Supporting Information

Facile Synthesis of Bimetallic Fluoride Heterojunctions on Defect-Enriched Porous Carbon Nanofibers for Efficient ORR Catalysts

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Supporting Methods

Synthesis of PCNFs, Cu@PCNFs, CuCoF$_2$@PCNFs. The spinning sol was prepared by a simple and environmentally friendly method. Specifically, 0.9 g of PVP was dissolved in 5.1 g of deionized water and then stirred by magnetic force for 1 h at room temperature. Then added 3 g of PTFE water emulsion and stirred for 2 h. Different from pure PCNFs, the preparation of metal doped PCNFs needed to add 0.5 mmol of Copper (II) acetate monohydrate (Cu(CH$_3$COO)$_2$·H$_2$O) and 0.5 mmol of Cobalt (II) acetate tetrahydrate (Co(CH$_3$COO)$_2$·4H$_2$O) into the spinning sol. After ball-milling for 1 h, the uniformly mixed sol was obtained. In addition, in order to increase the nitrogen loading, 0.5 g of melamine powder was also added into the spinning sol. Then, the prepared sol was transferred to a 10 ml of syringe container. During electrospinning under high voltage, the charged droplets at the front end of the syringe were accelerated, stretched and pulled onto the receiving roller with a speed of 60 r/min, and the fiber felt similar to nonwovens could be obtained. In this experiment, the voltage was set as 20 kV, the liquid flow rate was 1 ml/h, and the distance between the needle and the receiver was 20 cm. In order to decrease the defects in the electrospun nanofibers, it was necessary to heat the as spun nanofiber membrane at a low temperature before the high-temperature calcination. The oxidation heating temperature was set as 250 °C. The oxidized fiber was then calcined at 900 °C for 2 h in N$_2$ atmosphere, and the heating rate was 5 °C/min.

Material Characterizations. The morphology and NP size of the obtained materials were observed through SEM (Hitachi S-4800) and field emission TEM (FE-TEM, JEN-2100F). The XRD measurements were examined using a D/Max-2550/PC

(Rigaku Co., Japan) at Cu Kα radiation (λ=1.5418 Å). XPS (Escalab 250Xi) was used to analyze the surface valence of the materials. N_2 adsorption-desorption isotherms were measured using a physisorption system (ASAP 2020, Micromeritics Co., USA), and the SSA and pore structures were calculated by Brunauer-Emmett-Teller and Horvath-Kawazoe (HK) models, respectively. FT-IR spectroscopy was carried out using a Nicolet iS10 spectrometer (Thermo Fisher Scientific Inc., USA). TG analysis was characterized by a thermogravimetric analysis (SDT Q600; TA Co., USA) with a heat rate of 10 °C/min under air atmosphere. The Raman data were characterized by Lab RAM HR Evolution, which has an excitation wavelength of 532 nm.

Electrochemical Characterization. The electrochemical measurements were performed in a three- electrode system by using CHI 660E electrochemical station and the rotating electrode (Pine Instrument Co, AFMSRCE 3699) at room temperature (25 °C). The three electrodes were composed of a glassy carbon electrode with catalyst as working electrode, a platinum mesh with an area of 1 cm^2 as counter electrode and saturated calomel as reference electrode. In the process of measurement, 30 min O_2 pre-scan and continuous gas bubbling are needed to achieve oxygen saturation. The catalyst inks were prepared by mixing 2 mg of catalyst materials with 45 μL (5 wt.%) of Nafion solution and 1 mL of ethanol and then undergoing an ultrasonic dispersion for 20 min. Then, 30 μL of the catalyst suspension was dropped onto the polished rotating disk electrode (RDE) and dried at room temperature naturally. The catalyst loading was calculated roughly as 0.3 mg/cm^2. For comparison, a commercial Pt/C (20 wt.%) catalyst was also prepared in the same way, and the catalyst loading was 0.1 mg/cm^2.

The cyclic voltammetry (CV) curves were recorded in O_2-saturated 0.1 M KOH solution at 50 mV/s from 0.2 to -1V. The linear sweep voltammetry (LSV) curves were carried out at 5 mV/s with varying rotating speed from 400 to 2025 rpm.

