

## Supporting Information

# Mn Cluster-Embedded N/F Co-Doped Carbon toward Mild Aqueous Supercapacitors

Chen Zheng <sup>1,†</sup>, Xu Han <sup>2,†</sup>, Fangfang Sun <sup>1</sup>, Yue Zhang <sup>1</sup>, Zihang Huang <sup>1,\*</sup> and Tianyi Ma <sup>3,\*</sup>

<sup>1</sup> Institute of Clean Energy Chemistry, Key Laboratory for Green Synthesis and Preparative Chemistry of Advanced Materials of Liaoning Province, College of Chemistry, Liaoning University, Shenyang 110036, China; zc13940417032@163.com (C.Z.); sff108250@163.com (F.S.); yuezhang1229@163.com (Y.Z.)

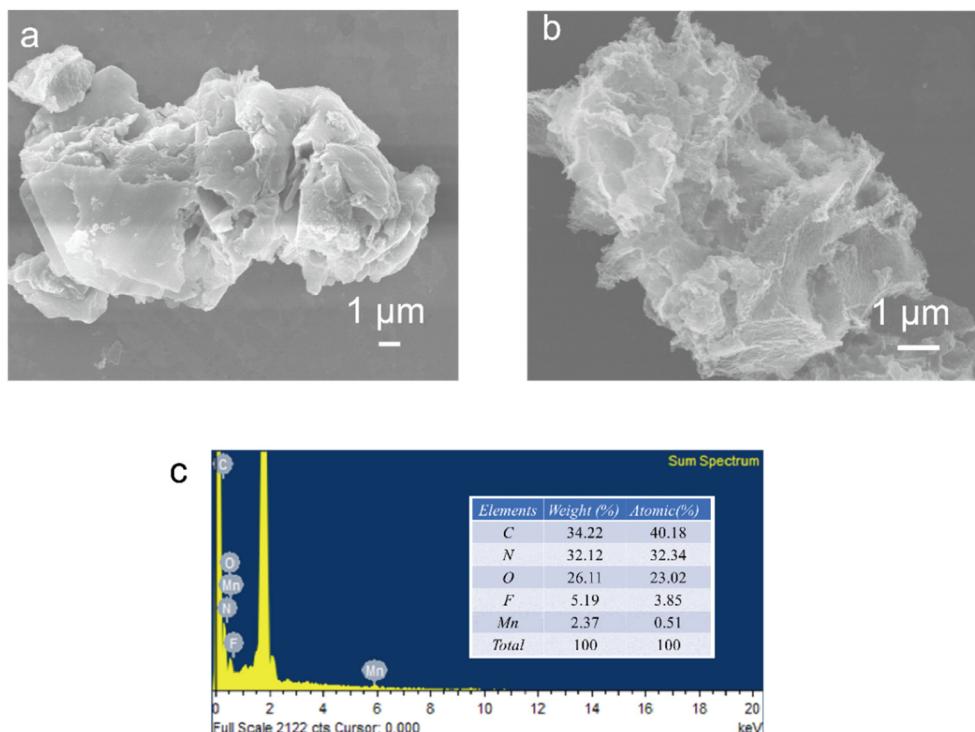
<sup>2</sup> Engineering Laboratory of Advanced Energy Materials, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China; hanxu@nimte.ac.cn

