Supporting Information

N- and O-doped Hollow Carbons Constructed by Self- and Extrinsic-activation for Oxygen Reduction Reaction and Flexible Zinc-Air batteries

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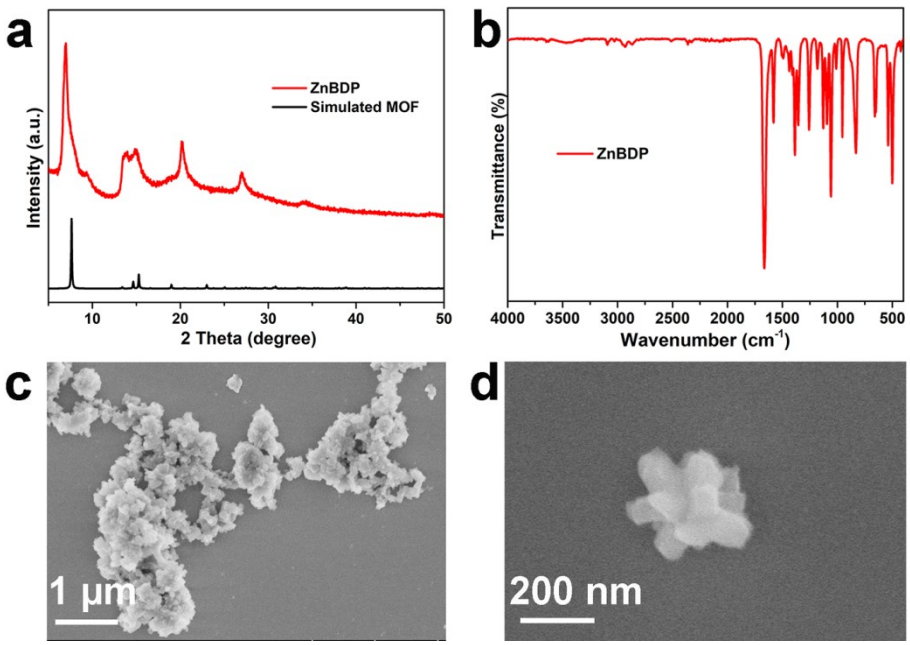

Figure S1. (a) The X-ray diffraction (XRD) patterns, (b) Fourier transformation infrared (FT-IR) spectrum, (c–d) scanning electron microscopy (SEM) images of ZnBDP (BDP = 1,4-(4-bispyrazolyl)benzene).

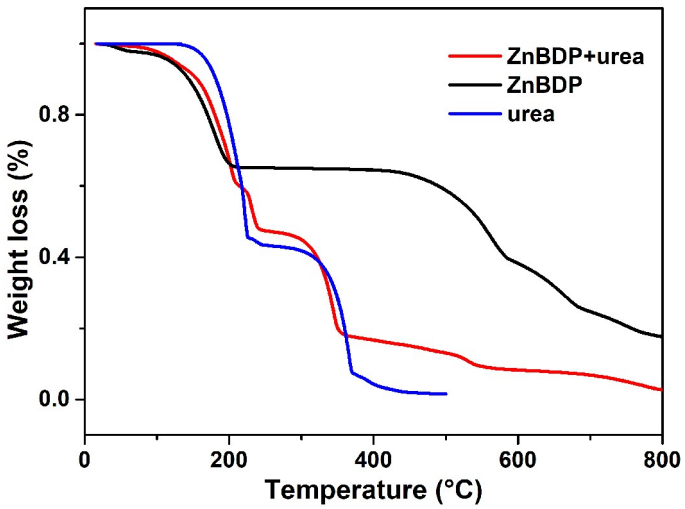

Figure S2. The TG of ZnBDP, urea, and the mixture of ZnBDP and urea (1 : 3 by weight).

