Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Graphene Oxide/Core-shell Structured Metal-Organic Frameworks Nano-sandwiches and Their Derived Cobalt/N-doped Carbon Nanosheets for Oxygen Reduction Reaction

Jing Wei, Yaoxin Hu, Yan Liang, Biao Kong, Zhanfeng Zheng, Jin Zhang, San Ping Jiang, Yongxi Zhao, Huanting Wang**

Experiment

Synthesis of GO/core-shell structured ZIF-8@ZIF-67: GO/core-shell structured ZIF-8@ZIF-67 was synthesized via ZIF-8 seed-mediated deposition approach. ZIF-8 seeds were firstly deposited on GO to synthesize GO/ZIF-8. Typically, $Zn(NO_3)_2$•$6H_2O$ (0.366 g) and 2-methylimidazole (Hmim, 0.811 g) were dissolved in 12 and 20 mL of methanol respectively. Then, $Zn(NO_3)_2$ solution (12 mL) was added into the 2-methylimidazole solution to obtain a clear solution. 8 mL of GO solution (1 mg/mL, in water/methanol, 1:4, *v*/*v*) was added to the above mixed solution immediately. After stirring for 3 h, the grey precipitation was collected by centrifugation (8000 rpm for 5 min) and washing with methanol at least three times. After drying at 50 ºC for 12 h, GO/ZIF-8 was prepared. Then, ZIF-67 was deposited on GO/ZIF-8. Typically, 15 mL of $Co(NO_3)_2$•6 H_2O (0.2185 g) methanol solution was added into 30 mL of methanol solution containing 0.3 g of GO/ZIF-8 for 5 min. Then 15 ml of 2-methylimidazole methanol solution containing 0.2465 g of 2-methylimidazole was added into the above solution and stirred for 15 min at room temperature. The product was collected by centrifugation and washed three times with methanol. The content of ZIF-67 deposited on GO can be adjusted by changing the concentration of Co^{2+} and Hmim solution. For example, GO/ZIF-8@ZIF-67-L and GO/ZIF-8@ZIF-67-H were synthesized using Co^{2+} solution with 0.0125 and 0.05 mol/L while the molar ratio of Co^{2+} to Hmim kept constant.

Synthesis of GO/ZIF-67: GO/ZIF-67 was synthesized via direct deposition route, which was similar to that of GO/ZIF-8 except for the amount of $Co(NO_3)_2$•$6H_2O$ (0.358 g).

Synthesis of Co/C composites: The Co/C composites were synthesized via the carbonization of GO/ZIF composites followed by acid etching. In a typical synthesis, GO/ZIF-8@ZIF-67 was carbonized at 700-900 ºC in Ar atmosphere. Then the obtained powders were immersed in 2 M HCl solution for 24 h to remove the exposed cobalt nanoparticles. The residual solid was collected and washed with water at least three times. After drying at 100 ºC for 1 day, the samples were denoted GO/ZIF-8@ZIF-67-*x* (*x*= 700, 800 and 900, refers the carbonization temperature). For comparison, GO/ZIF-8 and GO/ZIF-67 were also treated using the same method, and the obtained materials were denoted GO/ZIF-8-900 and GO/ZIF-67-900.

Characterization: Scanning electron microscopy (SEM) images were taken with a field-emission scanning electron microscope (FEI Nova NanoSEM 450). Transmission electron microscopy (TEM) images were taken by a FEI Tecnai G2 F20 operated at an accelerating voltage of 200 kV. The samples were first dispersed in ethanol. A drop of the dispersion was supported on a copper grid with holey carbon films and then dried, prior to TEM characterization. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a Kratos AXIS Ultra DLD system with Al Kα radiation as an X-ray source for radiation. Powder X-ray diffraction (PXRD) patterns were recorded in the 2θ range of 5-80° at room temperature using a Miniflex 600 diffractometer (Rigaku, Japan) in a transmission geometry using Cu Kα radiation (15 mA and 40 kV) at a scan rate of 2 °/min and a step size of 0.02 °. Nitrogen adsorption/desorption isotherms were measured at -196 °C with a Micromeritics 3Flex Analyzer. The samples were degassed in a vacuum at 180 °C for at least 12 h before the test. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area using the adsorption data at p/p_0 range of 0.05 ~ 0.25. The pore size is calculated using nonlocal density functional theory (NLDFT) method.

Electrochemical measurements: Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed using a μAutolab electrochemical analyzer in a conventional three-electrode electrochemical cell. A Pt wire auxiliary electrode, a saturated Ag/AgCl (saturated with 3 M KCl) reference electrode, and rotating disk working electrode were used. 4 mg of catalysts (or commercial Pt/C, 20 wt%, from Sigma-Aldrich, Australia) were dispersed in 1 mL of ethanol (containing 0.03 mL of 5.0 wt % Nafion) solution under ultrasonic agitation to form a homogeneous catalyst ink. Then 5 μL of the catalyst ink was dropped on the surface of the polished rotating disk electrode (5 mm diameter, 0.196 cm^2) and dried at room temperature. The nonprecious metal catalyst loadings are ~ 0.1 mg cm^{-2} in 0.1 M KOH and ~ 0.2 mg cm^{-2} in