<sup>3</sup> School of Science, RMIT University, Melbourne, VIC 3000, Australia

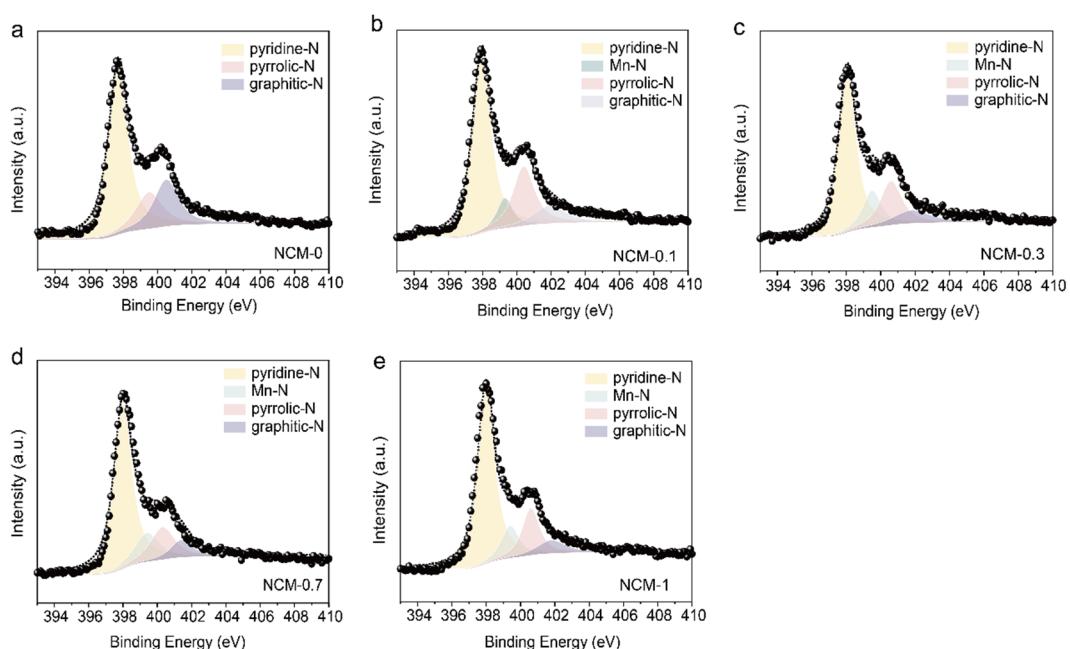
\* Correspondence: huangzihang@lnu.edu.cn (Z.H.); tianyi.ma@rmit.edu.au (T.M.)

† These authors contributed equally to this work.