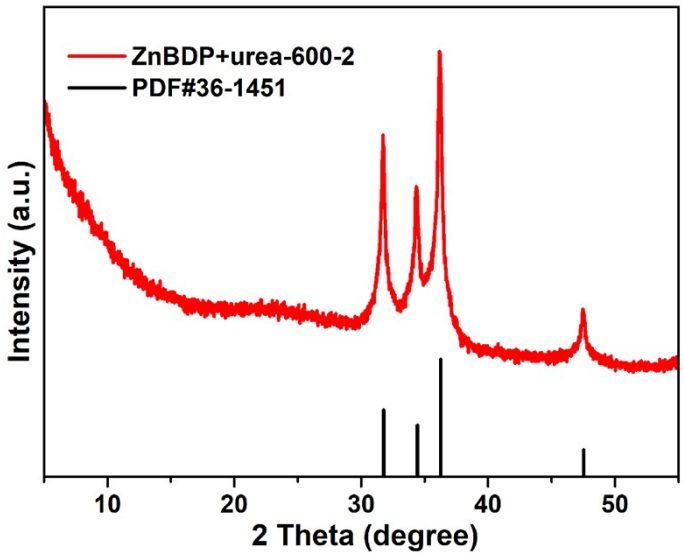

Figure S3. The XRD pattern of the mixture of ZnBDP (1 : 3 by weight) pyrolysized under Ar flow at 600 °C for 1 h. As shown, the Zn was transformed into ZnO during pyrolysis.

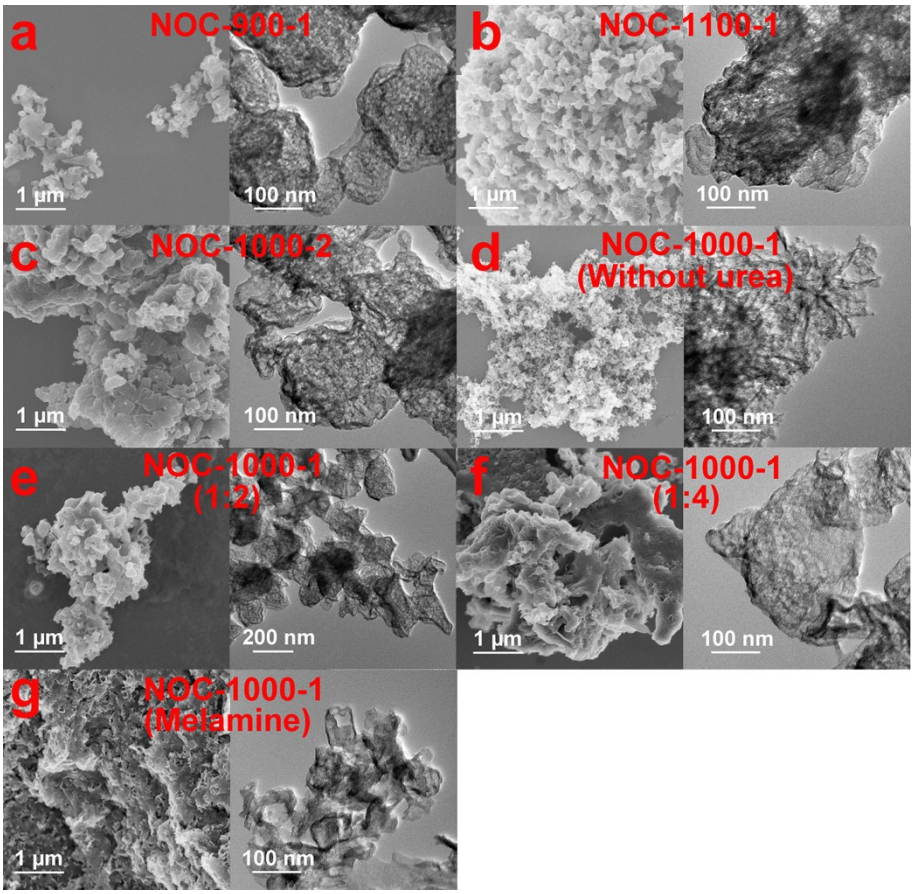

Figure S4. The SEM images and TEM images of derived carbon catalysts under different conditions. Viewing from the images, it is apparent that the presence of sacrificial extrinsic activator was of great significance for the formation of hollow carbons.

