Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

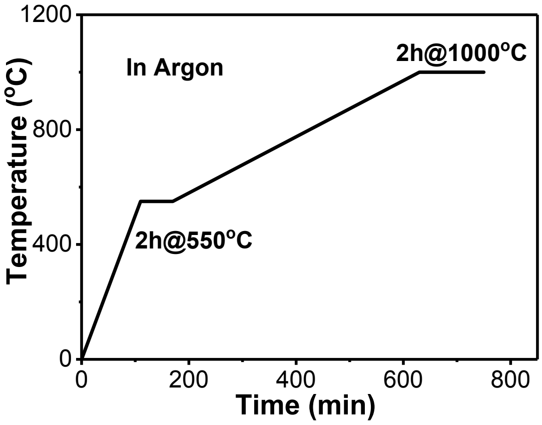


Fig. S1 The relationship of pyrolysis temperature and annealing time.

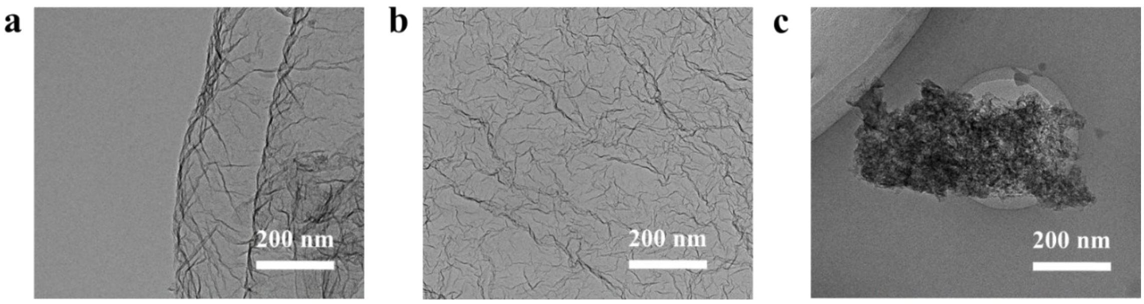


Fig. S2 TEM images of corresponding samples: (a) NC-NPC-5/1; (b) NC-NPC-10/1; (c) NC-NPC-20/1.

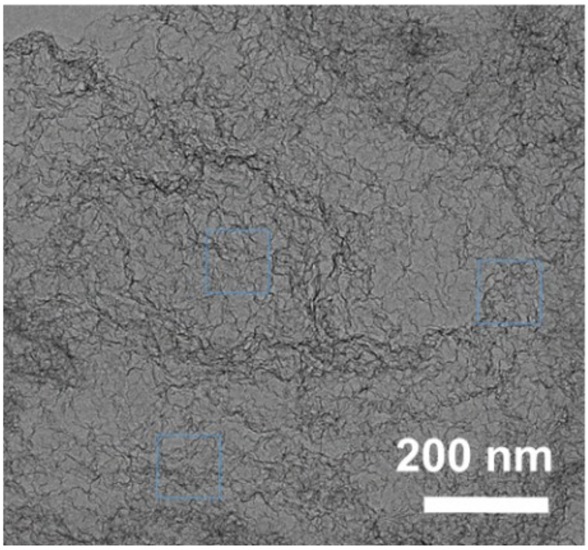
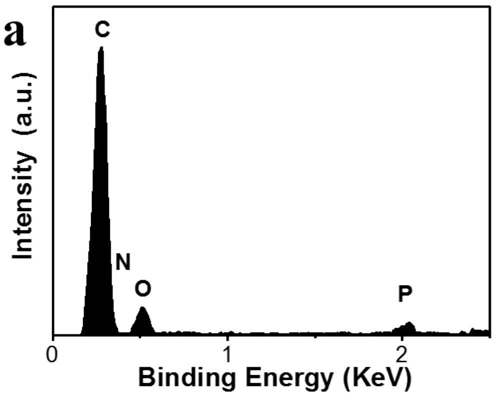


Fig. S3 The TEM image of NC-NPC-15/1 for calculating the crumple density.

