Supplementary data of

# Comparative study of undoped, boron-doped, and boron/fluorine dual-doped carbon nanoparticles via solution plasma as catalysts for oxygen reduction reaction

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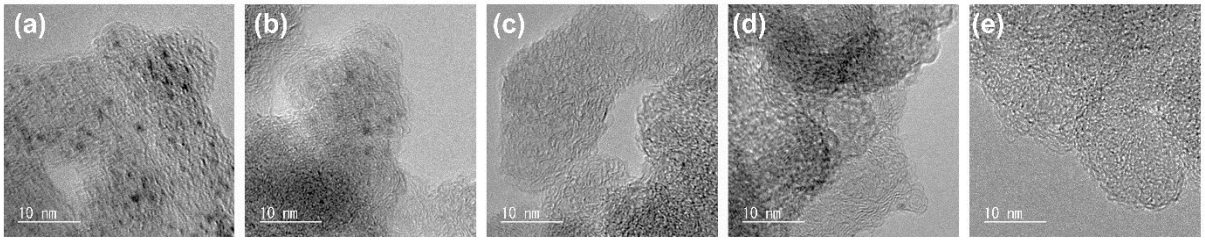


**Fig. S1** TEM images of the obtained products from (a) toluene, and toluene with addition of (b) TPBO, (c) TFPB, (d) TDFPB and (e) TTFPB via SP.

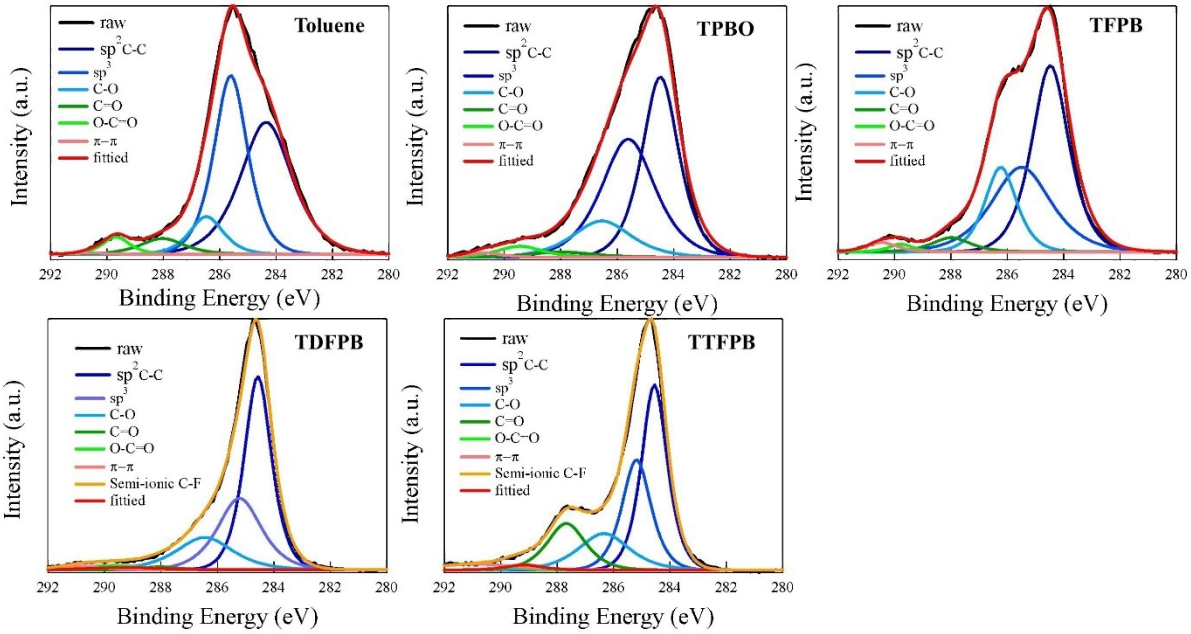


**Fig. S2** High-resolution XPS C 1s spectra of the obtained products from (a) toluene, and toluene with addition of (b) TPBO, (c) TFPB, (d) TDFPB and (e) TTFPB via SP.

The in-plane crystallite size, $L_a$, can be determined by using the Tuinstra–Koenig relation as following:

$$L_a = C\lambda^4(I_D/I_G)^{-1} \quad \text{(S1)}$$

where C is a constant ($2.4 \times 10^{-10}$ nm$^{-3}$) and λ is the Raman excitation wavelength (532.1 nm).