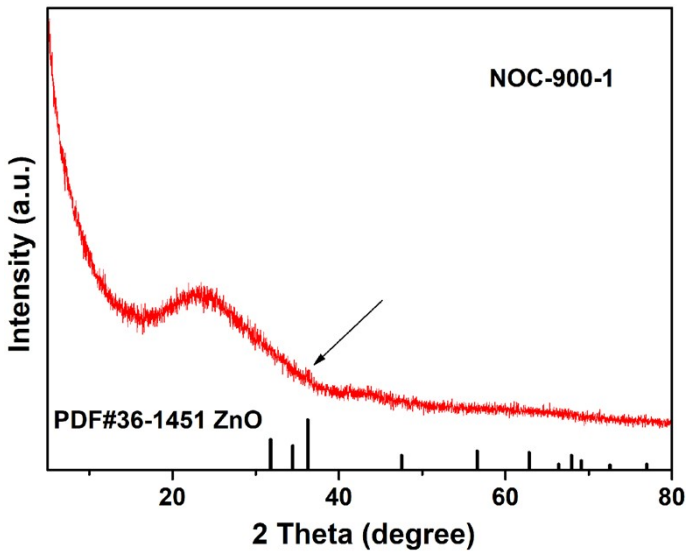

Figure S5. The XRD patterns of NOC-900-1. Herein, an additional peak located at 36.3° could assign to the (101) of ZnO.