0.1 M $HClO_4$. The loading of Pt/C is 0.1 mg cm^{-2} in both alkaline and acidic condition. Argon and O_2 were used to achieve oxygen-free and oxygen-rich environments. The electrolyte was saturated with Ar (or O_2) before test. The CV curves were recorded at a scan rate of 50 mV/s, and the RDE curves were recorded at a scan rate of 10 mV/s. A flow of O_2 was maintained over the electrolyte during LSV test to ensure O_2 saturation. The numbers of electrons transferred (n) during ORR was calculated by Koutecky-Levich equation at various electrode potentials:

$$\frac{1}{J}=\frac{1}{J_L}+\frac{1}{J_K}=\frac{1}{B\omega^{0.5}}+\frac{1}{J_K}$$

$$B=0.62nFC_0D_0^{2/3}v^{-1/6}$$

where J is the measured current density, J_K and J_L are the kinetic and diffusion-limiting current densities, ω is the angular velocity, n is transferred electron number, F is the Faraday constant (96485 C mol^{-1}), C_0 is the bulk concentration of O_2 (1.2×10^{-6} mol cm^{-3} for 0.1 M KOH, 1.26×10^{-6} mol cm^{-3} for 0.1 M $HClO_4$), D_0 is the diffusion coefficient of O_2 (1.9×10^{-5} cm^2 s^{-1} in 0.1 M KOH, 1.93×10^{-5} cm^2 s^{-1} in 0.1 M $HClO_4$), and v is the kinematic viscosity of the electrolyte (0.01 cm^2 s^{-1} in 0.1 M KOH, 0.01009 cm^2 s^{-1} in 0.1 M $HClO_4$).

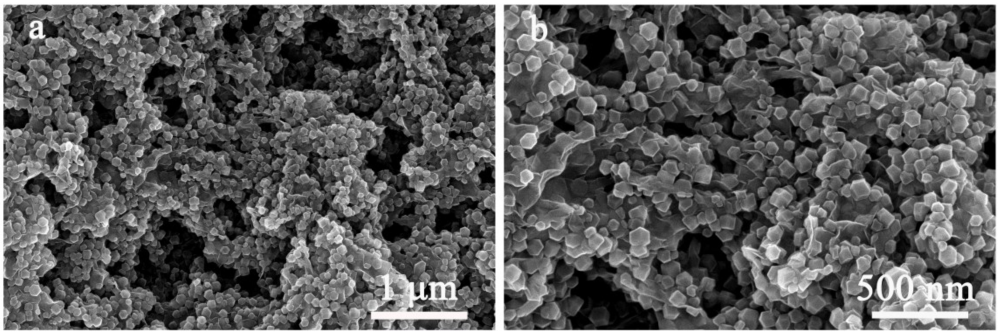

Figure S1 (a, b) SEM images of GO/ZIF-67 synthesized by direct deposition of ZIF-67 on GO.

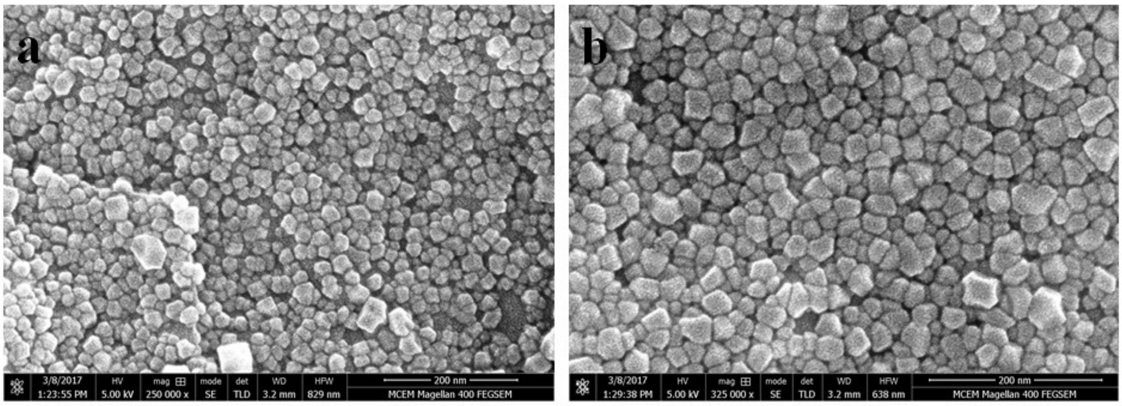

Figure S2 High resolution SEM images of (a) GO/ZIF-8 and (b) GO/ZIF-8@ZIF-67. The SEM images reveal that the distance between the ZIF crystals become smaller after coating of ZIF-67, indicating a successful deposition of ZIF-67 on the surface of ZIF-8.

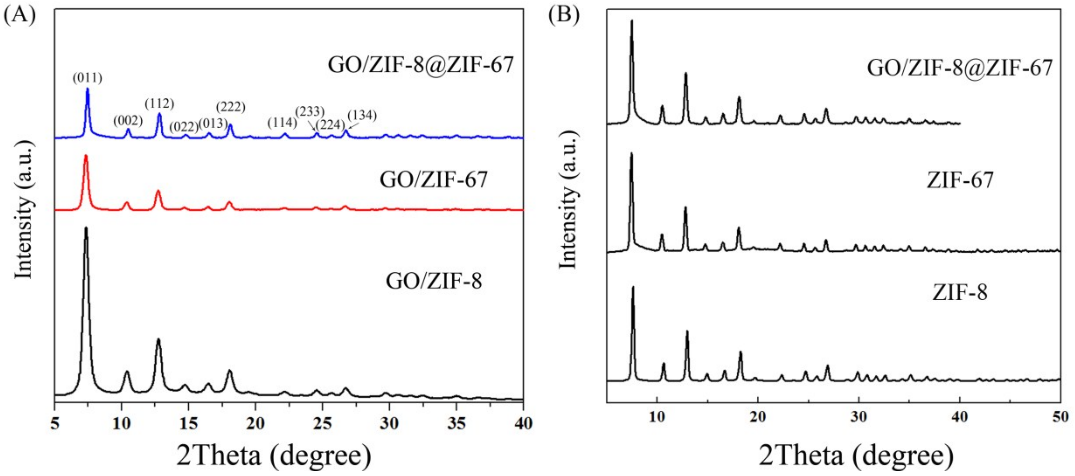

Figure S3 XRD patterns of (A) GO/ZIF-8, GO/ZIF-67 and GO/ZIF-8@ZIF-67; and (B) ZIF-8, ZIF-67 and GO/ZIF-8@ZIF-67, respectively. All the materials reveal the typical diffraction peaks of ZIF.

