Electronic Supporting information

Fe/N co-doped graphitic carbon bulb for high-performance oxygen reduction reaction

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I. Experimental Section

Synthesis of Fe/N-gCB

In a typical synthesis of Fe/N-gCB, 1 ml of 1 M $FeCl_3$ solution was added drop by drop to a 10 ml of 0.05 M $K_4Fe(CN)_6$ solution at room temperature with stirring. The sediment (PB) was filtered, washed and dried at 50 °C overnight in vacuum. The PB was then heated in a tube furnace from room temperature to 550 °C with temperature ramping of 3 °C per minute, kept for 3 hours and cooled to room, under N_2 protection. The PPB was washed with 20 ml of 0.1 M HCl, filtered and washed with water and dried, resulting the Fe/N-gCB.

Synthesis of e-rGO, N-rGO and $Fe(OH)_x$/N-rGO

Graphite flake (3 g) was mixed with concentrated H_2SO_4 (12 ml), $K_2S_2O_8$ (2.5 g), and P_2O_5 (2.5 g). The mixture was kept at 90 °C for 6 h, then cooled to room temperature and diluted with 0.5 L of DI water. The suspension was filtered and washed with DI water. The solid was dried in vacuum at 50 °C overnight. The pretreated graphite was put into cold (0 °C) concentrated H_2SO_4 (120 mL). Then, $KMnO_4$ (15 g) was added gradually under stirring and the temperature of the mixture was kept to be below 20 °C by ice cooling. The mixture was stirred at 40 °C for 3 h, and then diluted with DI water (250 mL) using ice bath cooling.

It was then stirred for 2 h, and then additional 0.7 L of DI water was added. 20 mL of 30% H_2O_2 was added to the mixture. It was washed with 1:10 HCl aqueous solution (1 L). The resulting graphite oxide was diluted to in DI water. Exfoliation was carried out by sonicating graphite oxide dispersion under ambient condition for 30 min, followed with centrifuging at 3000 rpm for 30 min to eliminate unexfoliated graphite.

To prepare e-rGO on electrodes, 50 µl 0.1 % GO solution was dipped on the disk of RRDE and dried under ambient conditon. The electrode was then used as the working electrode in the electrochemical setup described below. Cyclic voltammetry (CV) was applied to the working electrode between 1.2 V and -0.2 V at 100 mV s^{-1} until steady CV curve was reached. During the CV, the GO was reduced to e-rGO.

To synthesize N-rGO, 5 ml of 25% NH_3 aqueous solution was added into 65 ml 0.1% GO solution. The solution was stirred at 90 °C for 12 h. After reduction, the N-rGO was filtered and washed with water and dispersed in water by supersonication.

To prepare Fe(OH)x/N-rGO, 10 µl of 0.1 M $FeCl_3$ was added to 10 ml of 0.02 % N-rGO suspension under sonication. Then 100 µl of 0.1 M NaOH was added. The products were centrifuged and washed with water and re-dispersed

Synthesis of N-MCN

In a typical synthesis N-MCN, a solution was prepared by mixing 80 mL ethanol and 200 mL of distilled water. Subsequently, 1 g F127, 1.3 g CTAB, and 2 g cysteine were added in the mixed solution under continuous stirring. Then, 2 g 3-aminophenol was added and stirred until a complete dissolution. Next, 2.8 mL of 37 wt% formaldehyde was dropped in and kept stirring for another 24 h at 25 °C. Finally, the mixture was transferred to autoclave and kept at 100 °C for another 24 h. The resulting resin was obtained by washing with water and ethanol for 3 times. In order to obtain N-MCN, The resin were carbonized under N_2 flow in the tube furnace. It were heated at rate of 1°C/min up to 350 °C, kept for 2 h, heated at 1 °C /min up to 700 °C and kept for 4 h.

Characterization

The thermogravimetric analysis (TGA) was measured with SETARAM ABSYSTM TGA. Transmission electron microscopy (TEM) images were taken with Tecnai F20. X-ray diffraction was taken by Rigaku Miniflex 600 with Cu Kα line. X-ray photoelectron spectroscopy (XPS) was taken by KRATOS Axis Ultra DLD with Al Kα line. Raman spectroscopy was taken with HORIBA LabRAM HR Evolution with 532 nm laser.

Electrochemical measurement

2 mg Fe/N-gCB was dispersed in 2 ml of 0.2 % nafion aqueous solution by supersonication. 50 µl of the catalyst ink was dipped onto the glassy carbon working electrode (5.61 mm in diameter) of a rotating ring-disk electrode (RRDE) and dried under ambient condition. The final catalyst loading on RRDE are about 0.2 mg cm^{-2}. When testing Pt/C, the loading is 0.2 mg cm^{-2}. The electrode was then used as the working electrode in a 3-electrode electrochemistry system where a Ag/AgCl (4 M KCl) electrode and a Pt wire were used as the reference electrode and counter electrode respectively. O_2 saturated 0.1 M KOH aqueous solution and 0.05 M H_2SO_4 aqueous solution were used as alkaline and acid electrolytes respectively. CV was applied to the working electrode between 0 V and 1.2 V (vs RHE, hereinafter the same) at 100 mV s^{-1} until steady CV curve was reached. When testing stability, the potential is set to 0.7 V for basic electrolyte and 0.3 V for acidic electrolyte, with O_2 inlet of 5 SCCM (standard cubic centimetres per minute).

