Electronic Supplementary Information

Electrospun ZIF-based hierarchical carbon fiber as efficient electrocatalyst for oxygen reduction reaction

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Experimental Section

Materials: Polyacrylonitrile (PAN, molecular weight=150000), 2-methylimidazole was obtained from Sigma-Aldrich. N,N-dimethylformamide (DMF, ≥99.9%), methanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Cobaltous nitrate hexahydrate ($Co(NO_3)_2·6H_20$), Zinc nitrate hexahydrate (Zn(NO3)2·6H2O) and sulfuric acid was purchased from Nanjing Chemical Reagent Co., Ltd. All chemicals were used as received without any further purification. Millipore water was used in all experiments.

Synthesis of Zn,Co-ZIF: Zn,Co-ZIF were synthesized by a reported method[1]. The typical preparation of Zn,Co-ZIF was described by the following procedure. $Co(NO_3)_2·6H_2O$ (1.57 g) and $Zn(NO_3)_2·6H_2O$ (8 g) were dissolved in 500 mL of methanol. 2-methylimidazole (11 g) was dissolved separately in 400 mL of methanol. The metal salt solution was then poured into the 2-methylimidazole solution, and the resulting solution was stirred for 2 h. The solid Zn,Co-ZIF product was collected by centrifugation and washed with methanol.

***Synthesis of ZCP-CFs*:** In a typical synthesis, 0.5 g of Zn,Co-ZIF was added into 5 mL DMF with sonication until the Zn,Co-ZIF were well dispersed. Then, 0.5 g PAN and 0.25 g $Co(NO_3)_2·6H_2O$ were added into the solution with stirring at 60 ^oC for 6h. The obtained Zn,Co-ZIF/Co^{2+}/PAN/DMF solution was used as a precursor for electrospinning of carbon fibers. During the electrospinning process, the precursor solution was transported to a metal needle with a flow rate of 5 μL min^{-1} by a syringe pump. A flat copper foil used as a fiber collector was put about 12 cm away under the needle. A positive direct current (DC) voltage of about 12-15 kV was applied between the needle and the collector to generate a stable continuous Zn,Co-ZIF/Co^{2+}/PAN-based fibers, which were denoted as ZCPF. The electrospun fibers were collected on an aluminum foil wrapped on the metal drum with a rotation speed of 300 rpm. The obtained fibers were pre-oxidized in an air atmosphere at 240 °C for 1 h (denoted as ZCPF-PO) and then carbonized at 700-1000 °C for 3 h in argon. The resultant Co-N doped composite

fibers were denoted as ZCPF-C. Finally, the unstable Co species were leached out in 1M H_2SO_4 solution and the obtained product was ZCP-CFs-T (T is the pyrolysis temperature). For comparison, Zn,Co-ZIF was directly carbonized into granular porous carbon (denoted as ZIF-C) at 900 ^oC followed by the acid etching process. Co^{2+}/PAN fibers were prepared without adding HMCSSs in the precursor solution. Through the similar process, Co, N-doped carbon fibers (CP-CFs) were synthesized.

[1] L. Shang, H. J. Y, X. Huang, T. Bian, R. Shi, Y. F. Zhao, G. I. N. Waterhouse, L. Z. Wu, C. H. Tung and T. R. Zhang, Adv. Mater., 2016, 28, 1668.

Characterization: TEM (transmission electron microscopy) analysis was conducted on an FEI Titan G2 60-300 transmission electron microscopy (TEM) operated at an accelerating voltage of 300 kV at Nanjing University of Science and Technology. It is equipped with a spherical aberration corrector under the objective lens, which allows for an information limit better than 0.08 nm. For imaging, it equipped with a Gatan Orius SC 1000B CCD (Charge Coupled Device) camera. SEM (scanning electron microscopy) analysis was conducted on FEI 250 system. The XPS (X-ray photoelectron spectroscopy) spectra were obtained by using a PHI Quantera Ⅱ ESCA System with Al Kα radiation at 1486.8V. N_2 adsorption and desorption isotherms were measured using Micromeritics ASAP-2020 at liquid nitrogen temperature (-196 ^oC). The specific surface area and the pore size distribution were calculated by using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method, respectively. The X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 advance powder diffraction system using Cu Kα (λ=1.5418Å) radiation. Raman spectra were collected on Renishaw in Via reflex spectrometer system.

