

Title	Cobalt doped JUC-160 derived functional carbon superstructures with synergetic catalyst effect for Li-SeS <sub>2</sub> batteries
Authors	Jin, Wen-wu;Li, He-Jun;Zou, Ji-zhao;Zhang, Qi;Inguva, Saikumar;Zeng, Shao-zhong;Xu, Guo-zhong;Zeng, Xie-rong
Publication date	2020-07-03
Original Citation	Jin, W.-W., Li, H.-J., Zou, J.-Z., Zhang, Q., Inguva, S., Zeng, S.-Z., Xu, G.-Z. and Zeng, X.-R. (2020) 'Cobalt doped JUC-160 derived functional carbon superstructures with synergetic catalyst effect for Li-SeS <sub>2</sub> batteries', <i>Microporous and Mesoporous Materials</i> , 306, 110438 (11pp). doi: 10.1016/j.micromeso.2020.110438
Type of publication	Article (peer-reviewed)
Link to publisher's version	<a href="https://doi.org/10.1016/j.micromeso.2020.110438">10.1016/j.micromeso.2020.110438</a>
Rights	© 2020, Elsevier B.V. All rights reserved. This manuscript version is made available under the CC BY-NC-ND 4.0 license. - <a href="https://creativecommons.org/licenses/by-nc-nd/4.0/">https://creativecommons.org/licenses/by-nc-nd/4.0/</a>
Download date	2024-05-06 02:37:47
Item downloaded from	<a href="https://hdl.handle.net/10468/12582">https://hdl.handle.net/10468/12582</a>



## Support information

# ***Cobalt doped JUC-160 Derived Functional Carbon Superstructures with Synergetic Catalyst Effect for Li-SeS<sub>2</sub> Batteries***

Wen-wu Jin <sup>a</sup>, He-Jun Li <sup>b</sup>, Ji-zhao Zou <sup>a,\*</sup>, Qi Zhang <sup>c</sup>, Saikumar Inguva <sup>d</sup>, Shao-zhong Zeng <sup>a</sup>, Guo-zhong Xu <sup>a</sup>, Xie-rong Zeng <sup>a,\*</sup>

*a. Shenzhen Key Laboratory of Special Functional Materials & Shenzhen Engineering Laboratory for Advance Technology of Ceramics, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, PR China.*

*b. State Key Laboratory of Solidification Processing, Carbon/Carbon Composites Research Center, Northwestern Polytechnical University, Xi'an 710072, PR China.*

*c. School of Aerospace, Transport and Manufacturing, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK.*

*d. School of Chemistry, University College Cork and Tyndall National Institute, Cork, T12YN60, Ireland.*

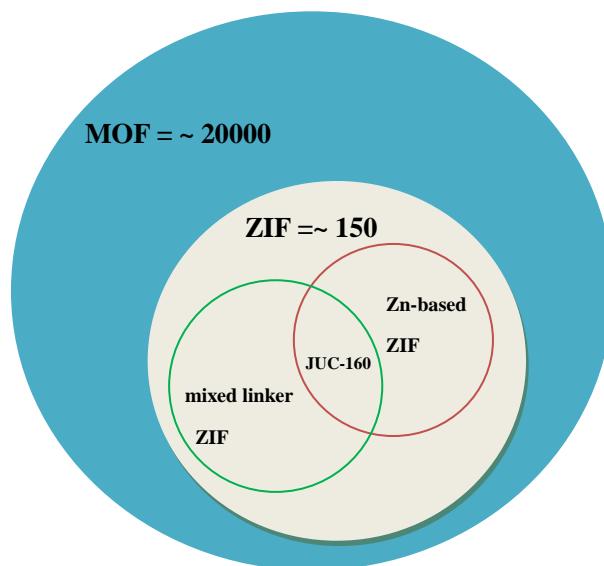
\* Correspondence: [zoujizhao@szu.edu.cn](mailto:zoujizhao@szu.edu.cn) (J Z.Zou); [zengxier@szu.edu.cn](mailto:zengxier@szu.edu.cn) (X R.Zeng)

**Keywords:** Cobalt-doped, ZIF, Self-assembled, Crystal-shape engineering, Li-SeS<sub>2</sub>

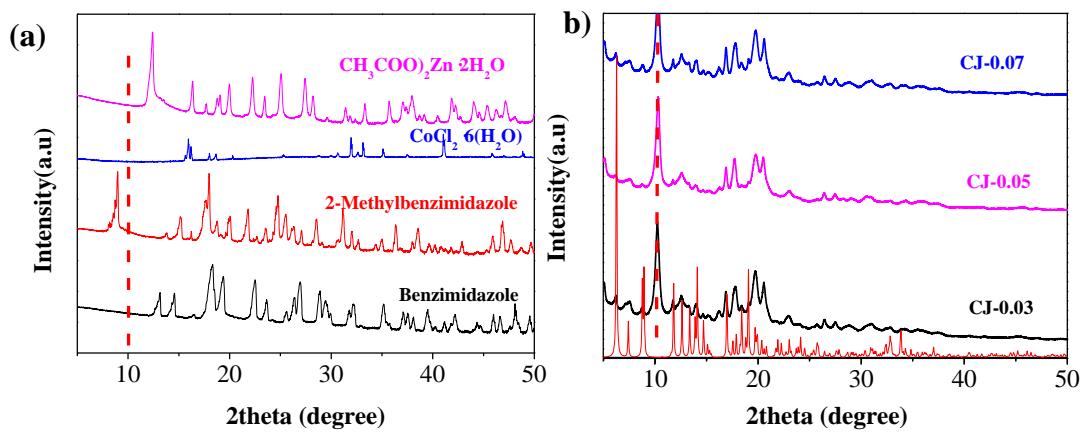
Table S1. List of abbreviations

ZIF	Zeolitic imidazolate frame-work (ZIF), a subfamily of metal organic framework (MOF) generated from an assembly of transition metal ions (i.e., Zn( II ), Co( II )) and N-rich imidazolate linkers
JUC-160	A ZIF material with zinc ion as the central ion
CJ-n	Cobalt doped ZIF prepared by adding $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in the synthesis of JUC-160, and based on the addition amount of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.03,0.05 and 0.07g), the cobalt doped JUC-160 is named as CJ-n (n=0.03,0.05 and 0.07)
PCJ-m	Cobalt doped JUC-160 was prepared by mixing 0.06g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and a certain amount of JUC-160, and based on the addition amount of JUC-160 (0.5,0.8 and 1.1 g), the cobalt doped JUC-160 is named as PCJ-m (m=0.5,0.8 and 1.1)
CNC-n	The carbonization products of CJ-n
PCNC-m	The carbonization products of PCJ-m
CNC-n/ $\text{SeS}_2$	Selenium sulfide-impregnated CNC-n
PCNC-m/ $\text{SeS}_2$	Selenium sulfide-impregnated PCNC-m

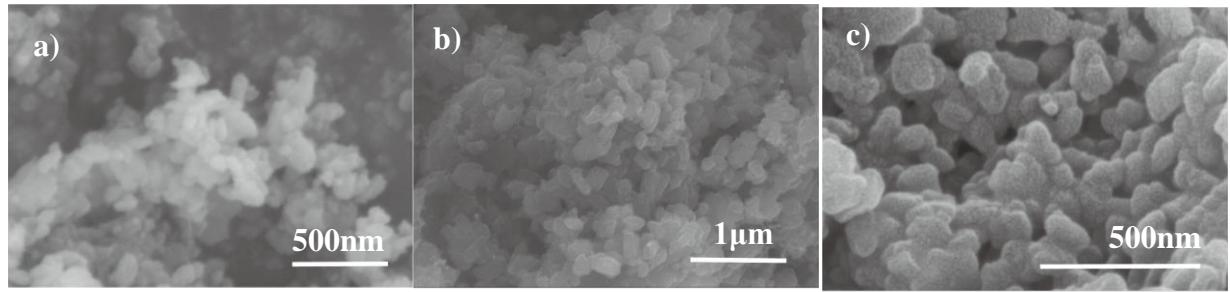
In order to better show the relationship between MOF, JUC-160, mixed linker ZIF and Zn-based ZIF, the following figure is drawn with the concept of aggregate in mathematics.