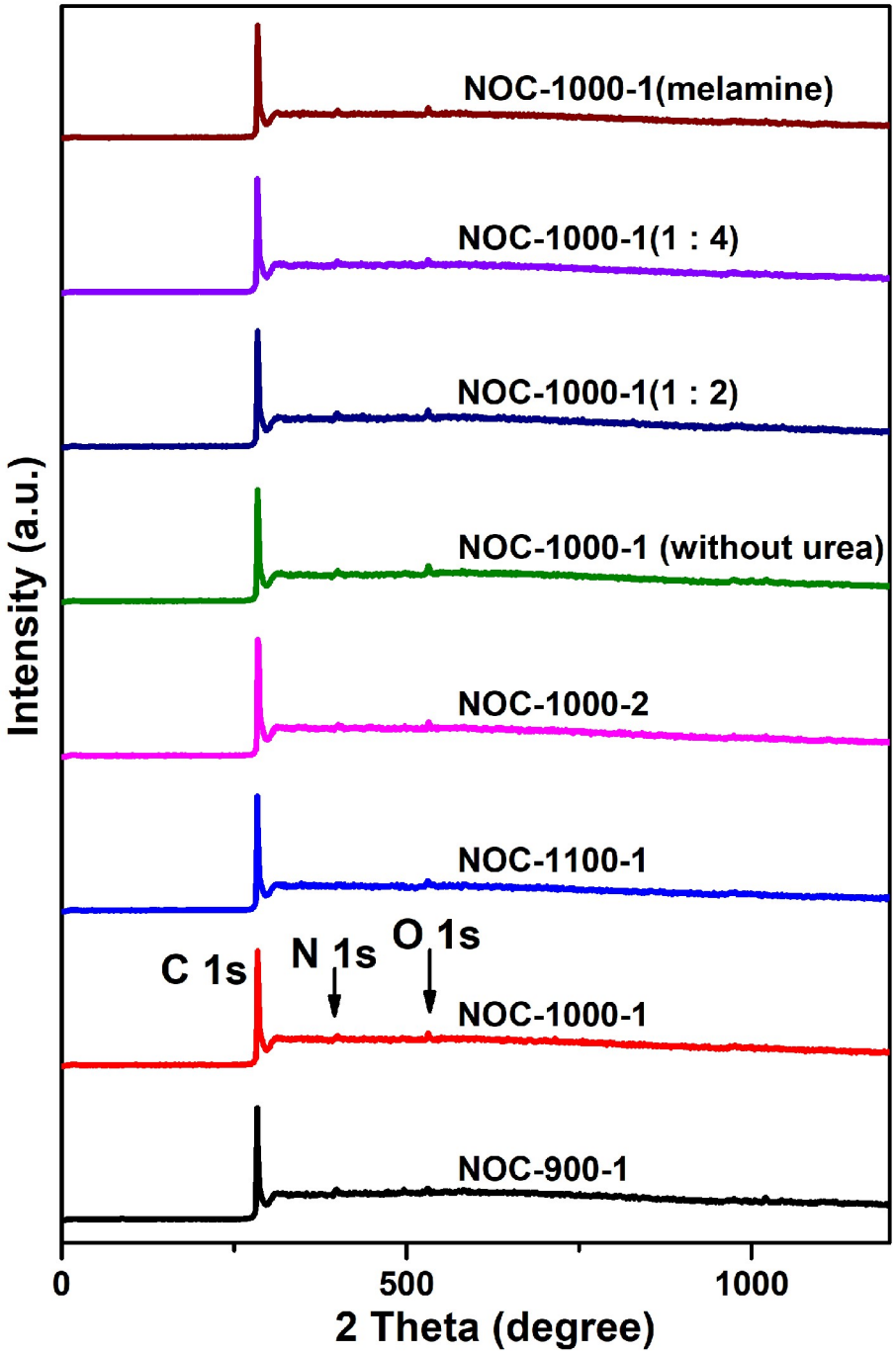

Figure S6. The full XPS spectra of the derived carbon catalysts pyrolysized under different conditions.