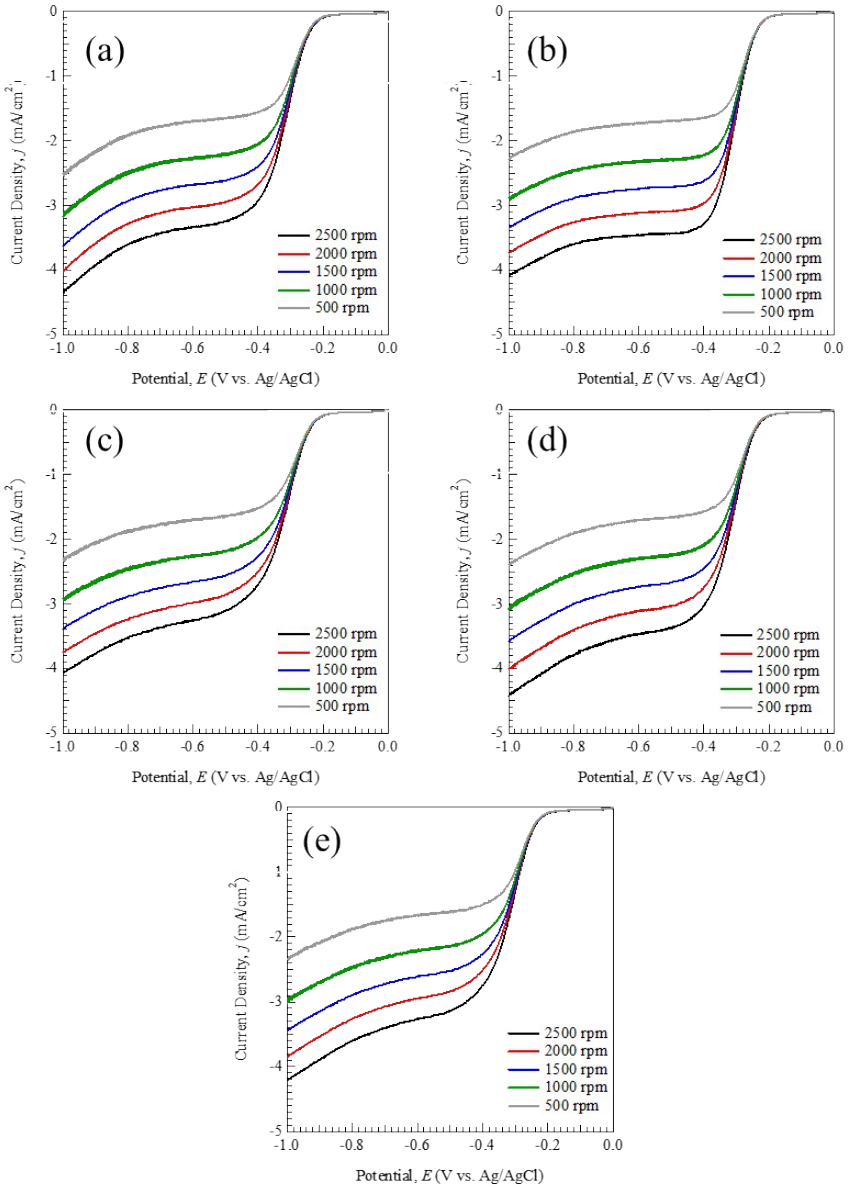


**Fig. S3** LSV measurement of the obtained products from (a) toluene, and toluene with addition of (b) TPBO, (c) TFPB, (d) TDFPB and (e) TTFPB via SP at on RRDE in an $O_2$-saturated 0.1 M KOH solution at a scan rate of 10 mV s$^{-1}$ and various rotational speeds.

Two different major pathways of ORR:

Four-electron pathway: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (S2)

Two-electron pathway: $O_2 + H_2O + 2e^- \rightarrow OH + HO_2^-$ (S3)

$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$ (S4)

Rotating ring disk (RDE) measurement can be used to verify the ORR pathway. A series of polarization curves was recorded at various rotation speeds (i.e., 500, 1000, 1500, 2000 and 2500 rpm), as shown in Figure S2. The result obviously showed that the current density in the diffusion-controlled region increases as increasing rotation speed, which referred to faster oxygen diffusion through the electrode surface. On the basis of the polarization curves recorded at various rotation speeds, the electron transfer number ($n$) per $O_2$ molecule involved in the ORR process can be determined by the Koutecky-Levich (K-L) equation given as below:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_K} + \frac{1}{B\omega^{1/2}} \quad \text{(S5)}$$

$$B = 0.62nFv^{-1/6}C_{O_2}D_{O_2}^{2/3} \quad \text{(S6)}$$

where $J$ is the measured current density, $J_K$ is the kinetic-limiting current density, $J_L$ is the diffusionlimiting current density, $\omega$ is the angular velocity of the disk in rad $s^{-1}$ ($\omega = 2\pi N/60$, N = the RDE rotation rate in rpm), $F$ is the Faraday constant (96485 C $mol^{-1}$), $D_{O_2}$ is the diffusion coefficient of $O_2$ in the electrolyte ($1.90 \times 10^{-5}$ $cm^2$ $s^{-1}$), $v$ is the kinematic viscosity of the electrolyte (0.01 $cm^2$ $s^{-1}$), and $C_{O_2}$ is the bulk concentration of $O_2$ in the electrolyte ($1.20 \times 10^{-6}$ mol $cm^{-3}$). The constant 0.62 is adopted when the rotation speed is expressed in radians per second (rad $s^{-1}$). The K–L plots of $J^{-1}$ versus $\omega^{-1/2}$ of all samples show a good linearity in the investigated potentials ranging from –1.0 and –0.3 V (Fig. S4). The parallel characteristics of linear fitting lines are observed in the potentials between –0.5 and –0.7 V, indicating a first-order ORR kinetic with respect to oxygen. The $n$ values calculated from the slope of the K–L plots are in the range between 2.00 and 2.70 with no obvious change with increasing fluorine doping content over the potential range between –1.0 and –0.3 V (Fig. S5).

