Efficient Metal-Free Electrocatalysts for Oxygen Reduction: Polyaniline-Derived N- and O-Doped Mesoporous Carbons

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Detailed Experimental Section

Reagents and Materials. Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) ($(PEG)_{20}(PPG)_{70}(PEG)_{20}$) (Pluronic® 123), average molecular weight of 5800 Da, was obtained from BASF. Tetraethyl orthosilicate (TEOS), sodium persulfate, aniline, cobalt(II) nitrate ($Co(NO_3)_2$), $FeCl_3$, hexane, hexamethyldisilazane (HMDS), and Pt/C (1% Pt) were purchased from Sigma-Aldrich. Hydrochloric acid solution and absolute ethanol (99.99%) were obtained from Fischer Scientific. *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane was acquired from Gelest, Inc.

Synthesis of SBA-15 Mesoporous Silica Functionalized with Organodiamine Groups (SBA-15/Diamine). SBA-15 was synthesized as reported previously.[1,2] Pluronic® 123 (4 g) was dissolved in a solution of HCl (20 mL) and distilled water (130 mL). After the temperature of the solution was adjusted to 45 °C, TEOS (8.5 g) was added in it. The solution was vigorously stirred for 20 h, and after which it was kept in an oven at 80 °C for 24 h. The as-prepared mesostructured silica was recovered by filtration, washed copiously with distilled water, and then dried under ambient conditions. Prior to template extraction, the external surface of the as-prepared mesostructured silica was modified with -$SiMe_3$ groups by stirring 4 g of the material in HMDS/toluene (5 mL/60 mL) solution for 18 h. This helped the external surface silanol groups of the as-prepared mesostructured silica to be coated with trimethylsilyl (-$SiMe_3$) groups. After this, the Pluronic® 123 template was removed by stirring the $SiMe_3$-functionalized mesostructured silica material (0.5 g) in 100 mL of diethyl ether:ethanol (1:1 ratio) solution for 5 h. This yielded $SiMe_3$-capped mesostructured silica (labeled here as Me-SBA-15). Organodiamine ("Diamine") groups were then grafted onto the inner channel walls of the Me-SBA-15 by stirring Me-SBA-15 (0.1 g) in a solution of *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (1.0 mL) and anhydrous toluene (100 mL) for 18 h at 80 °C. The resulting material was washed with copious amount of ethanol, and dried under ambient conditions, giving a mesoporous material, labeled as "SBA-15/Diamine", whose external surface is functionalized with -Me groups and whose internal surfaces were functionalized with -alkyldiamine groups.

Synthesis of Polyaniline (PANI) within the Pores of SBA-15 (PANI/SBA-15 Nanocomposite Materials). SBA-15/Diamine (100 mg) was treated with 1 mol/L hydrochloric

acid (10 mL) containing sodium persulfate (600 mg). After stirring for 2 h at room temperature, the solid material was recovered from the solution by filtration and washed with distilled water to remove any residual persulfate ions that are not electrostatically immobilized in it. The resulting solid material, denoted as SBA-15/Diammonium-Persulfate, was stirred in a solution containing aniline (150 μL) and 1 mol/L hydrochloric acid (10 mL) in an ice bath (0-5 °C) for 4 h. This led to polymerization of aniline into PANI, as seen by the color changes of the sample from white to green. The solid material was recovered by filtration and washed copiously with acetone:ethanol (1:1 ratio). It was then treated with 1.0 M ammonia solution (10 mL), filtered, washed several times with distilled water and let to dry under ambient conditions. This gave the material PANI/SBA-15.

Metal-Doped PANI/SBA-15. Cobalt(II), Fe(III) or mixed Cobalt(II)/Fe(III) ions were chelated onto PANI/SBA-15 by stirring PANI/SBA-15 (50 mg) in 0.1 mmol/L aqueous solutions containing the corresponding metal salts (2 mL). The solution was stirred for 6 h, and after which the solid material was recovered by centrifugation, washed with ethanol, and then dried under ambient conditions.

Table S1. Metal concentration in the metal-doped PANI/SBA-15 materials.

Sample	$[Co^{2+}]$		$[Fe^{3+}]$	
	mmol/g	Wt. %	mmol/g	Wt. %
PANI/SBA-15-$[Co^{2+}]$	4	2.36×10^{-2}	-	-
PANI/SBA-15-$[Fe^{3+}]$	-	-	4	2.23×10^{-2}
PANI/SBA-15-$[Co^{2+}]/[Fe^{3+}]$	2	1.18×10^{-2}	2	1.12×10^{-2}

Thermal Treatment (Pyrolysis) of PANI/SBA-15 Containing with or without Metals. Pyrolysis the samples was performed by keeping samples in an alumina boat within a temperature-programmable tube furnace under a flow of argon with a flow rate of 30 mL/min. First, the temperature of the furnace was increased at a low rate ramp of 1 °C/min from ambient temperature to reach to two temperature plateaus of 200 and 300 °C. The time span in each plateau was 2 h. After the 300 °C, the temperature was increased once again to the final pyrolysis temperature (600, 700, 800 or 900 °C) with a ramp of 10 °C/min. The temperature is kept at the

final pyrolysis temperature for 2 h. The sample was then cooled down to room temperature with a ramp of 10 °C/min.

Etching of Mesoporous Silica. The SBA-15 mesoporous silica template around the resulting carbon-based samples was removed (or dissolved) by stirring the former with 1 mol/L NaOH solution at 100 °C for 2 h. After the pyrolysis, the obtained powder was dispersed in 1 mol/L NaOH solution (~10 µg/mL). The solutions were placed in polypropylene vials and kept in an oven at 100 °C for 4 h to age. After this, the powder was recovered using high speed centrifugation (12000 rpm – 8064 RCF). The powder was repeatedly washed with distilled water and centrifuged until the Ph of the solution became neutral.

Electrochemical Measurements

Preparation of Working Electrodes. Typically, 10 mg of the PDMC sample was added in 2 mL of propanol/water solution (1:3 v/v) with 210 µL of 5% Nafion solution. The dispersion was sonicated for 30 min to form an electrocatalyst ink. By carefully drop casting 4 µL of the resulting electrocatalyst onto a glassy carbon electrode having 5 mm diameter, the working electrodes were prepared. The final catalyst load was 100 µg/cm^2. Please note that the axes corresponding to currents presented in all electrochemical measurements and graphs were all normalized to the geometrical area of the electrodes.

Cyclic Voltammetry. Cyclic voltammetry analyses of the samples and electrocatalysis using the materials as electrocatalysts were conducted using a Versastat-3 from PAR (Princeton Applied Research) instrument. A three-electrode configuration consisting of a saturated calomel electrode as the reference electrode, a platinum wire (diameter: 0.1 mm) as the counter electrode and the glassy carbon electrode (GCE) containing the powdered PDMC samples on it as the working electrode was employed. The voltammograms were obtained at scan rate of 20 mV s^{-1}. The CV was performed in 0.1 KOH solution saturated with oxygen (O_2) or nitrogen (N_2)

Rotating Disc Electrode (RDE). The kinetics of the ORR reaction catalyzed by the samples were analyzed using a rotate disk electrode (RDE, Pine Research Instrumentation) connected to a Pine Bipotentiostat (Pine Research Instrumentation) assembled with a rotator (Pine Research Instrumentation). Here also, like in the case of cyclic voltammetry measurements above, a three-electrode configuration consisting of a saturated calomel electrode as the reference electrode, a platinum wire (diameter: 0.25 mm) as the counter electrode and glassy

carbon electrode with the powdered PDMC samples on it as the working electrode was employed. The working electrode was prepared using the method above described. The working electrode was scanned cathodically at a rate of 5 mV·s^{-1} with varying rotating speeds ranging from 400 rpm to 2,400 rpm.

The number of electrons transferred (n) in the oxygen reduction reaction (ORR) was determined using the Koutecky–Levich (K-L) equation (Eqn. 1):

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$ Eqn. 1

$$\text{where} = 0.62nFC_o(D_o)^{2/3}v^{-1/6},$$

j_k is kinetic current, j_l is diffusion-limiting current, n is the overall number of transferred electrons during O_2 reduction, F is Faraday constant (96,500 C·mol^{-1}), A is the geometric area of the electrode (cm^2), k is rate constant for oxygen reduction, C_0 is the saturated O_2 concentration in the electrolyte, D_O is the diffusion coefficient of O_2 in the electrolyte, v is the kinetic viscosity of the solution, and ω is the angular frequency of the rotation in terms of rad·s^{-1}.