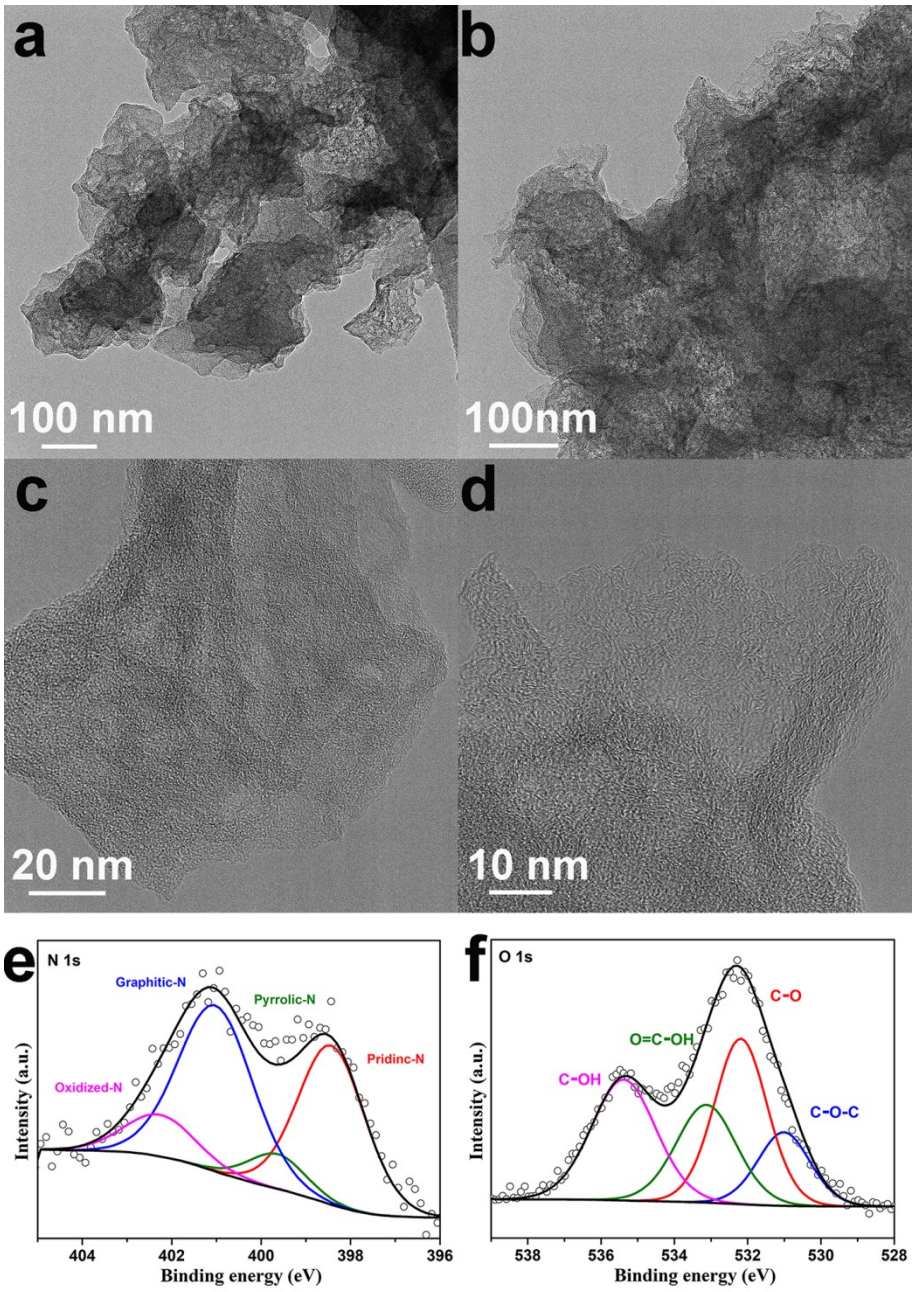

Figure S7. The ORR polarization curve and the corresponding ring current of (a) 20 wt% Pt/C and (b) NOC-1000-1 recorded on the RRDE.

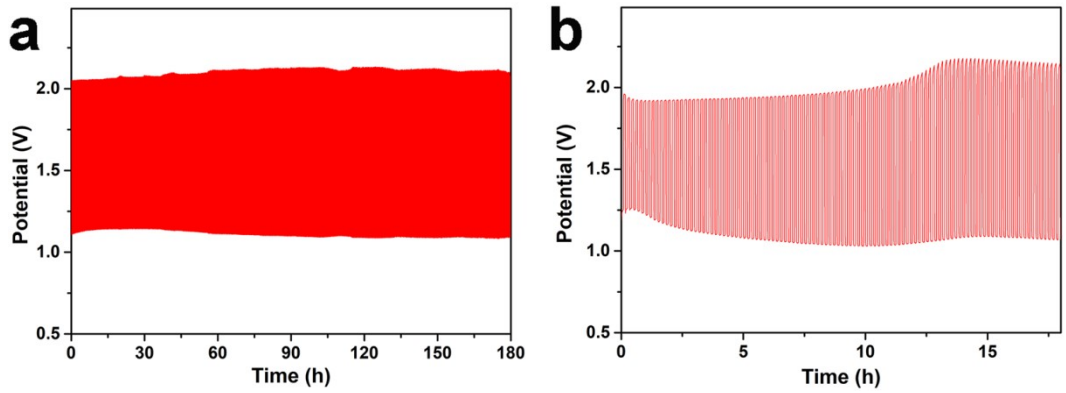

Figure S8. Cycling performance of rechargeable Zn-air batteries with the (a) NC+RuO_2 and (b) 20 wt% Pt/C+RuO_2 cathodes at 5 mA cm^{-2}.

Table S1. The relative content of pyridinic N, pyrrolic N, graphitic N and oxidized N in the derived carbon catalysts.

