Supplemental Information

Light-weight 3D Co-N-doping hollow carbon spheres as efficient electrocatalyst

for zinc-air battery

Shengmei Chen^{a,b}, Junye Cheng^{a,b,d}, Longtao Ma^b, Shanke Zhou^c, Xiuwen Xu^b, Chunyi Zhi^b,

Wenjun Zhang ^{a,b}, Linjie Zhi ^{c,*}, J Antonio Zapien ^{a,b,*}

^a Center of Super-Diamond and Advanced Films (COSDAF) City University of Hong Kong, Kowloon,

Hong Kong 999077 and City University of Hong Kong, Shenzhen Research Institute, Shenzhen,

Guangdong, P. R. China

^b Department of Materials and Science Engineering, City University of Hong Kong, Kowloon, Hong

Kong 999077

^c CAS Center of Excellence for Nanoscience, Key Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology, Beijing 100190, P. R. China

^d Guangdong Provincial Key Laboratory of Micro/Nano Optomechatronics Engineering, College of

Mechatronics and Control Engineering, Shenzhen University, Shenzhen 518060, China

E-mail addresses: apjazs@cityu.edu.hk (J. A. Zapien), zhilj@nanoctr.cn (L.J. Zhi).



Fig. S1 (a) SEM image of 0.05-Co-NHCs; (b) SEM image of 0.15-Co-NHCs.



Fig. S2 High-resolution XPS N 1s (a, c) and Co 2p (b, d) of 0.05-Co-NHCs and 0.15-Co-NHCs.



Fig. S3 The A.C impedance plots of catalysts NHCs, 0.05-Co-NHCs, 0.1-Co-NHCs and 0.15-Co-NHCs.



Fig. S4 CV curves in the region of 0.1-0.2 V at scan rate from 2 to 10 mVs⁻¹ and corresponding liner fitting capacitive current vs. scan rates to estimate the C_{dl} : 7.01 mF cm⁻² for NHCs (a, b), 12.00 mF cm⁻² for 0.05-Co-NHCs (c, d), 22.28 mF cm⁻² for 0.1-Co-NHCs (e, f) and 14.22 mF cm⁻² for 0.15-Co-NHCs (g, h).



Fig. S5 (a, d, g, j) CV curves of different catalysts recorded at 100 mV s⁻¹ in N₂ and O₂ saturated 0.1 M KOH solution; (b, e, h, k) LSV curves of different catalysts at different rotation speeds; (c, f, i, l) K-L plots of different catalysts at different potentials with corresponding electron transfer number.



Fig. S6 (a, d, g, j) CV curves of different catalysts recorded at 100 mV s⁻¹ in N₂ and O₂ saturated 0.1 M KOH solution; (b, e, h, k) LSV curves of different catalysts at different rotation speeds; (c, f, i, l) K-L plots of different catalysts at different potentials with corresponding electron transfer number.



Fig. S7 (a) CV curves of commercial Pt-C catalyst recorded at 100 mV s⁻¹ in N₂ and O₂ saturated 0.1 M KOH solution; (b) LSV curves of commercial Pt-C catalyst at different rotation speeds; (c) K-L plots of commercial Pt-C catalyst at different potentials with corresponding electron transfer number.



Fig. S8 Digital image of assembled zinc-air battery using 0.1-Co-NHCs as catalyst to display open-circuit voltage and different color LED powered by two of the assembled zinc-air batteries in series.

| | | | % N | | | | | |
|-------------|-------|-------|------|---------|--------|-------|-------|-------|
| | % C | % 0 | % Co | N total | Pyri-N | Co-N | Qua-N | Oxi-N |
| NHCs | 91.23 | 4.07 | 0.00 | 4.68 | 24.59 | 0.00 | 73.79 | 1.62 |
| 0.05Co-NHCs | 85.77 | 12.30 | 0.13 | 1.69 | 8.07 | 16.57 | 61.02 | 14.34 |
| 0.1 Co-NHCs | 89.00 | 8.52 | 0.29 | 2.19 | 9.65 | 32.71 | 39.87 | 17.76 |
| 0.15Co-NHCs | 91.05 | 6.51 | 0.39 | 2.26 | 14.24 | 18.20 | 57.71 | 9.85 |