The RDE experiment was performed using 0.1 mol/L KOH solution saturated with O_2. The number of electrons transferred (n) and j_k were obtained from the slope and intercept of the Koutecky−Levich plots ($1/j$ vs $\omega^{-0.5}$) respectively, and by using parameters $C_0 = 1.2 \times 10^{-3}$ mol L^{-1}, $D_0 = 1.9 \times 10^{-5}$ cm s^{-1}, and $v = 0.1$ m^2 s^{-1}.
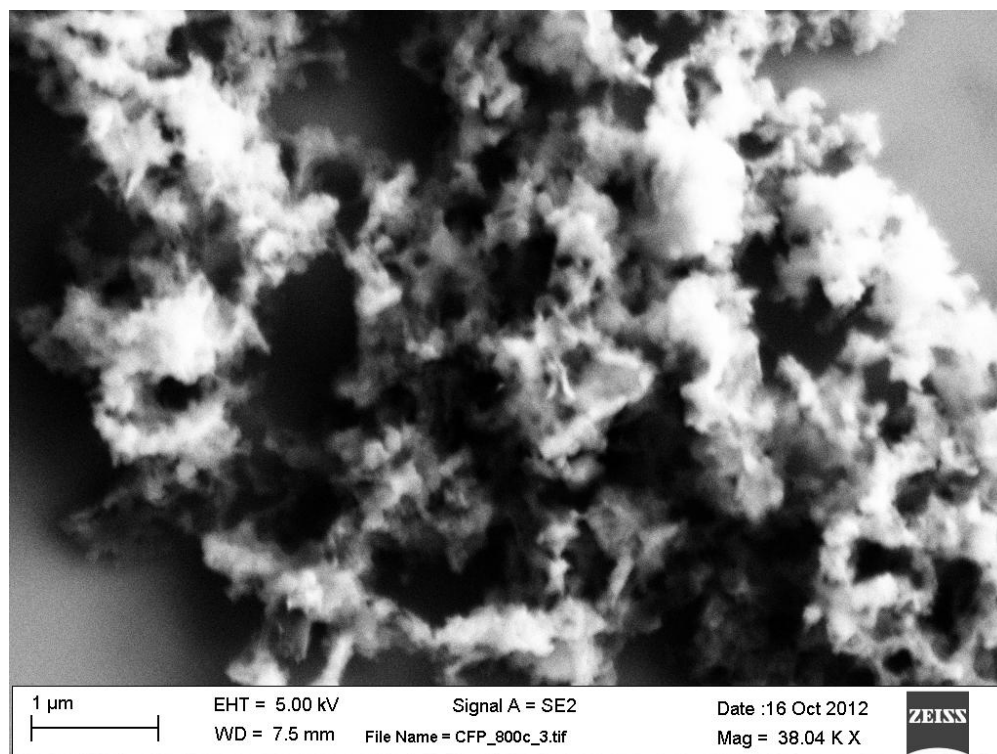
Calibration of Reference Electrode. All electrochemical measurements were carried out using a saturated calomel electrode (SCE) as reference. The SCE reference electrode was used to calibrate in the electrolyte solution used in the present work (0.1 mol/L KOH) saturated with hydrogen (H_2). As in this system hydrogen evolution and hydrogen oxidation can occur on a platinum working electrode depending on electric potential on the working electrode, the inter-conversion point between the anodic currents due to the hydrogen oxidation