Electrochemical measurements: Electrochemical measurements were conducted using a computer-controlled potentiostat (CHI 760C, CH Instrument, Shanghai) with a three-electrode electrochemical cell. The standard three-electrode electrochemical cell was fabricated using a catalysts-modified glassy carbon as the working electrode, platinum wire as the counter

electrode, and Ag/AgCl as the reference electrode. The working electrodes were fabricated as follows: first, 10 mg of the as-synthesized samples was mixed with 1 mL of DI water/isopropanol (1:1). The obtained suspension (10 μL) was dropped onto a g rotating disk electrode (RDE, 5 mm diameter, 0.196 cm^2 geometric surface areas). Through measurement, the loading mass of carbon spheres was 0.255 mg cm^{-2}. After drying, a Nafion solution (0.5 wt % in isopropanol) was coated on the sample as the binder. The cyclic voltammetry (CV) tests of the samples in O_2-saturated 0.1 M aqueous KOH solutions were performed in the potential range of 0.2 to -1.0 V with a scan rate of 10 mV s^{-1}. Linear sweep voltammograms (LSV) were acquired through the rotating disk electrode (RDE) technique in O_2-saturated 0.1 M KOH at a scan rate of 10 mV s^{-1} from 0.2 to -1.0 V under various rotation speeds (225-2500 rpm). The stability test was tested at the potential that the ORR limiting current was trended to be reached. Therefore, the stability test was performed at a potential of -0.26 V in O_2-saturated 0.1 M KOH solution for the chronoamperometry at room temperature with the working electrode rotating at 1600 rpm.

The electron transfer number (n) was calculated from the Koutecky-Levich (K-L) equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\,\omega^{1/2}}$$

$$n = \frac{B}{0.2F(Do_2)^{2/3}\,(v)^{-1/6}Co_2}$$

$$j_k = nFkC_0$$

Where j_k is the kinetic current, B can be determined from the slope of the K-L plots. F is the Faraday constant (F=96485 C mol^{-1}), Do_2 is the diffusion coefficient of O_2 (1.9×10^{-5} cm^2 s^{-1}), υ is the kinetic viscosity of the electrolyte (υ = 0.01 cm^2 s^{-1}) and Co_2 is the bulk concentration of O_2 (1.2×10^{-6} mol cm^{-3}), n is the overall number of electrons gained per O_2, k is the electron transfer rate constant.

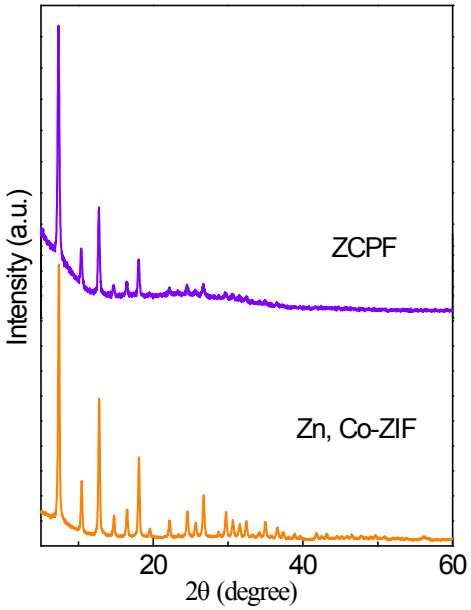

Figure S1. XRD patterns of Zn, Co-ZIF and ZCPF.