The crumple density can be obtained by directly counting the crumples from TEM images. As shown in Fig. S3, we randomly chose three blue squares in TEM image of NC-NPC-15/1, in which the area of each square is 10000 nm^{-2}. And then we counted the number of crumple in each square of 21 crumples, 26 crumples and 28 crumples. Thus the crumple density can be determined to be 2500 μm^{-2} for NC-NPC-15/1.



b

Elements	Weight(%)	Atomic(%)
C K	82.88	87.44
O K	7.39	5.85
N K	5.52	4.99
P K	4.21	1.72
Total	100	100

Fig. S4 (a) The energy dispersive spectroscopy (EDS) of NC-NPC-15/1 shows the presence of C, O, N, and P elements. (b) The corresponding proportions of the C, O, N, P elements.

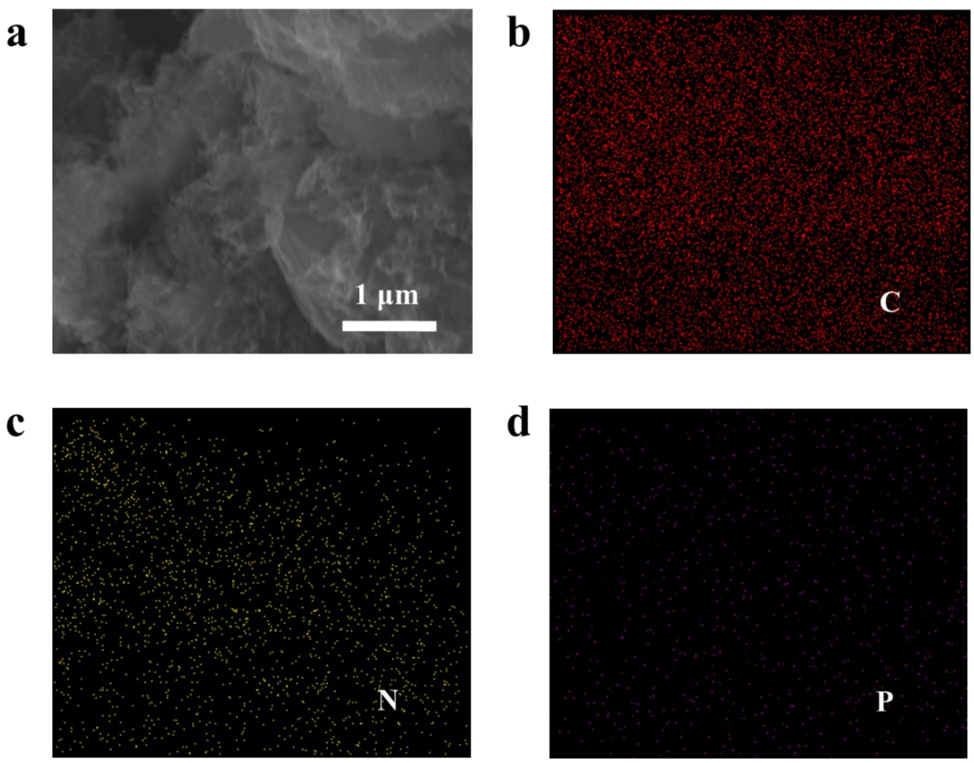


Fig. S5 (a) SEM image of NC-NPC-15/1. The element mapping images of (b) carbon, (c) nitrogen and (d) phosphorus element, respectively.

Elements	Weight(%)
C K	81.13
O K	8.49
N K	6.06
Total	95.68

Fig. S6 The weight contents of the C, O, N elements in the elemental analysis of NC-NPC-15/1.

Elements	Weight(%)	Atomic(%)
C K	81.95	86.91
O K	7.24	5.76
N K	5.86	5.33
P K	4.95	2.03
Total	100	100

Fig. S7 The proportions of the C, O, N, P elements in the X-ray photoelectron spectroscopy (XPS) of NC-NPC-15/1.