In the mixed control region of mass transfer and kinetics, the total reaction current satisfies the Koutecky-Levich equation, and the electron transfer number were calculated by K-L equation. The equation is as follows:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_K} + \frac{1}{B\omega^{\frac{1}{2}}}$$
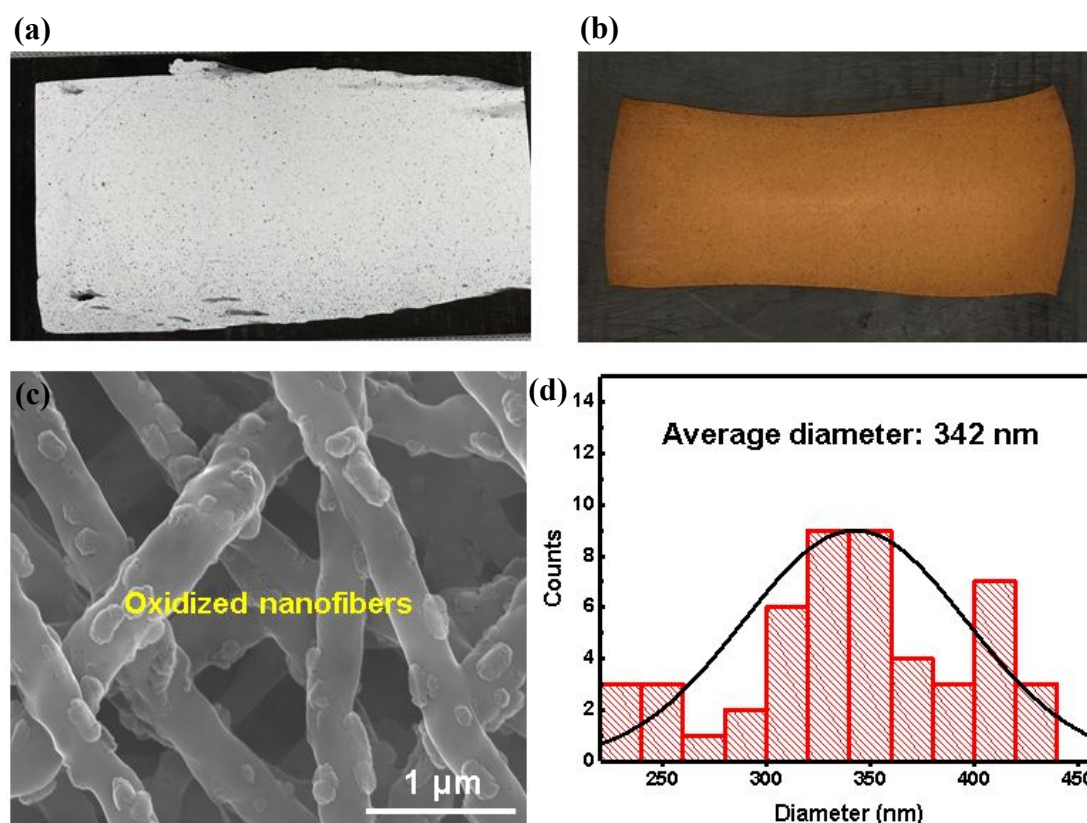
$$B = 0.62nFC_0(D_0)^{2/3}v^{-1/6}$$