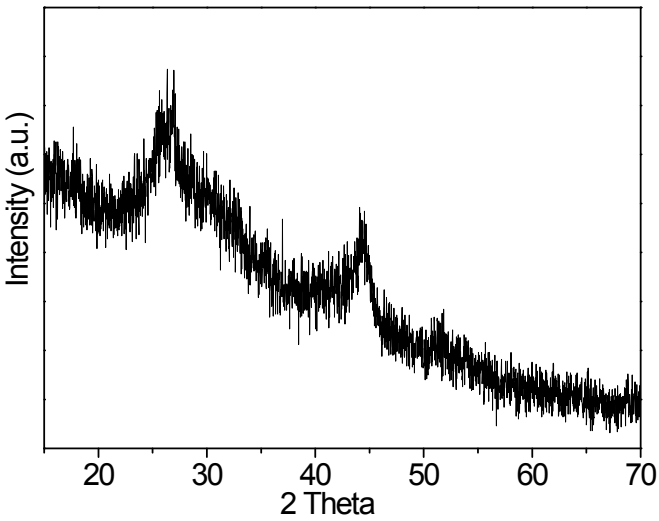

Figure S2. XRD patterns of ZCPF-C

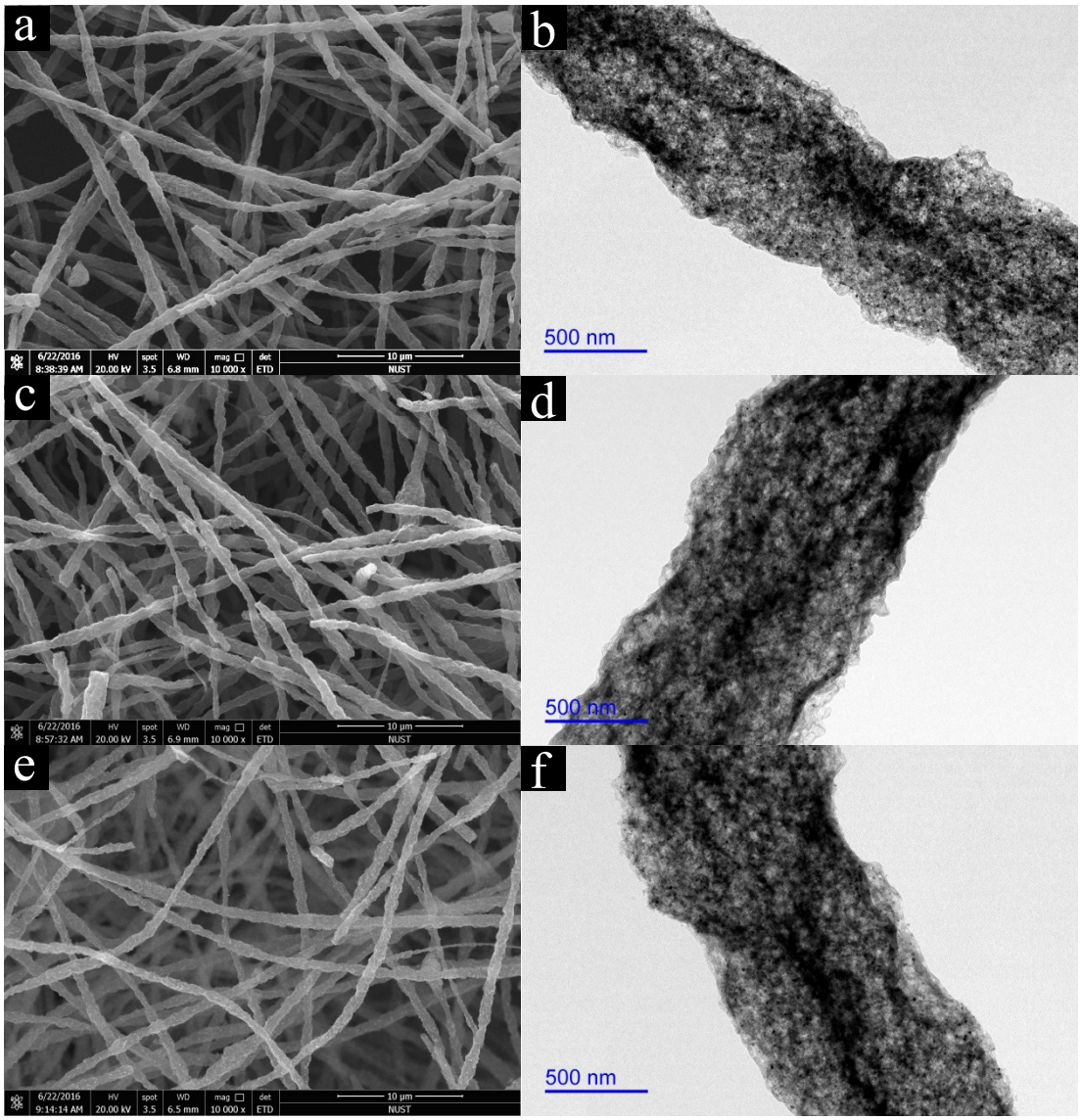

Figure S3. (a, c, e) SEM images of ZCP-CFs-7, ZCP-CFs-8, ZCP-CFs-10, (b, d, f) TEM images of ZCP-CFs-7, ZCP-CFs-8, ZCP-CFs-10.