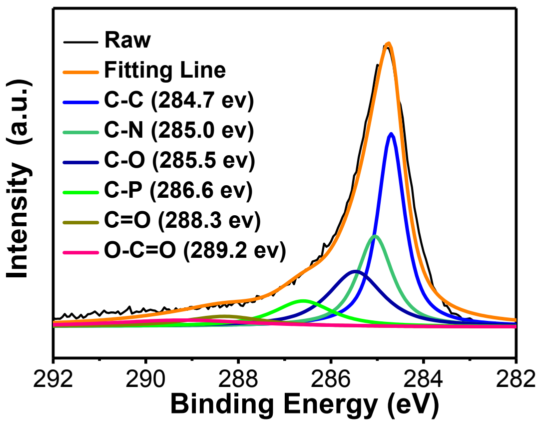


Fig. S8 The high-resolution XPS of C 1s peaks of NC-NPC-15/1.

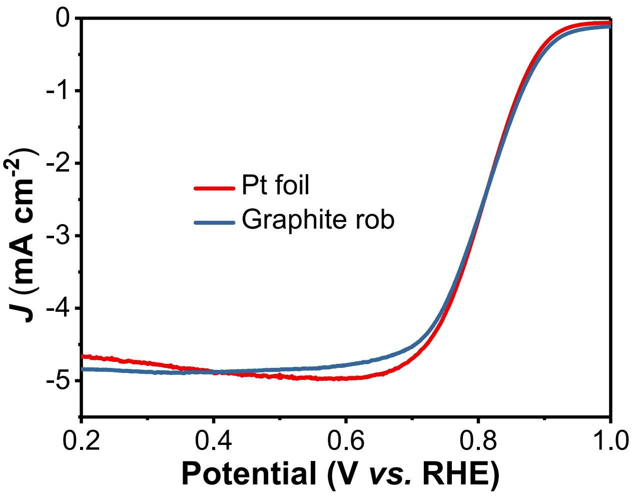


Fig. S9 LSVs of NC-NPC-15/1 catalysts with Pt and highly oriented pyrolytic graphite rob as counter electrodes at a rotation speed of 1600 rpm in oxygen-saturated 0.1 M KOH solution, scan rate: 10 mV s^{-1}. The two LSV curves show similar trend, indicating there is no any Pt contamination during the ORR testing process.

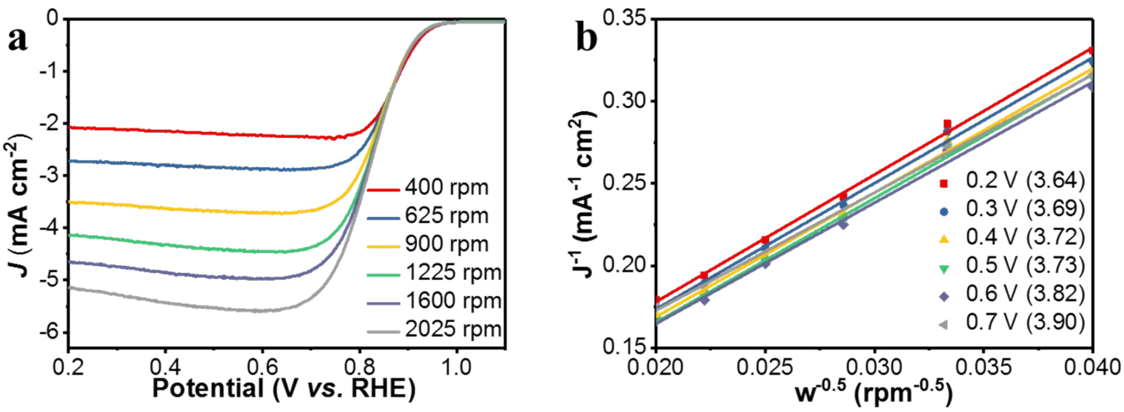


Fig. S10 (a) The LSV of the NC-NPC-15/1 sample measured on RDE at different rotation speeds. (b) Koutecky-Levich plots of different samples at various potentials. Inset parentheses show the corresponding electron transfer number (n).