and due to the hydrogen evolution was used as the standard point for the RHE (Reversible Hydrogen Electrode) scale in this work. In the experiment, linear sweep voltammetry was carried out in a three electrode setup using a platinum foil as working electrode (1 cm^2 dipped in the solution), a platinum wire (0.25 mm diameter) as a counter electrode and the saturated calomel electrode as reference. The solution (0.1 mol/L KOH) was purged with H_2 gas prior the analysis for approximately 30 minutes.
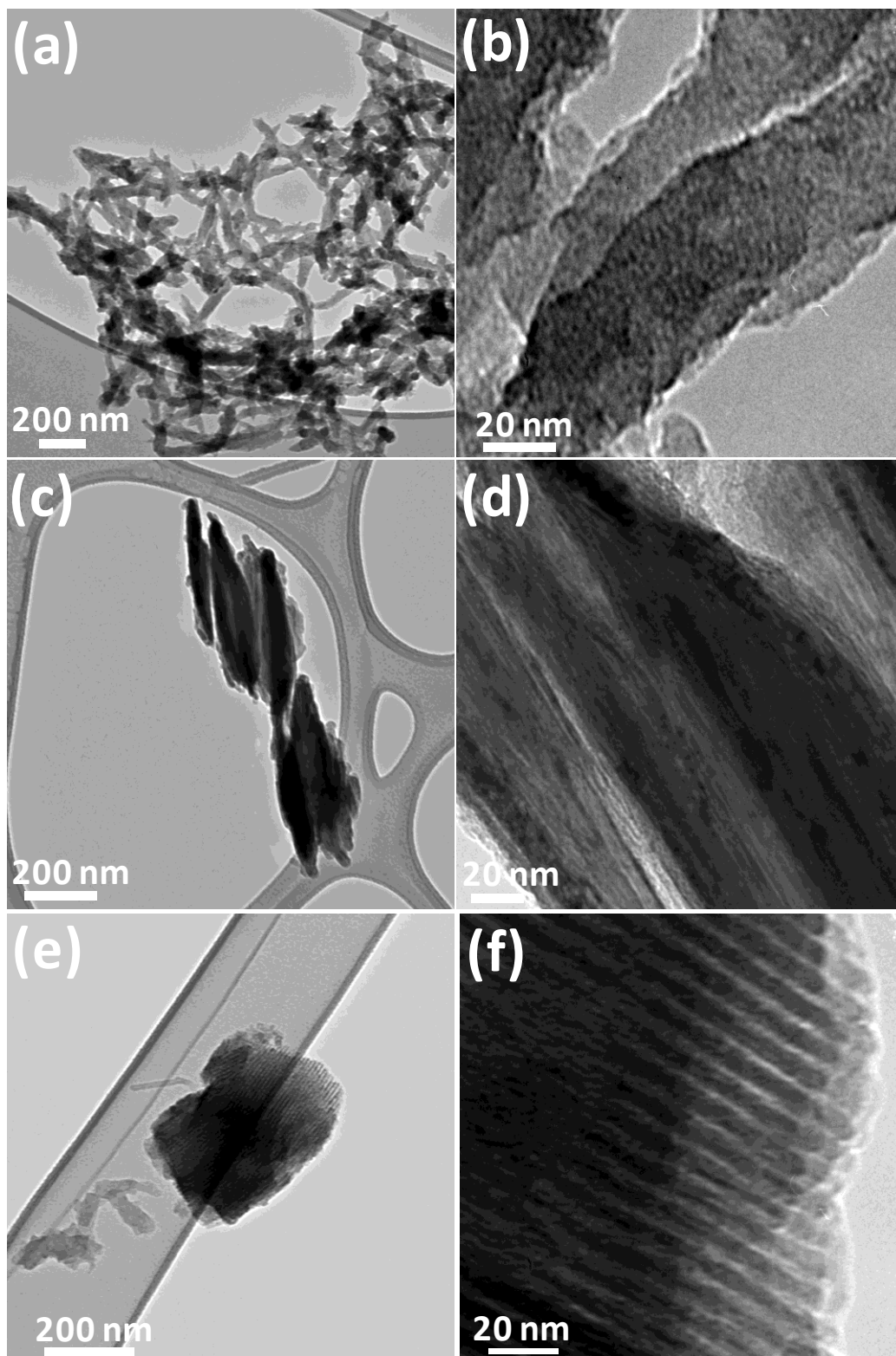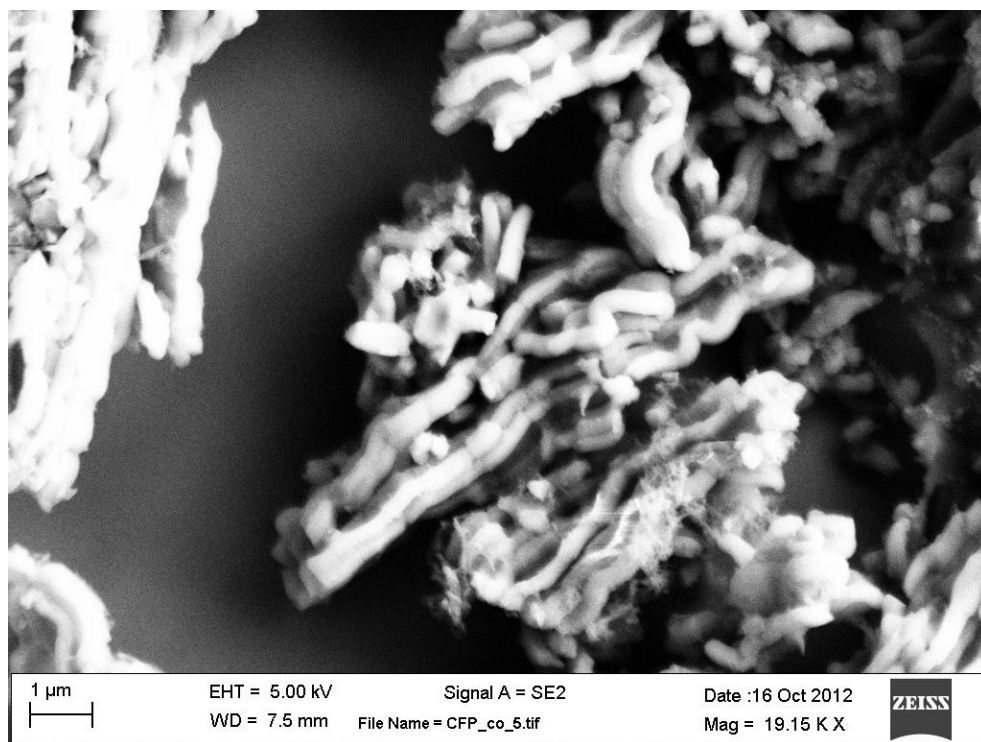
Figure S1. TEM images of mesoporous carbons (PDMCs) obtained by carbonization of PANI/SBA-15 at 600 ºC (*a,b*) and 800 ºC (*c,d*), and PANI/SBA-15 containing Co^{2+} ions at 800 ºC (PDMC-Co) (*e,f*).
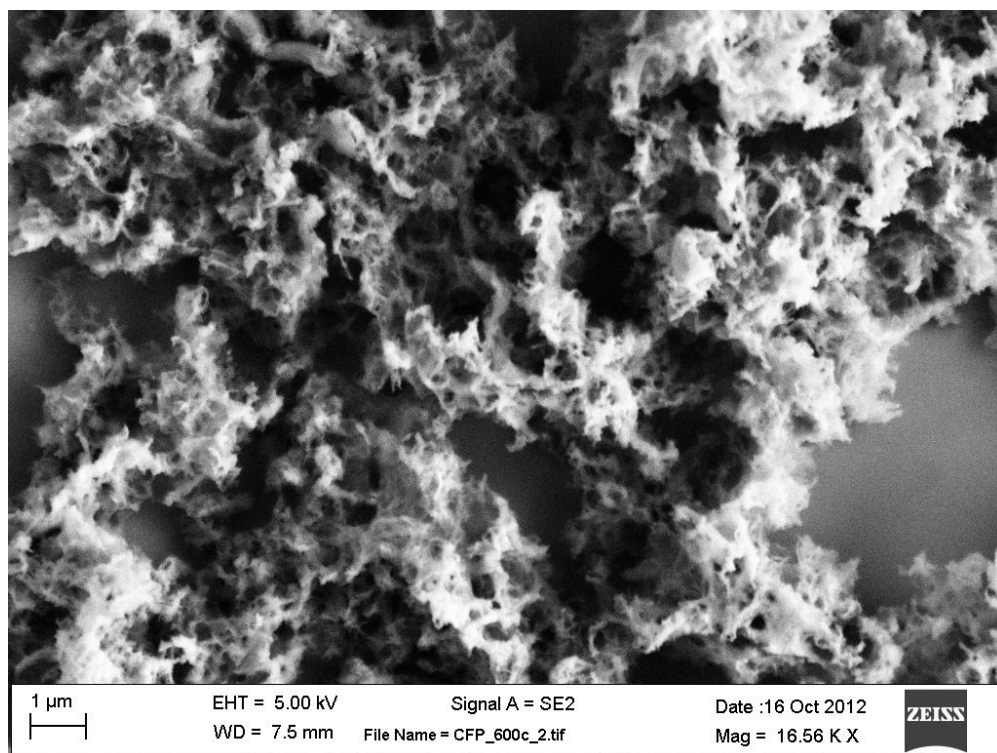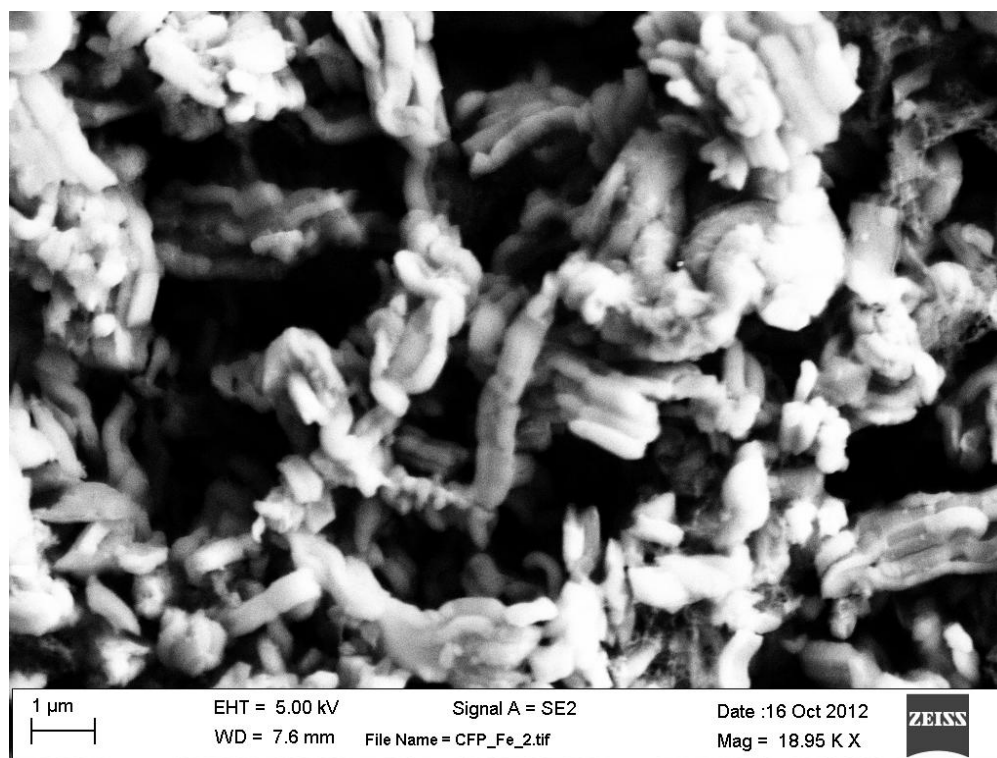
Figure S2. SEM images of the PDMC-600, the PDMC sample synthesized at 600 °C.