II. Supporting Figures

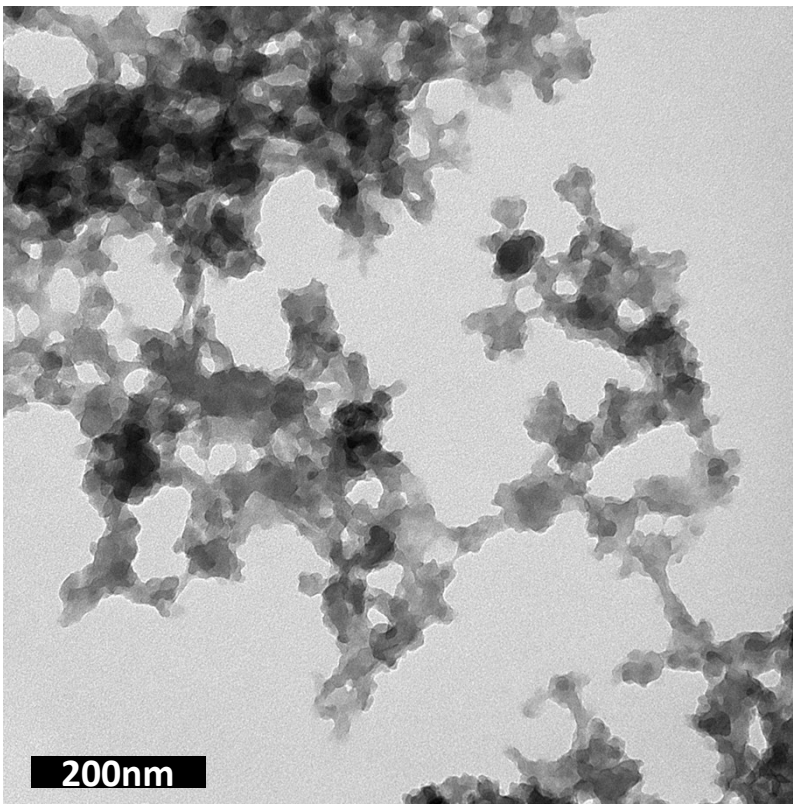

Figure S1. TEM image of PB.

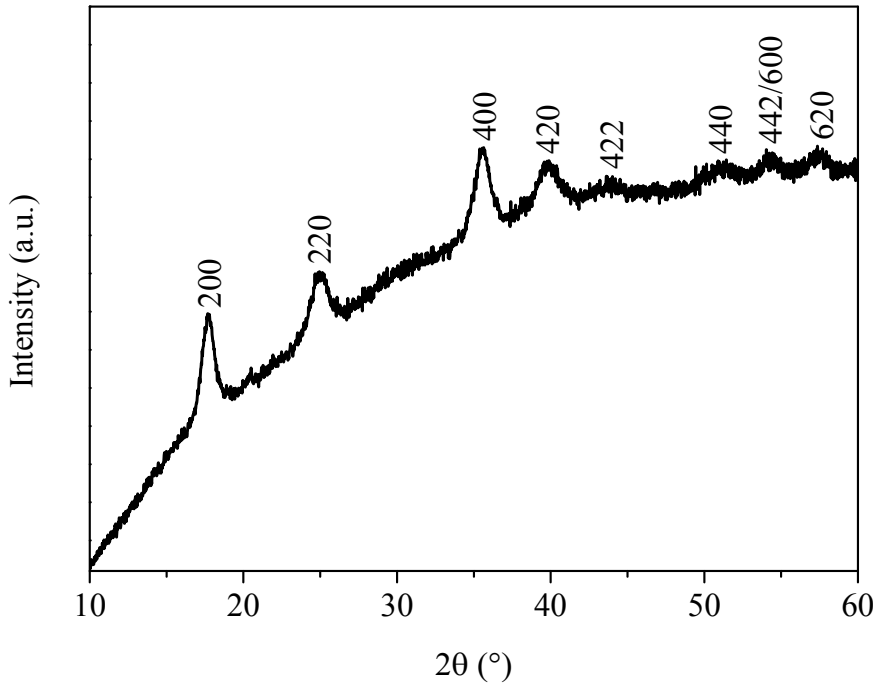

Figure S2. XRD pattern of PB.

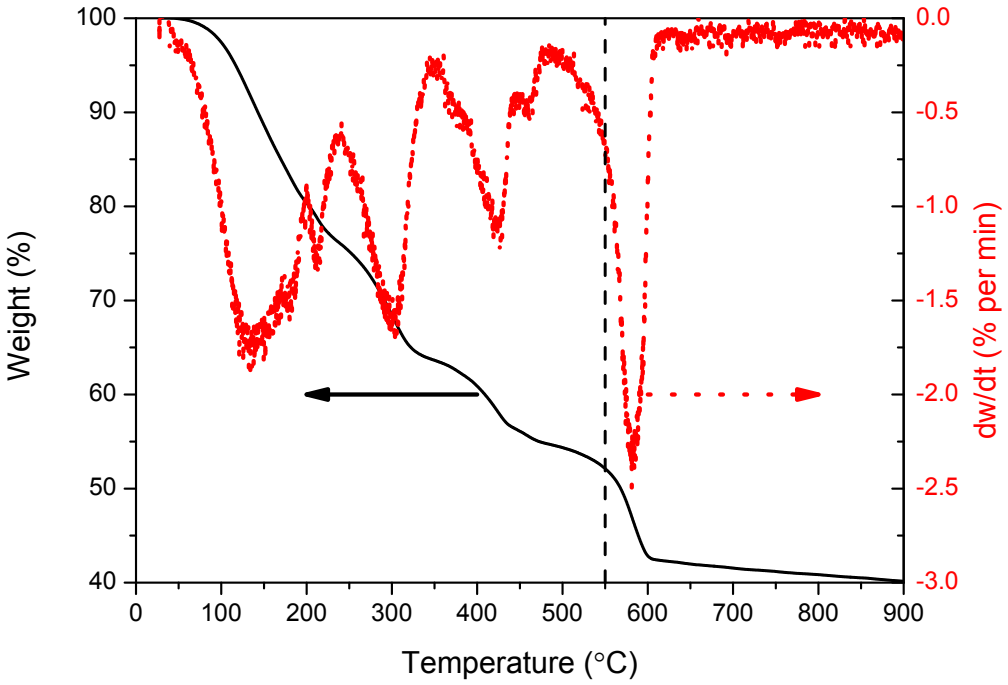

Figure S3. TGA of Pyrolysis of PB in N_2.