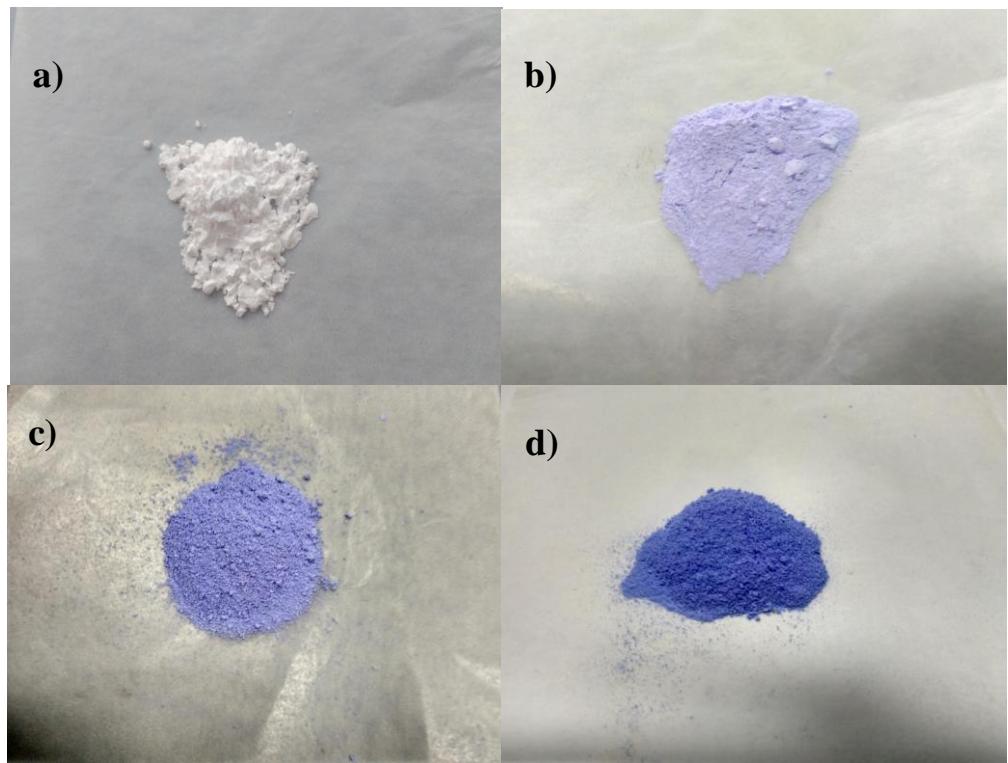
**Fig.S1. the relationship between MOF, JUC-160, mixed linker ZIF and Zn-based ZIF.**



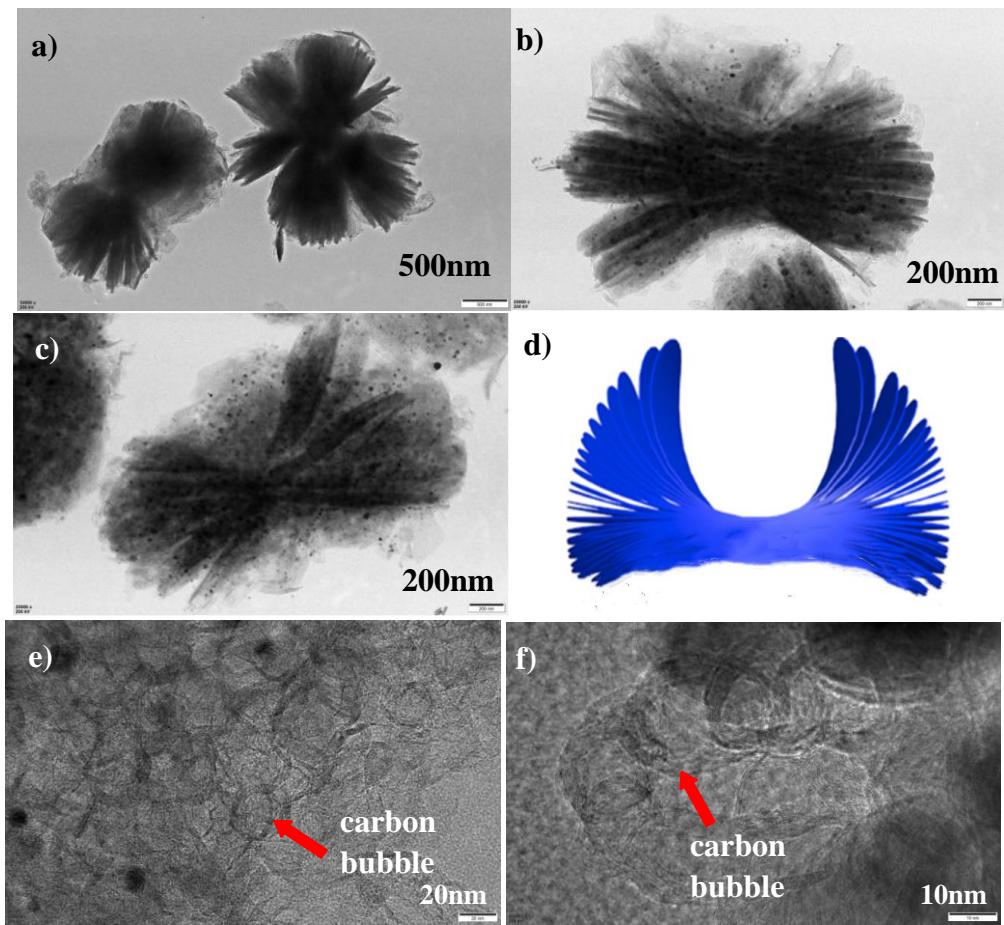
**Fig.S2.(a)**The chemical used in the experiment and its XRD characteristic peak; **(b)** X-ray diffraction (XRD) patterns of calculated the JUC-160 and CJ-n.