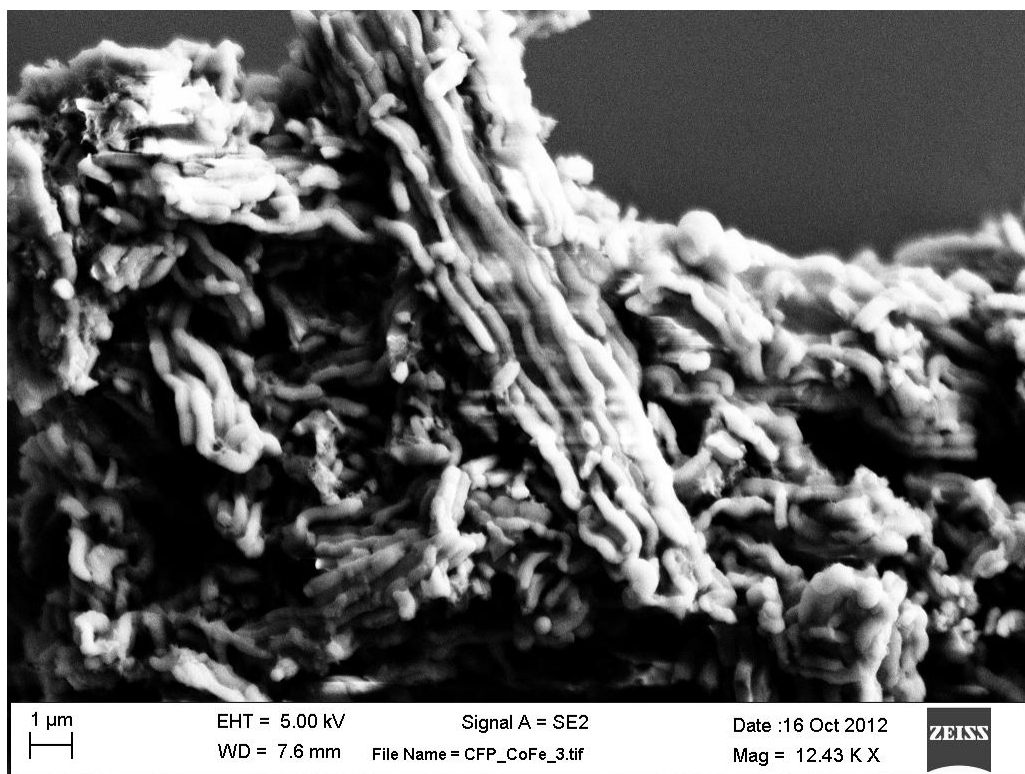**Figure S3.** SEM image of the PDMC-800, the PDMC sample synthesized at 800 °C.

