

## Supporting Information

### **Synthesis of graphene anchored with atomically isolated cobalt from a promising graphite-like supramolecule**

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## Experimental Section

### Synthesis of *g*-SOM

Mixture of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.2621 g, 0.9 mmol),  $(\text{NH}_4)_5\text{[p-sulfonato-calix[4]arene]}$  (0.4968 g, 0.6 mmol), bpdo (2, 2'-bipyridine-N, N'-dioxide, 0.5076 g, 2.7 mmol) with the ratio of 3:2:9 was dissolved in 15 ml hot methanol aqueous solution. Red precipitate was obtained after cooling to room temperature. Red crystals of the *g*-SOM were obtained after the filtrate evaporates at room temperature for a few days.

### Synthesis of *b*-SOM

Mixture of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.8337 g, 2.87 mmol),  $(\text{NH}_4)_5\text{[p-sulfonato-calix[4]arene]}$  (1.5462 g, 1.92 mmol), 2, 2'-bipyridine (1.3448 g, 8.61 mmol) with the ratio of 3:2:9 was dissolved in 20 ml methanol aqueous solution. With stirring at 60°C, the solvent was evaporated to 5ml. Then the mixed solution was cooled to room temperature, and a red precipitate was obtained after standing for 4 hours. Filter and wash twice with 5 ml ice ethanol. Finally dried in the air and collected red solid.

### Synthesis of CoN-graphene and CoN-C

The as-synthesized *g*-SOF and *b*-SOF power were transferred into a tube furnace and then heated to 800 °C for 3h at a ramp of 3 °C/min under  $\text{N}_2$  gas flow and then naturally cooled to room temperature. The carbonized material was then leached by 0.5 M  $\text{H}_2\text{SO}_4$  solution at 80°C for 8 h to remove the unstable Co species. The product was collected by centrifuging, washing with ultra-pure water several times and then dried in an oven at 70°C overnight.

### Materials Characterization

Power X-ray diffraction patterns were acquired by X-ray diffraction (Bruker AXS D8-Focus, Germany) with Cu-K $\alpha$  radiation. Scanning electron microscopy (SEM, Hitachi SU8000, Japan) and transmission electron microscopy (TEM, Titan G260-300, USA) was used to study

the morphology and nanostructure of the samples. Aberration-corrected high-angle annular dark field scanning transmission electron microscopy (AC-HAADF-STEM) images were obtained on a Themis Z (FEI, USA) equipped with energy-dispersive X-ray spectroscopy (EDS) mapping, and the accelerating voltage was 200.0 KV. Fourier transform infrared spectrometry (FTIR, NEXUS 870, USA) was used to investigate the detailed structure of the samples. X-ray photoelectron spectroscopy (XPS) results were obtained on an Escalab 250XI spectrometer (ThermoFisher, USA). The synchrotron-based X-ray absorption spectroscopy (XAS) was measured at the Beijing Synchrotron Radiation Facility (1W1B, BSRF). N<sub>2</sub> adsorption-desorption isotherms were measured using an ASAP 2020 (Micromeritics Instrument Corporation, USA). Atomic force microscopy (AFM) measurement was carried out to measure the thickness of the sample (Dimension Icon. Veec Instruments/Bruker, Germany). Raman microscope (inVia Reflex, Renishaw, Germany) was performed to reveal the graphitization degree of the samples. Thermogravimetric analysis (TG) was measured by STA 449F3 (NETZSCH, Germany). The metal contents were verified by the inductively coupled plasma-optical emission spectroscopy (ICP-OES). Non-metallic element contents were confirmed by Elemental analysis (Vario EL Cube, Elementar, Germany).