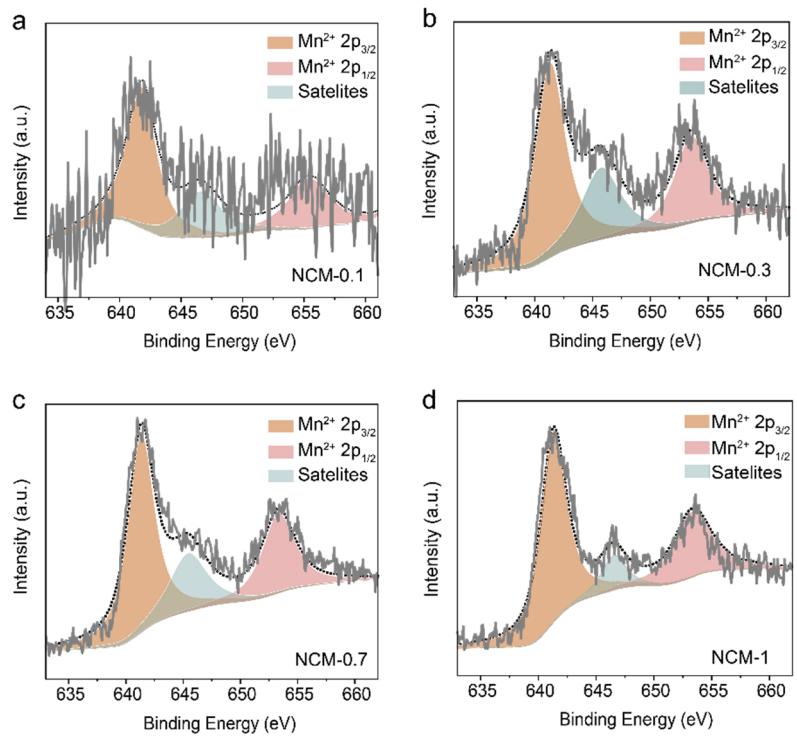
## Supplementary Figures and Tables



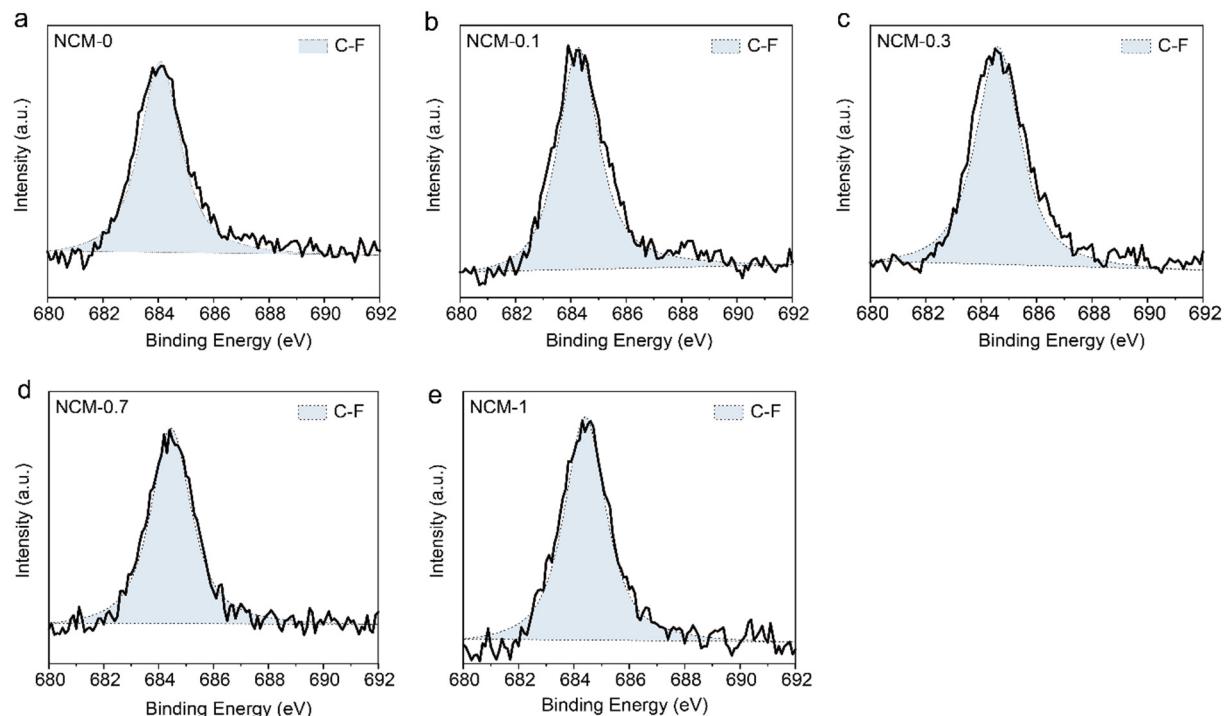
**Figure S1.** SEM image of (a) the NC; (b) the NCM-0; (c) EDS spectra collected for NCM-0.5 sample.



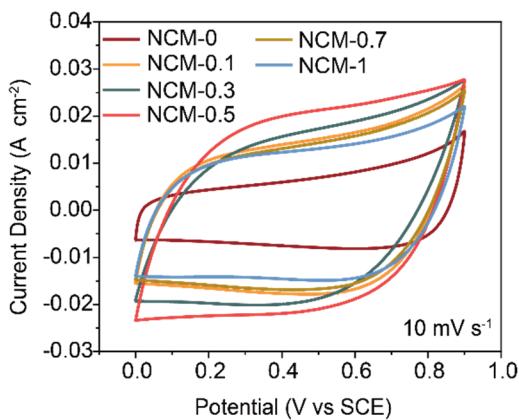
**Figure S2.** High resolution XPS spectrums of N 1s of (a) NCM-0; (b) NCM-0.1; (c) NCM-0.3; (d) NCM-0.7; (e) NCM-1.



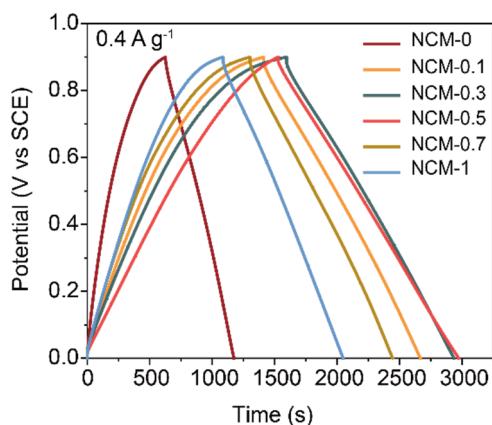
**Figure S3.** High resolution XPS spectrums of Mn 2p of (a) NCM-0.1; (b) NCM-0.3; (c) NCM-0.7; (d) NCM-1.



