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Supplementary Information

Simple one-step synthesis of fluorine-doped carbon nanoparticles as potential alternative metal-free electrocatalysts for oxygen reduction reaction

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Fig. S1 SEM/EDS elemental mapping images of FCNP-4 showing the distribution of (b) carbon, (c) oxygen, and (d) fluorine.



Fig. S2 High-resolution XPS C 1s spectra of CNP and FCNPs. The enlarged view in the inset shows the evolution of the peak of semi-ionic C–F bond.



Fig. S3 High-resolution XPS O 1s spectra with deconvolution and peak assignments of CNP and FCNPs. The spectra can be resolved into two components, including C=O/O-C=O (O_I: 532.4 \pm 0.1 eV), C-O-C/COOH/C-OH (O_{II}: 533.5 \pm 0.2 eV).



Fig. S4 CV curves of all samples on GC electrodes in 0.1 M KOH solution saturated with N_2 (dashed line) and O_2 (solid line) at a scan rate of 50 mV s⁻¹: (a) CNP, (b) FCNP-1, (c) FCNP-2, (d) FCNP-3, and (e) FCNP-4.



Fig. S5 LSV curves of all samples on a GC-RDE in an O_2 -saturated 0.1 M KOH solution at various rotation speeds from 225 to 2500 rpm (10 mV s⁻¹): (a) CNP, (b) FCNP-1, (c) FCNP-2, (d) FCNP-3, and (e) FCNP-4.



Fig. S6 The K–L plots at the potentials between –1.0 and –0.35 V derived from the LSV curves in Fig. S5: (a) CNP, (b) FCNP-1, (c) FCNP-2, (d) FCNP-3, and (e) FCNP-4.



Fig. S7 Electron transfer number (*n*) of all samples calculated from the K–L plots at the potentials from -1.0 to -0.35 V.



Fig. S8 Kinetic-limiting current density (J_K) of all samples calculated from the K–L plots in the mixed kinetic-diffusion control region (from -0.45 to -0.35 V).

Rotating-ring disk electrode (RRDE) measurement

A certain amount of 5 µl of catalyst ink was applied onto a rotating ring-disk electrode (RRDE), which consists of a glassy carbon disk (disk diameter: 4 mm, A = 0.126 cm²) surrounded by a Pt ring (inner/outer-ring diameter: 5.0/7.0 mm). The catalyst loading is approximately 0.2 mg_{cat} cm⁻².

To investigate the ORR mechanisms and kinetics on the catalysts, the LSV measurements were performed on a RRDE at a rotation speed of 1600 rpm with a scan rate of 10 mV s⁻¹. The corresponding ring current was simultaneously measured with a Pt ring electrode by applying a constant potential of 0.5 V. The electron transfer number (*n*) per O₂ molecule involved in the ORR and the percentage of O₂ molecules that are reduced to HO₂⁻ can be calculated based on the ring and disk currents (Fig. S9) using the following equations:

$$n = 4 \times \frac{I_D}{I_D + I_R / N} \tag{S1}$$

$$HO_{2}^{-}\% = 200 \times \frac{I_{R} / N}{I_{D} + I_{R} / N}$$
(S2)

where I_D and I_R are the disk and ring currents, respectively. *N* is the collection efficiency. The *N* value in our system was calibrated in 0.1 M KOH with a 10 mM K₃Fe(CN)₆ electrolyte, which was estimated to be approximately 0.43.



Fig. S9 LSV-RRDE curves of the ORR for all samples in an O_2 -saturated 0.1 M KOH at a rotation speed of 1600 rpm (10 mV s⁻¹).



Fig. S10 (a) The calculated electron number transfer (*n*) and (b) HO_2^- yields for all samples at the potentials from -0.3 to -1.0 V.