### **X-ray crystal structure determination**

The single-crystal X-ray data was collected on a Bruker SMART 1000 CCD diffractometer with Cu K $\alpha$  radiation using the  $\omega$ -scan mode. Data were corrected for absorption using the SADABS program, and solution and refinement of the structure were performed using the SHELX-97 software package. Crystal/refinement details for 1: C<sub>136</sub>H<sub>96</sub>Co<sub>3</sub>N<sub>20</sub>O<sub>50</sub>S<sub>8</sub>,  $M= 3243.60$ , The compound 1 crystallized in the space group  $C2/m$ , monoclinic,  $a=36.8976(5) \text{ \AA}$ ,  $b=36.999(5) \text{ \AA}$ ,  $c= 15.455(5) \text{ \AA}$ ,  $\alpha=90.000(5)^\circ$ ,  $\beta=98.502(5)^\circ$ ,  $\gamma=90.000(5)^\circ$ ,  $V= 20867.8(12) \text{ \AA}^3$ ,  $Z=4$ ,  $T= 157 \text{ K}$ ,  $\lambda=1.54178 \text{ \AA}$ ,  $R_{\text{int}} = 0.1130$ ; A total of 144900 reflections were collected in the range  $1.12 < \theta < 27.01$ , of which 22727 were unique.  $\text{GOF}=1.140$ ,  $R_1=0.1646$ ,  $wR_2$  (all data) = 0.3576. Many atoms (C59-C68, N7-N8, S1-S4, O1-

O13, O23-O25) were refined by disorder. Non-hydrogen atoms were refined anisotropically except (C59-C68, N7-N8, O1-O13, O23-O25). In this structure, the location of  $\text{NH}_4^+$  cations can't be determined by X-ray diffractions. The high  $R_1$  and  $wR_2$  of SOF-1 is due to the weak crystal diffraction quality, the disorder of the  $[\text{Co}(\text{bpdo})_2 \cdot 2\text{H}_2\text{O}]^{2+}$  and molecular water. The contribution from the water solvent was subtracted from the observed data by SQUEEZE method as implemented in PLATON. CCDC-2020238 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### **Electrochemical Measurements**

The catalytic performance of the samples was evaluated by a three-electrode cell, which consists of a working electrode (RDE,  $0.1256 \text{ cm}^2$ ; RRDE,  $0.2475 \text{ cm}^2$ ), a counter electrode (graphite rod) and a reference electrode (Hg/HgO, 1M KOH). For the working electrode preparation, 2mg of catalyst was suspended in 1 ml solution containing 0.78 ml deionized water, 0.2 ml ethanol and 0.02 ml Nafion. After sonicated for 1 hour to form a well-dispersed ink, a certain volume of the ink was deposited onto the GC electrode to achieve a specific mass loading of  $1.14 \text{ mg cm}^{-2}$  for nonprecious catalysts. The loading of commercial 20 wt% Pt/C was  $0.286 \text{ mg cm}^{-2}$ . The electrolyte (1 M KOH) was first purged with  $\text{N}_2/\text{O}_2$  for 30 minutes to make sure it was  $\text{N}_2/\text{O}_2$  saturated before the measurement, and  $\text{N}_2/\text{O}_2$  continued flowing during testing. Electrochemical tests data was obtained by a CHI 760E electrochemical workstation equipped with a rotating system (AFCPRBE). Cyclic voltammetry tests were first performed to activate the catalysts until repeatable curves were obtained. Linear-sweep voltammetry (LSV) measurements were scanning at a rate of  $5 \text{ mV s}^{-1}$ . For RRDE tests, the ring potential was kept at 1.2 V vs. RHE. The potential were transferred to standard reversible hydrogen (RHE) for analyzing based on the formula:  $E_{\text{vs RHE}} = E_{\text{vs Hg/HgO}} + 0.926 \text{ V}$  in 1 M KOH.

Koutecky-Levich (K-L) formula can be used to calculate the electron transfer number (n) of the catalysts:

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_d} = \frac{1}{I_k} + \frac{1}{B\omega^{1/2}}$$

$$B = 0.62nFD_0^{2/3}\nu^{-1/6}C_0$$

where I is the measured current densities, the  $I_k$  and  $I_d$  represent the kinetic and diffusion-limiting current densities,  $\omega$  is the angular speed of the RDE, n is the electron transfer number of the ORR, F is the Faraday constant,  $D_0$  is the diffusion coefficient of  $O_2$  in 1 M KOH,  $\nu$  is the kinetic viscosity of solvent and  $C_0$  is the saturated concentration of  $O_2$ .