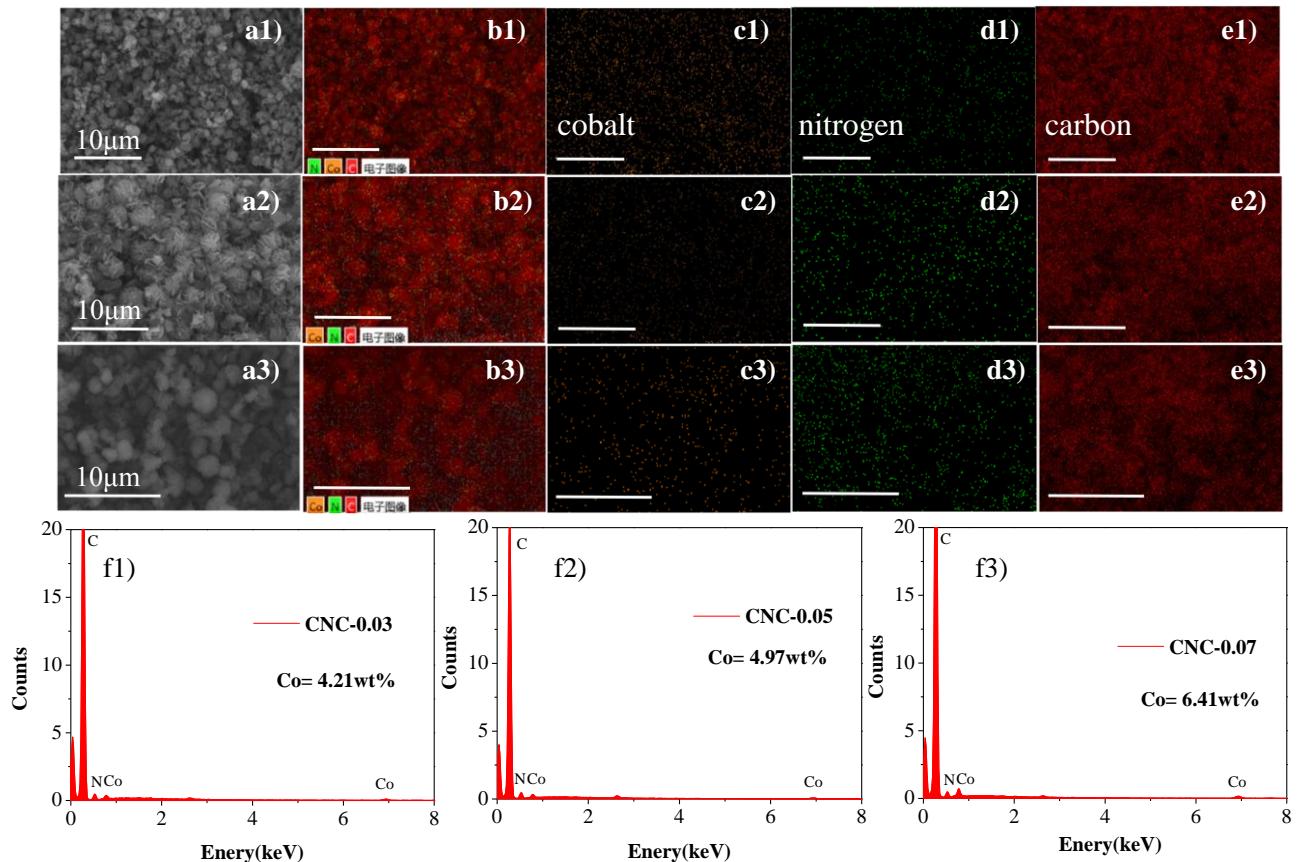
**Fig.S3.** JUC-160 (a) and their derived carbon materials (b,c).



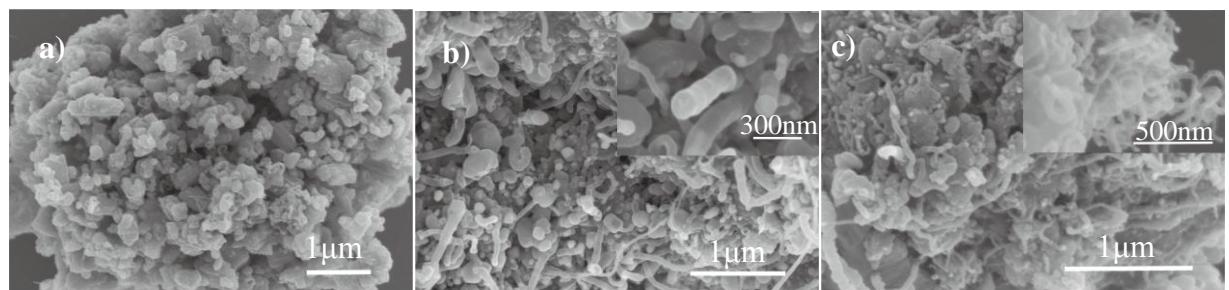
**Fig.S4.** The photographs of (a) JUC-160, (b) CJ-0.03, (c) CJ-0.05 and (d) CJ-0.07.



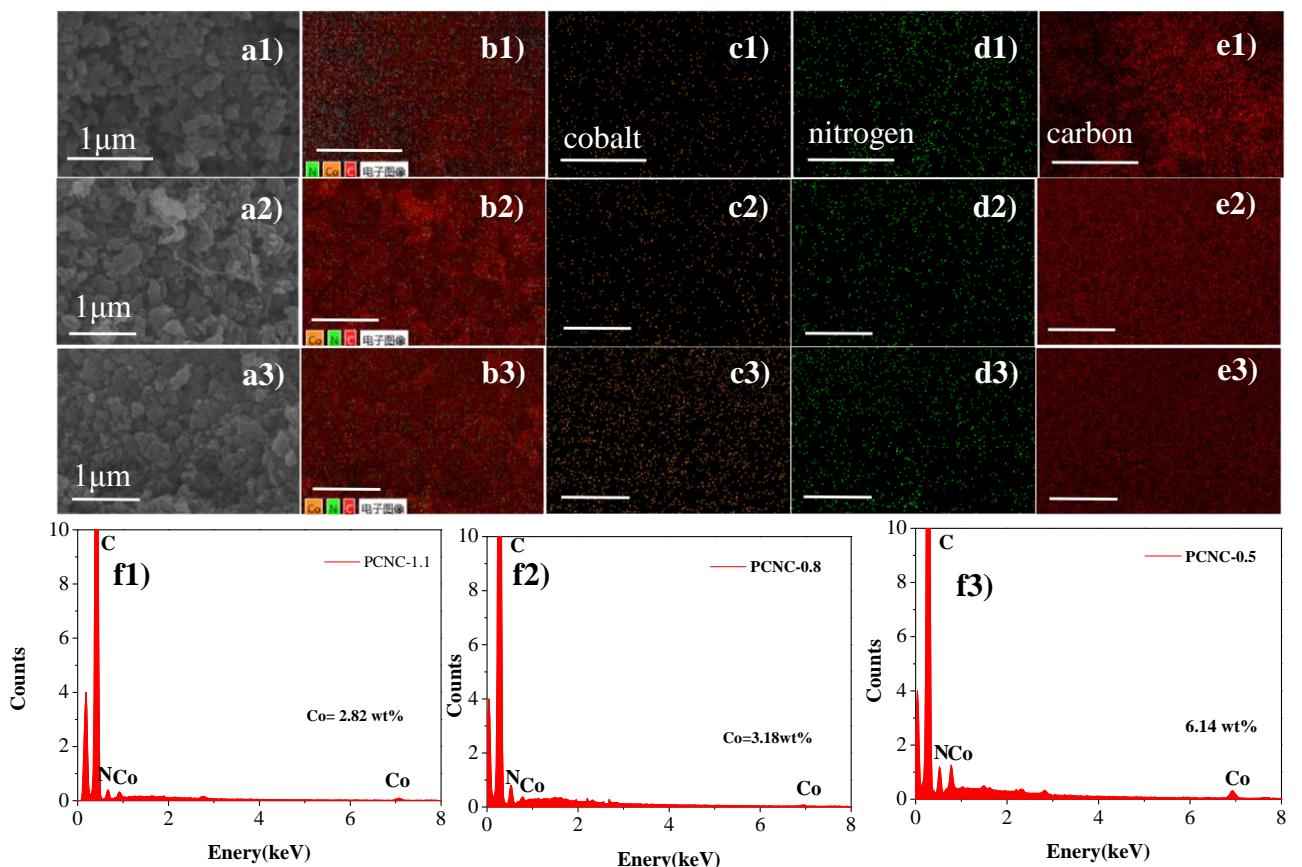
**Fig.S5. TEM images of the CNC-0.05 (a-c) and the open-book-like model (d); The hollow carbon bubble structures of CNC-0.05(e-f).**



**Fig.S6. SEM image of (a1~a3) CNC-n and the corresponding EDS elemental maps for cobalt(c1~c3), nitrogen (d1~d3), carbon(e1~e3) and all elements combined (b1~b3). The scale bar is 10μm; elemental spectrum(f1~f3).**



**Fig.S7. SEM image of (a) PCNC-1.1, (b) PCNC-0.8 and (c) PCNC-0.5.**



**Fig.S8.** SEM image of (a1~a3) PCNC-m and the corresponding EDS elemental maps for cobalt(c1~c3), nitrogen (d1~d3), carbon(e1~e3) and all elements combined (b1~b3). The scale bar is 1μm; elemental spectrum(f1~f3).