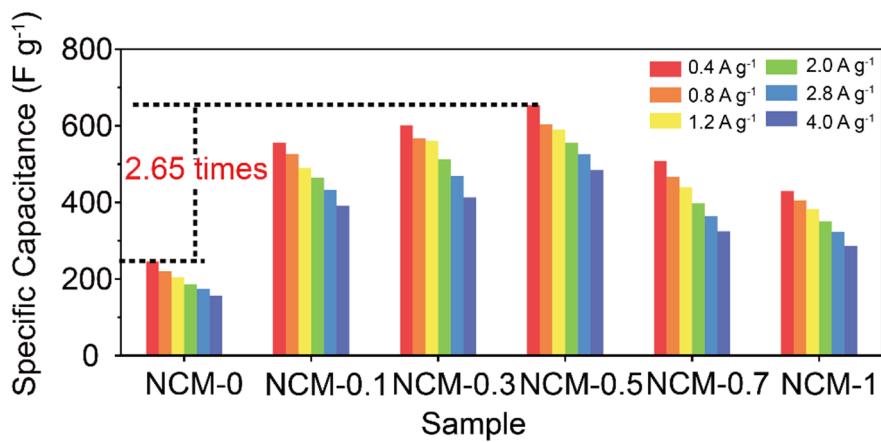
**Figure S4.** High resolution XPS spectrums of F 1s of (a) NCM-0; (b) NCM-0.1; (c) NCM-0.3; (d) NCM-0.7; (e) NCM-1.



**Figure S5.** CV curves of NCM-x ( $x=0, 0.1, 0.3, 0.5, 0.7, 1$ ) at the scanning rate of  $10 \text{ mV s}^{-1}$ .



**Figure S6** GCD profiles of the NCM-x ( $x=0, 0.1, 0.3, 0.5, 0.7, 1$ ) at the current density of  $0.4 \text{ A g}^{-1}$ .



**Figure S7** the specific capacitance of the NCM-x ( $x=0, 0.1, 0.3, 0.5, 0.7, 1$ ) at

various current densities.

**Table S1.** Comparison of specific capacitance, rate capability and cycling stability of NCM-0.5 with recently reported carbon-based electrodes.

Electrode	Maximum Specific Capacitance	Minimum Specific Capacitance	Rate Capability	Capacitance Retention
HPC-700 <sup>[1]</sup>	412.5 F g <sup>-1</sup> @ 0.5 A g <sup>-1</sup>	253 F g <sup>-1</sup> @ 50 A g <sup>-1</sup>	61.3%	99.6% (10000)
NIPCG <sup>[2]</sup>	673 F g <sup>-1</sup> @ 1 A g <sup>-1</sup>	481 F g <sup>-1</sup> @ 10 A g <sup>-1</sup>	71.5%	95% (1000)
B/N-CNS <sup>[3]</sup>	423 F g <sup>-1</sup> @ 0.2 A g <sup>-1</sup>	125 F g <sup>-1</sup> @ 50 A g <sup>-1</sup>	29.5%	100% (30000)
pCA-KOH-700 <sup>[4]</sup>	467 F g <sup>-1</sup> @ 1 A g <sup>-1</sup>	330 F g <sup>-1</sup> @ 10 A g <sup>-1</sup>	70.6%	85.7% (10000)
HPC-700 <sup>[5]</sup>	330 F g <sup>-1</sup> @ 1 A g <sup>-1</sup>	221 F g <sup>-1</sup> @ 20 A g <sup>-1</sup>	66.9%	90.5% (10000)
NS-PCM-1000 <sup>[6]</sup>	461.5 F g <sup>-1</sup> @ 0.1 A g <sup>-1</sup>	187 F g <sup>-1</sup> @ 10 A g <sup>-1</sup>	40.5%	90% (23000)
NCNF2-900 <sup>[7]</sup>	224 F g <sup>-1</sup> @ 0.5 A g <sup>-1</sup>	149 F g <sup>-1</sup> @ 10 A g <sup>-1</sup>	66.5%	97% (10000)
N/S-HCS <sup>[8]</sup>	280 F g <sup>-1</sup> @ 1 A g <sup>-1</sup>	134 F g <sup>-1</sup> @ 50 A g <sup>-1</sup>	47.8%	94.4% (10000)
AHPC <sup>[9]</sup>	576 F g <sup>-1</sup> @ 1 A g <sup>-1</sup>	460.8 F g <sup>-1</sup> @ 10 A g <sup>-1</sup>	80%	95% (10000)
900N-Ti <sub>2</sub> CT <sub>x</sub> <sup>[10]</sup>	327 F g <sup>-1</sup> @ 1 A g <sup>-1</sup>	282 F g <sup>-1</sup> @ 10 A g <sup>-1</sup>	86.2%	96.2% (5000)
MAC-N-0.5 <sup>[11]</sup>	385 F g <sup>-1</sup> @ 0.2 A g <sup>-1</sup>	332 F g <sup>-1</sup> @ 20 A g <sup>-1</sup>	86.3%	100% (10000)
NOPC-2 <sup>[12]</sup>	527 F g <sup>-1</sup> @ 1 A g <sup>-1</sup>	246 F g <sup>-1</sup> @ 200 A g <sup>-1</sup>	46.7%	94.3% (20000)
N-GQD@cZIF-8/CNT <sup>[13]</sup>	540 F g <sup>-1</sup> @ 0.5 A g <sup>-1</sup>	332.1 F g <sup>-1</sup> @ 20 A g <sup>-1</sup>	61.5%	90.9% (8000)
HHCF <sup>[14]</sup>	361 F g <sup>-1</sup> @ 1 A g <sup>-1</sup>	182 F g <sup>-1</sup> @ 100 A g <sup>-1</sup>	50.4%	95.8% (10000)
NPCN <sup>[15]</sup>	267 F g <sup>-1</sup> @ 1 A g <sup>-1</sup>	145 F g <sup>-1</sup> @ 50 A g <sup>-1</sup>	54%	_____
FCL700 <sup>[16]</sup>	505.4 F g <sup>-1</sup> @ 0.1 A g <sup>-1</sup>	216.1 F g <sup>-1</sup> @ 20 A g <sup>-1</sup>	42.7%	70.3% (2000)
KNOSC <sup>[17]</sup>	402.5 F g <sup>-1</sup> @ 1 A g <sup>-1</sup>	308.5 F g <sup>-1</sup> @ 100 A g <sup>-1</sup>	76.6%	90% (30000)