For RRDE analysis, the peroxide percentage ( $H_2O_2$  %) and the electron transfer number (n) were calculated by the following formula:

$$H_2O_2(\%) = 200 \times \frac{I_R/N}{I_D + I_R/N}$$

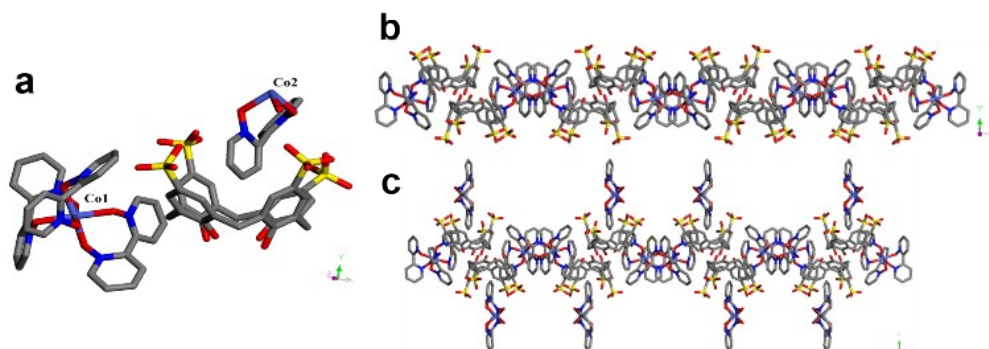
$$n = 4 \times \frac{I_D}{I_R/N + I_D}$$

where  $I_D$  and  $I_R$  represent the disk and ring current, N is the ring collection efficiency of RRDE (0.26).

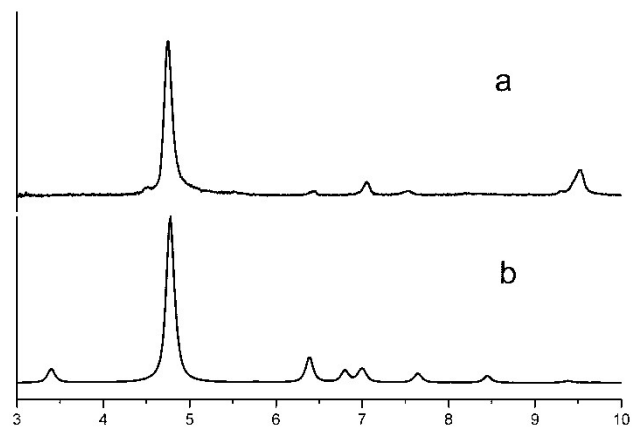
### **DMFC assembly and performance tests**

Catalyst ink was prepared using the following weight ratio: catalyst/isopropanol/deionized water/5 wt% Nafion of 1/12/12/11. The catalyst ink was sprayed onto one side of a 5 cm<sup>2</sup> carbon paper (TGP-H-060, Toray) after ultrasonic treated for 1 h until the loading reached 2 mg cm<sup>-2</sup>. The prepared catalysts (or commercial Pt black) were used as cathode catalyst while 20 wt.% Pt/C was used as anode catalyst. The anode electrode, porous membrane and cathode electrode were then assembled together with the fuel reservoir and current collectors by screws at a certain pressure to form a passive fuel cell. 5 M KOH + 1 M methanol solution was used as fuel and electrolyte and ambient air was used as oxidant.

Polarization curves of the air-breathing fuel cells were collected by Arbin battery test system at 25 °C.