Table S1. Textural parameters and proportion of carbon, oxide, nitrogen and iron calculated by XPS of the samples

Samples	BET surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	C content (%)	O content (%)	N content (%)	Co content (%)
ZCP-CFs-7	317.0	0.40	84.5	7.6	7.8	0.1
ZCP-CFs-8	426.5	0.48	86.8	6.4	6.4	0.2
ZCP-CFs-9	515.2	0.54	88.3	5.7	5.8	0.2
ZCP-CFs-10	529.7	0.56	92.3	4.3	3.3	0.1

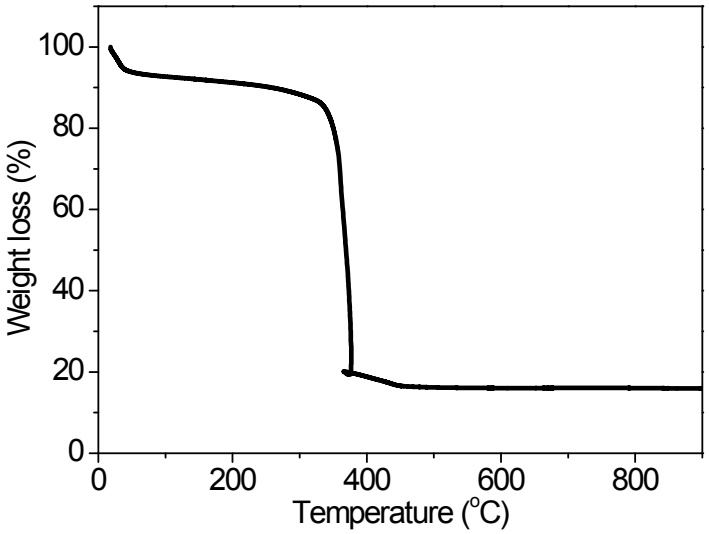

Figure S4. Figure S4. TGA curve of ZCP-CFs-9 treated in air with a heating rate 5 °C/min.

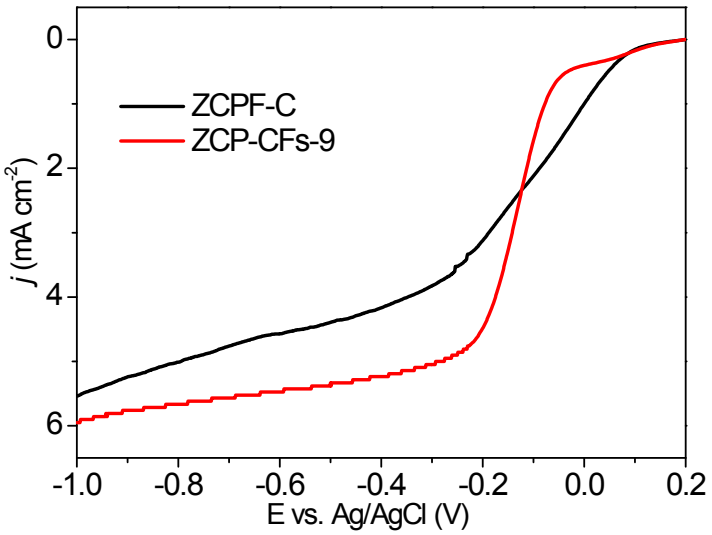

Figure S5. Polarization curves of ZCP-CFs-9 and ZCPF-C in O2-saturated 0.1 M KOH at a rotation rate of 1600 rpm