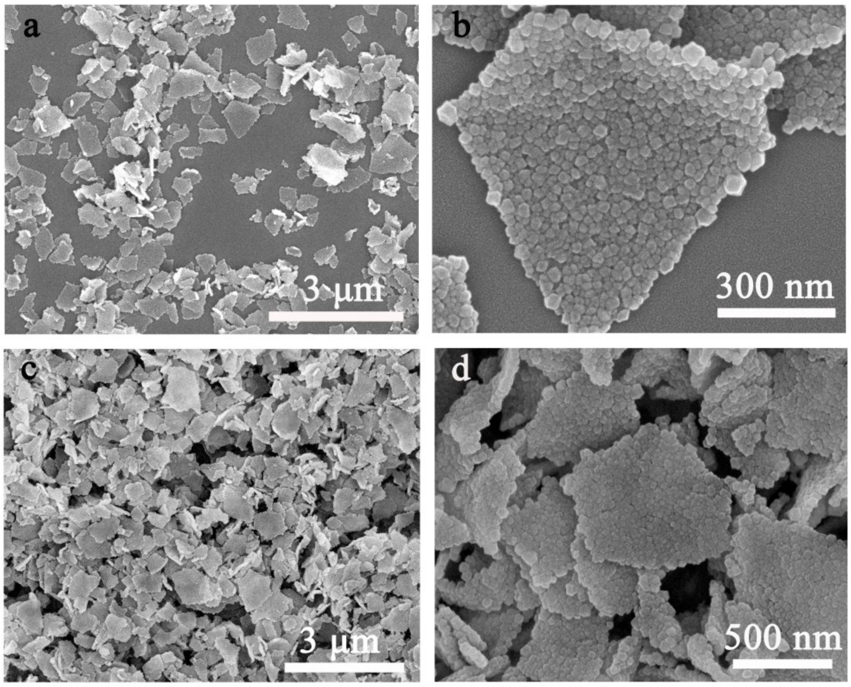

Figure S4 SEM images of (a, b) GO/ZIF-8@ZIF-67-L and (c, d) GO/ZIF-8@ZIF-67-H using different concentrations of Co ions solution as a Co source.

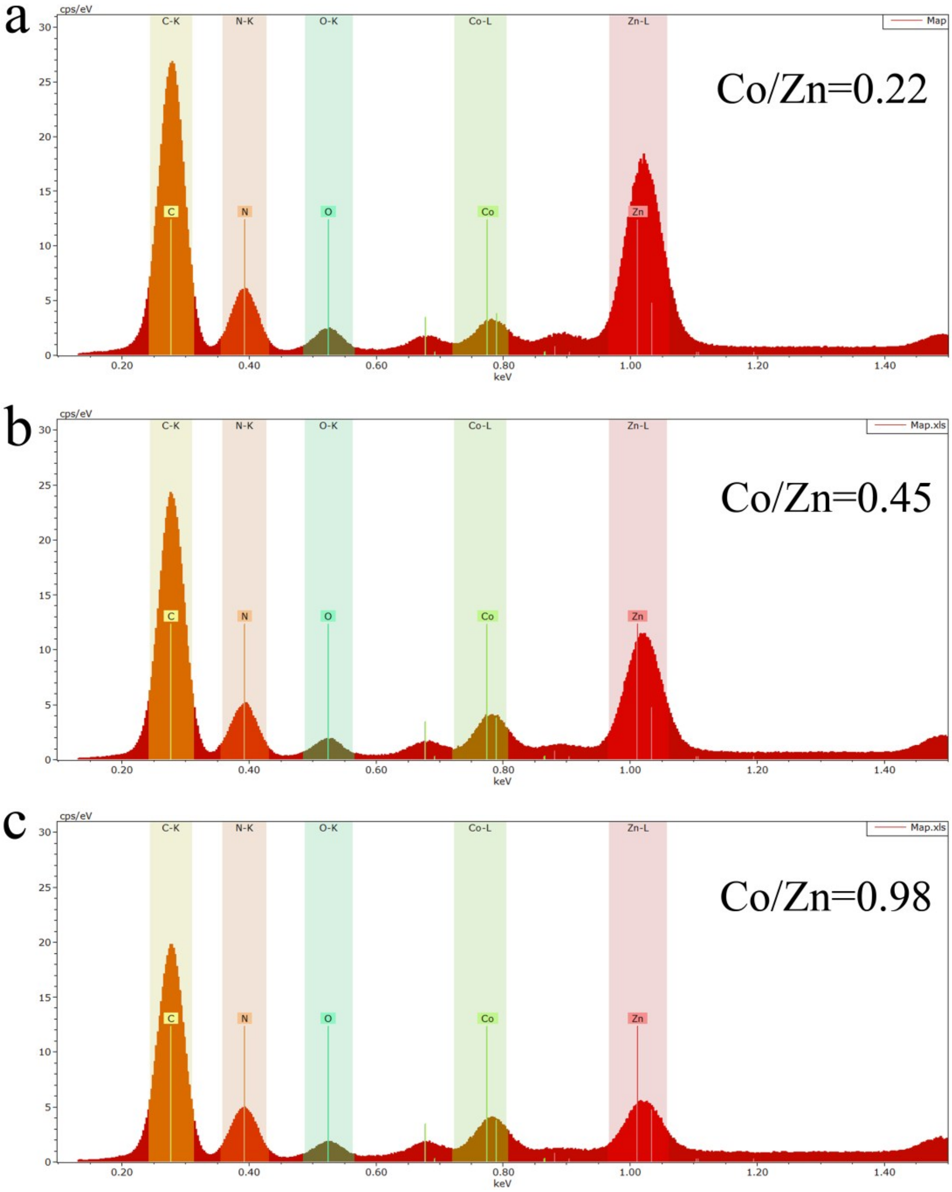

Figure S5 EDX spectra for (a) GO/ZIF-8@ZIF-67-L, (b) GO/ZIF-8@ZIF-67 and (c) GO/ZIF-8@ZIF-67-H from the SEM images. The atom ratio of Co to Zn in the GO/MOF composites increases as the initial concentrations of Co ions solution increase.