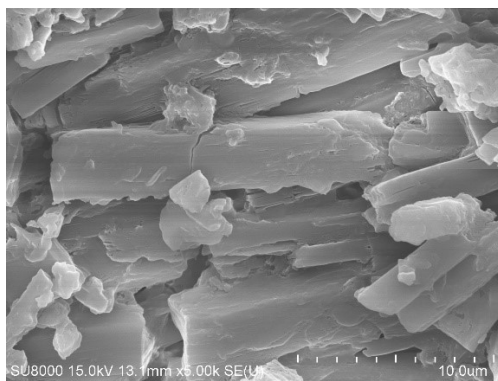


**Scheme S1.** (a) The asymmetric unit of *g*-SOM, water molecules and  $\text{NH}_4^+$  have been omitted for clarity. In the asymmetric unit, there are one  $[\text{Co}(\text{bpdo})_3]^{2+}$ , half disorder  $[\text{Co}(\text{bpdo})_2 \cdot 2\text{H}_2\text{O}]^{2+}$ , two  $\text{NH}_4^+$ , one *p*-sulfonatocalix[4]arenes and water molecules. The *p*-sulfonatocalix[4]arenes take on an overall charge of -5, with one of the phenolic hydroxyl groups being deprotonated. (b) A layer structure consist of the *p*-sulfonatocalix[4]arene and the  $[\text{Co}(\text{bpdo})_3]^{2+}$  (viewed down the *c* direction). (c) The layer with many cavities as a host for  $[\text{Co}(\text{bpdo})_2 \cdot 2\text{H}_2\text{O}]^{2+}$ .

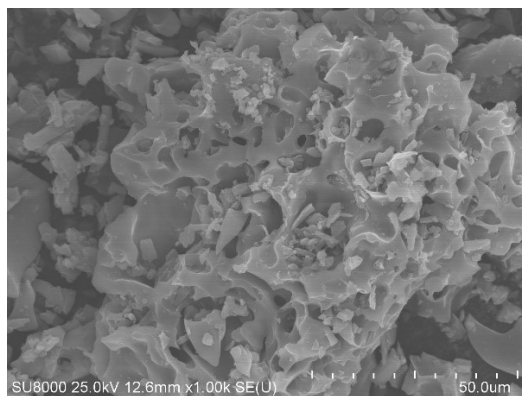


**Fig. S1.** (a) Powder XRD pattern of g-SOM; (b) simulated XRD pattern from single crystal data.

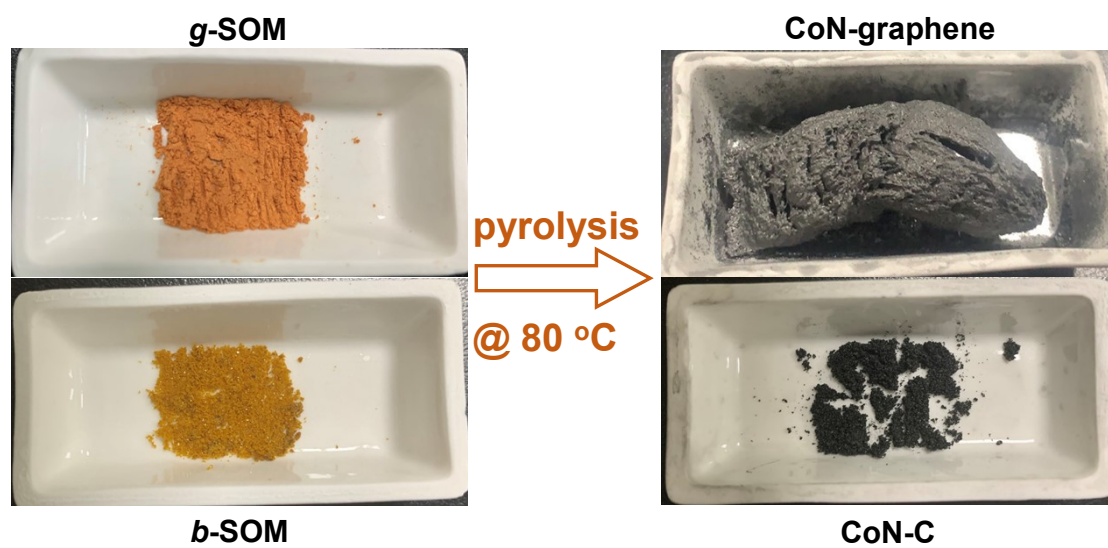




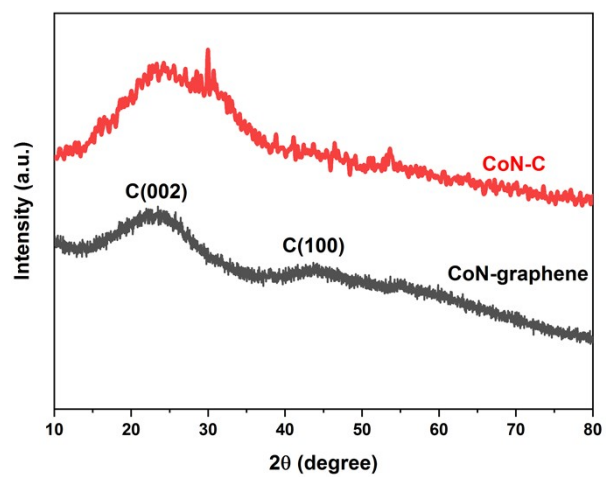
**Fig. S2.** SEM image of *b*-SOM.