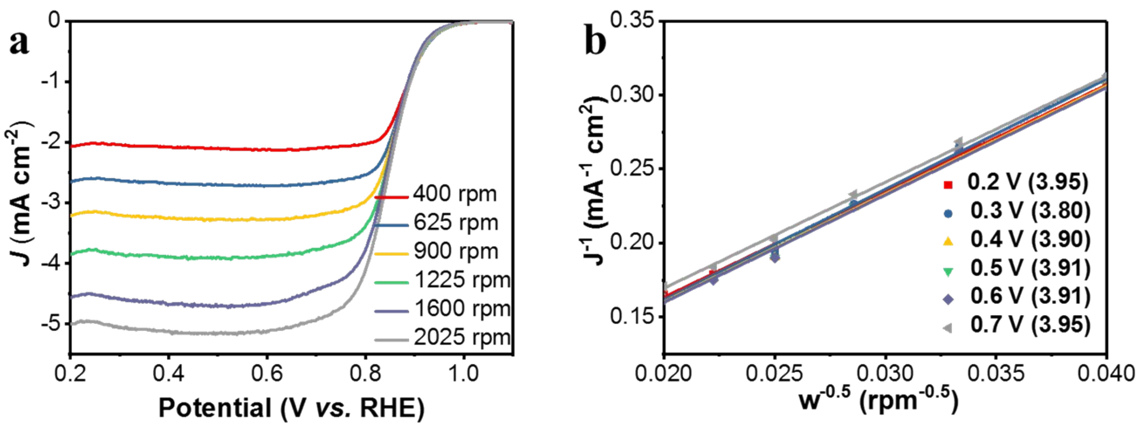


Fig. S11 (a) The LSV of the commercial Pt/C catalyst measured on RDE at different rotation speeds. (b) Koutecky-Levich plots of different samples at various potentials. Inset parentheses show the corresponding electron transfer number (n).

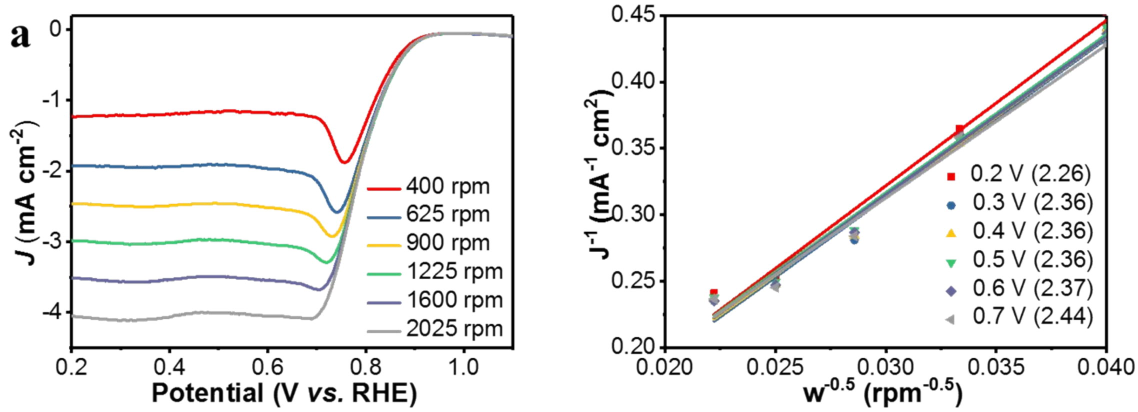


Fig. S12 (a) The LSV of the NC-NPC-5/1 catalyst measured on RDE at different rotation speeds. (b) Koutecky-Levich plots of different samples at various potentials. Inset parentheses show the corresponding electron transfer number (n).