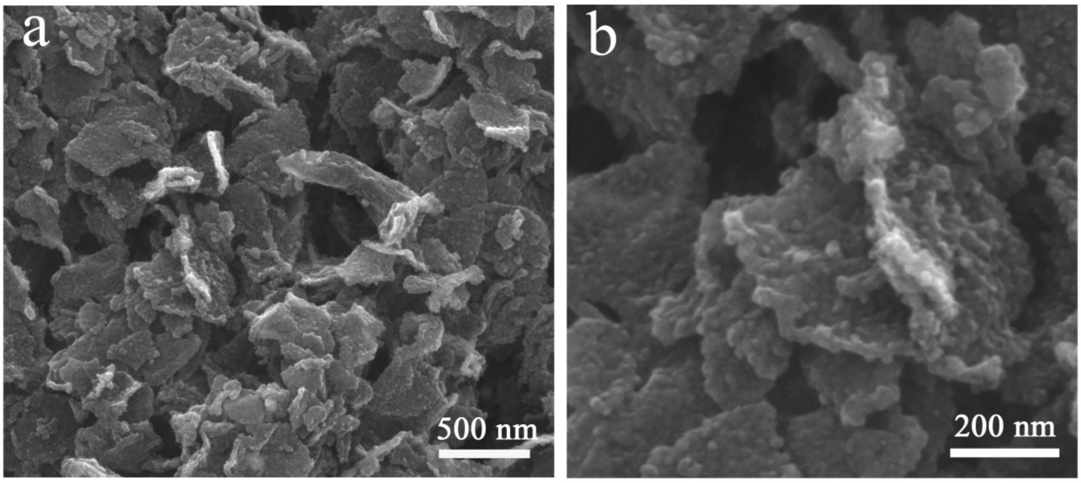

Figure S6 SEM images of GO/ZIF-8@ZIF-67-900 synthesized by carbonization of GO/ZIF-8@ZIF-67 at 900 ºC in Ar followed by acid etching.

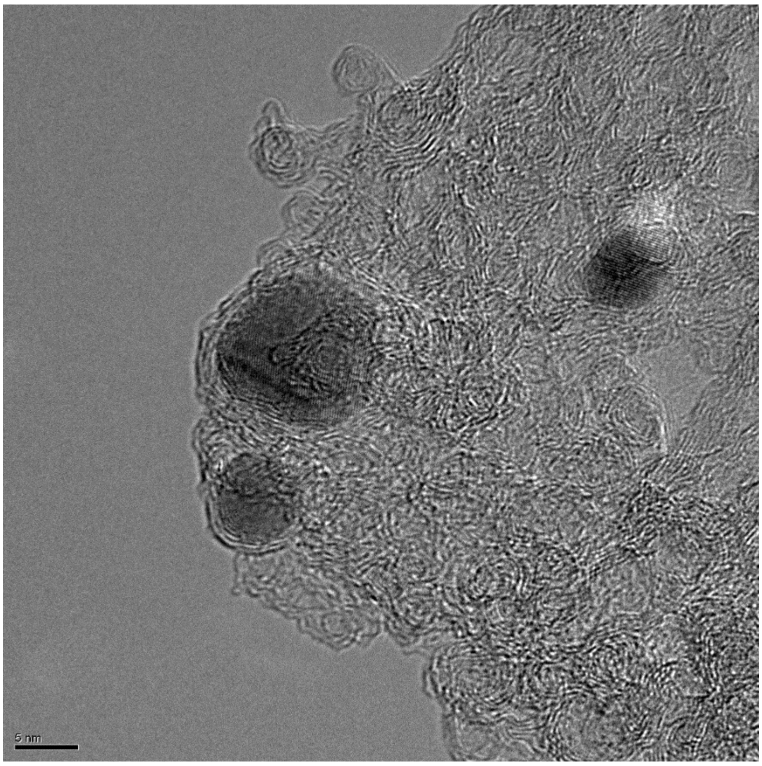

Figure S7 High-resolution TEM image of GO/ZIF-8@ZIF-67-900. The high crystalline cobalt nanoparticles were encased by the graphitic carbon layer.