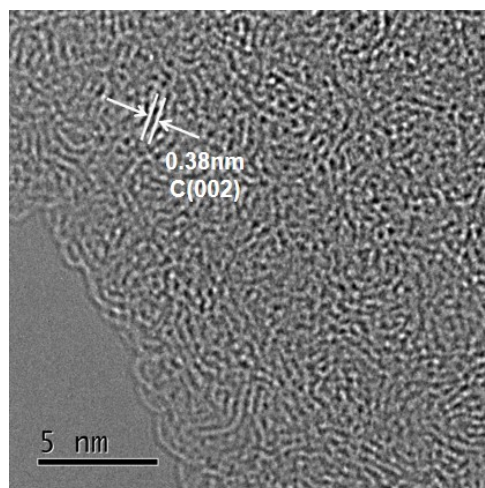
**Fig. S3.** SEM image of CoN-C.



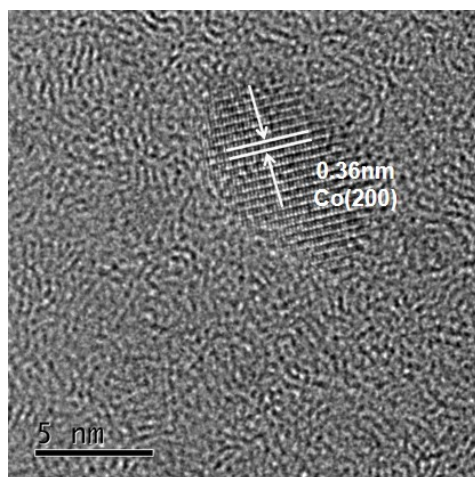
**Fig. S4.** Photographs of g-SOF and b-SOF before and after pyrolysis.



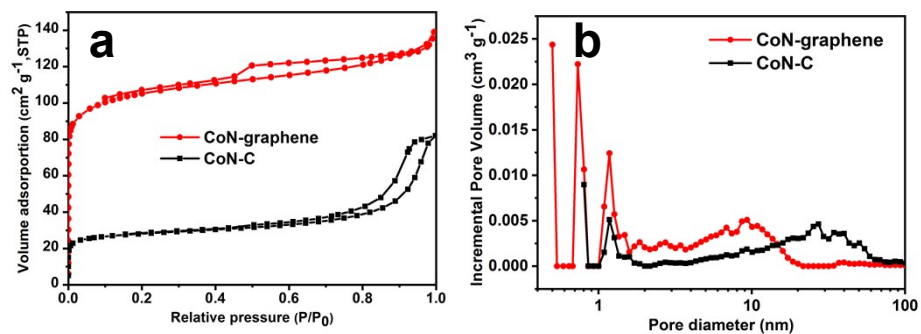
**Fig. S5.** XRD patterns of CoN-graphene and CoN-C.



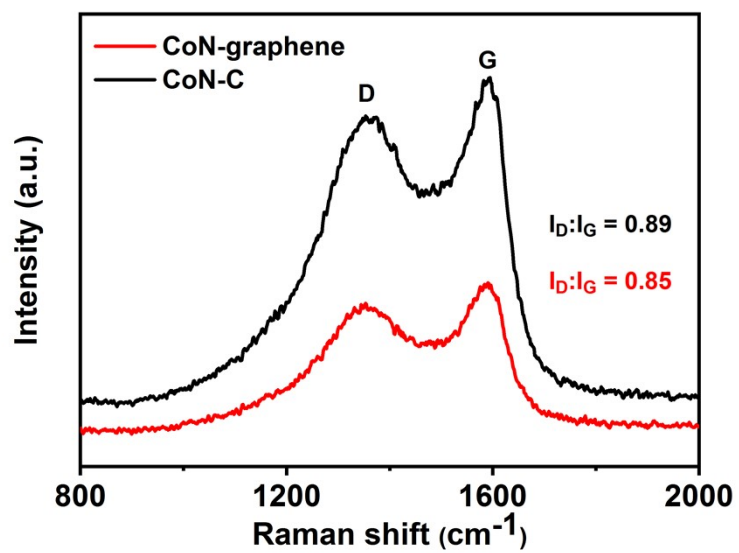
**Fig. S6.** HR-TEM image on CoN-graphene sheet.



