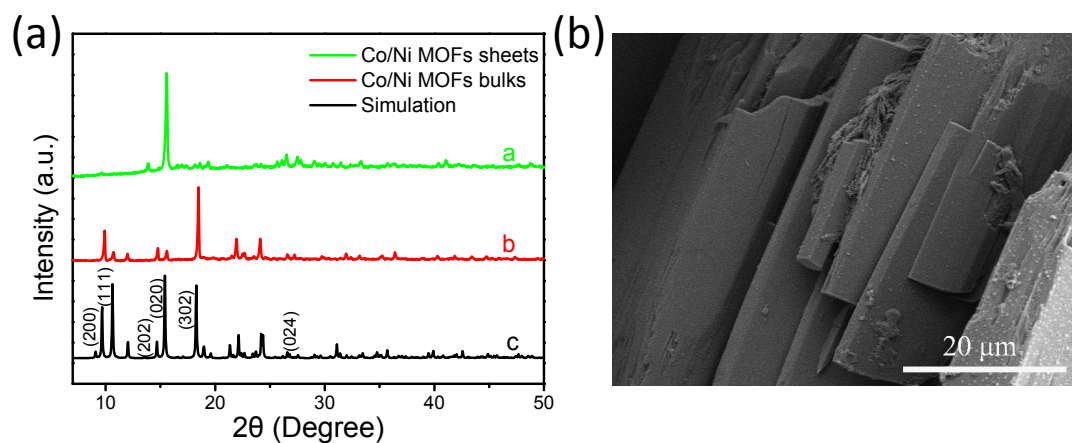


Fig. S2 (a) XRD patterns of the as-prepared Co/Ni MOFs. Co/Ni MOFs bulks (line b) were obtained by similar synthetic method with 2D Co/Ni MOFs nanosheets except for reaction temperature of 120°C for 12 h under hydrothermal conditions; (b) SEM image of Co/Ni MOFs bulks.

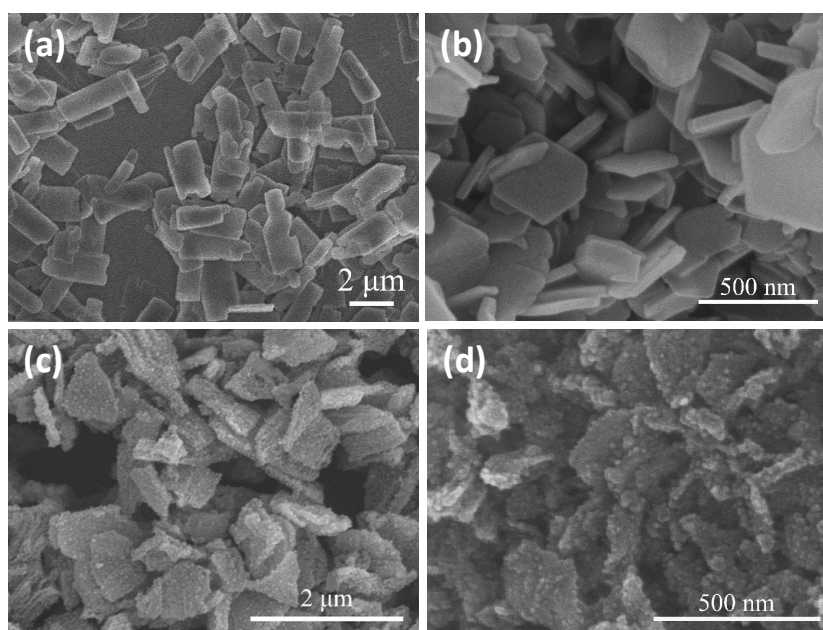


Fig. S3 SEM images of (a) Co-MOFs; (b) Ni-MOFs; (c) Co@SNC and (d) Ni@SNC.