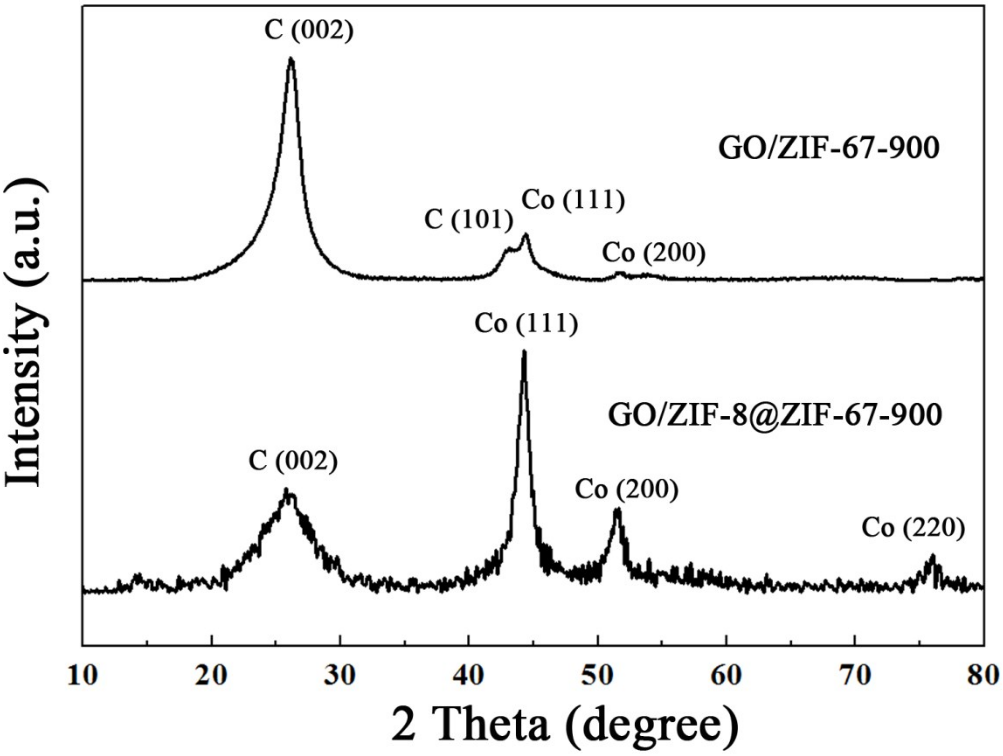

Figure S8 XRD patterns of cobalt/carbon composites synthesized by carbonization of GO/ZIF-8@ZIF-67 and GO/ZIF-67 at 900 °C respectively.

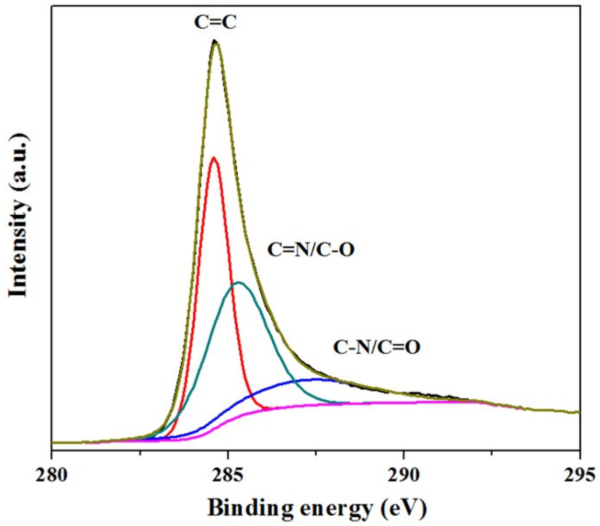

Figure S9 The high-resolution C 1s spectrum of GO/ZIF-8@ZIF-67-900. For C 1s spectrum, the dominated peak positioned at 284.58 eV is attributed to C=C, while the peaks at 285.24 and 287.25 eV are ascribed to C=N/C-O and C-N/C=O respectively.

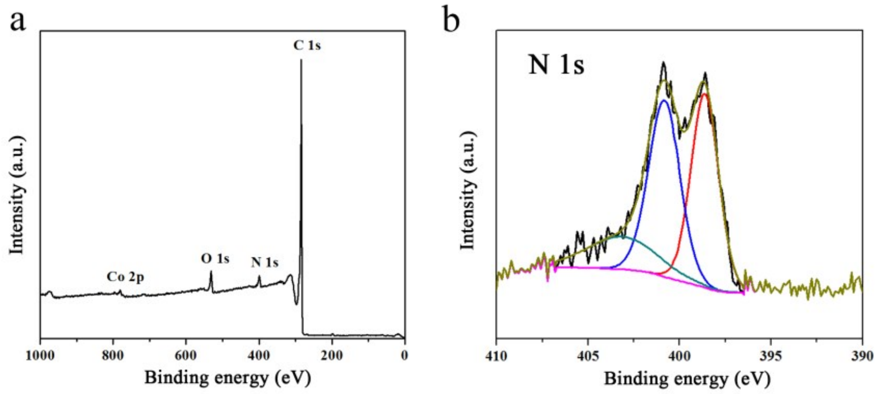

Figure S10 (a) XPS spectrum and (b) high resolution N 1s spectrum for GO/ZIF-67-900.

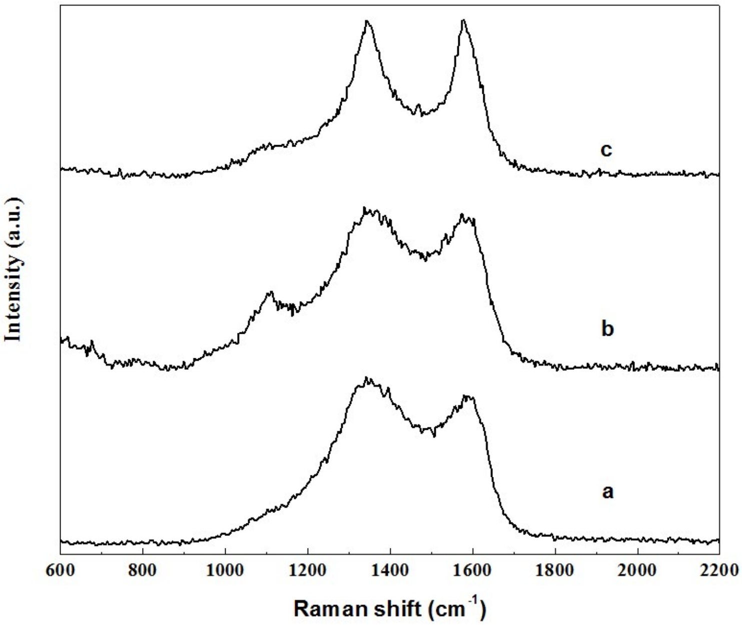

Figure S11 Raman spectra of (a) GO/ZIF-8-900, (b) GO/ZIF-8-67-900 and (c) GO/ZIF-67-900. As the ratio of cobalt to zinc increases, the I_D/I_G decreases, indicating the increasing graphitization degree of the carbon composites. The band at around 1100 cm^{-1} is from the glass substrate for loading of the samples.