Table S2, Synthesis conditions of CJ-n

CJ-n	Derived carbon	Benzimidaz ole (g)	2-methylbenzi midazole (g)	Zn(Ac) <sub>2</sub> ·2H <sub>2</sub> O (g)	CoCl <sub>2</sub> ·6 H <sub>2</sub> O (g)
CJ-0.03	CNC-0.03	0.29539	0.26432	0.49394	0.03399
CJ-0.05	CNC-0.05	0.29541	0.26439	0.49357	0.05558
CJ-0.07	CNC-0.07	0.29543	0.26435	0.494071	0.07131

Table S3, Synthesis conditions of PCJ-m

PCJ-( JUC-160(g)/ CoCl <sub>2</sub> .6H <sub>2</sub> O=0.06g)	Derived carbon	JUC-160 (g)	CoCl <sub>2</sub> .6H <sub>2</sub> O (g)	ethanol (ml)
PCJ-0.5	PCNC-0.5	0.50722	0.06973	40ml
PCJ-0.8	PCNC-0.8	0.82162	0.06979	40ml
PCJ-1.1	PCNC-1.1	1.182	0.06970	40ml

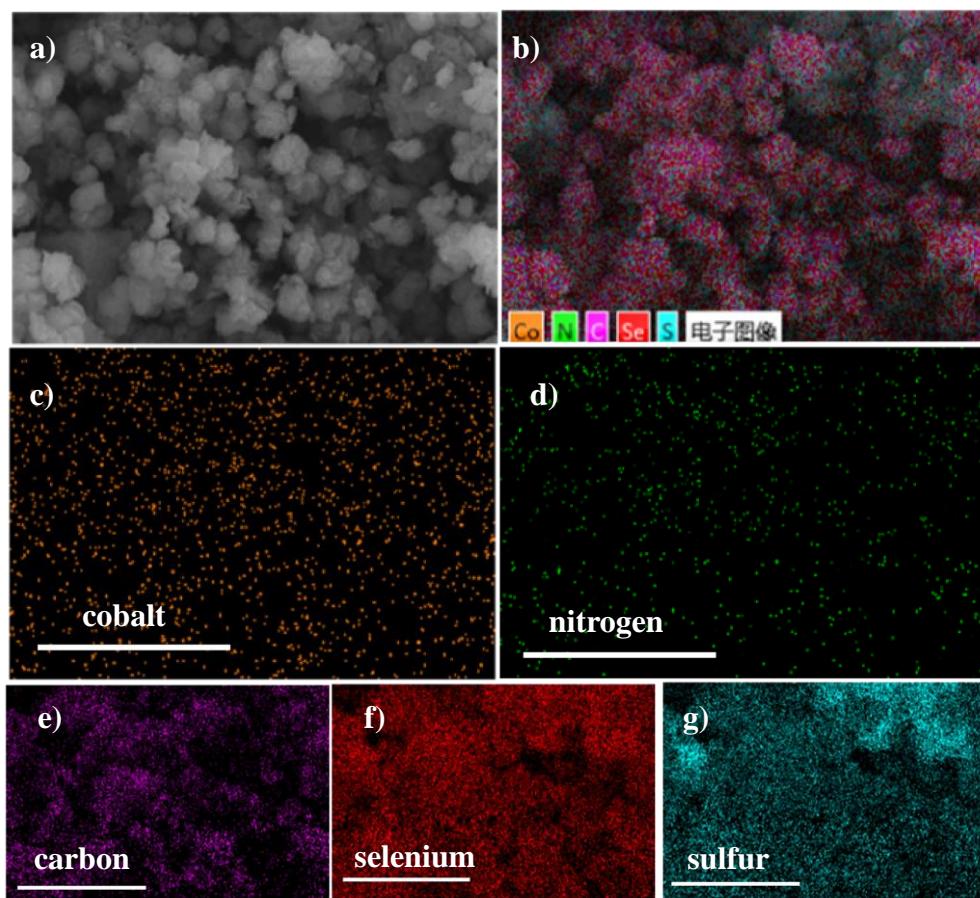
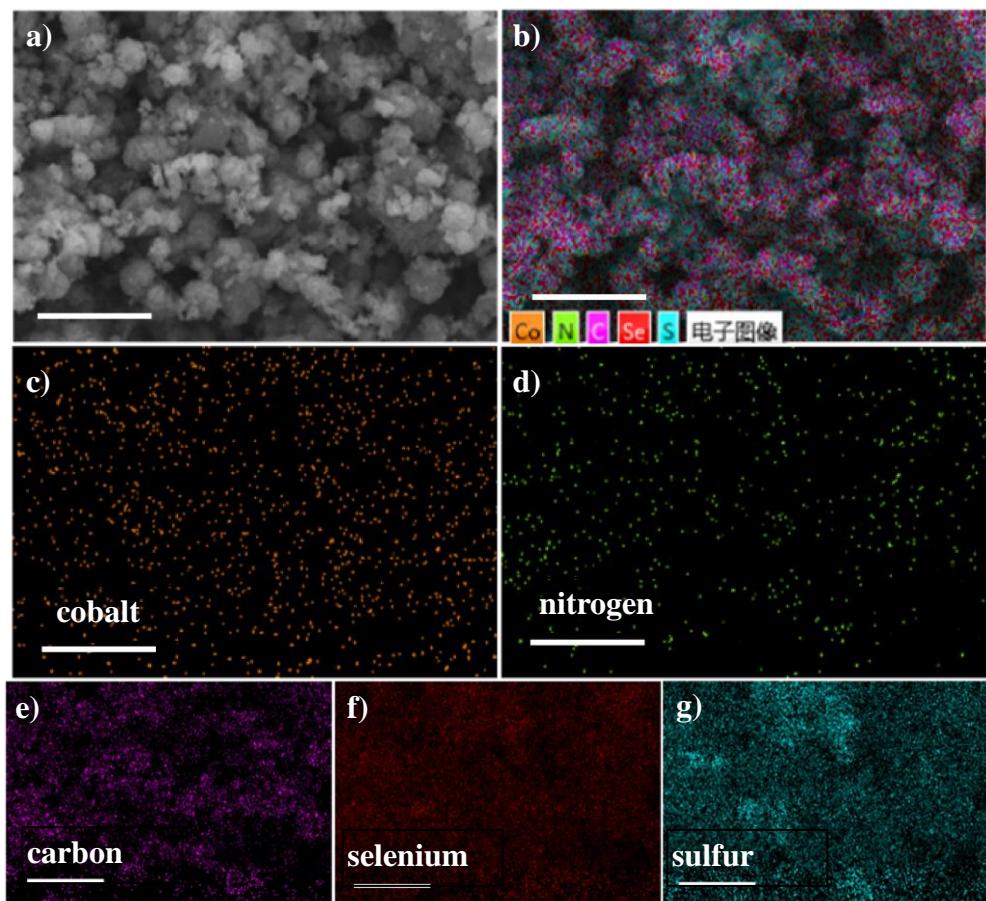
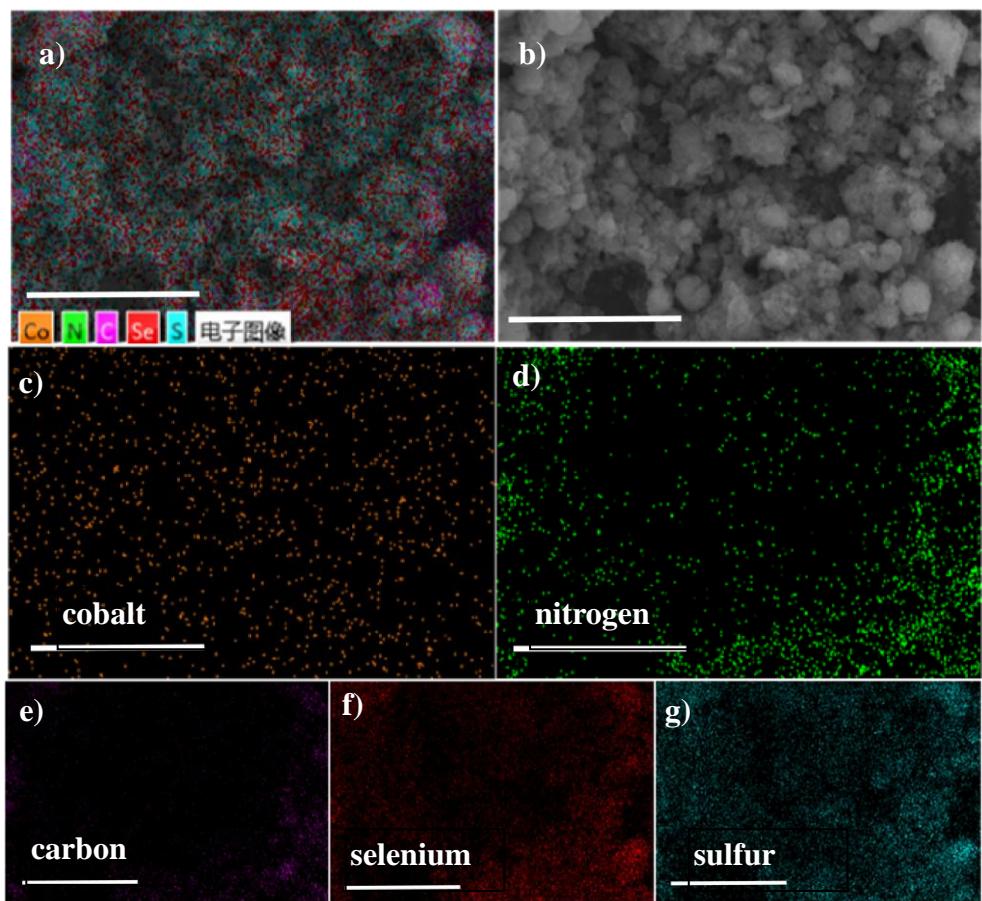


