Supplementary Information

In situ solution plasma synthesis of nitrogen-doped carbon nanoparticles as metal-free electrocatalysts for the oxygen reduction reaction

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Fig. S1 Particle size distribution of NCNP-70 deduced from bright-field TEM image.



Fig. S2 XPS survey spectra of CNP, NCNP-30, NCNP-50, and NCNP-70. The vertical dashed line indicates the position of N 1s peak.



Fig. S3 High-resolution XPS spectra of all catalysts: (a) C 1s, (b) N 1s and (c) O 1s.

| Sample | XPS N1s spectra | | | | | |
|---------|-------------------------------|-------------------------------|-------------------------------|--------------------------------------|--|--|
| | Pyridinic-N (N _P) | Pyrrolic-N (N _{PR}) | Graphitic-N (N _G) | Pyridinic N-oxide (N _{OX}) | | |
| NCNP-30 | 41.1% | 10.4% | 40.3% | 8.2% | | |
| NCNP-50 | 43.7% | 8.5% | 42.3% | 5.5% | | |
| NCNP-70 | 38.9% | 8.7% | 46.6% | 5.8% | | |

Table S1 Relative amount of different nitrogen bonding configurations obtained from the qualitative analysis of high-resolution XPS N 1s spectra of NCNP-30, NCNP-50, and NCNP-70 in Fig. S3b.



Fig. S4 CV curves of the ORR for (a) CNP, (b) NCNP-30, (c) NCNP-50, and (d) NCNP-70 modified on GC electrodes in a 0.1 M KOH solution saturated with N₂ (black dashed line) and O₂ (blue solid line).



Fig. S5 LSV curves of the ORR for all catalysts in an O_2 -saturated 0.1 M KOH solution at a scan rate of 10 mV s⁻¹ and different rotation speeds from 225 to 2500 rpm: (a) CNP, (b) NCNP-30, (c) NCNP-50, and (d) NCNP-70.



Fig. S6 K–L plots at potentials from –0.4 to –0.6 V on the basis of LSV data in Fig. S5 of (a) CNP, (b) NCNP-30, (c) NCNP-50, and (d) NCNP-70.



Fig. S7 Electron transfer number (*n*) obtained from the K–L plots (Fig. S6) as a function of potential from -0.4 to -0.6 V: (a) CNP, (b) NCNP-30, (c) NCNP-50, and (d) NCNP-70.

| _ | E _{onset} (V vs. Ag/AgCl) | $J_{\rm K}$ (mA cm ⁻²) | n _{K-L} | <i>n</i> _{RRDE} | HO ₂ ⁻ yield (%) |
|---------|---------------------------------------|------------------------------------|------------------|--------------------------|---|
| GC | -0.31 | 7.87 | 2.38 | 2.34 | 83.0 |
| 20%Pt/C | -0.09 | 19.6 | 4.05 | 3.85 | 7.65 |
| CNP | -0.22 | 10.8 | 2.42 | 2.40 | 81.4 |
| NCNP-30 | -0.21 | 13.9 | 2.56 | 2.62 | 68.6 |
| NCNP-50 | -0.20 | 14.1 | 2.65 | 2.71 | 64.9 |
| NCNP-70 | -0.17 | 14.5 | 2.80 | 2.86 | 59.5 |

Table S2 Electrochemical results of bare GC electrode, 20%Pt/C, CNP, NCNP-30, NCNP-50, and NCNP-70 obtained at a potential of -0.4 V. The onset potential (E_{onset}) is determined from LSV-RRDE curve.



Fig. S8 Comparative CV curves with (solid line) and without the introduction of 3 M methanol (dashed line) of NCNP-70 (b) and 20 wt% Pt/C.