**Fig. S7.** HR-TEM image on CoN-C.

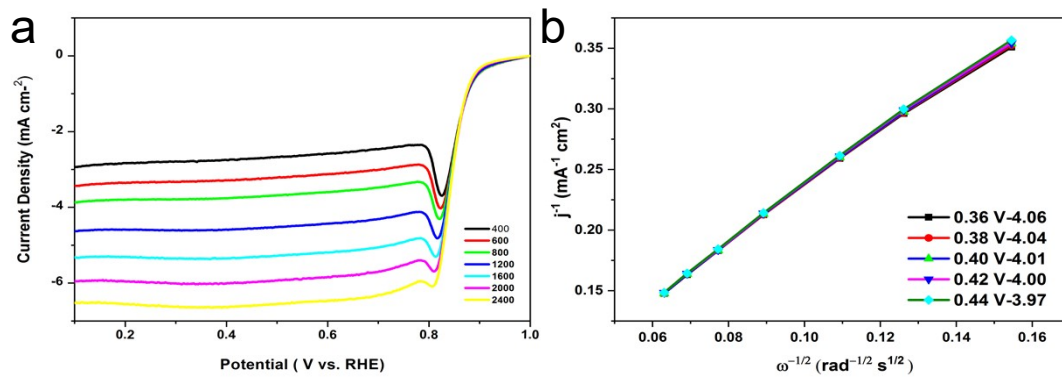


**Fig. S8.** (a) nitrogen adsorption-desorption isotherm curves of CoN-graphene and CoN-C. (b) The corresponding pore diameter distribution plots.