$$J_K = nFkC_0$$

Where J is the measured current density (mA/cm²), J_L and J_K represent the limiting and kinetic current density (mA/cm²), ω is the angular velocity of the rotating disk electrode during the experiment, F is the Faraday constant (96485 C/mol), C_0 (1.2 × 10⁻⁶ mol / ml) and D_0 (1.9 × 10⁻⁵ cm²/s) are the volume concentration and diffusion coefficient of O_2 saturated 0.1 M KOH electrolyte, v (0.01 cm²/s) is the viscosity of the electrolyte and K is the electron transfer rate constant. The unit of angular velocity (rad/s) needs to be further converted as follows:
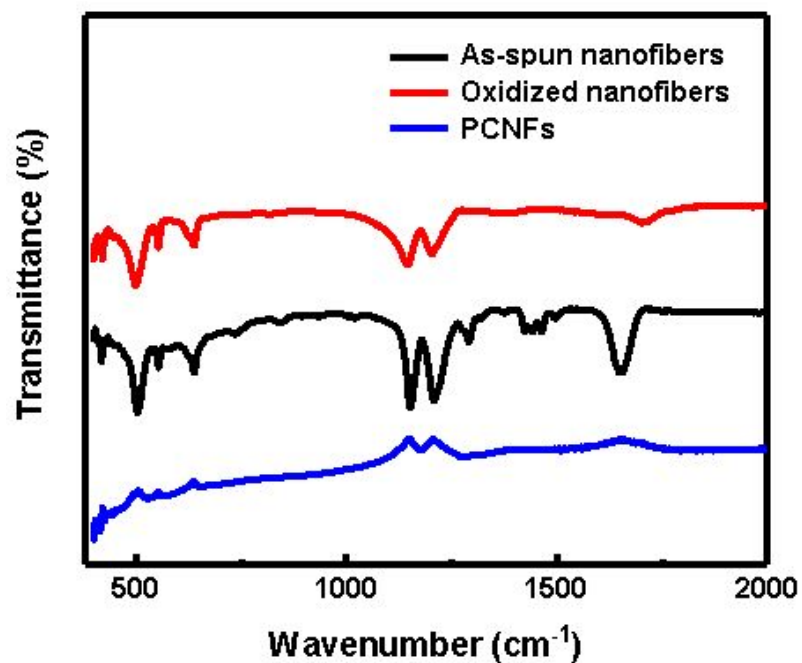
$$rad/s^1 = \frac{2\pi * rmp}{60}$$

Supporting Figures

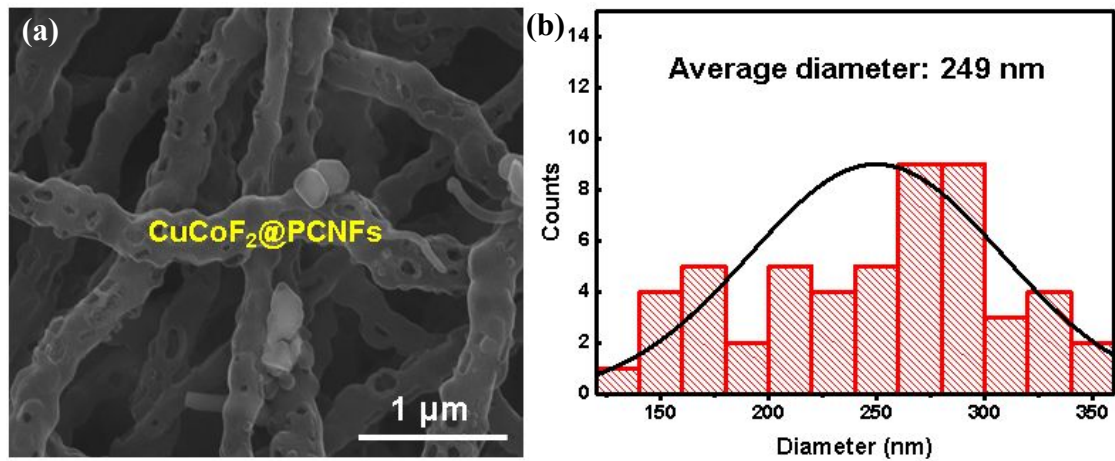

Figure S1. Photos of the stable spinning sol, the electron micrograph of the electrospun nanofiber film and the fiber diameter distribution. (**a**) The water based stable sol for electrospinning. (**b**) The SEM image of an electrospun nanofiber film and the normal distribution curve of fiber diameter. The average diameter of the fiber was ~230 nm.