| 1 μm | EHT = 5.00 kV | Signal A = SE2 | Date :16 Oct 2012 | ZEISS |
| | WD = 7.5 mm | File Name = CFP_co_5.tif | Mag = 19.15 K X | |

Figure S4. SEM image of PDMC/Co, the PDMC sample containing Co, synthesized at 800 °C.

| 1 μm | EHT = 5.00 kV | Signal A = SE2 | Date :16 Oct 2012 | ZEISS |
| | WD = 7.6 mm | File Name = CFP_Fe_2.tif | Mag = 18.95 K X | |

Figure S5. SEM image of PDMC/Fe, the PDMC sample containing Fe, synthesized at 800 °C.

1 µm EHT = 5.00 kV Signal A = SE2 Date :16 Oct 2012 ZEISS
WD = 7.6 mm File Name = CFP_CoFe_3.tif Mag = 12.43 K X

Figure S6. SEM image of PMMC-CoFe, the PDMC samples containing Co and Fe and synthesized at 800 °C.
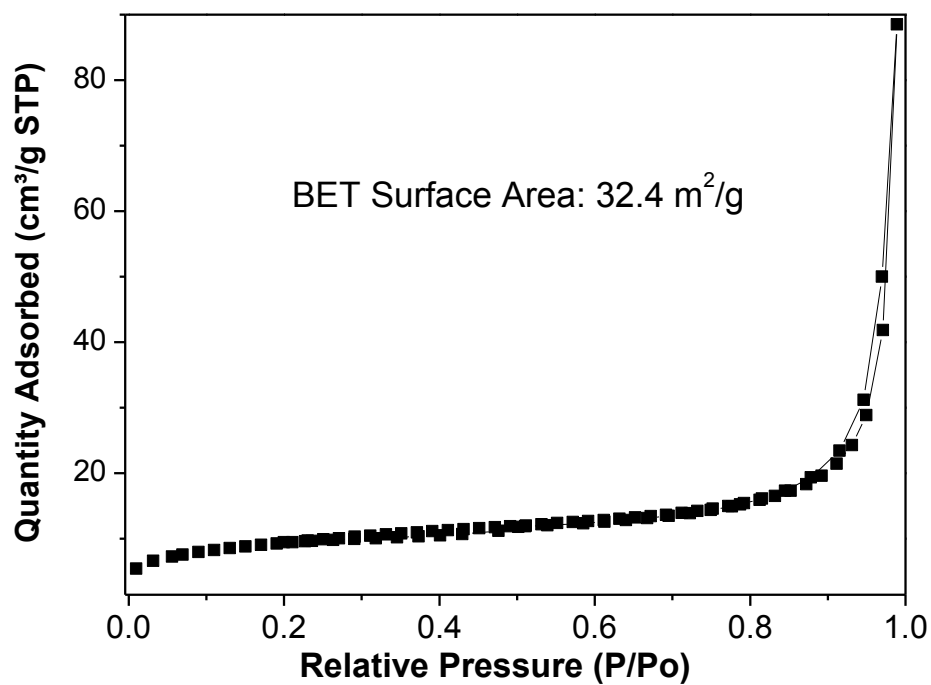
Figure S7. N_2 adsorption/desorption isotherm of PDMC.
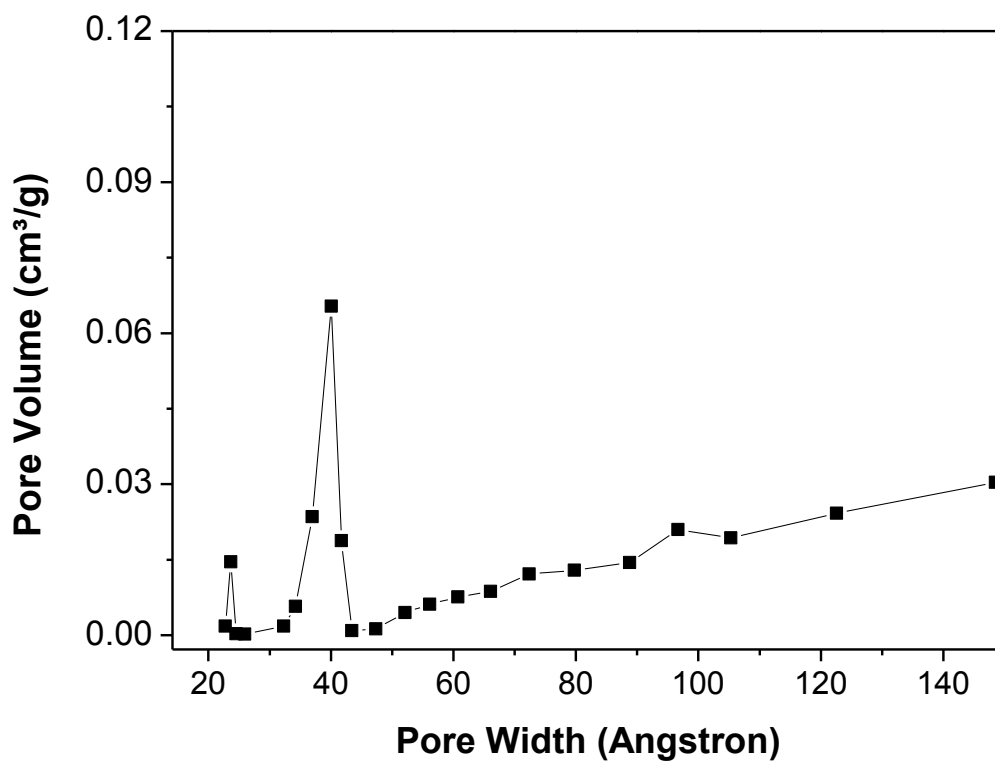
Figure S8. BJH pore size distribution curve of PDMC.
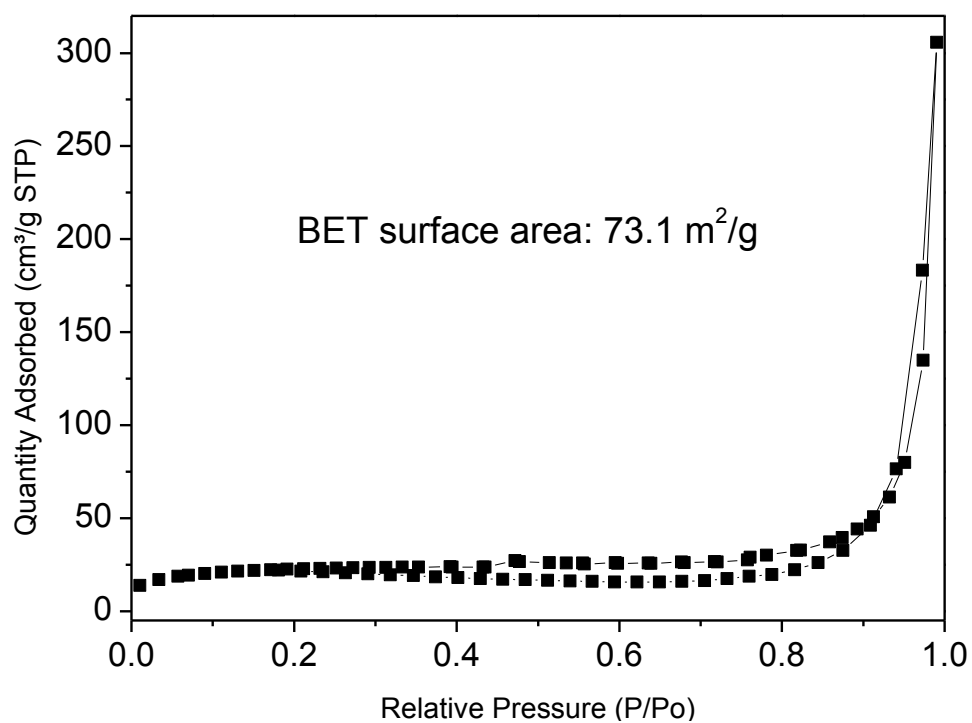
Figure S9. N_2 adsorption/desorption isotherm of PDMC-Co.
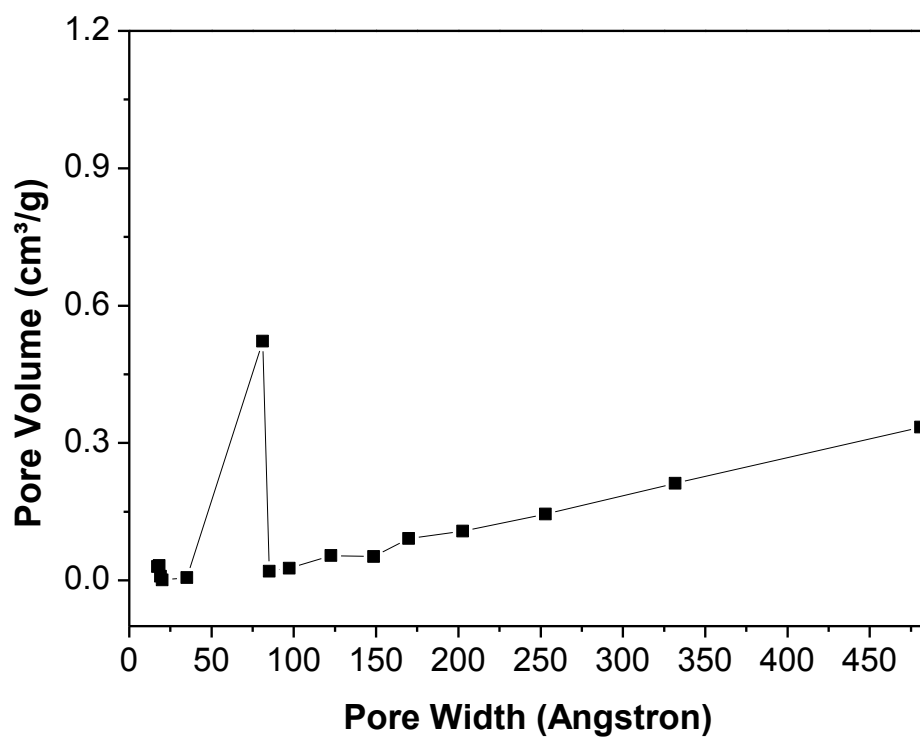
Figure S10. BJH pore size distribution curve of PDMC-Co.
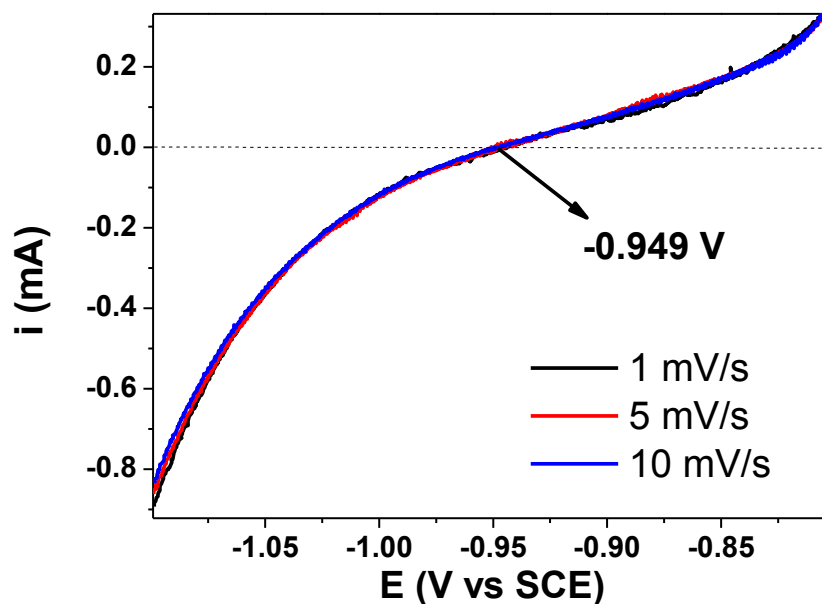
Figure S11. Linear sweep voltammograms obtained at different scan rate for 0.1 KOH solution saturated with hydrogen (H$_2$).