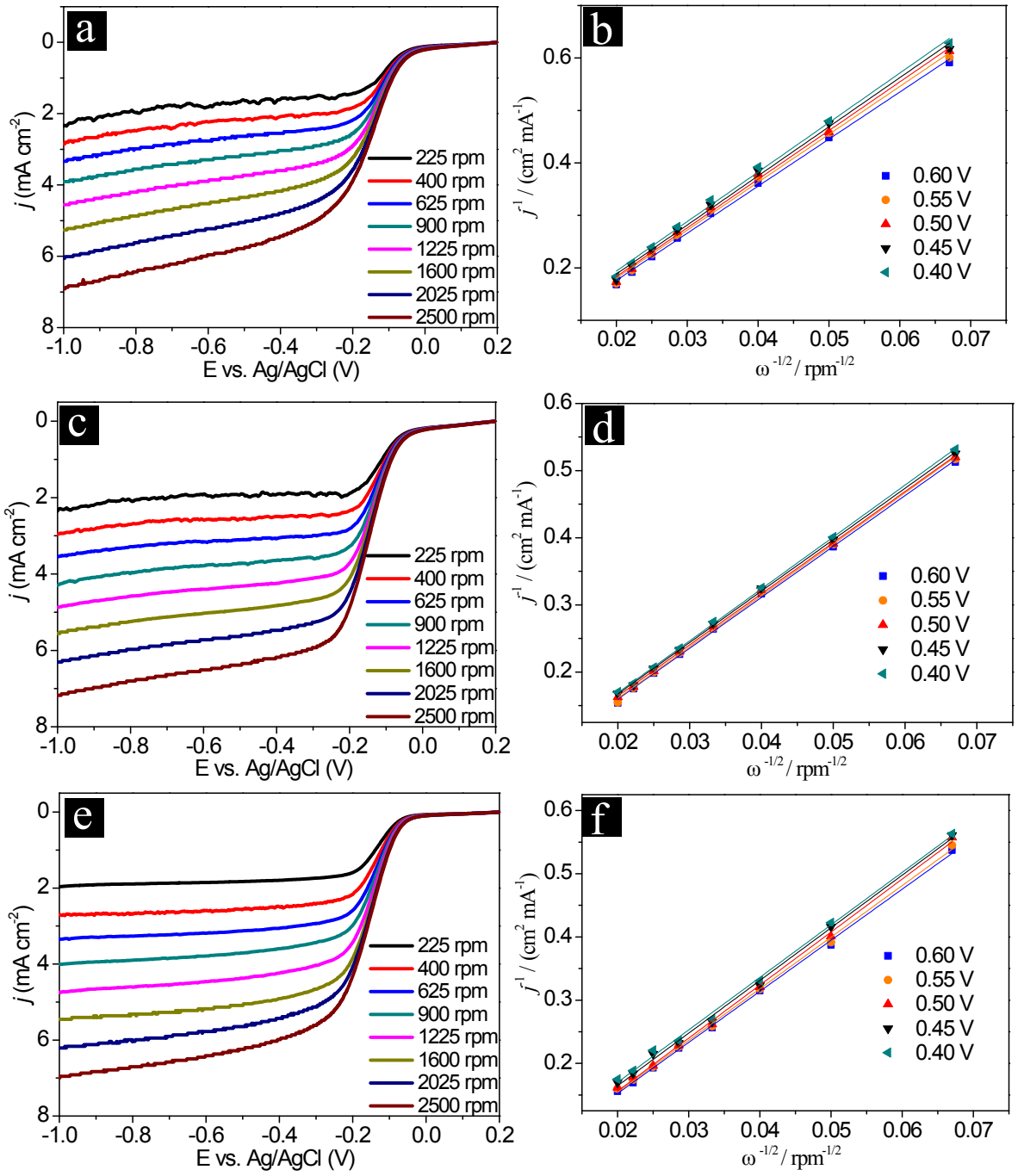

Figure S6. (a, c, e) Polarization curves of ZCP-CFs-7, 8, and 10 in O_2-saturated 0.1 M KOH at different rotation rates, (b, d, f) Koutecky-Levich plots of ZCP-CFs-7, 8, and 10 derived from polarization curves in (a, c, e) at different electrode potentials.

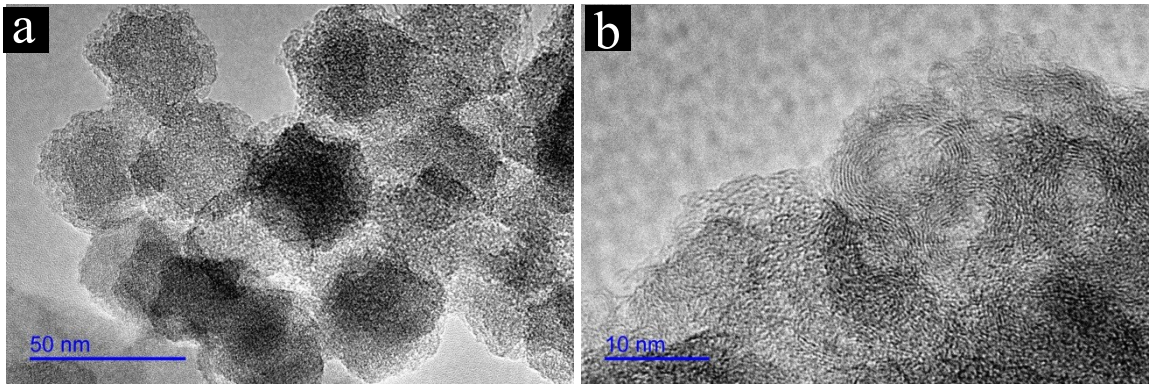

Figure S7. (a, b) TEM images of ZIF-C.