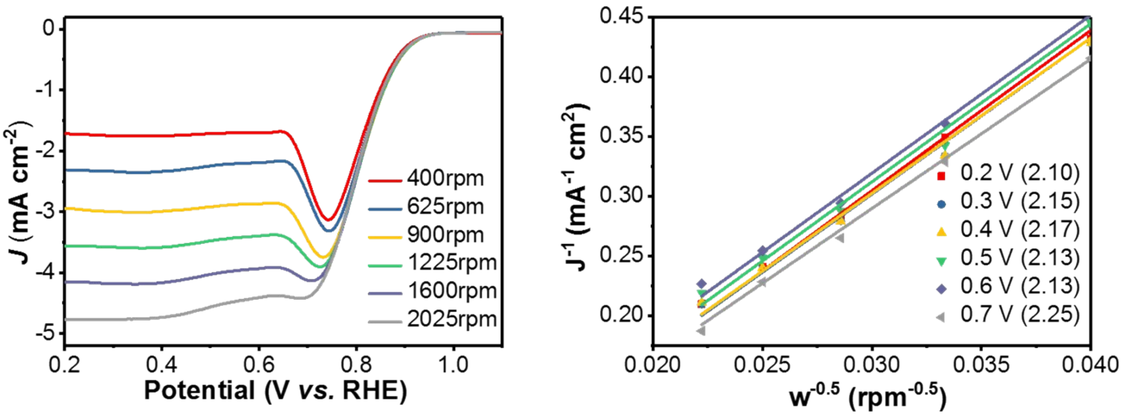


Fig. S13 (a) The LSV of the NC-NPC-10/1 catalyst measured on RDE at different rotation speeds. (b) Koutecky-Levich plots of different samples at various potentials. Inset parentheses show the corresponding electron transfer number (n).

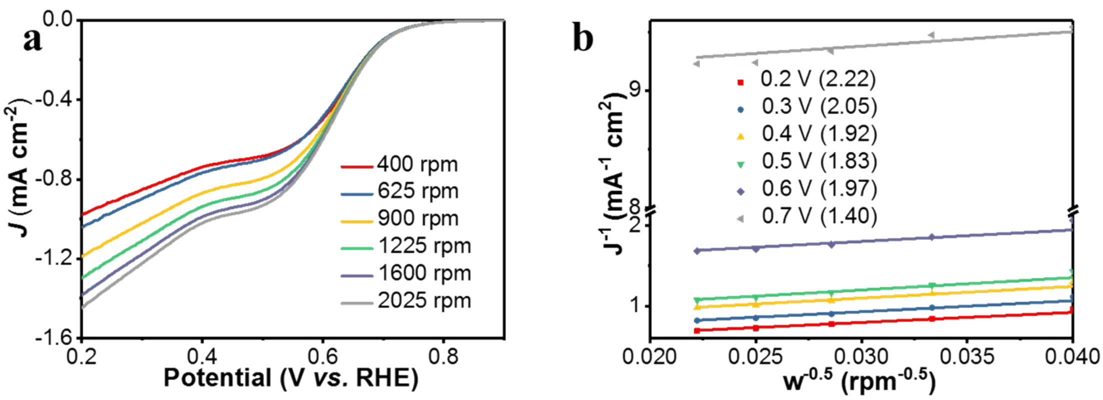


Fig. S14 (a) The LSV of the NC-NPC-20/1 catalyst measured on RDE at different rotation speeds. (b) Koutecky-Levich plots of different samples at various potentials. Inset parentheses show the corresponding electron transfer number (n).