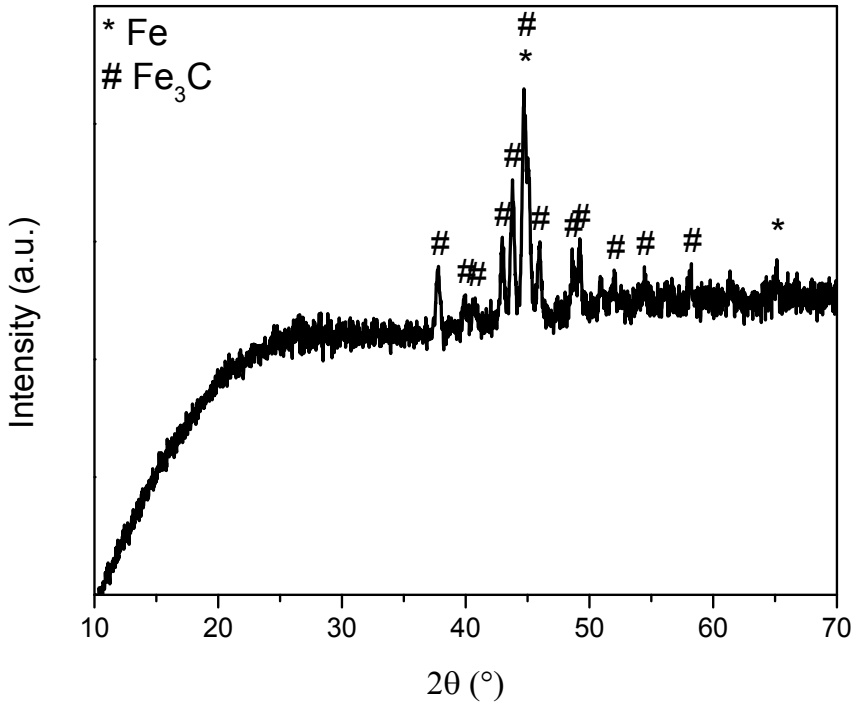

Figure S4. XRD of PPB at 900 °C.

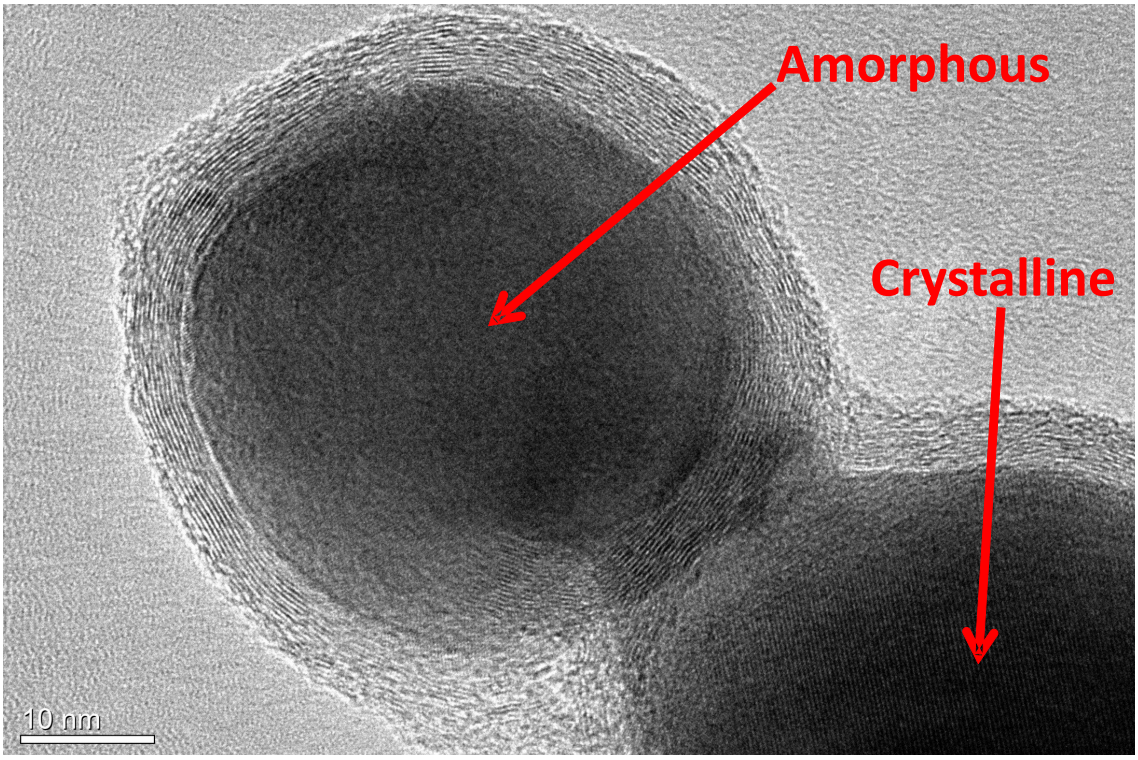

Figure S5. TEM image of PPB.