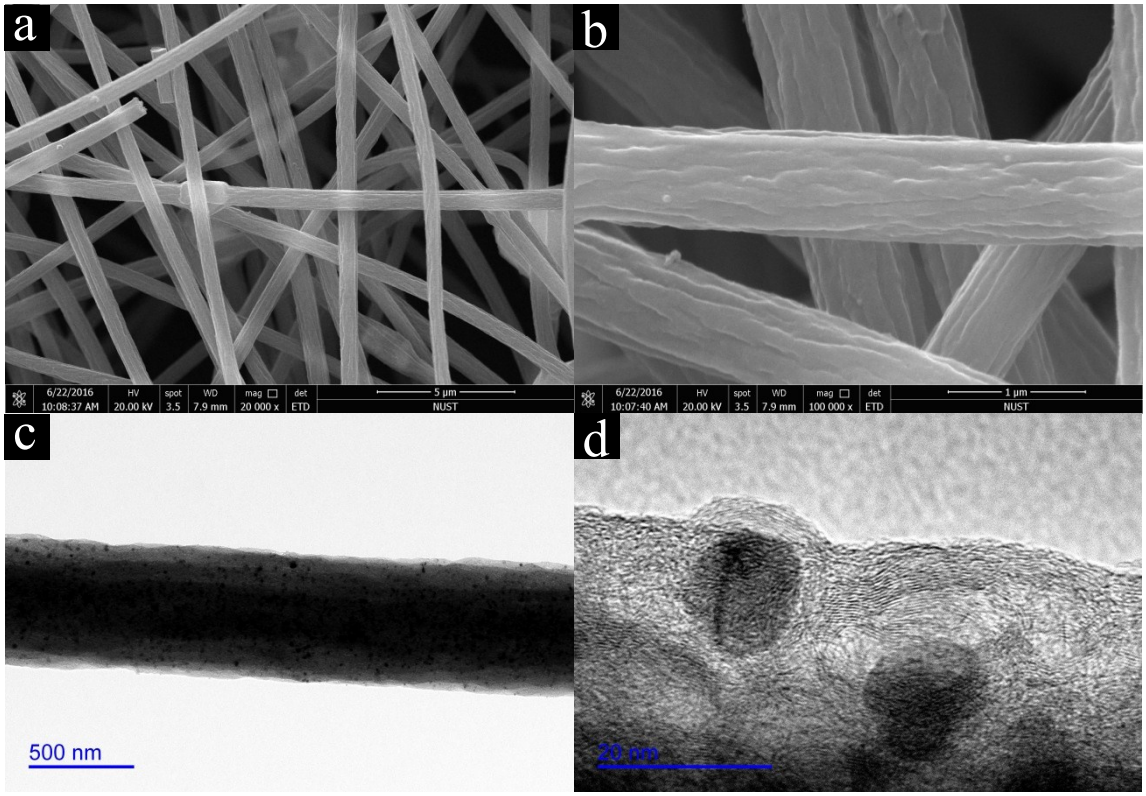

Figure S8. (a, b) SEM images, (c, d) TEM images of CP-CFs.

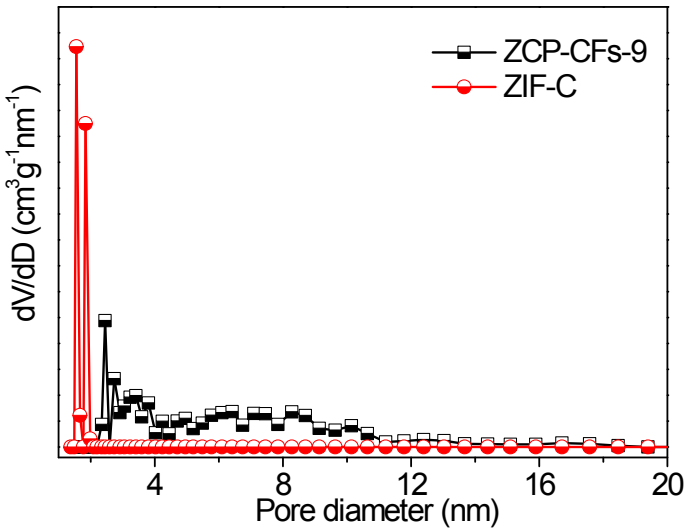

Figure S9. Pore size distribution of ZCP-CFs-9 and ZIF-C.