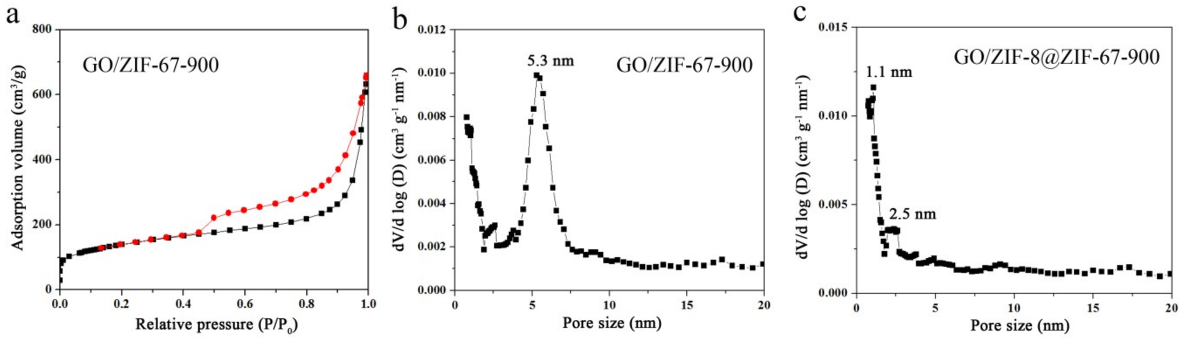

Figure S12 (a) N_2 sorption isotherms and (b) NLDFT pore size distributions for GO/ZIF-67-900. (c) NLDFT pore size distributions for GO/ZIF-8@ZIF-67-900.

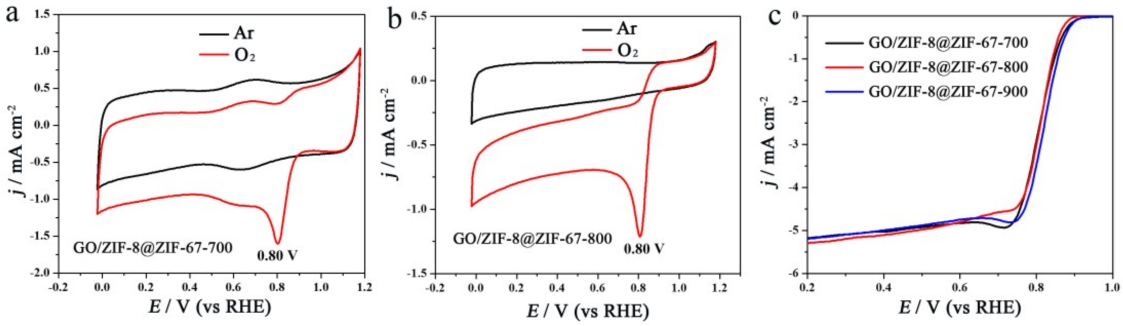

Figure S13 Cyclic voltammetry (CV) curves for (a) GO/ZIF-8@ZIF-67-700 and (b) GO/ZIF-8@ZIF-67-800 in Ar (or O_2)-saturated 0.1 M KOH solution. (c) Linear scan voltammogram (LSV) curves for GO/ZIF-8@ZIF-67-700, GO/ZIF-8@ZIF-67-800 and GO/ZIF-8@ZIF-67-900 respectively in O_2-saturated 0.1 M KOH solution with a rotating speed of 1600 rpm.

As the carbonization temperature is one key parameter to the preparation of catalysts, the catalysts prepared by carbonization of GO/ZIF-8@ZIF-67 at 700 and 800 ºC (denoted GO/ZIF-8@ZIF-67-700 and GO/ZIF-8@ZIF-67-800) were also used for ORR. The oxygen reduction peaks for both GO/ZIF-8@ZIF-67-700 and GO/ZIF-8@ZIF-67-800 are observed at about 0.80 V (*vs*. RHE). GO/ZIF-8@ZIF-67-900 show highest oxygen reduction potential among these three samples, indicating 900 ºC is possible the optimized temperature. In this work, 900 ºC is thus selected to carbonize other catalytic precursors for further investigation.

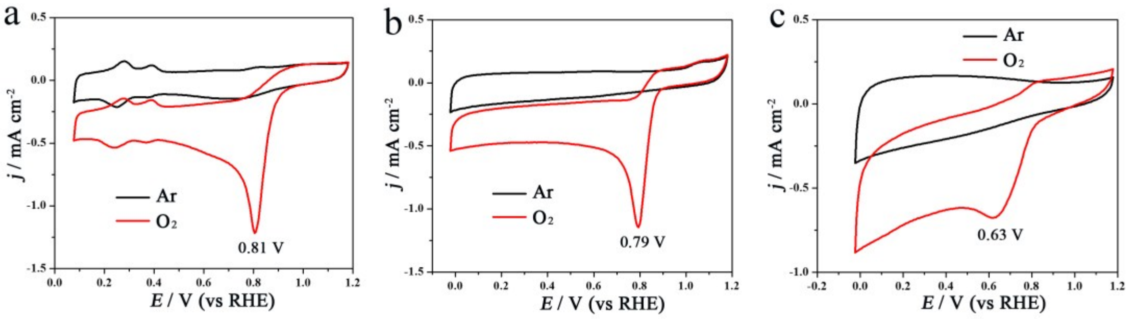

Figure S14 CV curves for Pt/C, GO/ZIF-67-900 and GO/ZIF-8-900 respectively in Ar (or O_2)-saturated 0.1 M KOH solution