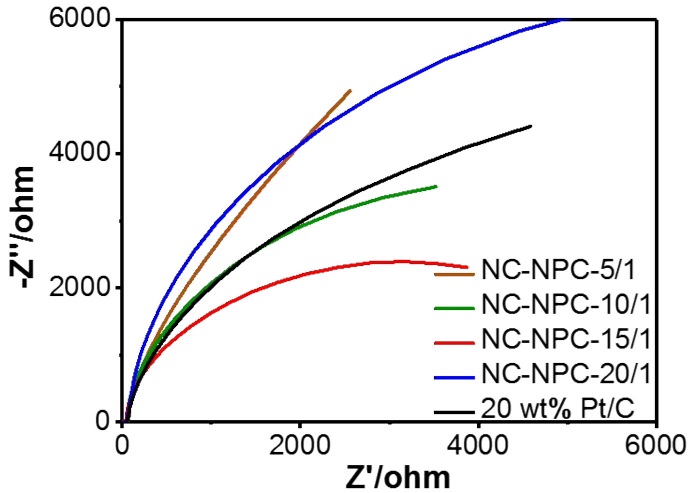


Fig. S15 Nyquist plots of NC-NPC-5/1, NC-NPC-10/1, NCN-PC-15/1, NC-NPC-20/1 and Pt/C, respectively.

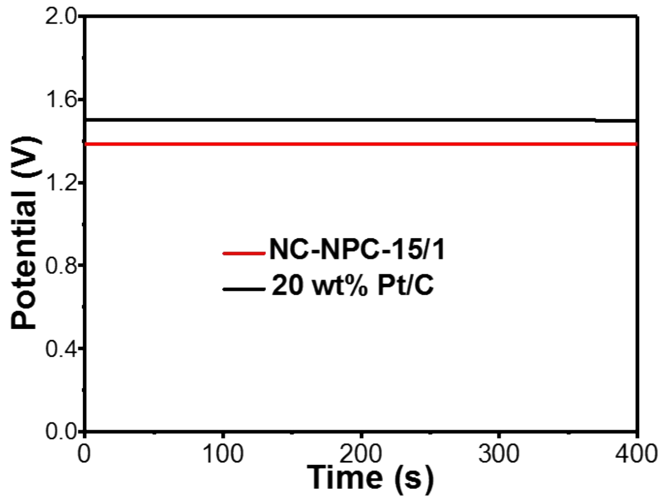


Fig. S16 The open-circle voltage of CNPC-15/1 and the commercial Pt/C based Zn–air battery.

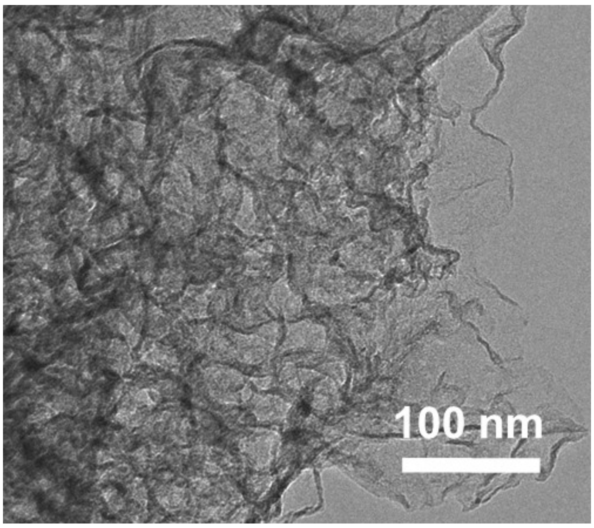


Fig. S17 The TEM images of the NC-NPC-15/1 after long time charge/discharge test of zinc–air battery cycling for 210 hours at 5 mA cm^{-2}.