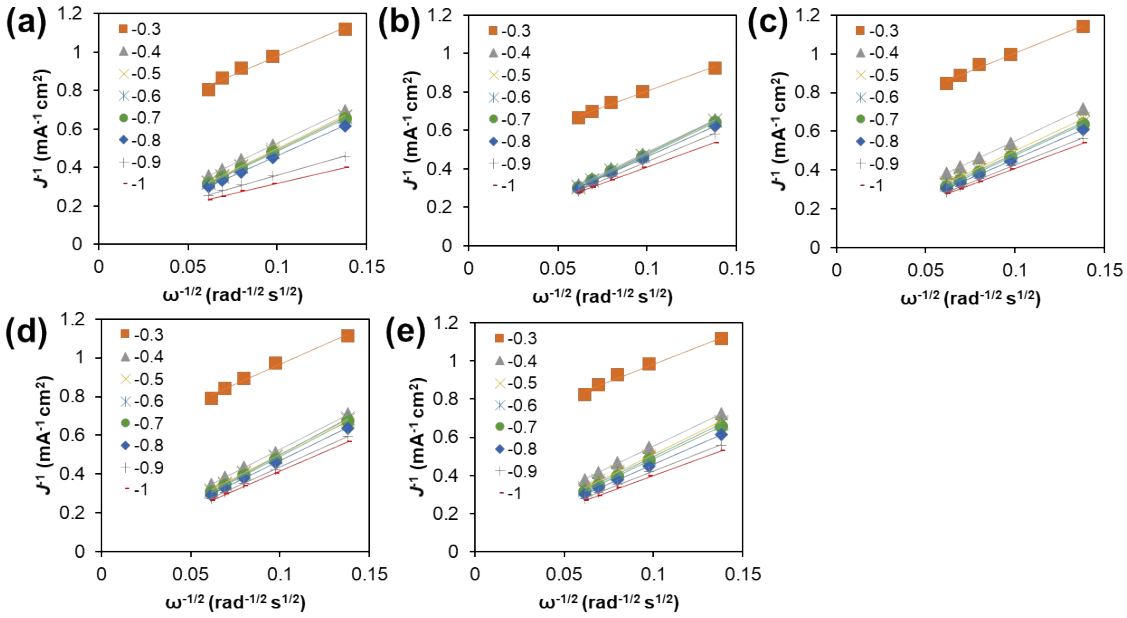


**Fig. S4** K–L plots of $J^{-1}$ versus $\omega^{-1/2}$ of the obtained products from (a) toluene, and toluene with addition of (b) TPBO, (c) TFPB, (d) TDFPB and (e) TTFPB via SP**.**

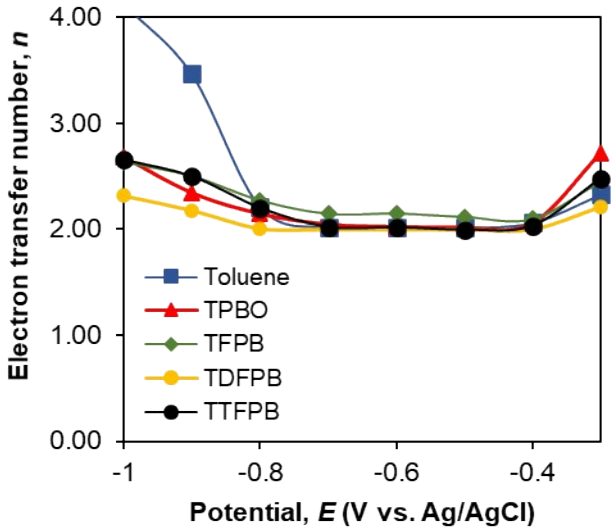


**Fig. S5** Electron transfer number ($n$) of all samples calculated from the K–L plots over the potential range between –1.0 and –0.3 V.

Equations for determining the overall electron transfer numbers and $HO_2^-$ yields related to the ORR have to be estimated on the basis of the disk and ring current:

$$\text{Electron transfer numbers, } n = 4 \times \frac{I_D}{I_D + I_R/N} \quad \text{(S7)}$$

$$HO_2^- \text{ yield} = 200 \times \frac{I_R/N}{I_D + I_R/N} \quad \text{(S8)}$$

where $I_D$ and $I_R$ are the disk and ring currents, respectively. $N$ is the collection efficiency of the ring electrode (0.43).