In Figure 1, the linear sweep voltammograms for different scan rate is presented. The system was swept in a cathode direction. The result showed that the interconversion between the hydrogen oxidation reaction and hydrogen evolution reaction occurred at -0.949 V versus SCE reference.

Based on this result, the following relation between SCE reference and reversible hydrogen electrode scale can thus be established (Eqn. 2):

$$E_{RHE} = E_{SCE} + 0.949\ V \qquad\qquad \text{Eqn. 2}$$

By using the above relation, all the electrochemical results presented in this work are corrected to RHE for comparison purposes.
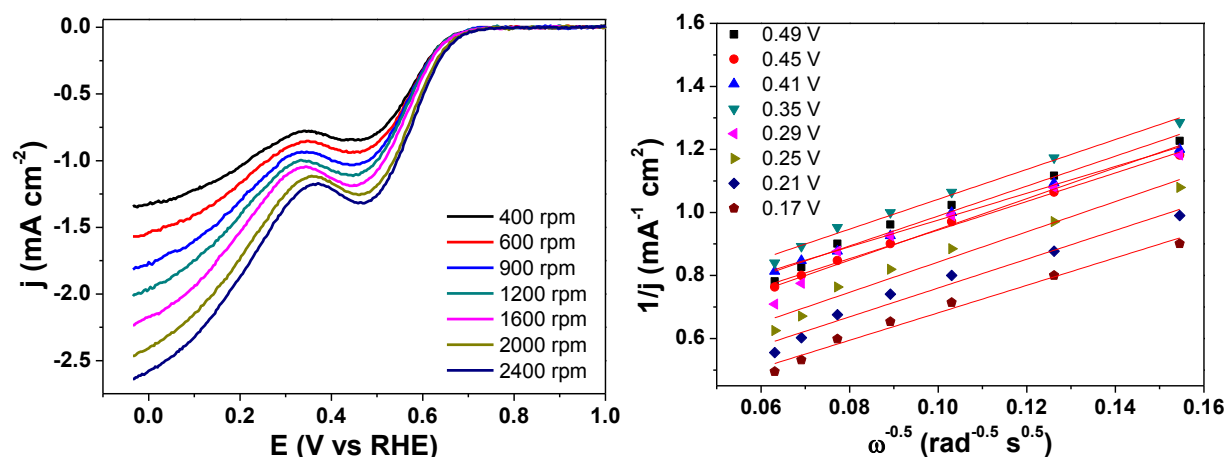
Figure S12. (Left Panel) RDE steady-state polarization curves for the ORR on the PDMC-600 °C electrocatalyst in O_2-saturated 0.1 M KOH solution at various rotating rates, as indicated next to the curves (in rpm) and (Right Panel) Koutecky-Levich plots for the ORR on the PDMC-600, the PDMC electrocatalyst made at 600 °C, at different electrode potentials.
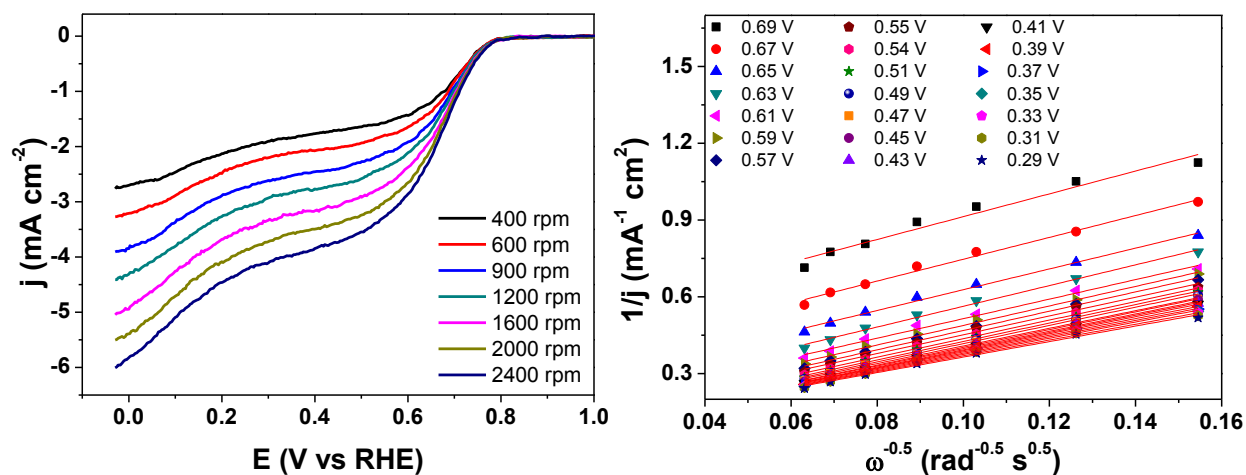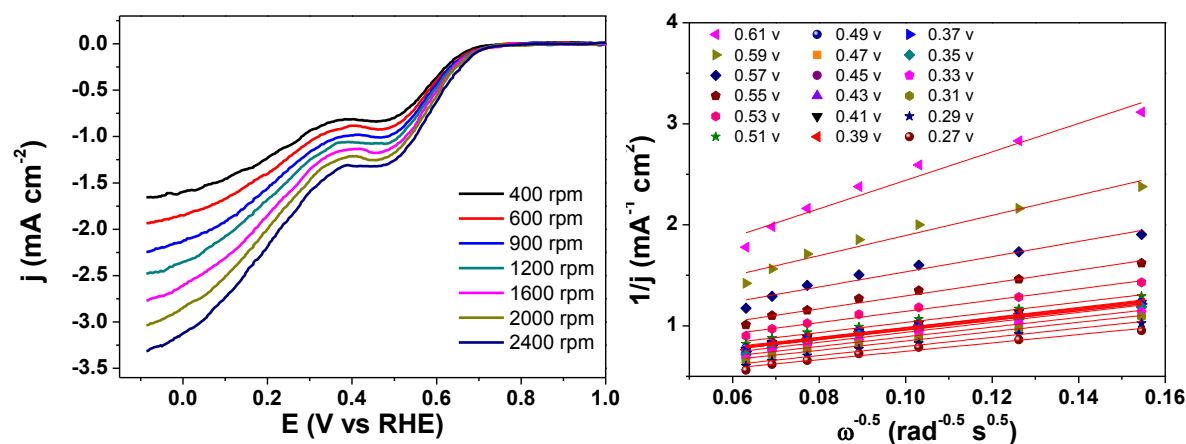

Figure S13. (Left Panel) RDE steady-state polarization curves of PDMC-700 (PDMC treated at 700 °C) electrocatalyst toward the ORR in O_2-saturated 0.1 M KOH solution at various rotating rates (as indicated in rpm within the graph) and (Right Panel) Koutecky-Levich plots of PDMC-700 electrocatalyst toward ORR at different electrode potentials.
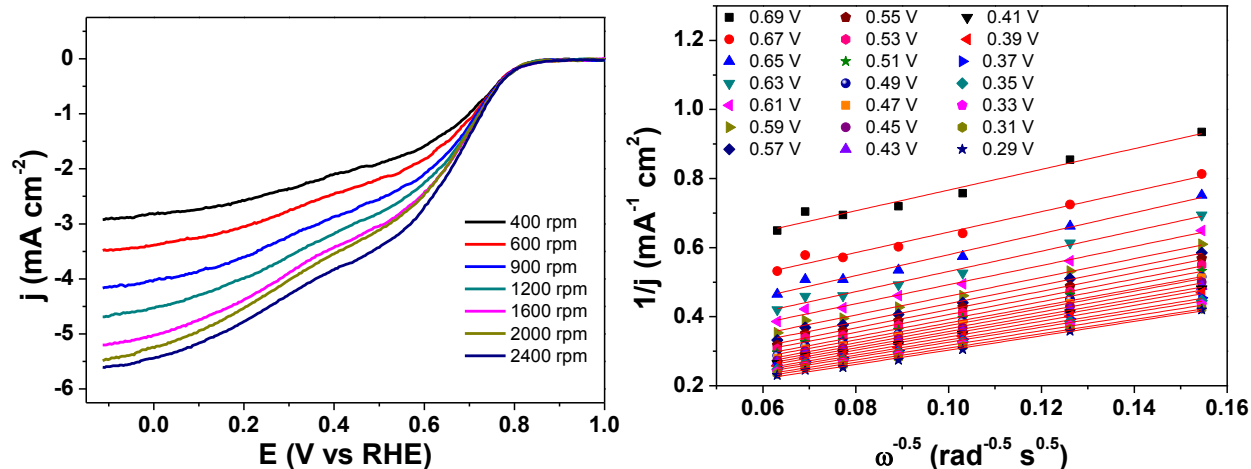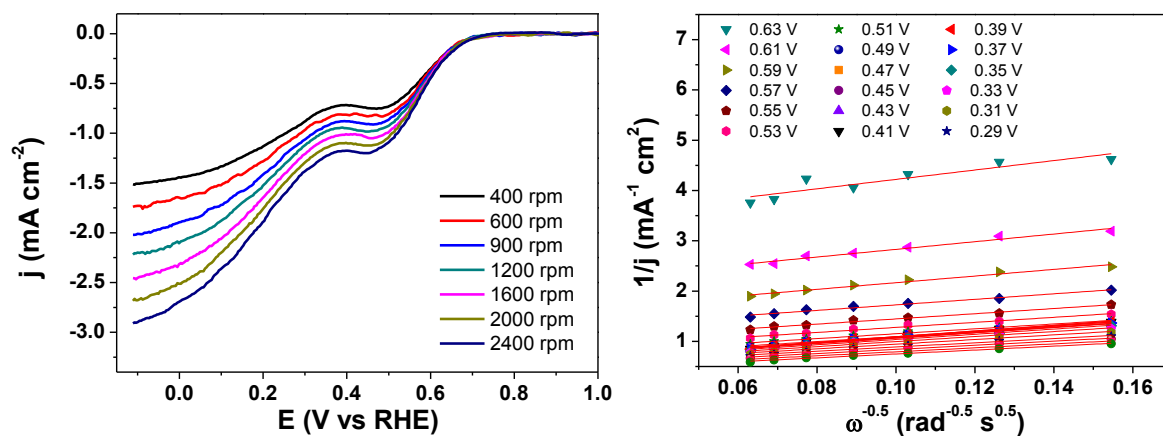
Figure S14. (Left Panel) RDE steady-state polarization curves for the ORR of PDMC-900 (the PDMC treated at 900 °C) electrocatalyst in oxygen-saturated 0.1 M KOH solution at various rotating rates in rpm, as indicated in the graphs and (Right Panel) Koutecky-Levich plots of PDMC-900 (the PDMC sample treated at 900 °C) electrocatalyst toward the ORR at different electrode potentials.
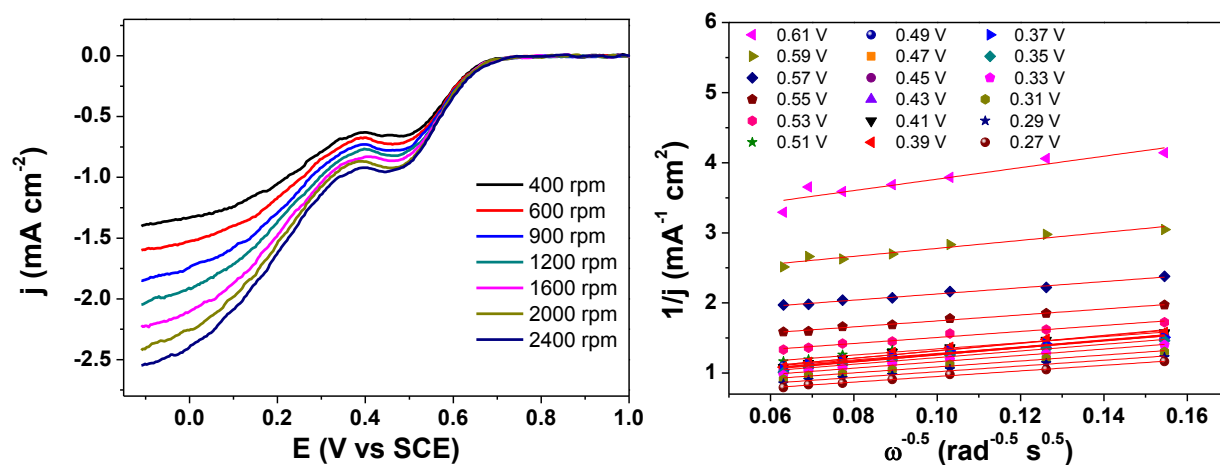