2D CoSNC <sup>[18]</sup>	360.1 F g <sup>-1</sup> @ 1.5 A g <sup>-1</sup>	204.5 F g <sup>-1</sup> @ 30 A g <sup>-1</sup>	56.8%	90% (2000)
N-CNFs-900 <sup>[19]</sup>	202 F g <sup>-1</sup> @ 1 A g <sup>-1</sup>	164 F g <sup>-1</sup> @ 30 A g <sup>-1</sup>	81.2%	97% (3000)
NCA-800 <sup>[20]</sup>	300 F g <sup>-1</sup> @ 0.5 A g <sup>-1</sup>	242 F g <sup>-1</sup> @ 10 A g <sup>-1</sup>	80.6%	98% (5000)
PCNS-6 <sup>[21]</sup>	470 F g <sup>-1</sup> @ 1 A g <sup>-1</sup>	338 F g <sup>-1</sup> @ 20 A g <sup>-1</sup>	72%	98% (50000)
2D-HPCs <sup>[22]</sup>	250 F g <sup>-1</sup> @ 0.5 A g <sup>-1</sup>	185 F g <sup>-1</sup> @ 10 A g <sup>-1</sup>	74%	96% (10000)
ZIF-8/ZTP <sup>[23]</sup>	341.2 F g <sup>-1</sup> @ 0.1 A g <sup>-1</sup>	181.3 F g <sup>-1</sup> @ 10 A g <sup>-1</sup>	53.1%	91.5% (50000)
TCNQ-CTF-800 <sup>[24]</sup>	383 F g <sup>-1</sup> @ 0.2 A g <sup>-1</sup>	197 F g <sup>-1</sup> @ 10 A g <sup>-1</sup>	51.4%	100% (10000)
MPC-800 <sup>[25]</sup>	430 F g <sup>-1</sup> @ 0.5 A g <sup>-1</sup>	327 F g <sup>-1</sup> @ 10 A g <sup>-1</sup>	76.0%	100% (10000)
<b>NCM-0.5</b>	<b>653 F g<sup>-1</sup> @ 0.4 A g<sup>-1</sup></b>	<b>484 F g<sup>-1</sup> @ 4 A g<sup>-1</sup></b>	<b>74.1%</b>	<b>40000 (97.4%)</b>