Content	Pyridinic N	Pyrrolic N	Graphitic N	Oxidized N	Pyridinic N + Graphitic N
NOC-900-1	46.04	7.56	39.36	7.05	85.4
NOC-1000-1	37.49	7.13	44.81	10.57	82.3
NOC-1100-1	16.39	5.29	62.11	16.21	78.5
NOC-1000-2	24.65	5.02	54.44	15.89	79.09
NOC-1000-1 (without urea)	32.27	9.97	42.32	15.44	74.59
NOC-1000-1(1:2)	32.62	12.12	42.52	12.74	75.14
NOC-1000-1(1:4)	30.73	7.73	46.63	14.91	77.36
NOC-1000-1 (melamine)	27.46	7.72	54.14	10.68	81.6

Table S2. Comparison of recently reported metal-free carbon catalysts for ORR in 0.1 M KOH electrolyte.

Catalyst	Heteroatom	E_{onset} (V vs.RHE)	$E_{1/2}$ (V vs.RHE)	OCV (V)	Peak power density of NOC-1000-1 (mW cm^{-2})	Peak power density of 20 wt% Pt/C+RuO_2 or IrO_2 (mW cm^{-2})	Durability	Ref.
NC-1000-1	N	0.977	0.867	1.63	140.55	105.69	180h/1080 cycles	This work
PANRGO-700	N	/	0.864	/	116.6	120.3	/	[1]
CMD-900-4	N, P	0.93	0.85	/	/	/	/	[2]
BN-PCN	N, B	0.91	0.84	1.387	193.6	117.9	100h	[3]
BN-CDs@CNT	N, B	0.92	0.8	/	/	/	/	[4]
HPNC-2	N	0.96	0.86	1.43	154	151	/	[5]
MCAC	N	0.87	0.8	1.383	139.1	/	200 cycles	[6]
10N-G-800	N	0.930	/	1.44	203	118	/	[7]
NPF-CNS-2	N, P, F	0.93	0.81	1.49	144	112	385 cycles	[8]
NC-800	N	/	0.85	/	/	/	/	[9]
O,N-graphene	N, O	1.01	0.842	1.43	152.8	119.8	160h	[10]
NPF@CNF-800	N, P, F	0.97	0.85	/	159	91	800 cycles	[11]
HPC(MV-c-PN)	N	0.95	0.855	/	80.1	57.0	/	[12]
10% F/BCN	N, B	0.92	0.79	/	/	/	/	[13]
N/C–N_P+N_G	N	0.98	0.86	1.70	126	121	/	[14]
NSMPC-2	N, S	0.967	0.858	1.48	153	/	100 cycles	[15]
GNP-900	N, O, P	0.96	0.824	/	/	/	/	[16]
P,S-CNS	N, P, S	0.95	0.82	/	225	/	40h	[17]
PNC-B	N, P	0.95	0.76	1.33	91.3	85.2	/	[18]
NHCP-1000	N	0.98	0.86	1.44	272	265	160	[19]
NDC-MS	N	/	0.88	1.495	174	132	72h	[20]
N, S@CM-1000	N, S	0.9	0.76	1.37	90	/	/	[21]
NrGO-90	N	0.82	0.52	/	/	/	/	[22]
N-GDY-900	N	1.01	0.83	1.54	84	/	300	[23]
NMC–1	N	0.96	0.82	/	/	/	/	[24]

Table S3. Comparison of the key parameters of flexible solid-state rechargeable ZABs from the reported literatures.