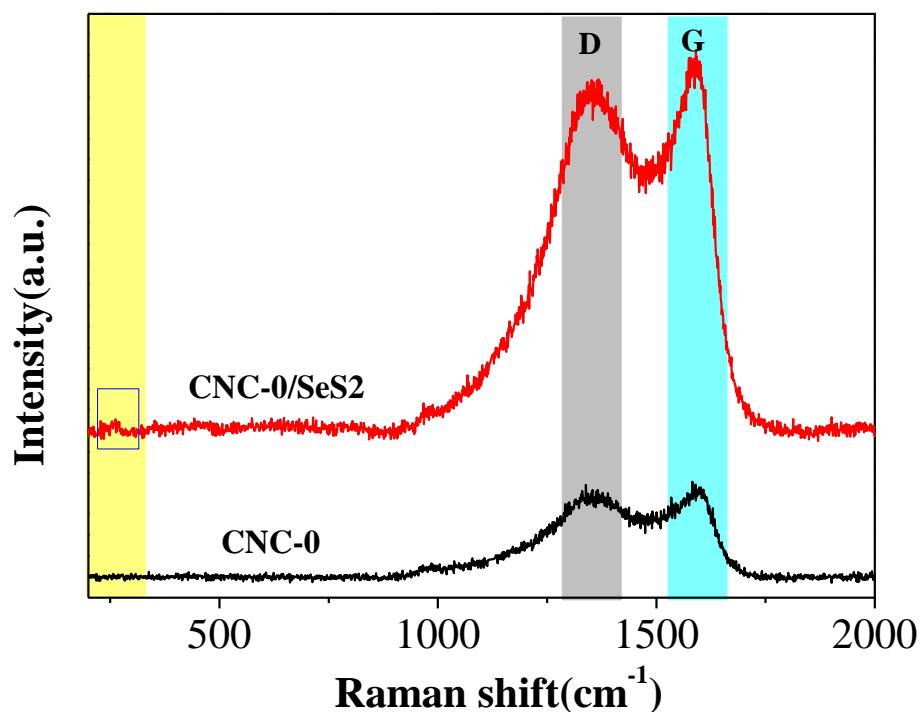
Fig. S9 . SEM image of (a) CNC-0.05/SeS<sub>2</sub> and the corresponding EDS elemental maps for cobalt(c), nitrogen (d), carbon (e), selenium (f) , sulfur (f) and all elements combined (b). The scale bar is 10μm.



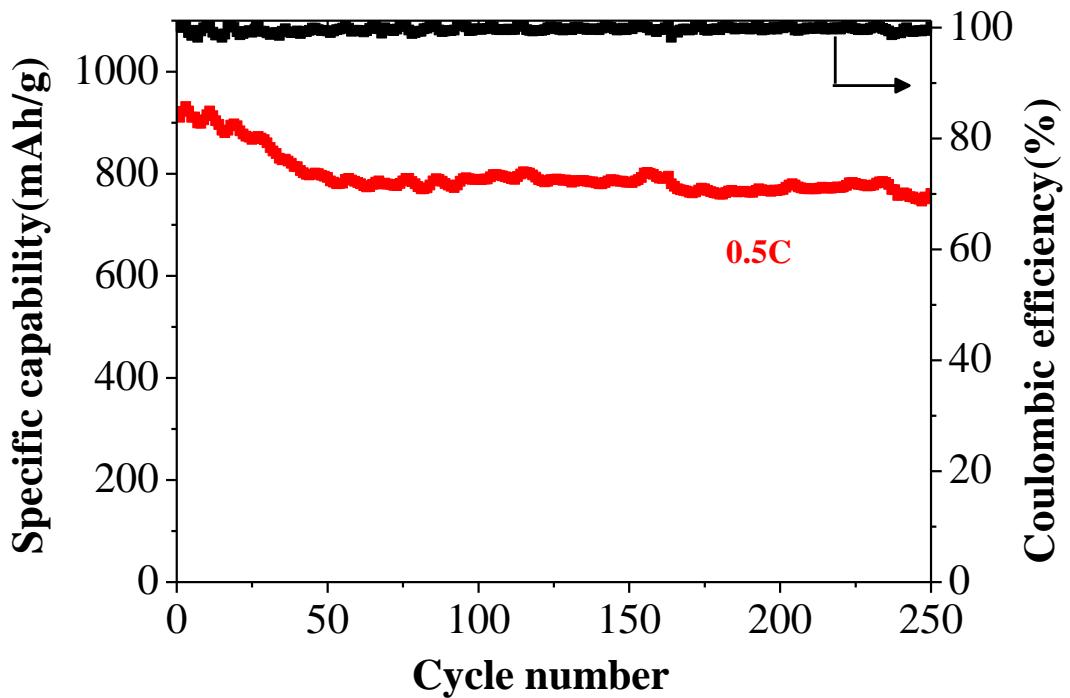
**Fig. S10 .** SEM image of (a) CNC-0.07/SeS<sub>2</sub> and the corresponding EDS elemental maps for cobalt(c), nitrogen (d), carbon (e), selenium (f) , sulfur (f) and all elements combined (b). The scale bar is 10μm.