## References

- [1] Wang, Y.; Liu, R.; Tian, Y.; Sun, Z.; Huang, Z.; Wu, X.; Li, B. Heteroatoms-doped hierarchical porous carbon derived from chitin for flexible all-solid-state symmetric supercapacitors. *Chemical Engineering Journal*, **2019**, *384*, 123263.
- [2] Chen, Z.; Zhao, S.; Zhao, H.; Zou, Y.; Yu, C.; Zhong, W. Nitrogen-doped interpenetrating porous carbon/graphene networks for supercapacitor applications. *Chemical Engineering Journal*, **2021**, *409*, 127891.
- [3] Hao, J.; Wang. J.; Qin; S.; Liu, D.; Li, Y. B/N co-doped carbon nanosphere frameworks as high-performance electrodes for supercapacitors. *Journal of Materials Chemistry A*, **2018**, *6*, 8053-8058.
- [4] Wei, X.; Wan, S.; Gao, S. Self-assembly-template engineering nitrogen-doped carbon aerogels for high-rate supercapacitors. *Nano Energy*, **2016**, *28*, 206-215.
- [5] Qian, X.; Miao, L.; Jiang. J.; Ping, G.; Xiong, W.; Lv, Y.; Liu, Y.; Gan, L.; Zhu, D.; Liu, M. Hydrangea-like N/O codoped porous carbons for high-energy supercapacitors. *Chemical Engineering Journal*, **2020**, *388*, 124208.
- [6] Lu, H.; Yang, C.; Chen, J.; Li, H.; Wang, J.; Wang, S. Tailoring Hierarchically

Porous Nitrogen-, Sulfur-Codoped Carbon for High-Performance Supercapacitors and Oxygen Reduction. *Small*, **2020**, *16*, 190584.

[7] Chen, H.; Liu, T.; Mou, J.; Zhang, W.; Jiang, Z.; Liu, J.; Huang, J.; Liu, M. Free-standing N-self-doped carbon nanofiber aerogels for high-performance all-solid-state supercapacitors. *Nano Energy*, **2019**, *63*, 103836.

[8] Miao, L.; Zhu, D.; Liu, M.; Duan, H.; Wang, Z.; Lv, Y.; Gan, Y. Cooking carbon with protic salt: Nitrogen and sulfur self-doped porous carbon nanosheets for supercapacitors. *Chemical Engineering Journal*, **2018**, *347*, 233-242.

[9] Zhao, G.; Chen. C.; Yu. D.; Sun, L.; Yang, C.; Zhang, H.; Sun, Y.; Besenbacher, F.; Yu, M. One-Step Production of O-N-S Co-Doped Three-Dimensional Hierarchical Porous Carbons for High-Performance Supercapacitors. *Nano Energy*, **2018**, *47*, 547-555.

[10] Yoon, Y.; Lee, M.; Kim, S. K.; Bae, G.; Song, W.; Sung, M.; Lim, J.; Lee, S. S.; Zyung. T.; An, K. S. A Strategy for Synthesis of Carbon Nitride Induced Chemically Doped 2D MXene for High-Performance Supercapacitor Electrodes. *Advanced Energy Materials*, **2018**, *8*, 1703173.

[11] Zhou, J.; Hou, L.; Lian, J.; Cheng, W.; Wang, D.; Gou, H.; Gao, F. Nitrogen-doped highly dense but porous carbon microspheres with ultrahigh volumetric capacitance and rate capability for supercapacitors. *Journal of Materials Chemistry A*, **2019**, *7*, 476-485.

[12] Hou, L.; Yang, W.; Li, Y.; Wang, P.; Jiang, B.; Xu, C.; Zhang, C.; Huang, G.; Yang, F.; Li, Y. Dual-template endowing N, O co-doped hierarchically porous carbon from potassium citrate with high capacitance and rate capability for supercapacitors. *Chemical Engineering Journal*, **2021**, *417*, 129289.

[13] Li, Z.; Liu, X.; Wang, L.; Bu, F.; Wei. J.; Pan, D.; Wu, M. Hierarchical 3D All-Carbon Composite Structure Modified with N-Doped Graphene Quantum Dots for High-Performance Flexible Supercapacitors. *Small*, **2018**, *14*, 1801498.

[14] Deng, X.; Li, J.; Zhu, S.; Ma, L.; Zhao, N. Boosting the capacitive storage performance of MOF-derived carbon frameworks via structural modulation for

supercapacitors. *Energy Storage Materials*, **2019**, 23, 491-498.