Figure S2. The direct view picture of the electrospun nanofiber film and the oxidized nanofiber film. (**a**) The precursor electrospun nanofiber film was white, and (**b**) the oxidized nanofiber membrane was brown. (**c**) SEM image of the oxidized nanofiber film at 250 °C and (**d**) the corresponding normal distribution of fiber diameter. The average diameter of the fiber was ~342 nm. Compared with the diameter of primary nanofibers, the diameter increased slightly.
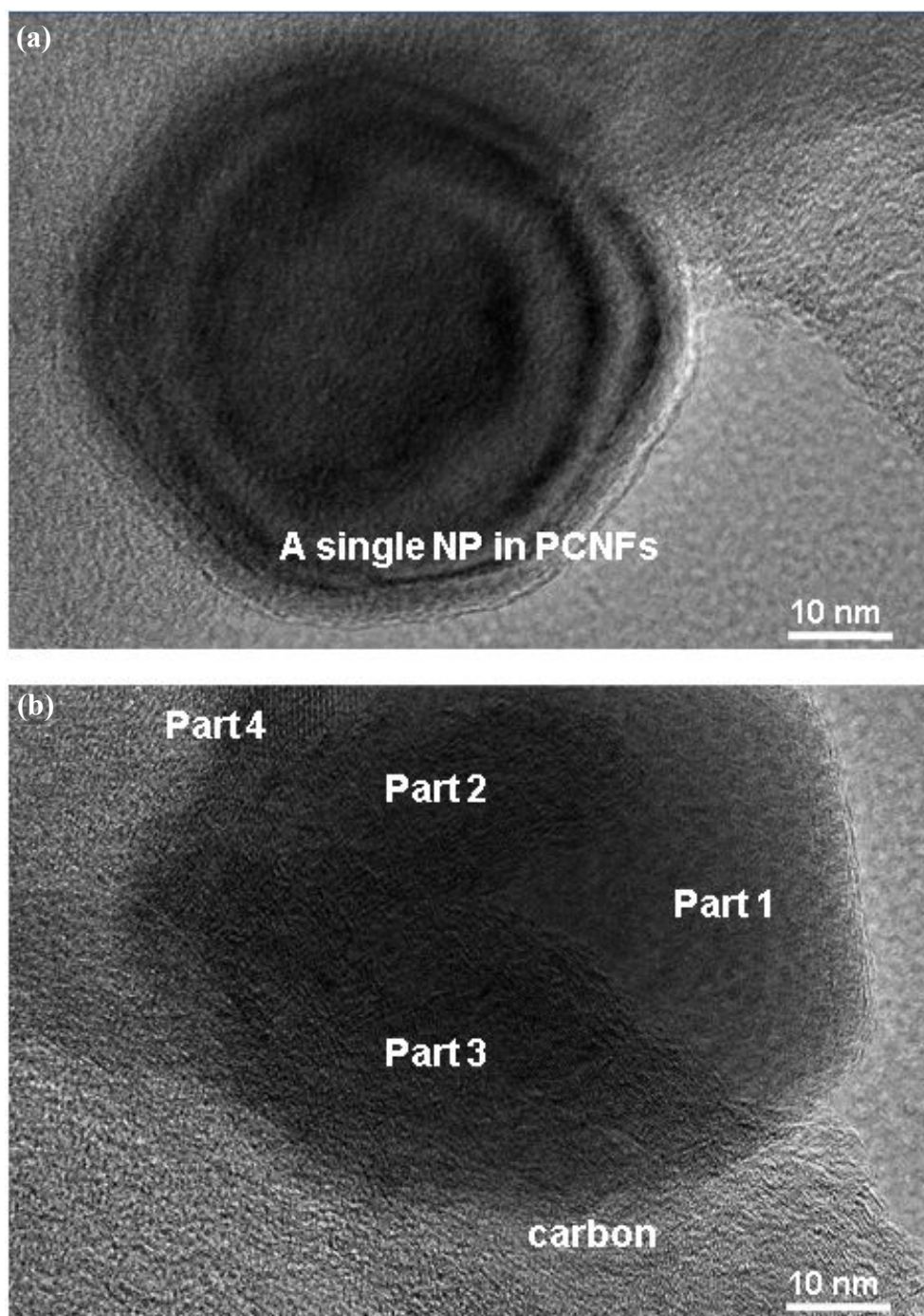
Figure S3. FTIR spectrogram of different samples. Compared with the precursor nanofiber film and the carbonized