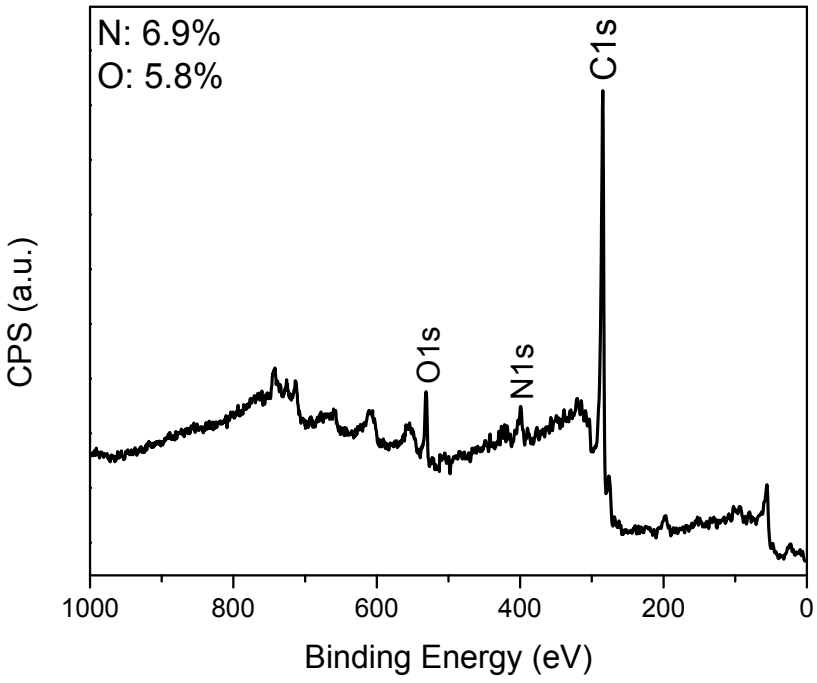

Figure S6. XPS of acid leached PPB from 600 °C.

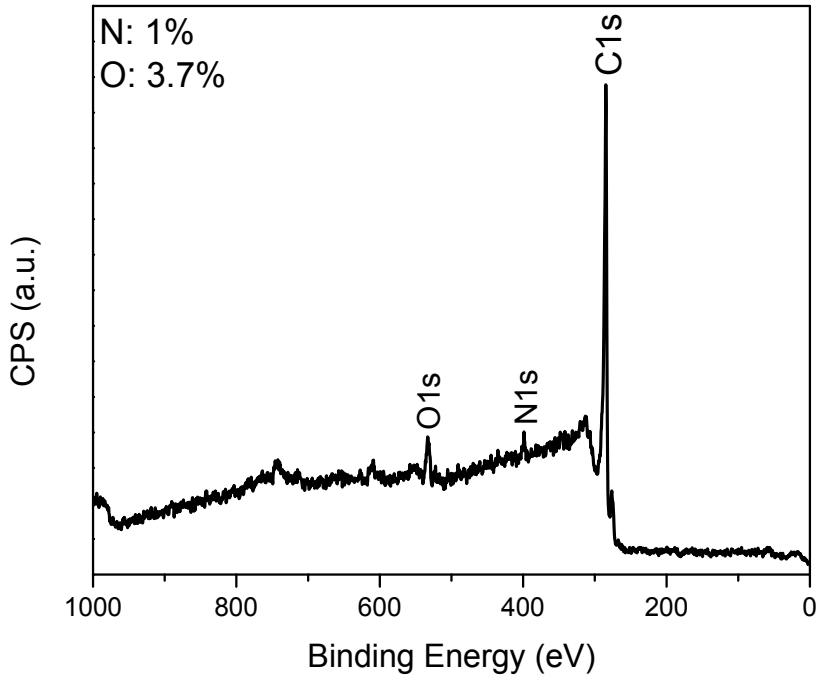

Figure S7. XPS of acid leached PPB from 700 °C.

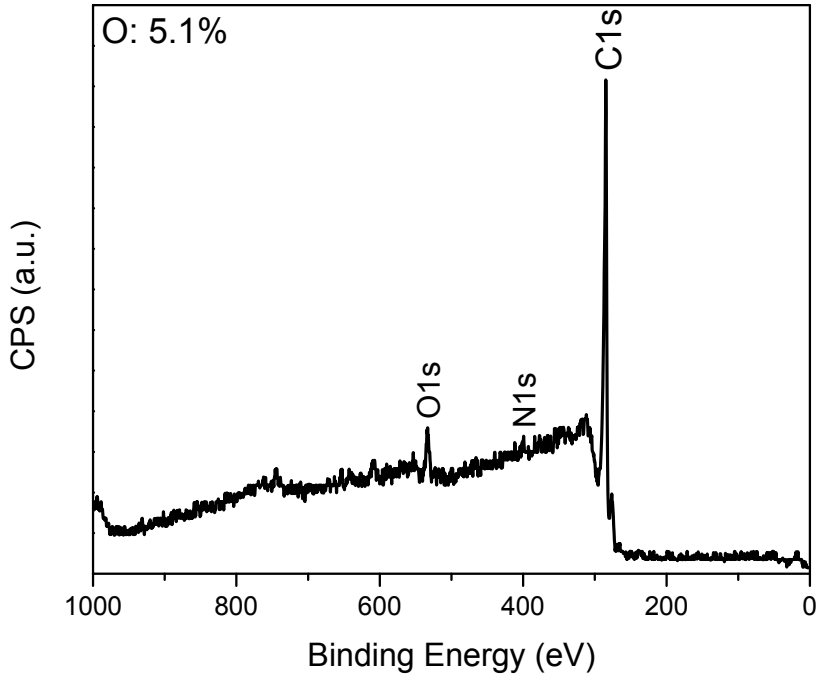

Figure S8. XPS of acid leached PPB from 800 °C.