Figure S15. (Left Panel) RDE steady-state polarization curves PDMC-Co electrocatalyst toward ORR in O_2-saturated 0.1 M KOH solution at various rotating rates (in rpm), as indicated in the curves and (Right Panel) Koutecky-Levich plots of PDMC-Co electrocatalyst toward ORR at different electrode potentials.

Figure S16. (Left Panel) RDE steady-state polarization curves of PDMC-Fe electrocatalyst toward ORR in O_2-saturated 0.1 M KOH solution at various rotating rates (in rpm), as indicated in the curves and (Right Panel) Koutecky-Levich plots PDMC-Fe electrocatalyst toward ORR at different electrode potentials.

Figure S17. (Left Panel) RDE steady-state polarization curves of on the PDMC-CoFe electrocatalyst toward ORR in O_2-saturated 0.1 M KOH solution at various rotating rates (in rpm), as indicated in the graph and (Right Panel) the Koutecky-Levich plots of PDMC-CoFe electrocatalyst toward ORR at different electrode potentials.
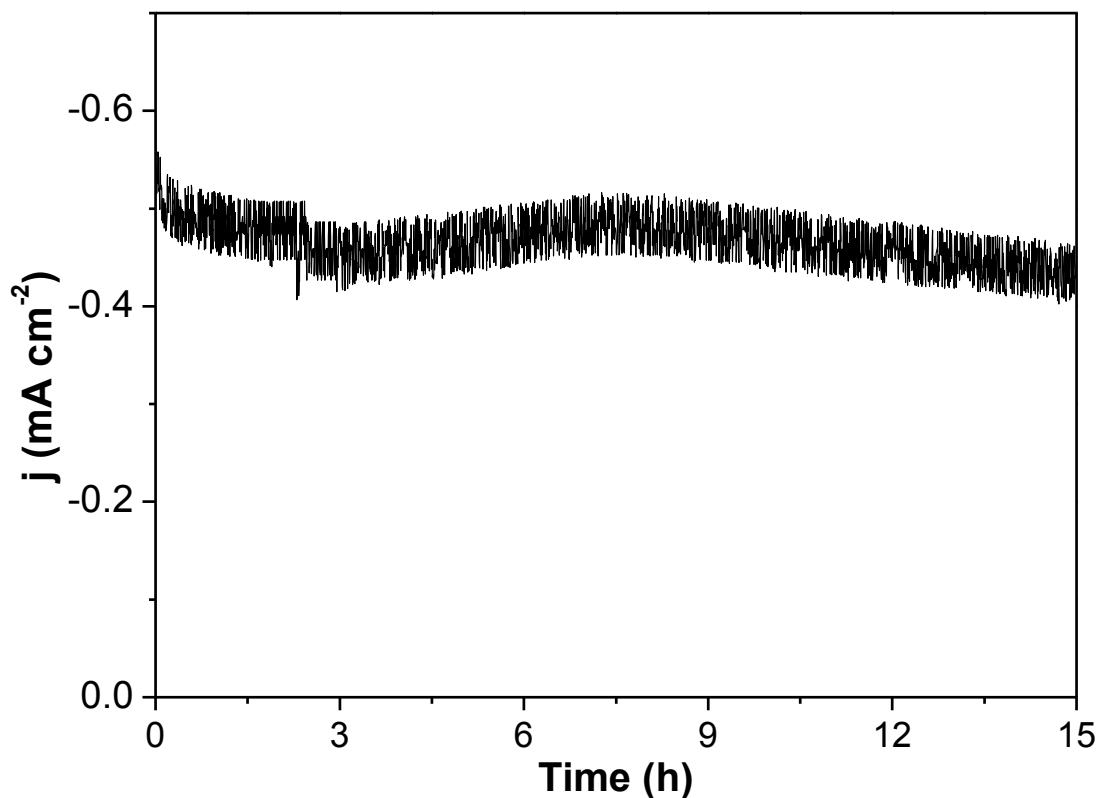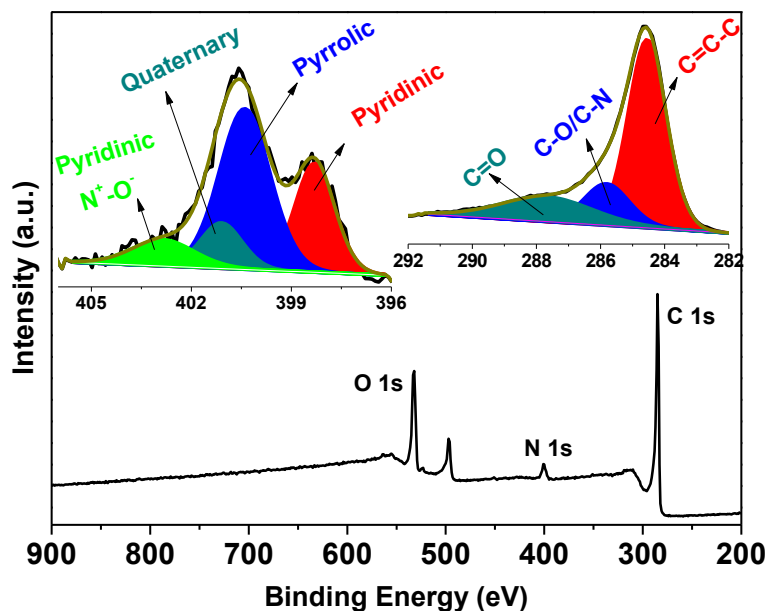
Figure S18. Chronoamperometric curves for PDMC in O_2 saturated 0.1 KOH at constant potential of 0.70 V vs RHE.
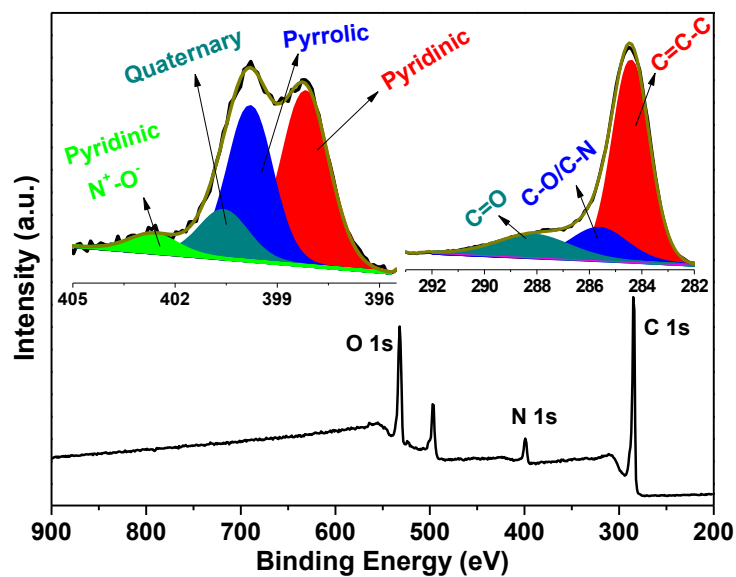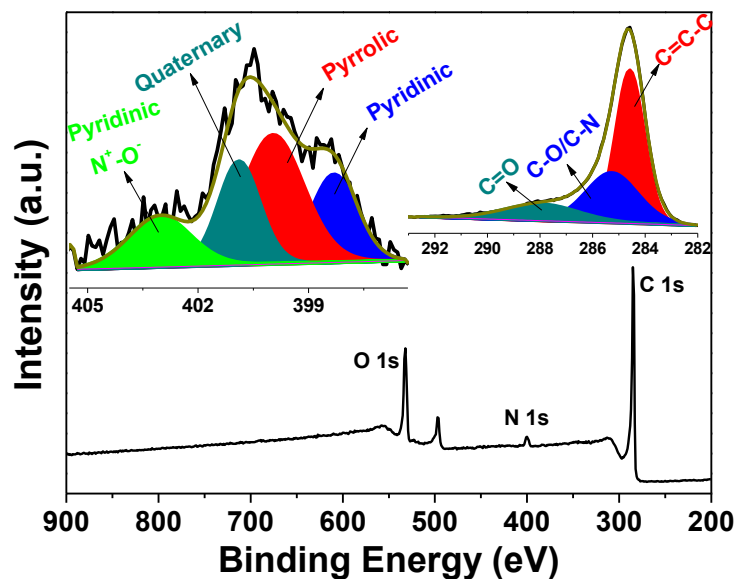