[15] Kale, V. S.; Hwang, M.; Chang, H.; Kang, J.; Chae, I. S.; Jeon, Y.; Yang, J.; Kim, J.; Ko, Y. J.; Piao, Y.; Hyeon, T. Microporosity-Controlled Synthesis of Heteroatom Codoped Carbon Nanocages by Wrap-Bake-Sublime Approach for Flexible All-Solid-State-Supercapacitors. *Advanced Functional Materials*, **2018**, 28, 1803786.

[16] Peng, Z.; Hu, Y.; Wang, J.; Liu, S.; Li, C.; Jiang, Q.; Lu, J.; Zeng, X.; Peng, P.; Li, F. F. Fullerene-Based In Situ Doping of N and Fe into a 3D Cross-Like Hierarchical Carbon Composite for High-Performance Supercapacitors. *Advanced Energy Materials*, **2019**, 9, 1802928.

[17] Peng, H.; Yao, B.; Wie, X.; Liu, T.; Kou, T.; Xiao, P.; Zhang, Y.; Li, Y. Pore and Heteroatom Engineered Carbon Foams for Supercapacitors. *Advanced Energy Materials*, **2019**, 9, 1803665.

[18] Cao, F.; Zhao, M.; Yu, Y.; Chen, B.; Huang, Y.; Yang, J.; Cao, X.; Lu, Q.; Zhang, X.; Zhang, Z.; Tan, C.; Zhang, H. Synthesis of Two-Dimensional CoS<sub>1.097</sub>/Nitrogen-Doped Carbon Nanocomposites Using Metal-Organic Framework Nanosheets as Precursors for Supercapacitor Application. *Journal of the American Chemical Society*, **2016**, 138, 6924-6927.

[19] Chen, L. F.; Zhang, X. D.; Liang, H. W.; Kong, M.; Guan, Q. F.; Chen, P.; Wu, Z. Y.; Yu, S. H. Synthesis of nitrogen-doped porous carbon nanofibers as an efficient electrode material for supercapacitors. *Acs Nano*, **2012**, 6, 7092-7102.

[20] Li, H.; Li, J.; Thomas, A.; Liao, Y. Ultra-High Surface Area Nitrogen-Doped Carbon Aerogels Derived From a Schiff-Base Porous Organic Polymer Aerogel for CO<sub>2</sub> Storage. *Advanced Functional Materials*, **2019**, 28, 1904785.

[21] Chen, C.; Yu, D.; Zhao, G.; Du, B.; Tang, W.; Sun, L; Sun, Y.; Besenbacher, F.; Yu, M. Three-dimensional scaffolding framework of porous carbon nanosheets derived from plant wastes for high-performance supercapacitors. *Nano Energy*, **2016**, 27, 377-389.

[22] Yao, L.; Wu, Q.; Zhang, P.; Zhang, J.; Wang, D.; Li, Y.; Ren, X.; Mi, H.; Deng,

L.; Zheng, Z. Scalable 2D Hierarchical Porous Carbon Nanosheets for Flexible Supercapacitors with Ultrahigh Energy Density. *Advanced Materials*, **2018**, *30*, 1706054.

[23] Yuksel, R.; Buyukcakir, O.; Panda, P. K.; Lee, S. H.; Jiang, Y.; Singh, D.; Hansen, S.; Adelung, R.; Mishra, Y. K.; Ahuja, R.; Ruoff, R. S. Necklace-like Nitrogen-Doped Tubular Carbon 3D Frameworks for Electrochemical Energy Storage. *Advanced Functional Materials*, **2020**, *30*, 1909725.

[24] Li, Y.; Zheng, S.; Liu, X.; Li, P.; Sun, L.; Yang, R.; Wang, S.; Wu, Z. S.; Bao, X.; Deng, W. Q. Conductive Microporous Covalent Triazine-Based Framework for High-Performance Electrochemical Capacitive Energy Storage. *Angewandte Chemie International Edition*, **2018**, *57*, 7992-7996.

[25] Ding, C.; Liu, T.; Yan, X.; Huang, L.; Ryu, S.; Lan, J.; Yu, Y.; Zhong, W. H.; Yang, X. An ultra-microporous carbon material boosting integrated capacitance for cellulose-based supercapacitors. *Nano-Micro Letters*, **2020**, *12*, 1-17.