Table S2. Textural parameters and proportion of carbon, oxide, nitrogen and iron calculated by XPS of the samples

Samples	BET surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	C content (%)	O content (%)	N content (%)	Co content (%)
ZIF-C	676.8	0.59	85.6	6.7	7.5	0.2
CP-CFs	183.1	0.25	88.8	5.2	5.9	0.1
ZCP-CFs-9	515.2	0.54	88.3	5.7	5.8	0.2

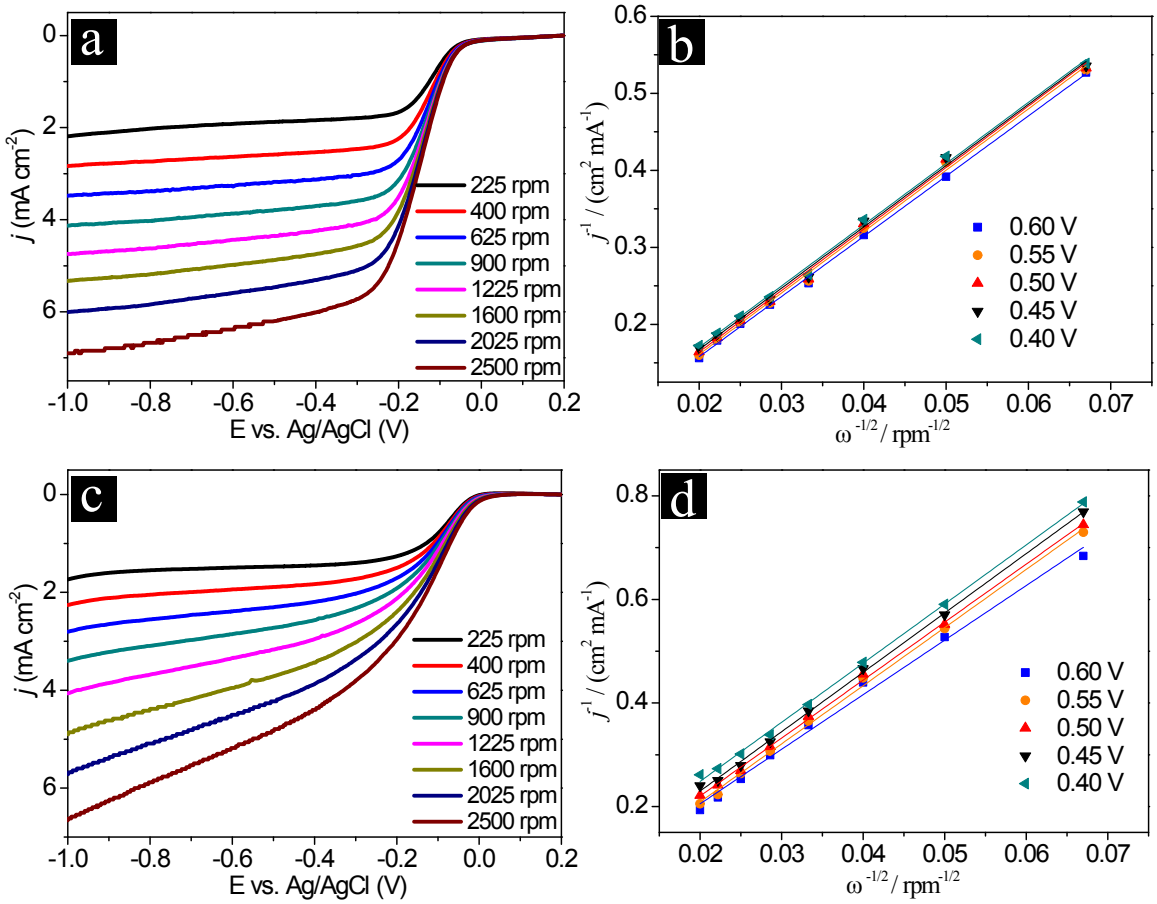

Figure S10. (a, c,) Polarization curves of ZIF-C and CP-CFs in O_2-saturated 0.1 M KOH at different rotation rates, (b, d) Koutecky-Levich plots of ZIF-C and CP-CFs derived from polarization curves in (a, c) at different electrode potentials.

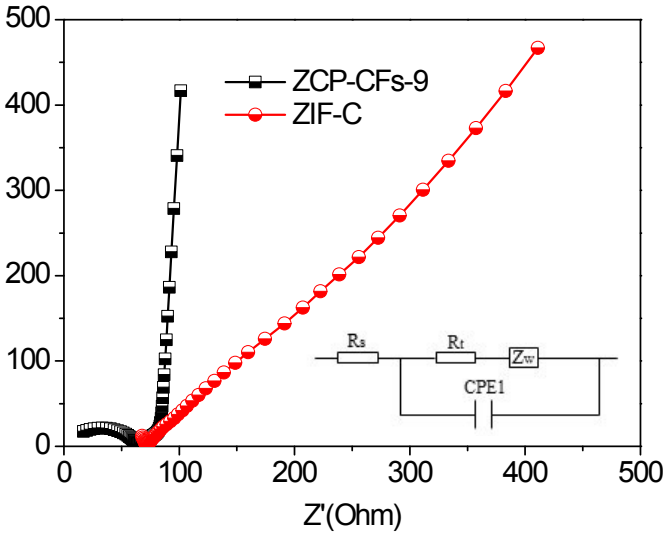

Figure S11. Electrochemical impedance spectroscopy of ZCP-CFs-9 and ZIF-C (Inset: the equivalent circuit diagram).