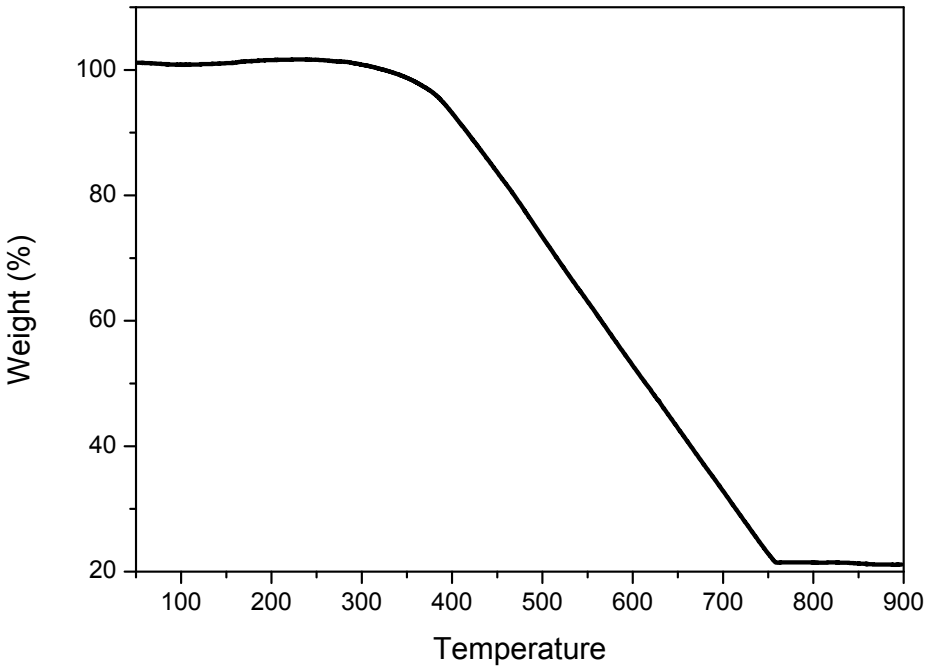

Figure S9. TGA of Fe/N-gCB in air.

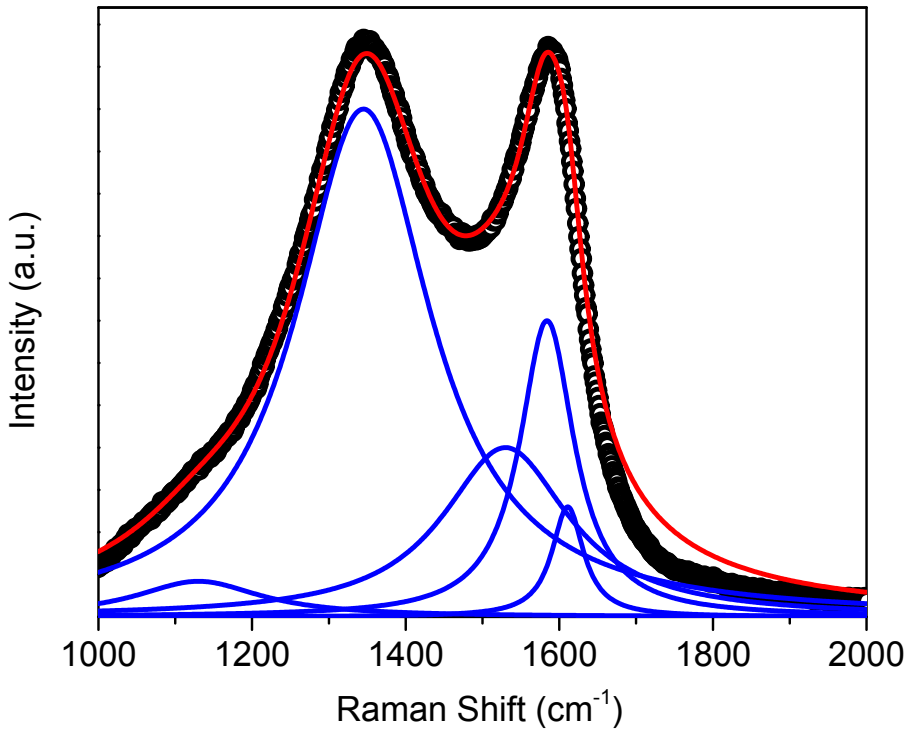

Figure S10. Raman spectrum of N-MCN.

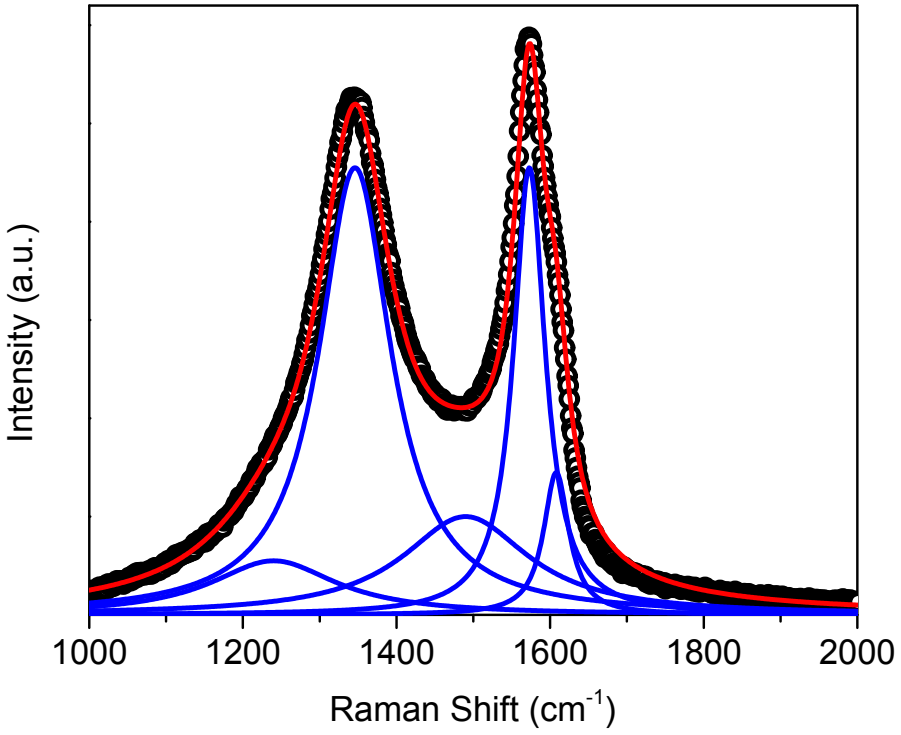

Figure S11. Raman spectrum of N-rGO.