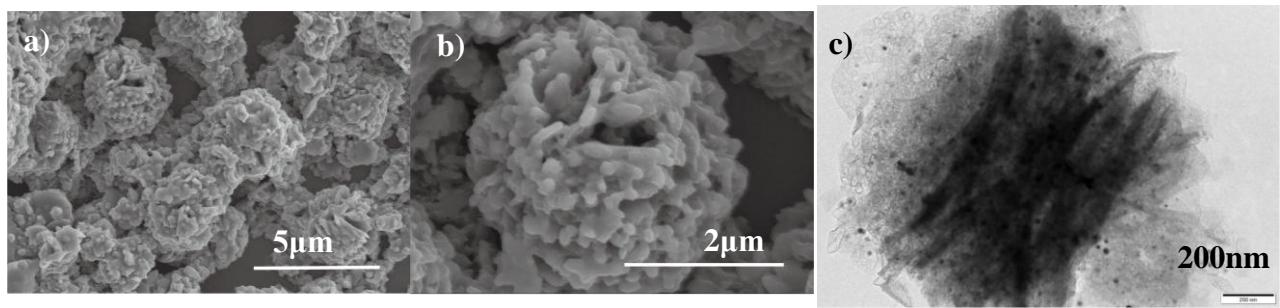
**Fig. S11.** SEM image of (a) CNC-0.03/SeS<sub>2</sub> and the corresponding EDS elemental maps for cobalt(c), nitrogen (d), carbon (e), selenium (f) , sulfur (f) and all elements combined (b). The scale bar is 10μm.



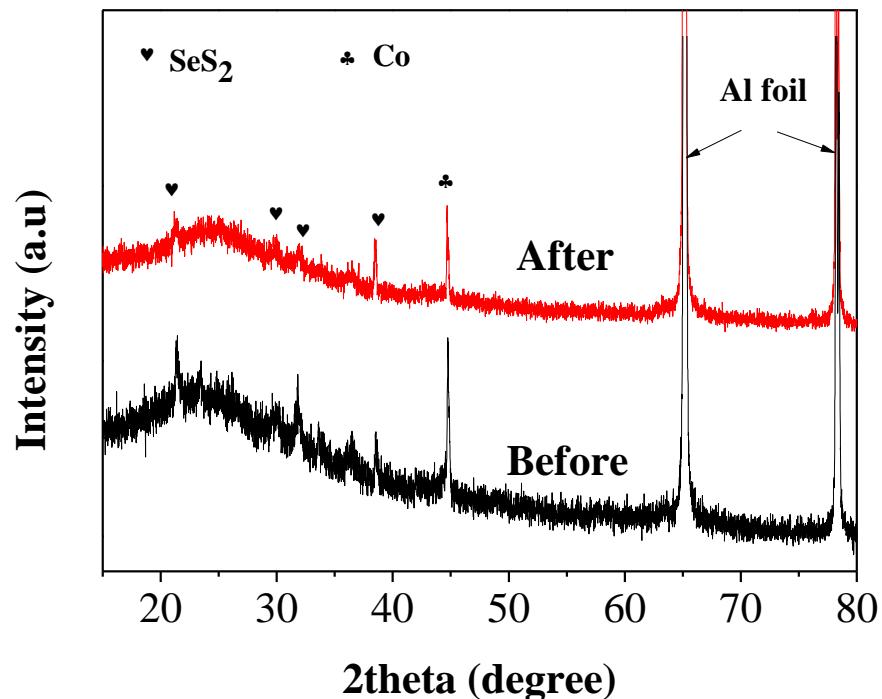
**Fig.S12.** Raman spectra of CNC-0 and CNC-0/SeS<sub>2</sub>.



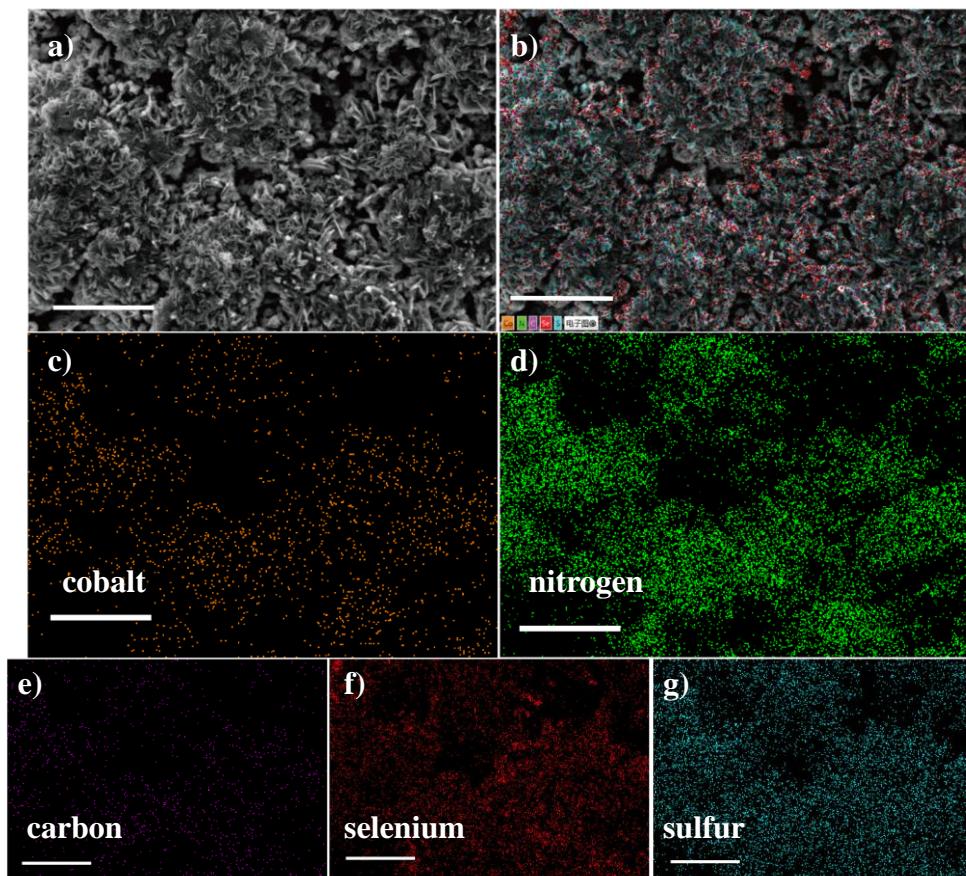
**Fig.13.** Cycle performance of the CNC-0.05/SeS<sub>2</sub> at 0.5C.



