# **Supporting information**

## Nitrogen and Fluorine-codoped Porous Carbons as Efficient Metal-free

### Electrocatalysts for Oxygen Reduction Reaction in Fuel Cells

Yanlong Lv<sup>1</sup>, Liu Yang<sup>1</sup> and Dapeng Cao<sup>\*,1, 2</sup>

<sup>1</sup> State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology,

Beijing 100029, People's Republic of China

<sup>2</sup> Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of

Chemical Technology, Beijing 100029, People's Republic of China

\*Email: caodp@mail.buct.edu.cn

### S1. Material Characterization

Scanning electron microscopic (SEM) images were obtained on a S7800 SEM instrument by dispersing the sample onto a silicon sheet and drying naturally. Transmission electronmicroscopic (TEM) images were recorded on a transmission electron microscope (TEM, Philips, Tecnai, F30) equipped with an energy dispersive spectrometer (EDS) analyzer. Fourier-transform infrared spectroscopy (FT-IR) spectroscopy was performed on a Nicolet 8700 instrument with the wave range of 4000-400 cm<sup>-1</sup>. Powder X-ray diffraction (PXRD) measurements were performed with D/MAX 2000 X-ray diffractometer with CuK $\alpha$  line ( $\lambda$ =1.54178 Å) as the incident beam. Raman spectra were collected by the LabRAM Aramis Raman Spectrometer (Horiba Jobin Yvon) using 514 nm laser as the excitation source. N<sub>2</sub> adsorption/desorption isotherms at 77 K were measured by a Micromeritics ASAP 2020. Pore size distribution data were calculated from the N<sub>2</sub> sorption isotherms based on the DFT model in the Micromeritics ASAP 2020 software package. X-ray photoelectron spectroscopy (XPS) analysis was performed on ThermoVG ESCALAB 250 equipped with an A1 K $\alpha$  X-ray source.

### **S2.** Electrochemical measurements

To evaluate ORR activity, all the electrochemical tests were performed in a standard three-electrode cell with a 1 cm<sup>2</sup> Pt net as the counter electrode and saturated calomel electrode as the reference electrode controlled by a CHI 760e electrochemistry workstation. The electrolyte was 0.1 M KOH, which was purged with high purity oxygen gas for at least 30 min before each measurement began. A flow of  $O_2$  was maintained during the recording of CVs. The CV measurement was also performed in a nitrogen

saturated electrolyte for comparison. The working electrode was cycle at least twenty times before formal recording. And the potential range is between 0 and 1.0 V vs. RHE. RDE and RRDE measurements were conducted with different rotating speeds from 400 to 2025 rpm by a RRDE-3A instruments device.

Koutecky-Levich plots were analyzed at various electrode potentials. The number of electrons transferred (n) were calculated by the slopes of the linear fitting on the basis of the following Koutecky-Levich equations

$$\frac{1}{J} = \frac{1}{J_l} + \frac{1}{J_k} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_k}$$
(e1)

$$J_k = nF\kappa C_0 \tag{e2}$$

$$B = 0.2nFC_0(D_0)^{\frac{2}{3}} v^{\frac{-1}{6}}$$
(e3)

where J is the measured current density,  $J_k$  and  $J_1$  are the kinetic- and diffusion-limiting current densities,  $\omega$  is the angular velocity of the disk ( $\omega$ =2 $\pi$ N, N is the linear rotation speed), n is the overall number of electrons transferred in oxygen reduction reaction, F is the Faraday constant (F=96485 C mol<sup>-1</sup>),  $\kappa$  is the electron-transfer rate constant, C<sub>0</sub> is the bulk concentration of O<sub>2</sub>, and  $\upsilon$  is the kinematic viscosity of the electrolyte. In 0.1 M KOH, the values can be determined: C<sub>0</sub>=  $1.2 \times 10^{-3}$  mol L<sup>-1</sup>; D<sub>0</sub>= $1.9 \times 10^{-5}$  cm s<sup>-1</sup>; v=0.1 m<sup>2</sup> s<sup>-1</sup>. The electron transfer number per O<sub>2</sub> and %HO<sub>2</sub><sup>-</sup> were calculated from the RRDE

The electron transfer number per  $O_2$  and  ${}^{\circ}_{0}HO_2$  were calculated from the RRDE measurement through the flowing equations

$$n = 4I_d / (I_d + I_r / N) \tag{e4}$$

$$\% HO_2^- = 200 \times \frac{I_r/N}{I_d + I_r/N}$$
 (e5)

where  $I_d$  is the disk current,  $I_r$  is the ring current and N is the current collection efficiency of Pt ring (N=0.42).



Figure S1. The pore size distribution of five as-synthesized samples obtained from non-local density functional theory. (a) N-Carbon-1000; (b) N,F-Carbon-1000; (c) N, F-Carbon-700; (d) N, F-Carbon-800; (e) N, F-Carbon-900.



Figure S2 Rotating-disk voltammograms of four N, F-Carbon-1000 in  $O_2$ -saturated 0.1 M HClO<sub>4</sub> with a sweep rate of 5 mV s<sup>-1</sup> at the rotating rate of 1600 rpm.