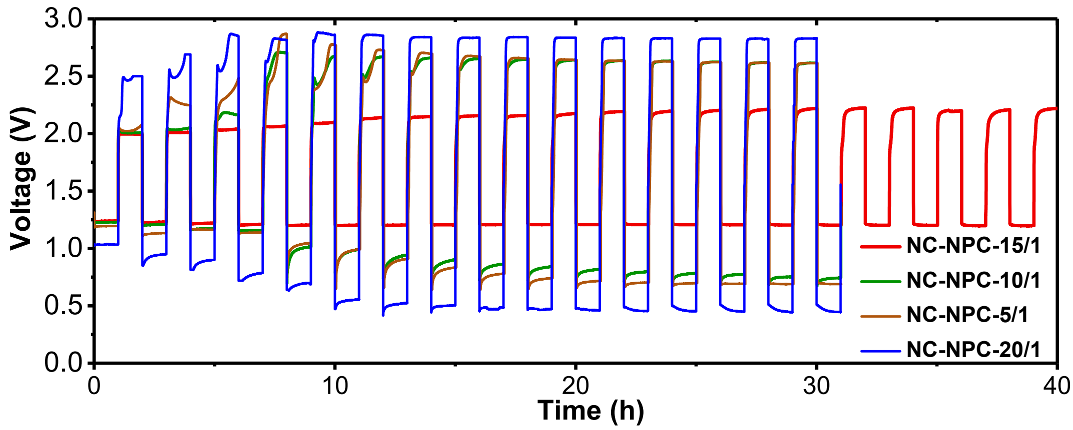


Fig. S18 Long-time charge/discharge test of zinc–air battery based on NC-NPC-5/1, NC-NPC-10/1, NC-NPC-15/1, NC-NPC-20/1 at 5 mA cm^{-2} with a cycle period of 60 min.

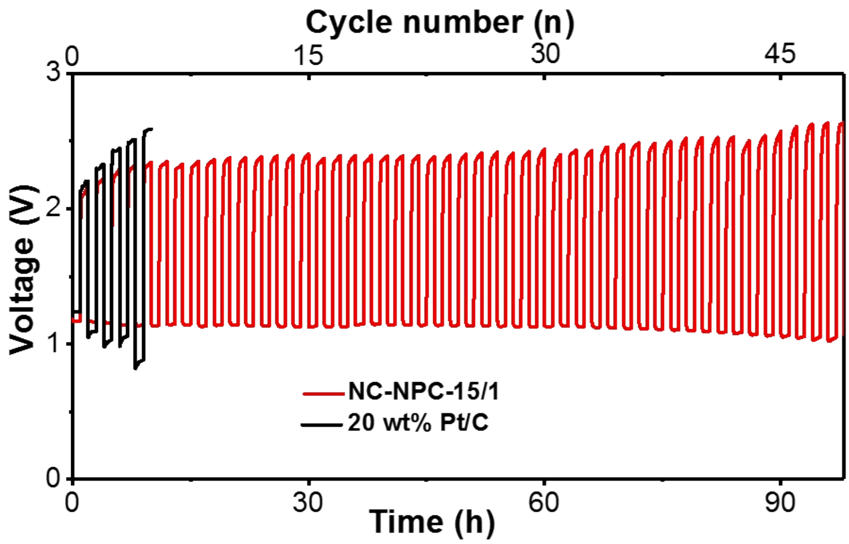


Fig. S19 Long time charging and discharging test of zinc–air battery based on CNPC-15/1 at 10 mA cm^{-2} with a cycle period of 2 h.

Table S1 The comparisons of carbon-based catalysts with different crumple densities.

Crumpled material	The number of crumple	The area (nm^2)	The density of crumple (μm^{-2})	Reference
NC-NPC-5/1	**15**	**40000**	**375**	**This work**
NC-NPC-10/1	**28**	**40000**	**700**	**This work**
NC-NPC-15/1	**25**	**10000**	**2500**	**This work**
Crumpled r-GO	6	40000	150	[1]
GO nanosheet	4	10000	400	[2]
Crumpled graphene	5	160000	31	[3]
Crumpled rGO ball	13	160000	81	[4]
Crumpled graphene	18	40000	450	[5]
Crumpled graphene	5	10000	500	[6]
Crumpled rGO	13	1000000	13	[7]
Crumpled graphene	14	250000	56	[8]
S,O-Crumpled graphene	27	40000	675	[9]
Crumpled N-$Ti_3C_2T_x$ sheet	7	40000	175	[10]
Crumpled carbon nanosheet	12	250000	48	[11]
Crumpled graphene	11	40000	275	[12]
Porous N-graphene foam	11	10000	1100	[13]
B,N-crumpled graphite layer	19	40000	475	[14]
Crumpled N-graphene sheet	47	250000	188	[15]
Edge rich graphene	9	10000	900	[16]
N-porous carbon sheet	38	40000	950	[17]
N-graphene mesh	8	10000	800	[18]

Table S2. The comparisons of ORR performances in 0.1 M KOH solution for various metal-free carbon based catalysts.