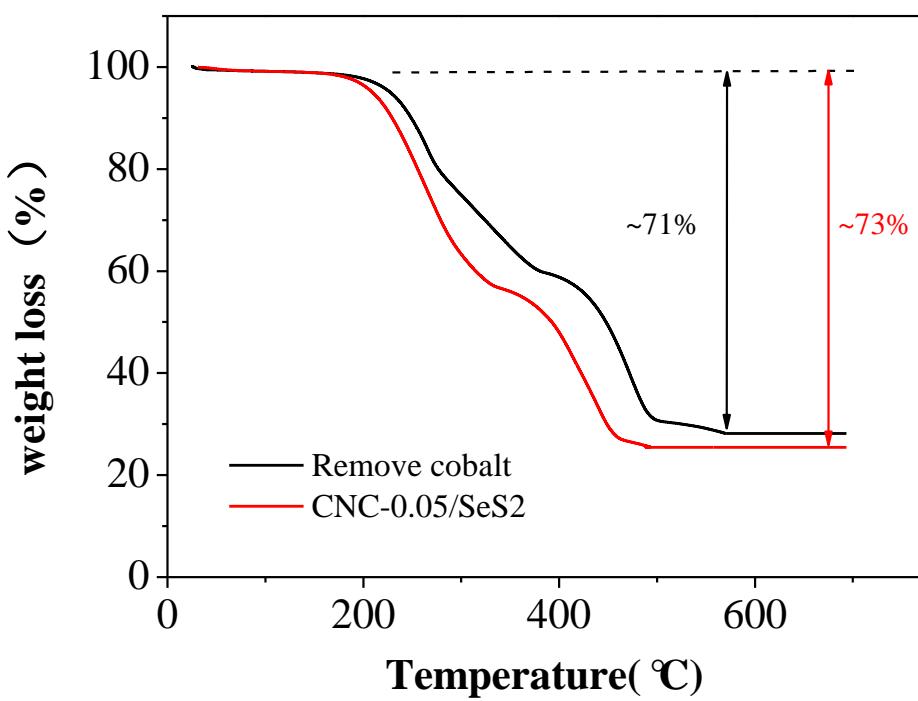
**Fig.S14.** (a-b) FESEM and (c) TEM images of the CNC-0.05/SeS<sub>2</sub> electrode after 100 cycles at a current density of 0.2C.



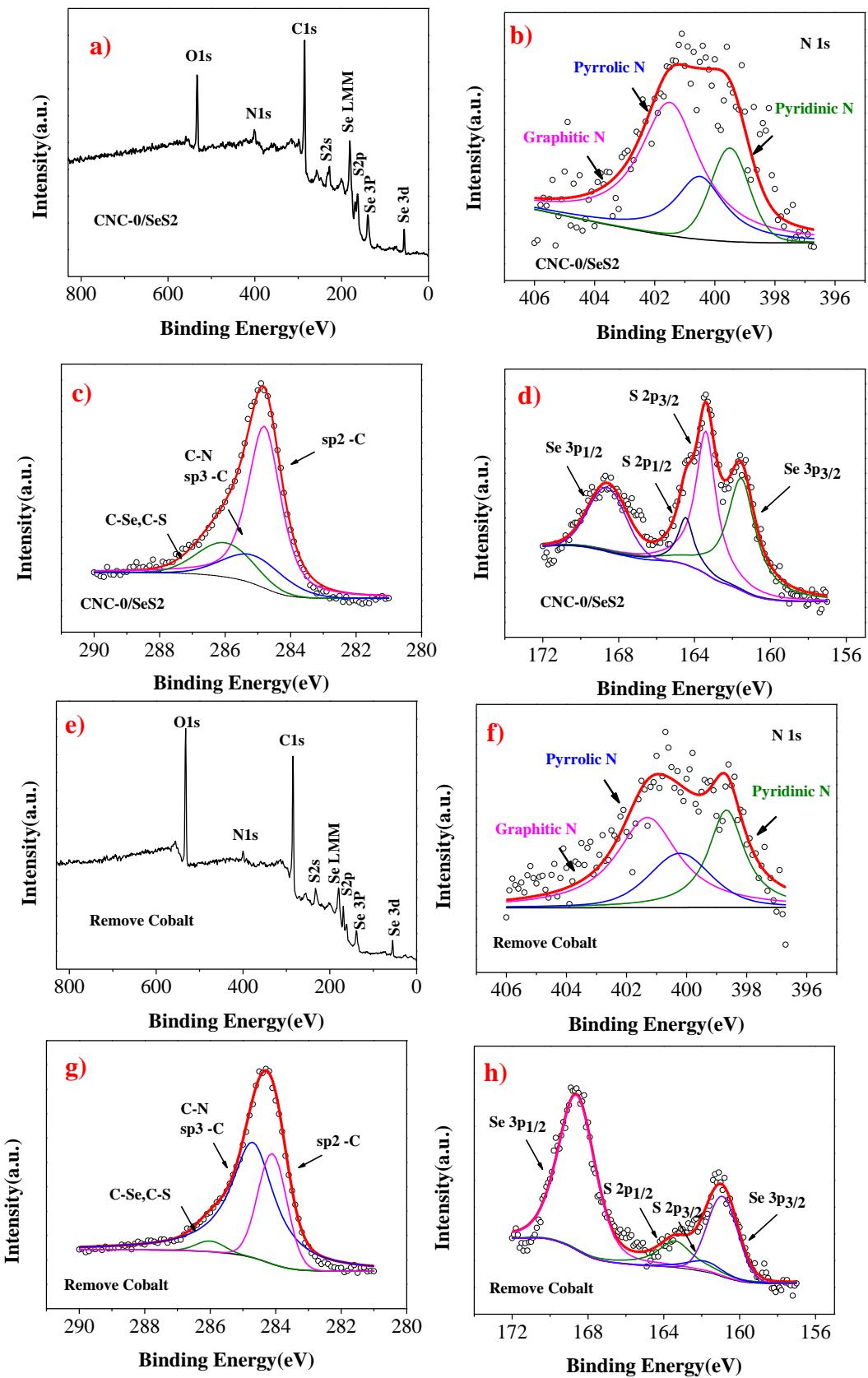
**Fig.S15.** XRD patterns of CNC-0.05/SeS<sub>2</sub> electrode on Al foil before and after 100 cycles at 0.2C.



**Fig. S16.** SEM image of (a) CNC-0.03/SeS<sub>2</sub> and the corresponding EDS elemental maps for cobalt(c), nitrogen (d), carbon (e), selenium (f) , sulfur (f) and all elements combined (b). of CNC-0.05/SeS<sub>2</sub> electrode after 100 cycles at 0.2C. The scale bar is 25μm.

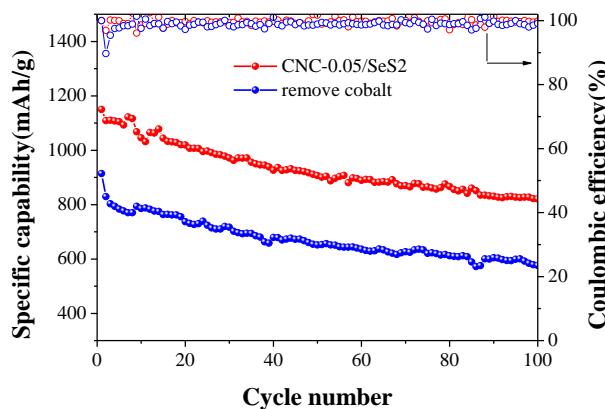


**Fig.S17. TGA curves of the CNC-0.05/SeS<sub>2</sub> and the samples of remove cobalt.**



**Fig.S18, (a) XPS survey spectrum of CNC-0/SeS<sub>2</sub>, (b-d) the corresponding high-resolution XPS**

spectra for N 1s and C 1s, S 2p/Se 3p, respectively; (e) XPS survey spectrum of the removing cobalt samples, (f–h) the corresponding high-resolution XPS spectra for N 1s and C 1s, S 2p/Se 3p, respectively.