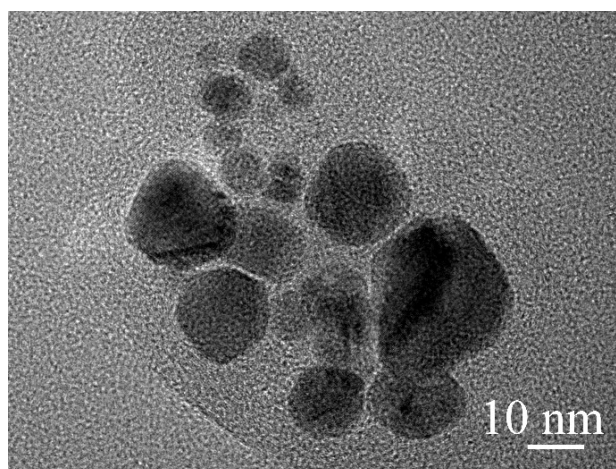


Fig. S4 TEM image of Co/Ni MOFs derived carbon material corresponding to EDX mapping images.

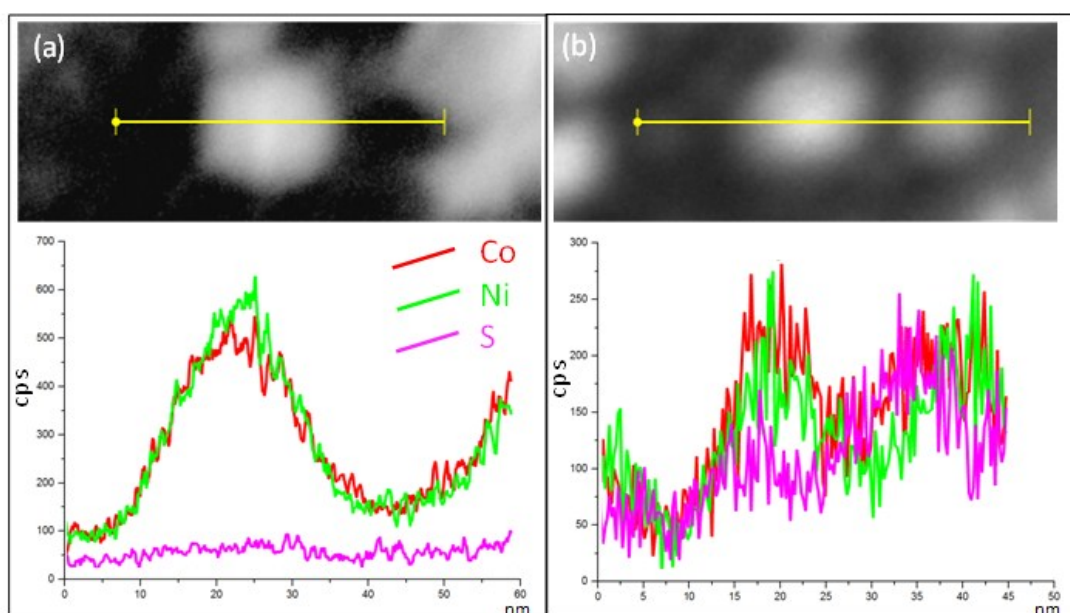


Fig. S5 STEM images of CoNi@SNC and line scanning spectra of element Co, Ni, and S. (a) CoNi alloy nanoparticles imbedded in S, N-doped carbon matrix; (b) CoNi alloy nanoparticles fused with Co_9S_8 .

Fig. S5 shows the STEM images and line scanning spectra of CoNi@SNC with different sample areas. In Fig. S5a, the lower and flat-distributed intensity curve of S than Co suggests that S atoms are doped in carbon matrix. However, the intensity curves of S, Co and Ni in Fig. S5b are almost identical, possibly implying a

combination of Co with S to form Co_9S_8 , which can be further confirmed by XPS characterization, as shown in Fig. 5d in the manuscript.