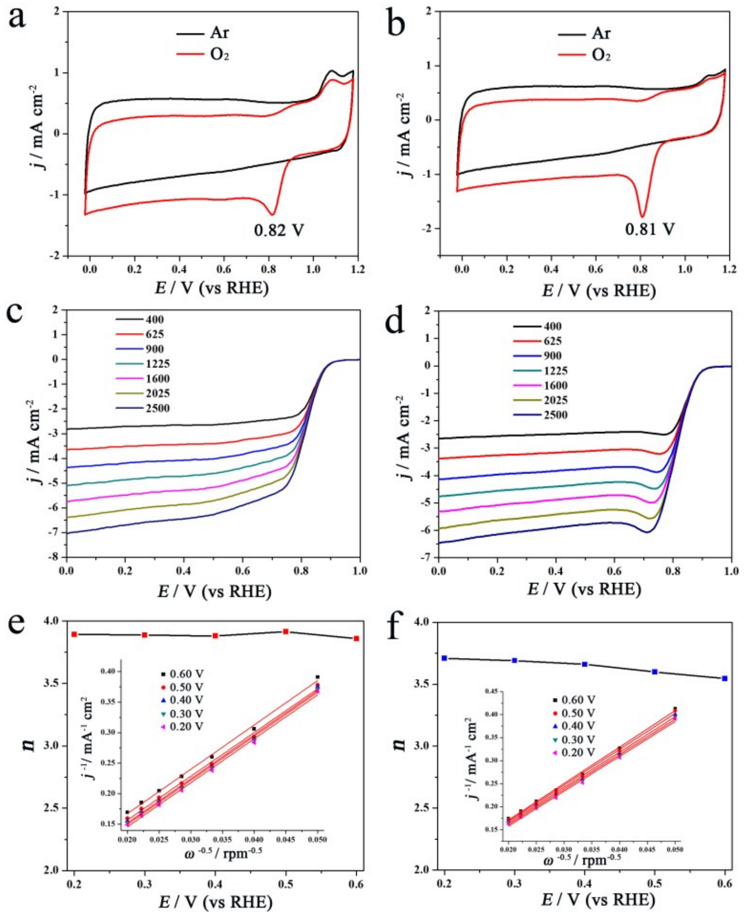

Figure S15 CV curves for (a) GO/ZIF-8@ZIF-67-L-900 and (b) GO/ZIF-8@ZIF-67-H-900 in 0.1 M KOH solution. LSV curves for (c) GO/ZIF-8@ZIF-67-L-900 and (d) GO/ZIF-8@ZIF-67-H-900 at different rotating speeds (400-2500 rpm). Electron transfer number for (e) GO/ZIF-8@ZIF-67-L-900 and (f) GO/ZIF-8@ZIF-67-H-900 calculated from K-L plots (insets).

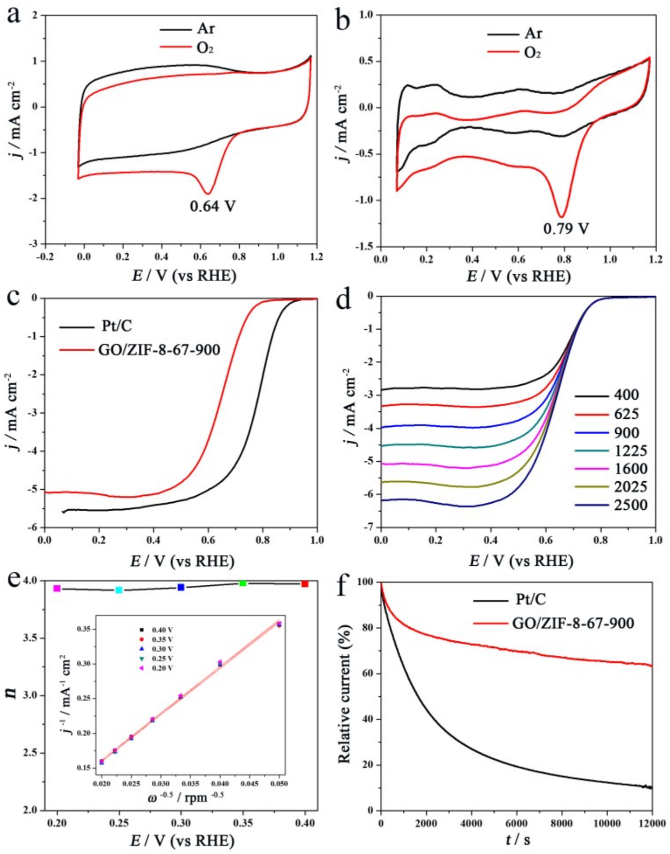

Figure S16 ORR performance of GO/ZIF-8@ZIF-67-900 in acidic conditions (0.1 M $HClO_4$). CV curves of (a) GO/ZIF-8@ZIF-67-900 and (b) Pt/C in Ar (or O_2)-saturated 0.1 M $HClO_4$ solution. (c) LSV curves for GO/ZIF-8@ZIF-67-900 and Pt/C at a rotating speed of 1600 rpm in O_2-saturated 0.1 M $HClO_4$ solution. (d) LSV curves for GO/ZIF-8@ZIF-67-900 at different rotating speeds (400-2500 rpm). (e) Electron transfer numbers and K-L plots (inset) for GO/ZIF-8@ZIF-67-900. (f) Current–time chronoamperometric response of Pt/C and GO/ZIF-8@ZIF-67-900 with a rotating speed of 1600 rpm in O_2-saturated 0.1 M $HClO_4$ solution.