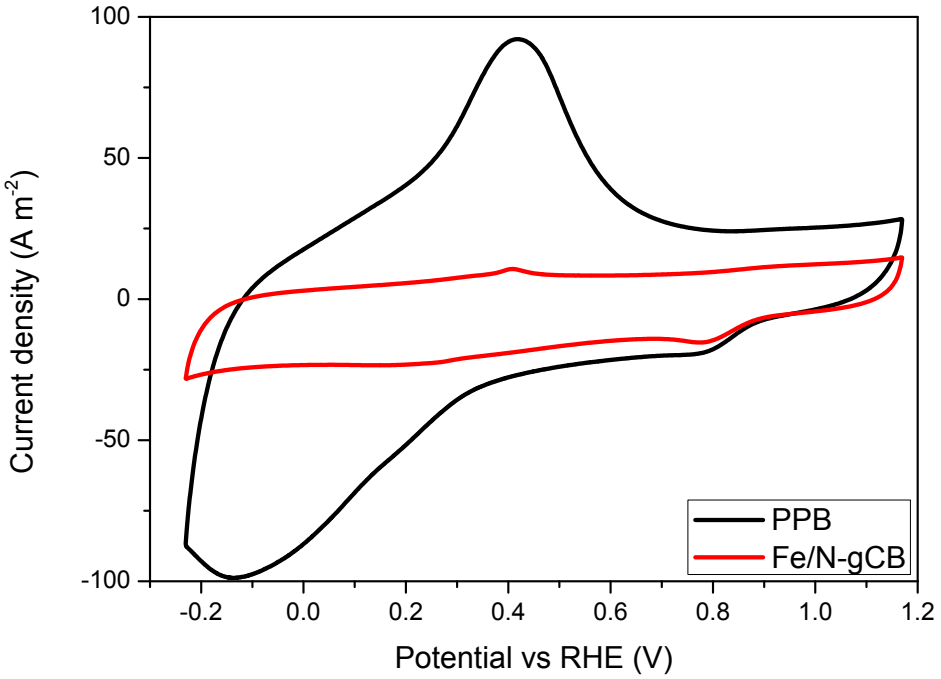

Figure S12. CVs of Fe/N-gCB and PPB in O_2 saturated 0.1 M KOH.

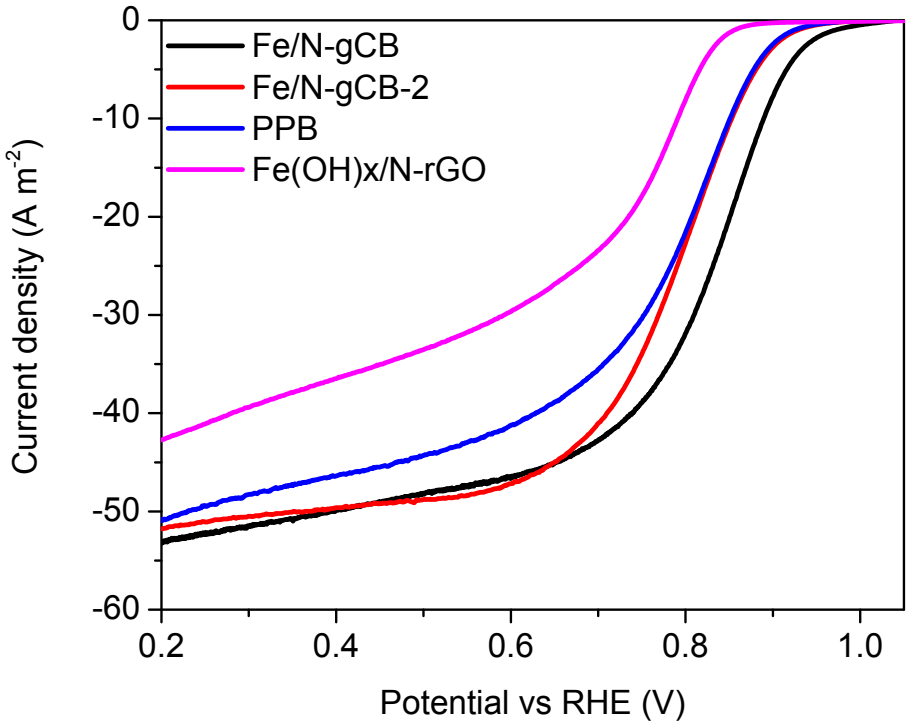

Figure S13. Normalized disk current at 1600 rpm in alkaline electrolyte.

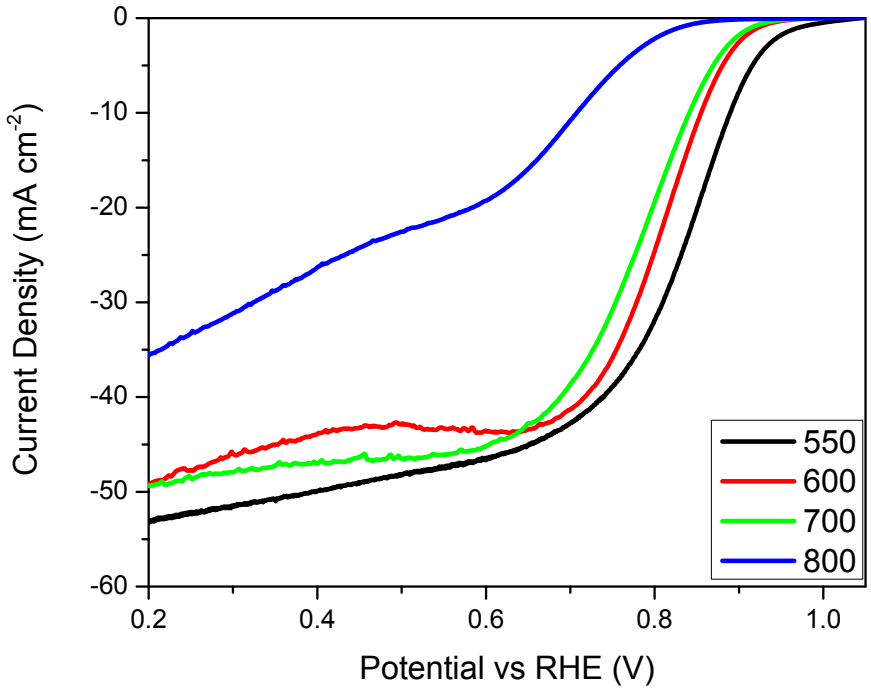

Figure S14. LSV of acid leached PPBs in alkaline electrolyte.