Table S1 Ratio analysis of the peaks in XPS spectrum in NHCs and Co based NHCs catalysts

Table S2 Comparison of the ORR performance between 0.1-Co-NHCs catalyst, commercial Pt-C and other reported catalysts in 0.1 M KOH electrolyte

| Electrocatalyst | Onset | Half-wave | Loading mass | Reference |
|----------------------|-----------|-------------|----------------|---------------------|
| | potential | potential | $(ug cm^{-2})$ | |
| | (V vs. | (V vs. RHE) | | |
| | RHE) | | | |
| 0.1-Co-NHCs | 0.99 | 0.81 | 217 | This work |
| Pt-C | 1.02 | 0.83 | 140 | This work |
| Fe-N/C-800 | 0.923 | 0.809 | 100 | J. Am. Chem. Soc., |
| | | | | 2014, 136, 11027. |
| N-doped carbon cubes | 0.92 | 0.80 | 400 | Nanoscale, |
| | | | | 2017, 9, 1059. |
| CoO@Co/N-rGO | 0.95 | 0.81 | - | J. Mater. Chem. A, |
| | | | | 2017,5,5865 |
| N, S-doped | 0.92 | 0.77 | 200 | Nano Energy, |
| Graphene sheets | | | | 2016, 19, 373 |
| NCNT/CoO-NiO-NiCo | 0.97 | 0.83 | 210 | Angew.Chem. Int.Ed. |
| | | | | 2015, 54,9654 |
| Fe-N-Doped Carbon | 0.94 | 0.83 | 100 | ACS Nano, |
| Capsules | | | | 2016, 10,5922 |
| CF-NG-Co | 0.97 | 0.85 | 140 | J. Mater. Chem. A, |
| | | | | 2018,6,489 |
| N-CG–CoO | 0.90 | 0.81 | 700 | Energ Environ Sci |
| | | | | 2014, 7, 609 |

Table S3 Comparison of the zin - air batteries performance between using 0.1-Co-NHCs catalyst, commercial Pt-C and other reported catalysts

| Electrocatalyst | Loading mass (g·cm ⁻²) | Power density (mW·cm ⁻²) | Round-trip Efficiency | Stability | Reference |
|---|--|--|--------------------------|--|---|
| 0.1-Co-NHCs | 1 | 239.8 | 60.6% | 11 min per cycle for 300 cycles; voltage gap increased ~0.1V | This work |
| Pt-C | 1 | 156 | 59.8% | 11 min per cycle for 300 cycles; voltage gap increased ~0.4V | This work |
| N-doped graphene | 0.5 | 65 | 60% | 60 min per cycle for 150 cycles; voltage gap increased ~0.2 V | Sci. Adv. 2016,2:e1501122. |
| FeCo-N-doped CNT | 2 | 89.3 | 32.3% | 10 min per cycle for 240 cycles; voltage gap increased ~0.03 V | Adv. Energy Mater. 2017, 1602420. |
| Co ₃ O ₄ -NCNT/SS | - | 160.7 | 61% | 20 min per cycle for 1500 cycles; voltage gap increased ~0.16 V | Adv. Mater. 2016, 28, 6421. |
| N, P-doped mesoporous carbon | 0.5 | 55 | 59% | 10 min per cycle for 180 cycles; voltage gap increased ~0.7 V | Nature Nanotech. 2015, 10, 444. |
| Atomically dispersed Fe-N | 1.25 | 102.7 | 57% | After 100cycles; voltage gap increased ~0.2 V | Angew. Chem. Int. Ed. 2017, 56, 610. |
| Co ₃ O ₄ /NPGC | 0.9 | - | 58.9% | After 85 hours; voltage gap increased ~0.05V | Angew.Chem .Int. Ed. 2016, 55, 4977 |
| Co ₄ N/CNW/CC | - | 174 | 61% | 20 min per cycle for 408 cycles; voltage gap increased ~0.01 V | J. Am. Chem. Soc. 2016, 138, 10226. |
| N/S hierarchically porous carbon | 1 | 151 | 61% | 11 min per cycle for 300 cycles; voltage gap increased ~0.085V | Energy Environ. Sci., 2017, 10, 742 |