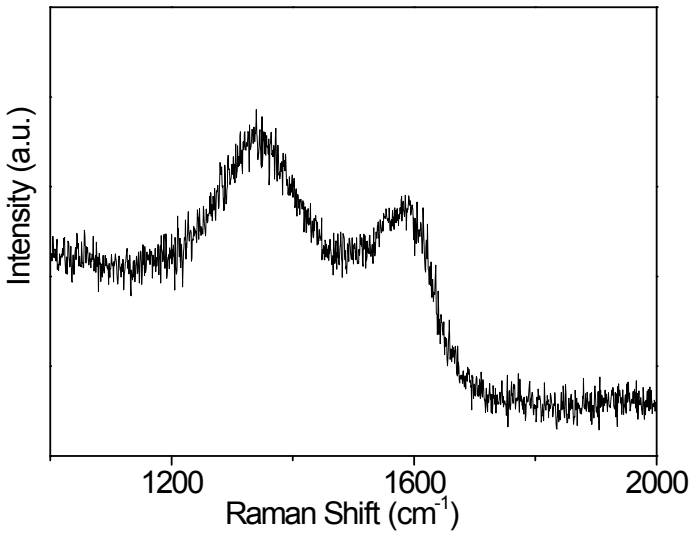

Figure S12. Raman spectrum of Pt/C.

Table S3. Comparison of ORR performance in 0.1 M KOH electrolyte of ZCP-CFs-9 with literature values.

Materials	Half-wave potential (V vs. Ag/AgCl)	Current density at -0.7 V (mA cm^{-2})	References
Fe-N-CNFs	-0.140	-5.12	Angew. Chem. Int. Ed. 2015, 54, 8179
Fe-N-C	0.86 (vs. RHE)	-5.8	Adv. Mater. 2015, 27, 2521
Fe-GO	<-0.40	-3.5	Angew. Chem. Int. Ed. 2014, 53, 1415
rGO/$(Co^{2+}$-THPP$)_7$	<-0.35	-3.2	Angew. Chem. Int. Ed. 2013, 52, 5585
FePc-Py-CNTs	0.915 (vs. RHE)	-5.3	Nat. Commun. 2013, 4, 2076
Fe-N/C	0.809 (vs. RHE)	-6.0	J. Am. Chem. Soc. 2014, 136, 11027
Fe-N-C-700	-0.178	-4.4	Chem. Eur. J. 2013, 19, 16170
CoP-CMP800	-0.18	-4.6	Adv. Mater. 2014, 26, 1450
C-COP-P-Co	0.80 (vs. RHE)	-5.8	Angew. Chem. Int. Ed. 2014, 53, 2433
Fe_3C/C-800	0.83 (vs. RHE)	/	Angew. Chem. Int. Ed. 2014, 53, 3675
NPC-Co45	0.79 (vs. RHE)	-5.5	Nano Res. 2013, 6, 293
Co_3O_4/N-rmGO	0.83 (vs. RHE)	-5.0	Nat. Mater. 2011, 10, 780
G-Co/CoO NPs	-0.176	-4.5	Angew. Chem. Int. Ed. 2012, 51, 11770
$MnFe_2O_4$/C	-0.154	-5.8	Nano Lett. 2013, 13, 2947
Fe_3O_4/N-Gas	<-0.40	-3.3	J. Am. Chem. Soc. 2012, 134, 9082
P-doped ordered mesoporous carbon	-0.30	-4.3	J. Am. Chem. Soc. 2012, 134, 16127
ZCP-CFs-900	-0.135 (0.805 vs. RHE)	-5.6	This work

Table S4. Comparison of economy in ZCP-CFs-9 with 20%Pt/C

Chemicals	Specifications	Price (¥)
$Zn(NO_3)_2 \cdot 6H_2O$	500 g	76.0
$Co(NO_3)_2 \cdot 6H_2O$	100 g	63.0
2-methylimidazole	500 g	808.5
methanol	500 Ml	12.0
DMF	500 Ml	17.0
PAN	100 g	2509.5
ZCP-CFs	1 g	107.5
20% Pt/C	1 g	580.0