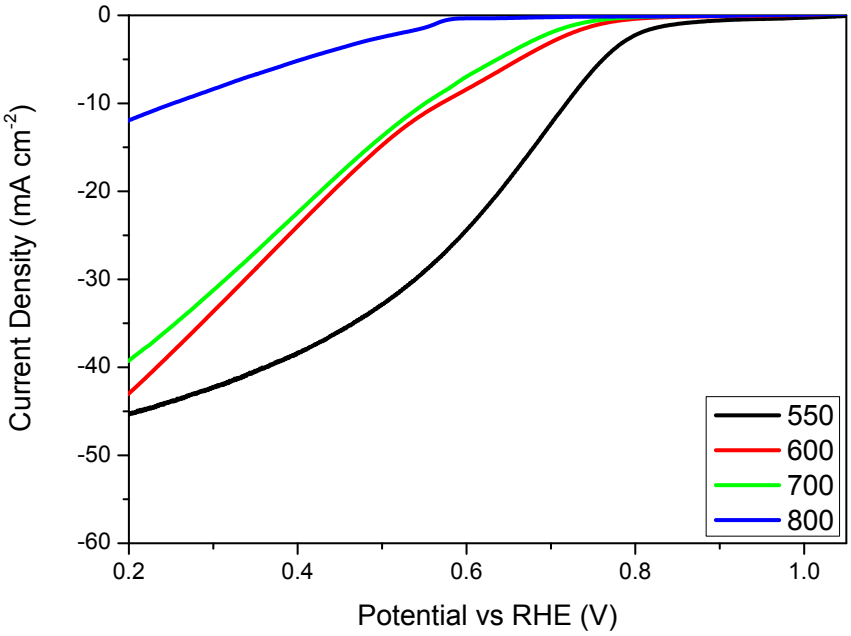

Figure S15. LSV of acid leached PPBs in acide electrolyte.

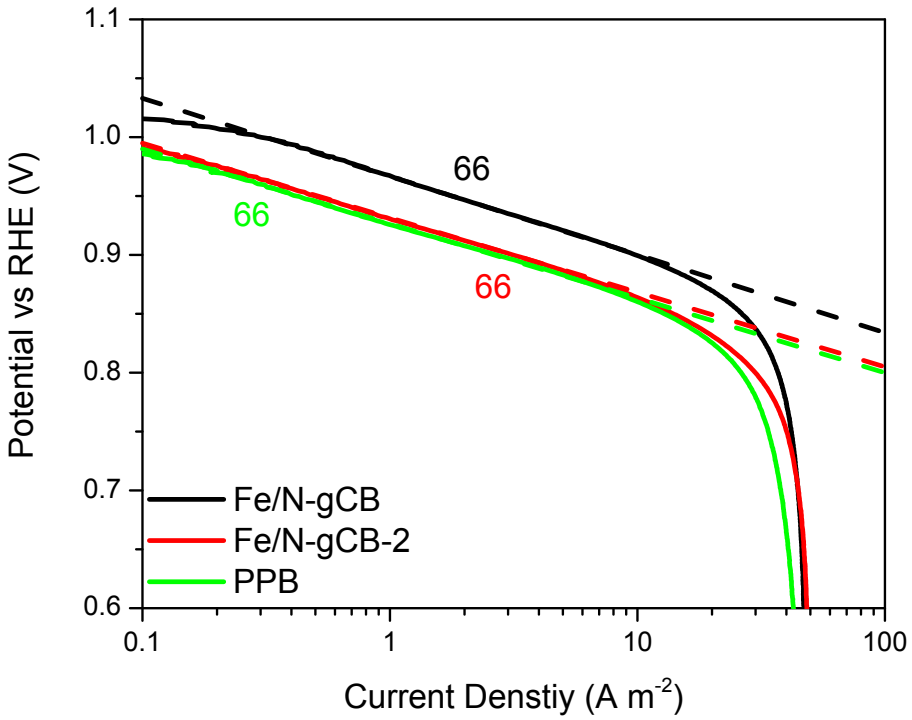

Figure S16. Tafel plots in alkaline electrolyte.