Catalyst	OCV (V)	power density of NOC-1000-1 (mW cm^{-2})	power density of 20 wt% Pt/C+RuO_2 or IrO_2 (mW cm^{-2})	Durability	Ref.
NC-1000-1	1.48	100.92	72.18	30 h/180 cycles	This work
F-ACET-500	/	52	/	42 h	[25]
NPF@CNF-800	1.33	64	51	120 cycles	[11]
N/E-HPC-900	1.34	36.2	/	80 h	[26]
N, S-CC	1.247	47	/	120 cycles	[27]
SilkNC/KB	/	32.3	26.7	30 cycles	[28]
CC-AC	1.367	52.3	/	1000 min	[29]
CNT@POF	1.39	22.3	/	/	[30]
FeCo/Se-CNT	1.405	37.5	/	20 h/120 cycles	[31]
UiO-66-NO_2 @CoCNT	/	26	28	/	[32]
FeP/Fe_2O_3@NPCA	1.42	40.8	/	500 min	[33]
NC-Co/CoNx	1.4	41.5	43.9	25 h	[34]
N, S-CC	1.25	47	/	120 cycles	[27]

Reference

[1] H. Begum, M. S. Ahmed, S. Jung, *J. Mater. Chem. A* **2021**, *9*, 9644.

[2] Z. Xing, R. Jin, X. Chen, B. Chen, J. Zhou, B. Tian, Y. Li, D. Fan, *Chem. Eng. J.* **2021**, *410*, 128015.

[3] Y. Kang, W. Wang, J. Li, S. Imhanria, Y. Hao, Z. Lei, *J. Power Sources* **2021**, *493*, 229665.

[4] Y. Pei, H. Song, Y. Liu, Y. Cheng, W. Li, Y. Chen, Y. Fan, B. Liu, S. Lu, *J. Colloid Interface Sci.* **2021**, *600*, 865.

[5] H. Liu, G. He, X. Liu, Y. Zhu, S. Eigler, L. Han, *ChemCatChem* **2021**, *13*, 3112.

[6] J. Liu, C. Wang, Y. Song, S. Zhang, Z. Zhang, L. He, M. Du, *J. Colloid Interface Sci* .**2021**, *591*, 253.

[7] C. Ou, H. Chen, H. Wang, Y. Liao, R. Li, H. Liu, *Electrochim. Acta* **2021**, *380*, 138256.

[8] Y. Zheng, H. Song, S. Chen, X. Yu, J. Zhu, J. Xu, K. A. I. Zhang, C. Zhang, T. Liu, *Small* **2020**, *16*, e2004342.

[9] J. Meng, Z. Liu, X. Liu, W. Yang, L. Wang, Y. Li, Y.-C. Cao, X. Zhang, L. Mai, *J. Mater. Sci. Techn.* **2021**, *66*, 186.

[10] R. Song, X. Cao, J. Xu, X. Zhou, X. Wang, N. Yuan, J. Ding, *Nanoscale* **2021**, *13*, 6174.

[11] Y. Zheng, S. Chen, K. A. I. Zhang, J. Zhu, J. Xu, C. Zhang, T. Liu, *ACS Appl. Mater. Interfaces* **2021**, *13*, 13328.

[12] Z. Duan, G. Han, H. Huo, Z. Lin, L. Ge, C. Du, Y. Gao, G. Yin, *ACS Sustain. Chem. Eng.* **2021**, *9*, 1264.

[13] M. A. Ahsan, T. He, K. Eid, A. M. Abdullah, M. L. Curry, A. Du, A. R. Puente Santiago, L. Echegoyen, J. C. Noveron, *J. Am. Chem. Soc.* **2021**, *143*, 1203.

[14] X. Zhang, X. Zhang, S. Zhao, Y. Q. Wang, X. Lin, Z. Q. Tian, P. K. Shen, S. P. Jiang, *Electrochim. Acta* **2021**, *370*, 137712.

[15] Z. Xu, L. Li, X. Chen, G. Xiao, *ACS Appl.Energy Mater.* **2021**, *4*, 1954.

[16] Z. Liu, M. Wang, X. Luo, S. Li, S. Li, Q. Zhou, W. Xu, R. Wu, *Appl. Surf. Sci.* **2021**, *544*, 148912.

[17] Y. Wang, N. Xu, R. He, L. Peng, D. Cai, J. Qiao, *Appl. Catal. B- Environ.* **2021**, *285*, 119811.