**Fig.S19, Cycle performance of the CNC-0.05/SeS<sub>2</sub> and remove cobalt at 0.2 C.**

**Table S4. A survey of electrochemical properties of the comparisons of cathode materials for Li-SeS<sub>2</sub> batteries.**

Category	Carbon SSA* ( $\text{m}^2 \text{g}^{-1}$ )	Precursor	SeS <sub>2</sub> content	Cycling stability	C-Rate-performance
CNC-0.05/SeS <sub>2</sub> (This work)	416	Cobalt doped JUC-160 (Template-free)	~73%	820.87 mAh g <sup>-1</sup> after 100 cycles at 0.2C/0.22 A g <sup>-1</sup> 760.93 mAh g <sup>-1</sup> after 250 cycles at 0.5C/0.56 A g <sup>-1</sup>	1067 mAh g <sup>-1</sup> (0.1C/0.11 A g <sup>-1</sup> ), 927 mAh g <sup>-1</sup> (0.2C/0.22 A g <sup>-1</sup> ), 822 mAh g <sup>-1</sup> (0.5C/0.56 A g <sup>-1</sup> ), 733 mAh g <sup>-1</sup> (1C/1.12 A g <sup>-1</sup> ), 634 mAh g <sup>-1</sup> (2C/2.24 A g <sup>-1</sup> ), 262 mAh g <sup>-1</sup> (5C/5.61 A g <sup>-1</sup> ), 158 mAh g <sup>-1</sup> (10C/11.23 A g <sup>-1</sup> )
MYS-Co <sub>4</sub> N@C/SeS <sub>2</sub> (Ref. <sup>1</sup> )	142	ZIF-67 (Template-free)	70%	996 mA h.g <sup>-1</sup> after 100 cycles at 0.22 A g <sup>-1</sup> 669 mA h.g <sup>-1</sup> after 300 cycles at 0.56 A g <sup>-1</sup>	962 mAh g <sup>-1</sup> (0.22 A g <sup>-1</sup> ), 866 mAh g <sup>-1</sup> (0.56 A g <sup>-1</sup> ), 735 mAh g <sup>-1</sup> (1.12 A g <sup>-1</sup> ), 610 mAh g <sup>-1</sup> (2.24 A g <sup>-1</sup> ), 460 mAh g <sup>-1</sup> (3.36 A g <sup>-1</sup> )

Co-N-C/SeS <sub>2</sub> (Ref. <sup>2</sup> )	296	ZIF-67 ( Template-free)	66.5%	970.2 mAh g <sup>-1</sup> after 200 cycles at 0.26 A g <sup>-1</sup>	1193.5 mAh g <sup>-1</sup> (0.13 A g <sup>-1</sup> ), 1080.7 mAh g <sup>-1</sup> (0.26 A g <sup>-1</sup> ), 928.2 mAh g <sup>-1</sup> (0.67 A g <sup>-1</sup> ), 760 mAh g <sup>-1</sup> (1.34 A g <sup>-1</sup> ), 604.1 mAh g <sup>-1</sup> (2.69 A g <sup>-1</sup> ), 439.7mAh g <sup>-1</sup> (5.38 A g <sup>-1</sup> ), 300.3 mAh g <sup>-1</sup> (8.07 A g <sup>-1</sup> ), 138.1 mAh g <sup>-1</sup> (10.76 A g <sup>-1</sup> )
NiCo <sub>2</sub> S <sub>4</sub> @NC /SeS <sub>2</sub> (Ref. <sup>3</sup> )	44.5	Dopamine hydrochloride ( NiCo <sub>2</sub> S <sub>4</sub> template)	66.7 %	556.45 mAh g <sup>-1</sup> after 800 cycles at 1.34 A g <sup>-1</sup>	1205.1 mAh g <sup>-1</sup> (0.13 A g <sup>-1</sup> ), 1021.2 mAh g <sup>-1</sup> (0.26 A g <sup>-1</sup> ), 871.6 mAh g <sup>-1</sup> (0.67 A g <sup>-1</sup> ), 776.6 mAh g <sup>-1</sup> (1.34 A g <sup>-1</sup> ), 673.5 mAh g <sup>-1</sup> (2.69 A g <sup>-1</sup> ),
SeS <sub>2</sub> @MCA (Ref. <sup>4</sup> )	—	mesoporous carbon aerogels ( Template-free)	49.3 %	308 mAh g <sup>-1</sup> after 130 cycles at 0.2 A g -1	1074 mAh g <sup>-1</sup> (0.25A g <sup>-1</sup> ), 731 mAh g <sup>-1</sup> (0.5A g <sup>-1</sup> ), 371mAh g <sup>-1</sup> (2A g <sup>-1</sup> ),
CMK-3/SeS <sub>2</sub> @PDA: (Ref. <sup>5</sup> )	—	CMK-3/SeS 2 @PDA ( Core-shell structure )	70%	783 mAh g <sup>-1</sup> after 150 cycles at 0.2 A g -1	1005 mAh g <sup>-1</sup> (0.2A g <sup>-1</sup> ), 864 mAh g <sup>-1</sup> (0.5A g <sup>-1</sup> ), 787mAh g <sup>-1</sup> (1A g <sup>-1</sup> ), 702mAh g <sup>-1</sup> (2A g <sup>-1</sup> ), 645mAh g <sup>-1</sup> (3A g <sup>-1</sup> ), 584mAh g <sup>-1</sup> (4A g <sup>-1</sup> ) 535mAh g <sup>-1</sup> (5A g <sup>-1</sup> )
CoS <sub>2</sub> @LRC/SeS <sub>2</sub> (Ref. <sup>6</sup> )	77.6	Co(Ac) 2 /PAN/PS paper	70%	745 mAh g <sup>-1</sup> after 100 cycles at 0.2A g -1	1096 mA hg <sup>-1</sup> (0.1A g <sup>-1</sup> ), 1038mA hg <sup>-1</sup> (0.2A g <sup>-1</sup> ), 846mA hg <sup>-1</sup> (0.5A g <sup>-1</sup> ), 686 mA hg <sup>-1</sup> (1A g <sup>-1</sup> ), 526mA hg <sup>-1</sup> (2A g <sup>-1</sup> ),

## Reference

- [1] Tao Chen, Weihua Kong, Mengting Fan, Zewen Zhang, Lei Wang, Renpeng Chen, Yi Hu, Jing Ma and Zhong Jin, Chelation-assisted formation of multi-yolk–shell Co<sub>4</sub>N@carbon nanoboxes for self-discharge-suppressed high-performance Li–SeS<sub>2</sub> batteries, J. Mater. Chem. A, 2019, 7, 20302–20309.

- [2] Jiarui He, Weiqiang Lv, Yuanfu Chen, Jie Xiong, Kechun Wen, Chen Xu, Wanli Zhang, Yanrong Li, Wu Qin , Weidong He, Direct impregnation of  $\text{SeS}_2$  into a MOF-derived 3D nanoporous Co–N–C architecture towards superior rechargeable lithium batteries, *J. Mater. Chem. A*, 2018, 6, 10466–10473
- [3] Bingshu Guo, Tingting Yang, Wenyan Du, Qianru Ma, a Long-zhen Zhang, Shu-Juan Bao, Xiaoyan Li, Yuming Chen, Maowen Xu, Double-walled N-doped carbon@ $\text{NiCo}_2\text{S}_4$  hollow capsules as  $\text{SeS}_2$  hosts for advanced Li– $\text{SeS}_2$  batteries, *J. Mater. Chem. A*, 2019, 7, 12276–12282
- [4] Zhian Zhang, Shaofeng Jiang, Yanqing Lai, Junming Li, Junxiao Song, Jie Li, Selenium sulfide@mesoporous carbon aerogel composite for rechargeable lithium batteries with good electrochemical performance, *Journal of Power Sources* 284 (2015) 95-102
- [5] Zhen Li, Jintao Zhang, Hao Bin Wu, and Xiong Wen (David) Lou , An Improved Li– $\text{SeS}_2$  Battery with High Energy Density and Long Cycle Life, *Adv. Energy Mater.* 2017, 1700281
- [6] Jintao Zhang , Zhen Li , Xiong Wen (David) Lou, A Freestanding Selenium Disulfide Cathode Based on Cobalt Disulfide-Decorated Multichannel Carbon Fibers with Enhanced Lithium Storage Performance, *Angew. Chem. Int. Ed.* 2017, 56, 1–7