nanofiber film, there were large amounts of C=C functional groups in the oxidized nanofiber film.
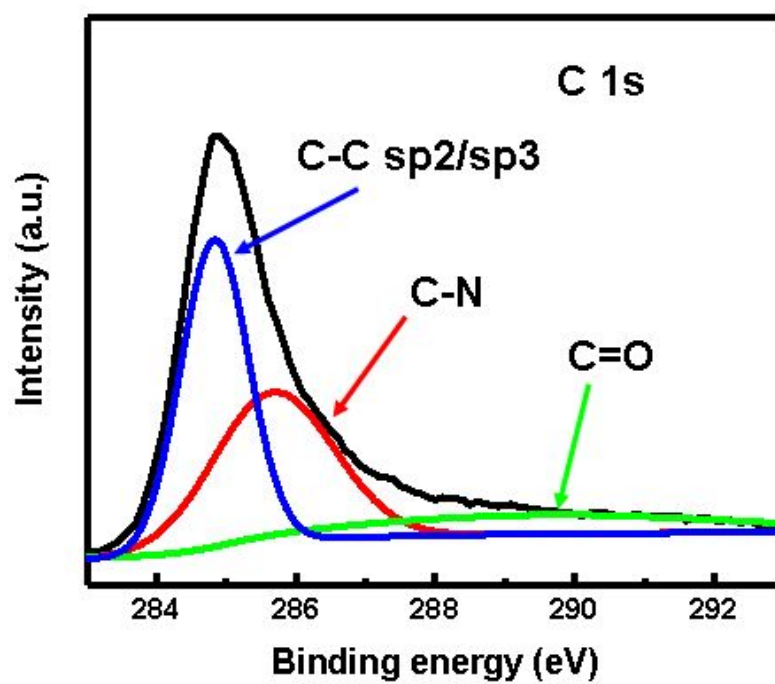
Figure S4. SEM image and the normal diameter distribution of the calcined nanofiber film. It was observed that the pores formed on the calcined nanofibers and heterojunctions were adsorbed on the nanofiber. The average diameter of the nanofiber was ~249 nm. Compared with the oxidized nanofiber, the diameter of the fiber decreased obviously.
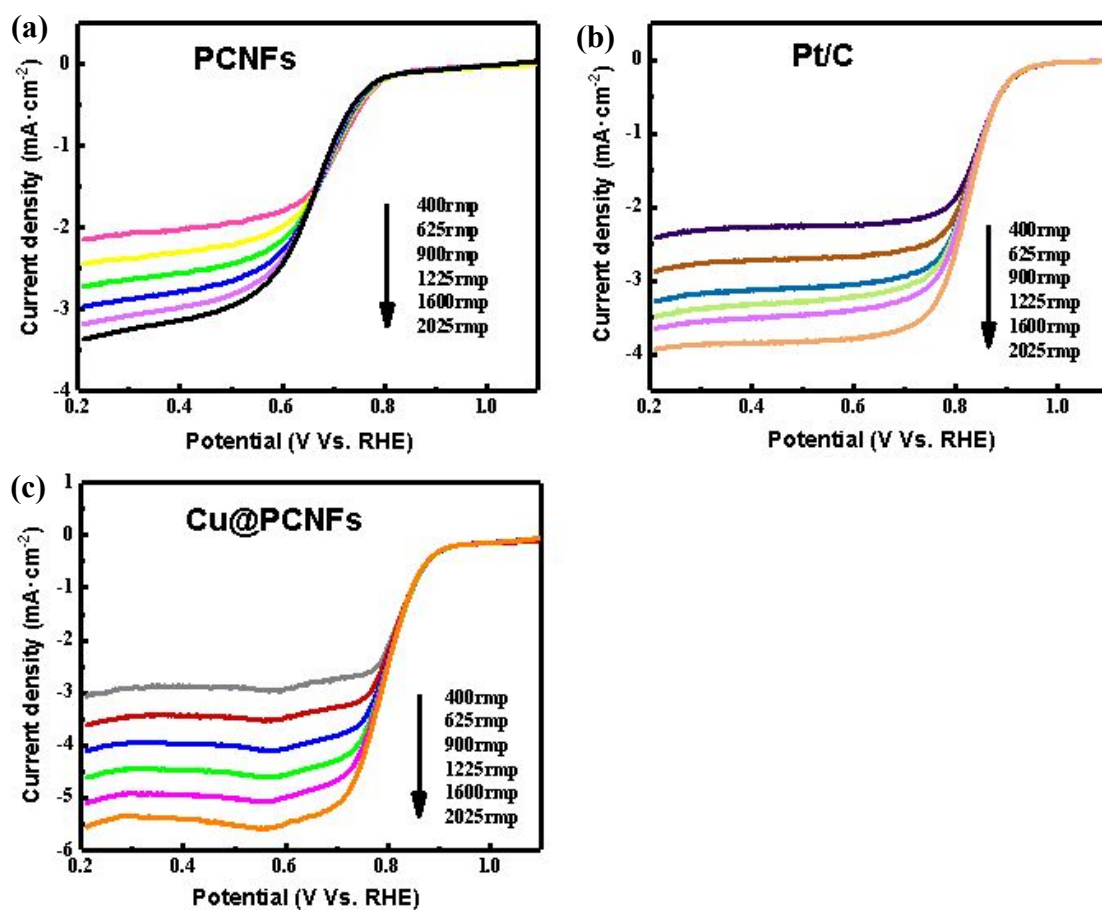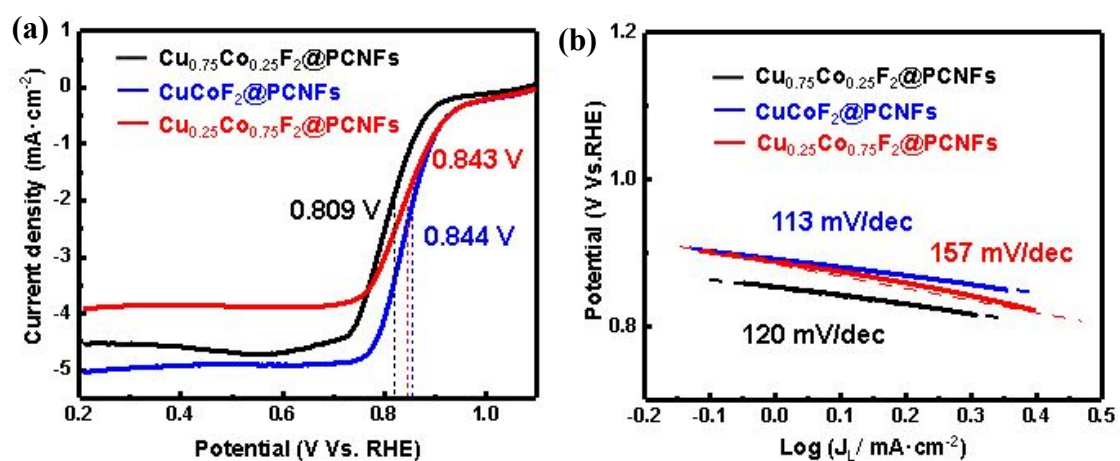
Figure S5. High resolution TEM images of the metallic NPs in PCNFs. (a) There were obvious graphite layers around the NPs, which show an obvious layered structure. **(b)** Further analysis of the internal lattice structure of the NPs shows the phenomenon of partition.

Figure S6. The high resolution of C 1s spectrum could be divided into three sub peaks: 284.8 eV (C-C), 285.6 eV (C-N) and 288.8 eV (C=O).

Figure S7. LSV curves of the other three electrodes at different rotation speeds. All these catalysts underwent a 4e⁻ transfer mechanism.

Figure S8. (**a**) LSV curves of the catalysts with different mole ratio of Cu and Co. (**b**) The corresponding Tafel plots of these electrodes.