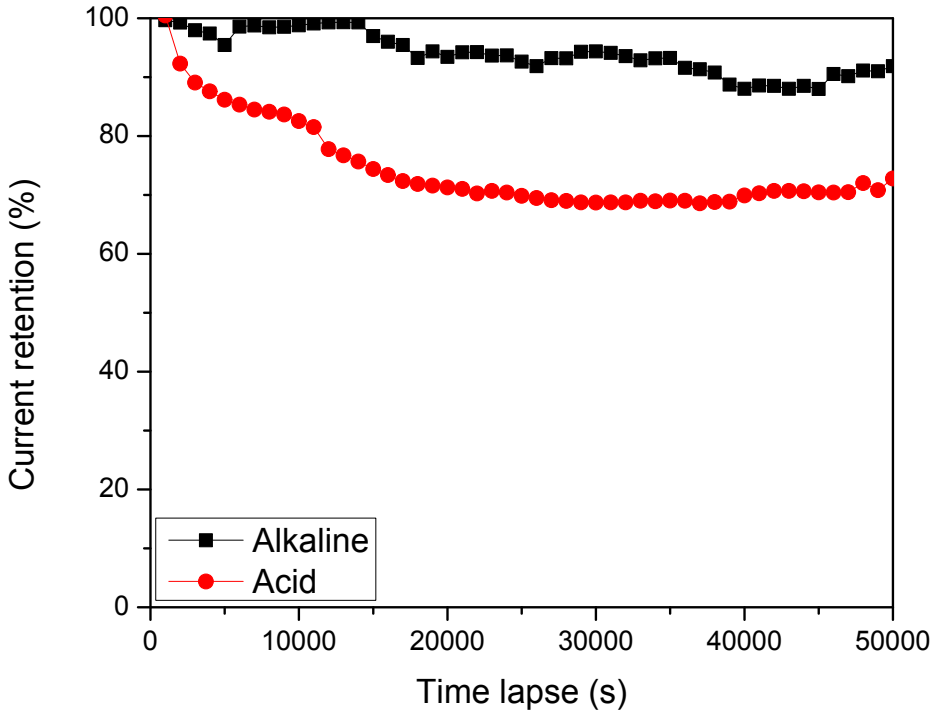

Figure S17. Stability of ORR of Fe/N-gCB in alkaline and acid electrolytes.

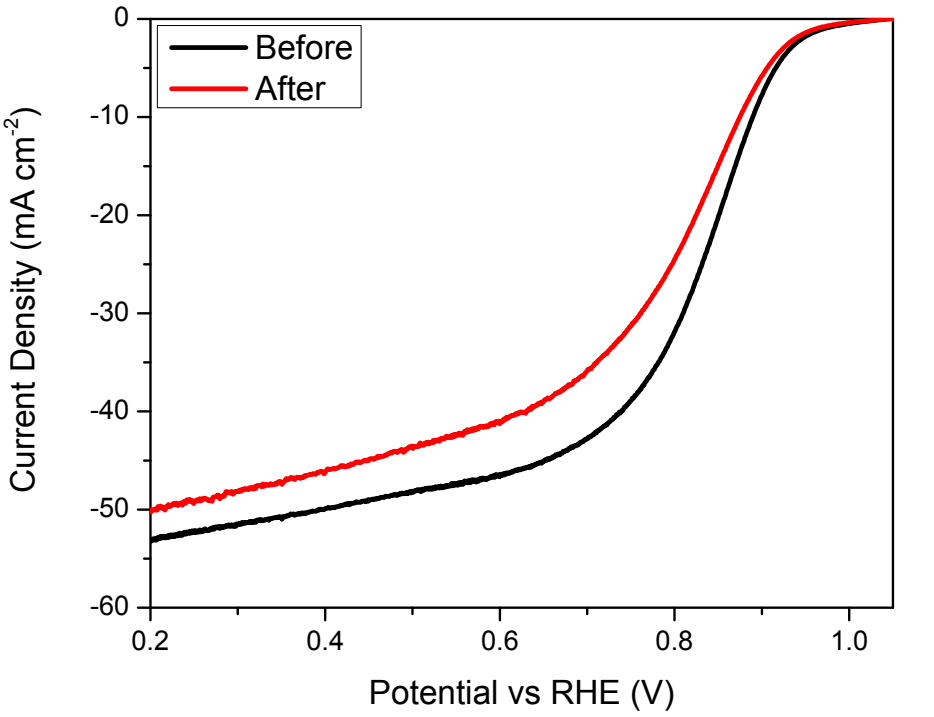

Figure S18. LSV of Fe/N-gCB before and after 50,000 s test in alkaline electrolyte.

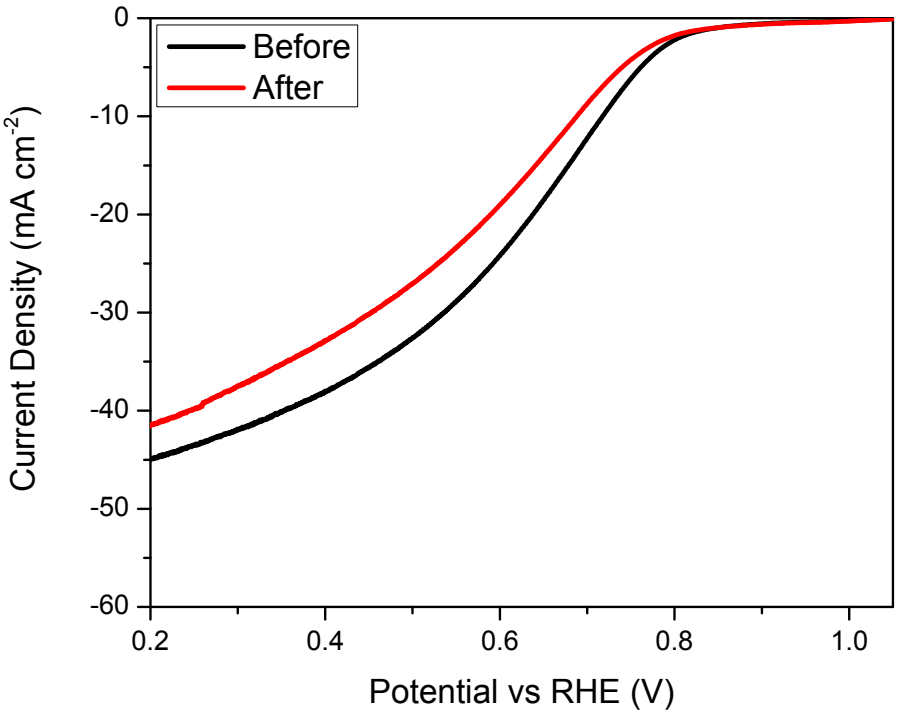

Figure S19. LSV of Fe/N-gCB before and after 50,000 s test in acid electrolyte.