Figure S19. XPS survey spectrum of PDMC-600 (sample obtained at 600 °C), with the N 1s and C 1s spectra shown in inset.
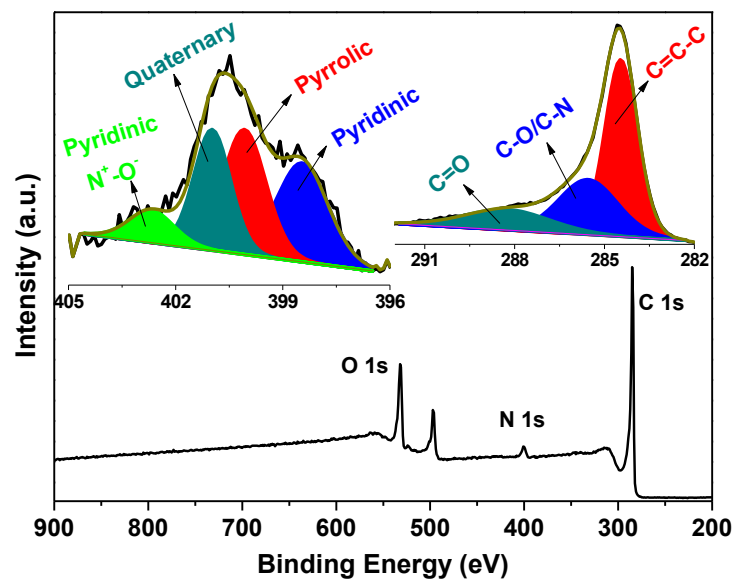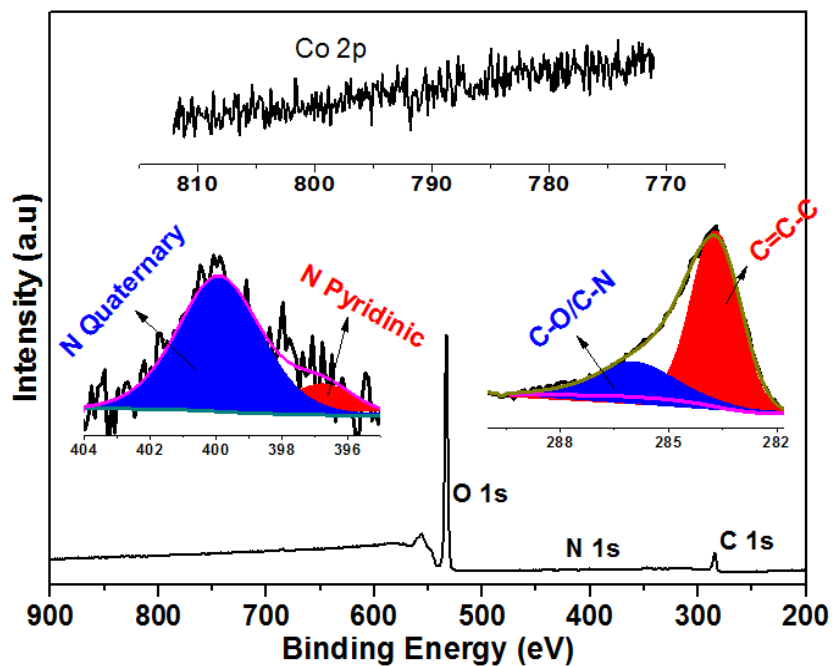
Figure S20. XPS survey spectrum of PDMC-700 (samples obtained at 700 °C) with the N 1s and C 1s spectra shown in inset.
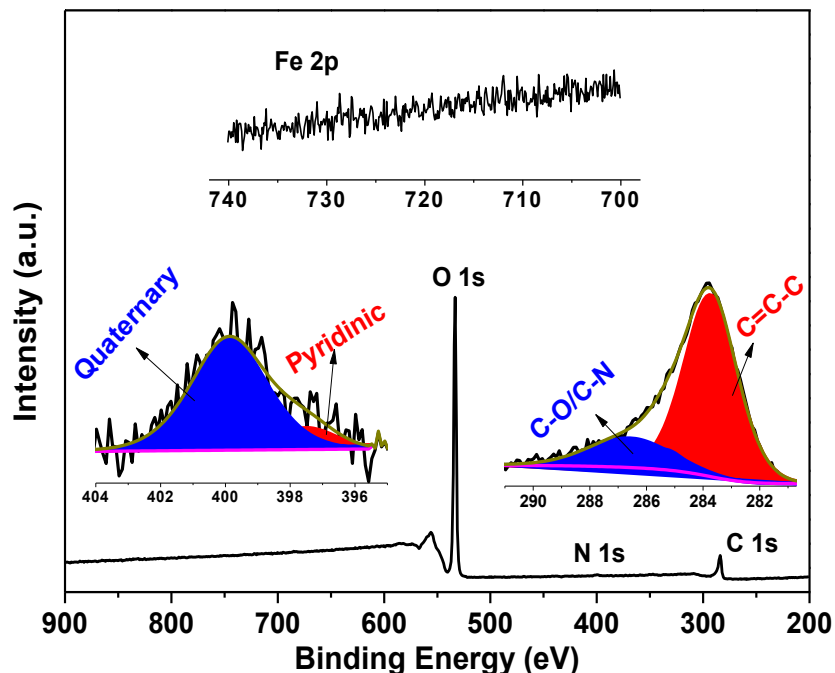

Figure S21. XPS survey spectrum of the PDMC-800 (sample obtained at 800 °C), with the N 1s and C 1s spectra shown in inset.
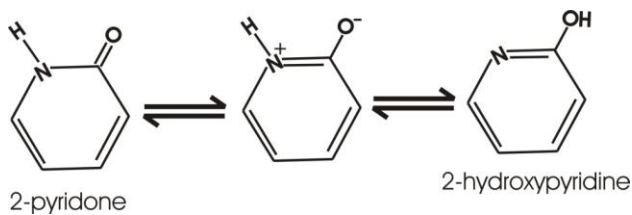
Figure S22. XPS survey spectrum of the PDMC-900 (sample obtained at 900 °C), with the N 1s and C 1s spectra shown in inset.
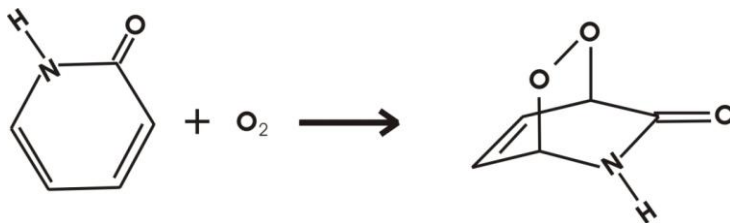

Figure S23. XPS survey spectrum of PDMC-Co, with the N 1s, C 1s and Co 2p spectra shown in inset.

Figure S24. XPS survey spectrum of PDMC-Fe, with the N 1s, C 1s and Fe 2p spectra shown in inset.

Figure S25. Tautomerization between 2-pyridone and 2 hydroxypyridine.

Figure S26. Representation of the addition reaction between molecular oxygen and a pyridone molecule, which lead to the formation of stable adduct. This process is easily verified when singlet oxygen is used.[3]

Supplementary Information References

(1) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548.

(2) Silva, R; Biradar, A. V.; Fabris, L; Asefa, T. *J. Phys. Chem. C* **2011**, *115*, 22810.

(3) Matsumoto, M.; Yamada, M.; Watanabe, N. *Chem. Commun.* **2005**, 483.