Table S1. ORR performance of M-N/C (M= Fe, Co) in recent literatures (electrode rotating speed is **1600 rpm**, in **0.1 M KOH solution**).

Materials	**Catalyst loading (mg/cm^2)**	**Onset potential (V *vs.* RHE)**	**Current density (mA/cm^2)**	**Electron transfer numbers**	**Reference**
GO/ZIF-8@ZIF-67-900	0.1	0.93	4.7 (at 0.60 V)	3.8-3.9	**This work**
Co-TA-800	0.3	0.95	4.2 (at 0.60 V)	3.7-4.0	*Angew. Chem. Int. Ed.* **2016**, *55*, 12470
Fe-TA-800	0.2	0.95	5.0 (at 0.60 V)	3.9-4.0	*Angew. Chem. Int. Ed.* **2016**, *55*, 12470
FP-Fe-TA-N-850	0.3	0.98	5.0 (at 0.60 V)	3.7-3.9	*Angew.Chem. Int. Ed.* **2016**, *55*, 1355.
Co_3O_4/NPGC	0.2	0.97	5.84 (at 0.60 V)	~ 4.0	*Angew.Chem. Int. Ed.* **2016**, *55*, 4977.
ZIF-67 derived NCNTFs	0.2	~1.0	~ 5 (at 0.60 V)	3.97-3.99	*Nature Energy*, **2016**, *1*, 15006.
Mesoporous Fe-N-Carbon materials	~0.08	0.98	4.81 (at 0.45 V)	>3.95	*J. Am. Chem. Soc.*, **2015**, *137*, 5555
Gelatin-derived carbon (IAG-C)	0.3	1.02	~ 6.3 (at 0.6 V)	3.9-4.0	*Sci. Adv.* **2015**, *1*, e1400035
Zn-ZIF/GO-800	0.2	0.92	5.2 (at 0.60 V)	4.0	*Adv. Funct. Mater.* **2015**, *25*, 5768
Fe-bidppz derived Fe-N/C-800	0.1	0.923	~ 6 (at 0.6 V)	~3.96	*J. Am. Chem. Soc.*, **2014**, *136*, 11027
ZIF derived P-CNCo-20	0.1	0.92	~ 6 (at 0.6 V)	3.9	*Adv. Mater.* **2015**, *27*, 5010
PCN-FeCo/C	0.2	1.00	~ 5 (at 0.6 V)	4.2 ± 0.1	*Adv. Mater.* **2015**, *27*, 3431
Fe_3C/NG-800	0.4	1.03	~ 6 (at 0.6 V)	3.89-4.0	*Adv. Mater.* **2015**, *27*, 2521

Fe-N-CNT-OPC	0.4	~0.96	~ 6 (at 0.5 V)	3.99	*Adv. Mater.* **2014**, *26*, 6074
Co$_{II}$-A-rG-O	0.6	0.88	4.5 (at 0.6 V)	3.5-3.9	*Angew. Chem. Int. Ed.* **2015**, *54*, 12622
Fe-N-CNFs	0.6	0.93	5.12 (at 0.26V)	3.93-3.95	*Angew. Chem. Int. Ed.* **2015**, *54*, 8179
FeX@NOMC	0.25	~0.90	~5.5 (at 0.5 V)	4	*Angew. Chem. Int. Ed.* **2015**, *54*, 1494

Table S2 ORR performance of metal-nitrogen doped carbon materials in recent literatures (electrode rotating speed is **1600 rpm**, in **0.1 M $HClO_4$ solution**)

Materials	**Catalyst loading (mg/cm^2)**	**Onset potential (V *vs*. RHE)**	**Current density (mA/cm^2)**	**Electron transfer numbers**	**Reference**
GO/ZIF-8@ZIF-67-900	0.2	0.81	5.1 (at 0.40 V)	3.9-4.0	**This work**
Co-TA-800	0.3	0.78	3.7 (at 0.40 V)	3.1-3.7	*Angew. Chem. Int. Ed.* **2016**, *55*, 12470
Fe-TA-800	0.2	0.84	5.1 (at 0.40 V)	3.8-3.9	*Angew. Chem. Int. Ed.* **2016**, *55*, 12470
FP-Fe-TA-N-850	0.3	0.83	4.4 (at 0.40 V)	~3.5	*Angew.Chem. Int. Ed*. **2016**, *55*, 1355
Co-Zn-ZIF/GO-800	0.3	0.85	4.2 (at 0.40 V)	4.0	*Adv. Funct. Mater*. **2015**, *25*, 5768
Fe-P-900	0.0395	0.84	~4 (at 0.40 V)	3.8	*J. Am. Chem. Soc*. **2015**, *137*, 3165
CPM-99Fe/C	0.6	0.875	~4.8 (at 0.40 V)	4.0	*J. Am. Chem. Soc*. **2015**, *137*, 2235
Fe-N/C-800	0.1	~0.9	6.09	3.92	*J. Am. Chem. Soc*. **2014**, *136*, 11027
PCN-FeCo/C	0.6	0.90	5.0	4.2	*Adv. Mater*. **2015**, *27*, 3431
Fe_3C/NG	0.4	0.92	~ 6	3.7-3.85	*Adv. Mater*. **2015**, *27*, 2521
$Zn(eIm)_2TPIP$	0.4	0.914	~5	~ 4	*Adv. Mater*. **2014**, *26*, 1093