Catalyst	Oneset potential (V *vs.* RHE)	Half-wave potential (V *vs.* RHE)	n (RDE)	Reference
NC-NPC-15/1	**0.96**	**0.85**	**3.9**	**This work**
20 wt% Pt/C	**0.99**	**0.87**	**3.95**	**This work**
N-carbon nanotube	0.97	0.84	3.9	[19]
N,P-CGHNs	0.94	0.82	4.0	[20]
N,P-mesoporous carbon	0.94	0.85	4.0	[21]
N-graphene ribbon network	0.92	0.84	3.9	[22]
N-CNTs-HGF	1.08	0.85	3.9	[23]
S-CN/PC	0.90	0.75	4.0	[24]
N-hollow carbon spheres	0.93	0.84	3.9	[25]
N-carbon nanosheets	0.90	0.76	3.9	[17]
N-graphene mesh	0.89	0.77	3.8	[18]
N,S- graphene	0.87	0.61	3.2	[26]
N- porous carbon	0.92	0.85	3.8	[27]
B,N-graphene	0.86	0.68	3.8	[28]
S-graphene	0.88	0.66	3.1	[29]
N,P- ordered carbon	0.95	0.82	3.7	[30]
N,S- carbon sheets	0.95	0.83	3.9	[31]
N-graphene	0.91	0.83	3.9	[32]
N,S,O-mesoporous carbon	0.85	0.73	3.5	[33]
N,S,O-nanoporous carbon	0.96	0.74	3.9	[34]
N,S-carbon nanosheet	0.92	0.77	3.9	[35]
N-nanoporous carbon fiber	0.97	0.82	4.0	[36]
N,S-porous carbon	0.99	0.85	3.9	[37]

Table S3. The comparisons of the state-of-the-art carbon-based cathodes for Zn-air battery in alkaline environment.

Catalyst	Current density ($mA\ cm^{-2}$)	Stability	Reference
NC-NPC-15/1	**5**	**2 h/cycle for 105 cycles; 210 h**	**This work**
NPMC-1000	2	10 min/cycle for 600 cycles; 100 h	[21]
P,S-CNS	25	12 min/cycle for 500 cycles; 100 h	[38]
PCN-CNF	20	10 min/cycle for 50 cycles; 8.3 h	[39]
NCNF-1000	10	10 min/cycle for 500 cycles; 83 h	[36]
N-GRW	2	1 h/cycle for 160 cycles; 160 h	[22]
2DBN-800	20	10 min/cycle for 66 cycles; 11 h	[40]
1100-CNS	10	10 min/cycle for 300 cycles; 50 h	[37]
NP-HPCS	5	20 cycles	[41]
2D-PPCN	10	10 min/cycle for 1000 cycles; 166.7 h	[42]
S-C_2NA	10	2 h/cycle for 375 cycles; 750 h	[43]
Co-N-CNTS	2	6.67 min/cycle for 144 cycles; 16 h	[44]
$Fe_{0.5}Co_{0.5}$ oxide/NrGO	10	2 h/cycle for 60 cycles; 120 h	[45]
$Co_3FeS_{1.5}(OH)_6$	2	20 min/cycle for 108 cycles; 36 h	[46]
$CoSb_3$@NCL-30	10	30 min/cycle for 120 cycles; 60 h	[47]
$CuCo_2O_4$/N-CNT	20	10 min/cycle for 240 cycles; 40 h	[48]
Ni_3FeN	10	20 min/cycle for 310 cycles; 103.3 h	[49]
Fe_3Pt/Ni_3FeN	10	2 h/cycle for 240 cycles; 480 h	[50]
$NiO/Ni(OH)_2$	1	70 min/cycle for 70 cycles; 82 h	[51]

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