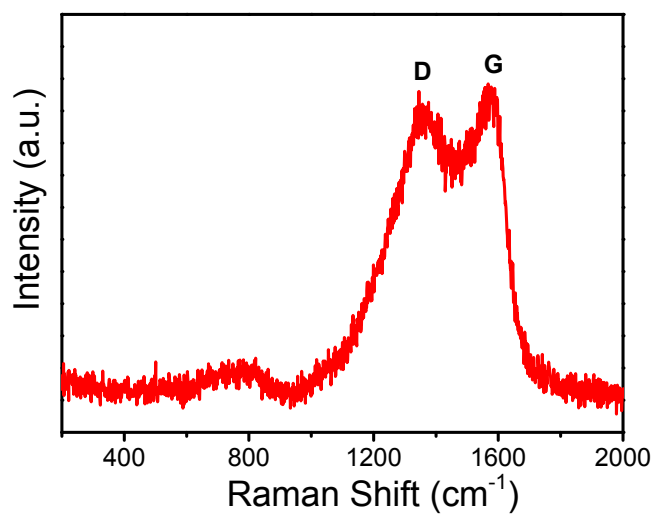


Fig. S6 Raman spectra of CoNi@SNC.

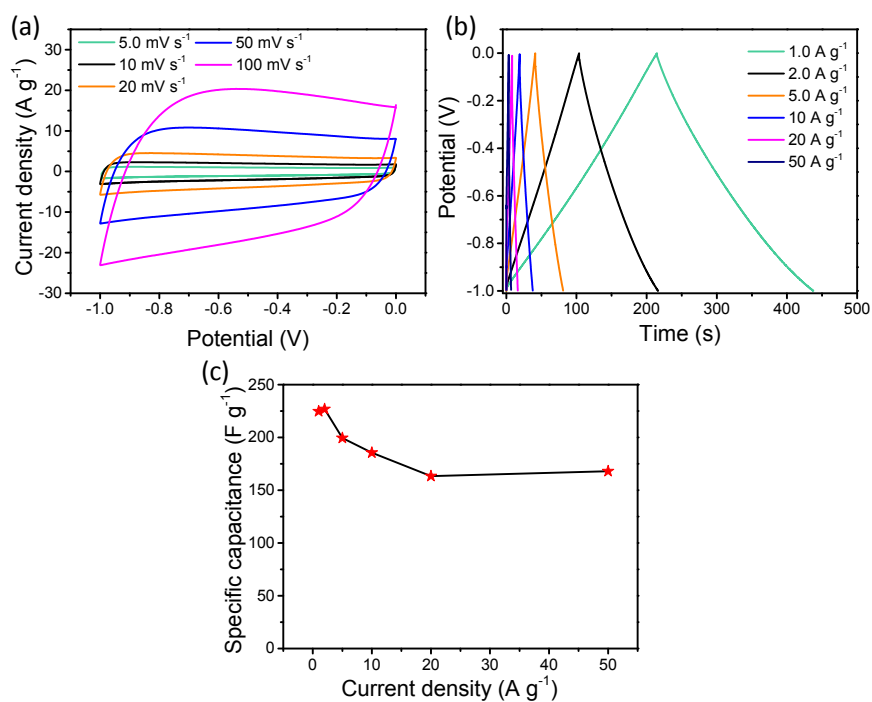


Fig. S7 The electrochemical performance of the activated carbon (AC) electrode in 6.0 M KOH electrolyte. (a) Cyclic voltammetry curves; (b) Galvanostatic charge-discharge curves; (c) Specific capacitance vs. current density.

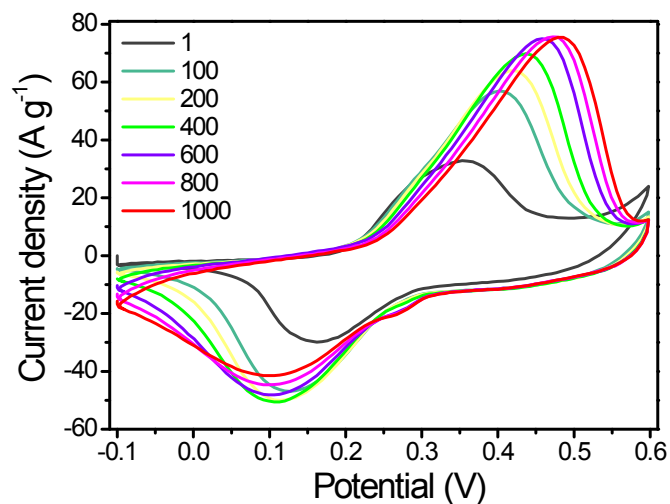


Fig. S8 CV curves at a scan rate of 50 mV s^{-1} with cycling times from 1th to 1000th.