[18] H. Yu, H. Zhang, Z. Zhang, *ChemCatChem* **2020**, *13*, 397.

[19] J. Yan, X. Zheng, C. Wei, Z. Sun, K. Zeng, L. Shen, J. Sun, M. H. Rümmeli, R. Yang, *Carbon* **2021**, *171*, 320.

[20] J.-J. Cai, Q.-Y. Zhou, X.-F. Gong, B. Liu, Y.-L. Zhang, Y.-K. Dai, D.-M. Gu, L. Zhao, X.-L. Sui, Z.-B. Wang, *Carbon* **2020**, *167*, 75.

[21] J. Yang, F. Xiang, H. Guo, L. Wang, X. Niu, *Carbon* **2020**, *156*, 514.

[22] D. Roy, S. Sarkar, K. Bhattacharjee, K. Panigrahi, B. K. Das, K. Sardar, S. Sarkar, K. K. Chattopadhyay, *Carbon* **2020**, *166*, 361.

[23] T. Lu, X. Hu, J. He, R. Li, J. Gao, Q. Lv, Z. Yang, S. Cui, C. Huang, *Nano Energy* **2021**, *85*, 106024.

[24] X. Li, Y. Zhao, Y. Yang, S. Gao, *Nano Energy* **2019**, *62*, 628.

[25] J. Deng, L. Wang, F. Jin, Y. H. Hu, *J. Mater. Chem. A* **2021**, *9*, 11145.

[26] X. Peng, L. Zhang, Z. Chen, L. Zhong, D. Zhao, X. Chi, X. Zhao, L. Li, X. Lu, K. Leng, C. Liu, W. Liu, W. Tang, K. P. Loh, *Adv. Mater.* **2019**, *31*, e1900341.

[27] Z. Zhao, Z. Yuan, Z. Fang, J. Jian, J. Li, M. Yang, C. Mo, Y. Zhang, X. Hu, P. Li, S. Wang, W. Hong, Z. Zheng, G. Ouyang, X. Chen, D. Yu, *Adv. Sci.* **2018**, *5*, 1800760.

[28] C. Wang, N.-H. Xie, Y. Zhang, Z. Huang, K. Xia, H. Wang, S. Guo, B.-Q. Xu, Y. Zhang, *Chem. Mater.* **2019**, *31*, 1023.

[29] K. Kordek, L. Jiang, K. Fan, Z. Zhu, L. Xu, M. Al‐Mamun, Y. Dou, S. Chen, P. Liu, H. Yin, P. Rutkowski, H. Zhao, *Adv.Energy Mater.* **2018**, *9*, 1802936.

[30] B.-Q. Li, S.-Y. Zhang, B. Wang, Z.-J. Xia, C. Tang, Q. Zhang, *Energy Environ. Sci.* **2018**, *11*, 1723.

[31] H. Zhang, M. Zhao, H. Liu, S. Shi, Z. Wang, B. Zhang, L. Song, J. Shang, Y. Yang, C. Ma, L. Zheng, Y. Han, W. Huang, *Nano Lett.* **2021**, *21*, 2255.

[32] S. Zeng, F. Lyu, L. Sun, Y. Zhan, F.-X. Ma, J. Lu, Y. Y. Li, *Chem. Mater.* **2019**, *31*, 1646.

[33] K. Wu, L. Zhang, Y. Yuan, L. Zhong, Z. Chen, X. Chi, H. Lu, Z. Chen, R. Zou, T. Li, C. Jiang, Y. Chen, X. Peng, J. Lu, *Adv. Mater.* **2020**, *32*, e2002292.

[34] C. Guan, A. Sumboja, W. Zang, Y. Qian, H. Zhang, X. Liu, Z. Liu, D. Zhao, S. J. Pennycook, J. Wang, *Energy Storage Mater.* **2019**, *16*, 243.