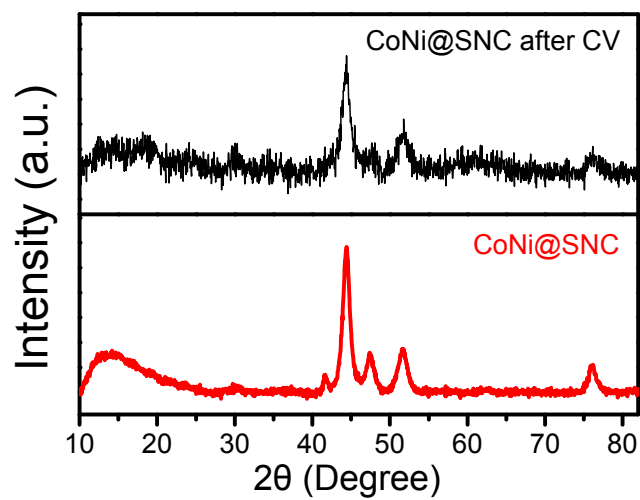


Fig. S9 XRD patterns of CoNi@SNC before and after CV test.

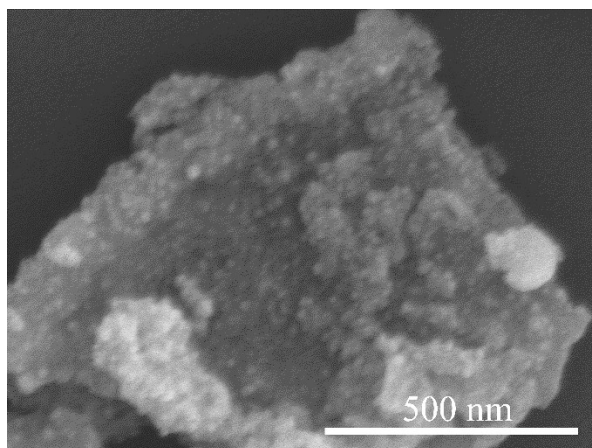


Fig. S10 SEM image of CoNi@SNC after CV test.

References

- 1 S. Liu, Q. Zhao, M. Tong, X. Zhu, G. Wang, W. Cai, H. Zhang and H. Zhao, *J. Mater. Chem. A*, 2016, **4**, 17080-17086.
- 2 S. Lee, J.-S. Kang, K. T. Leung, S. K. Kim and Y. Sohn, *Appl Surf Sci*, 2016, **386**, 393-404.
- 3 H. G. Ranjbar, M. Soleimani and H. R. Nader, *New J. Chem.*, 2016, **40**, 9187-9193.
- 4 P. Wen, P. Gong, J. Sun, J. Wang and S. Yang, *J. Mater. Chem. A*, 2015, **3**, 13874-13883.
- 5 J. Yang, C. Zheng, P. Xiong, Y. Li and M. Wei, *J. Mater. Chem. A*, 2014, **2**, 19005-19010.
- 6 F. Cao, M. Zhao, Y. Yu, B. Chen, Y. Huang, J. Yang, X. Cao, Q. Lu, X. Zhang, Z. Zhang, C. Tan and H. Zhang, *J Am Chem Soc*, 2016, **138**, 6924-6927.
- 7 H. Hu, Bu Y. Guan and Xiong W. Lou, *Chem*, 2016, **1**, 102-113.
- 8 S. He, Z. Li, J. Wang, P. Wen, J. Gao, L. Ma, Z. Yang and S. Yang, *RSC Adv.*, 2016, **6**, 49478-49486.