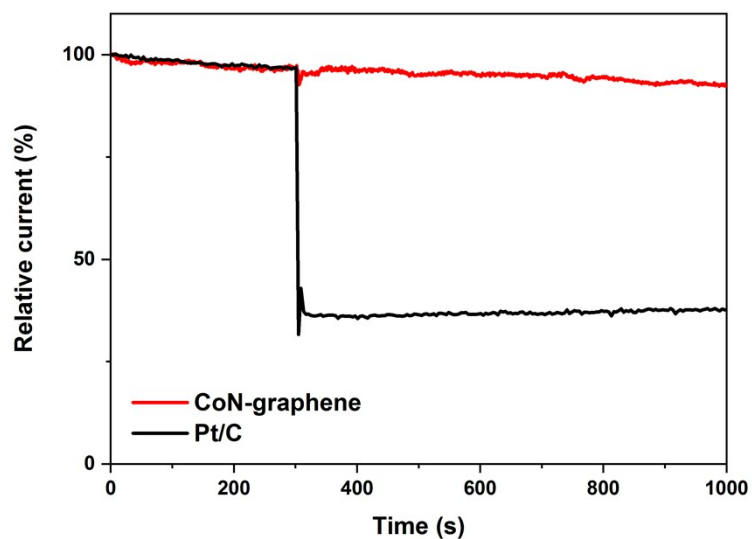


**Fig. S9.** Raman spectra of the CoN-graphene and CoN-C catalysts.

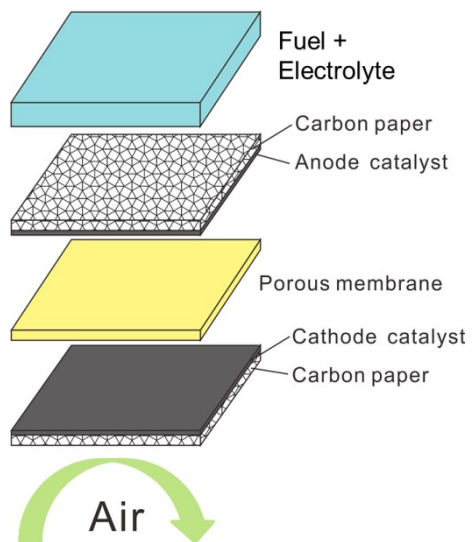




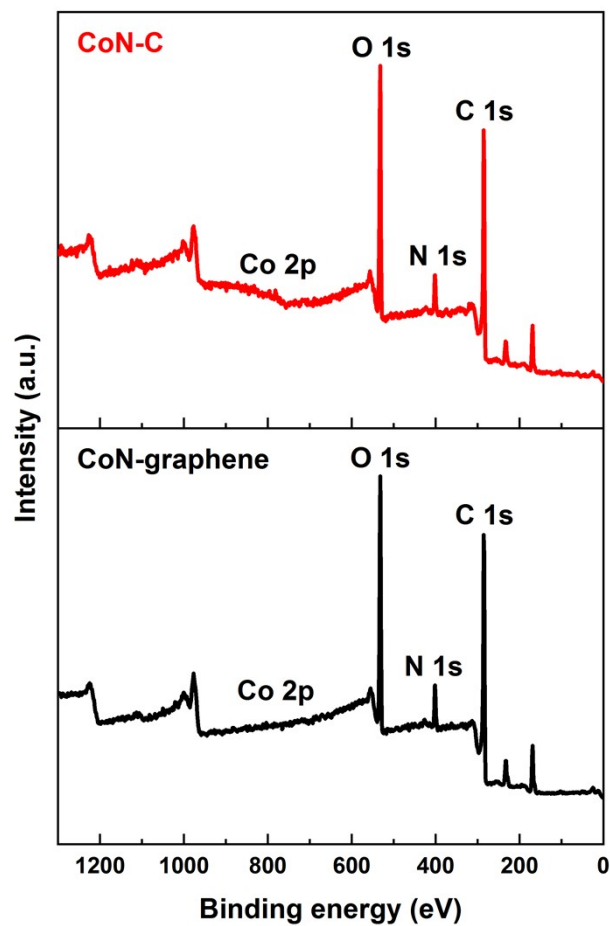
**Fig. S10.** (a) LSV curves collected at various rotating speeds and (b) the calculated linear Koutecky Levich (K-L) plots at different potentials for CoN-graphene.



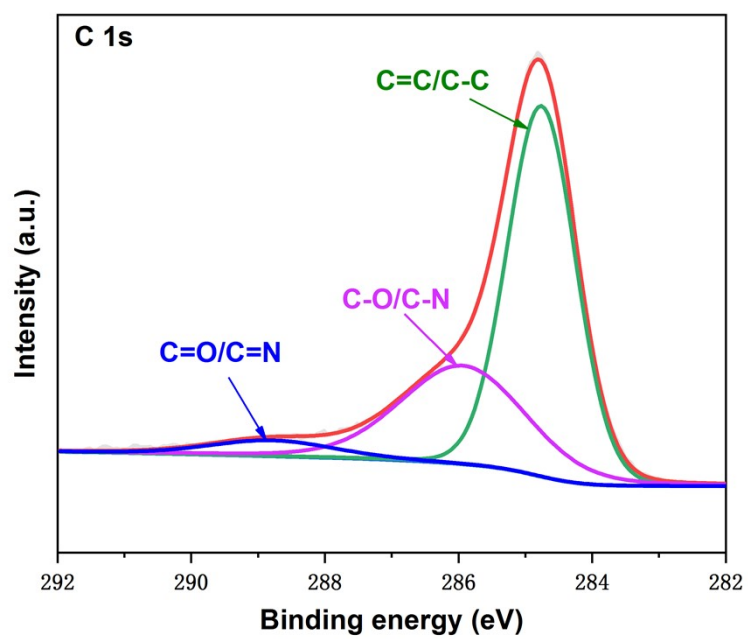
**Fig. S11.** Chronoamperometric(CA) responses of CoN-graphene and Pt/C after the addition of 1M methanol in O<sub>2</sub> saturated 1M KOH solution.



**Fig. S12.** Configuration of the anion exchange membrane free DMFC used for direct methanol/isopropanol fuel cell measurements.



**Fig. S13.** XPS survey spectra of the CoN-C and CoN-graphene.



**Fig. S14.** C 1s XPS spectrum of CoN-graphene.

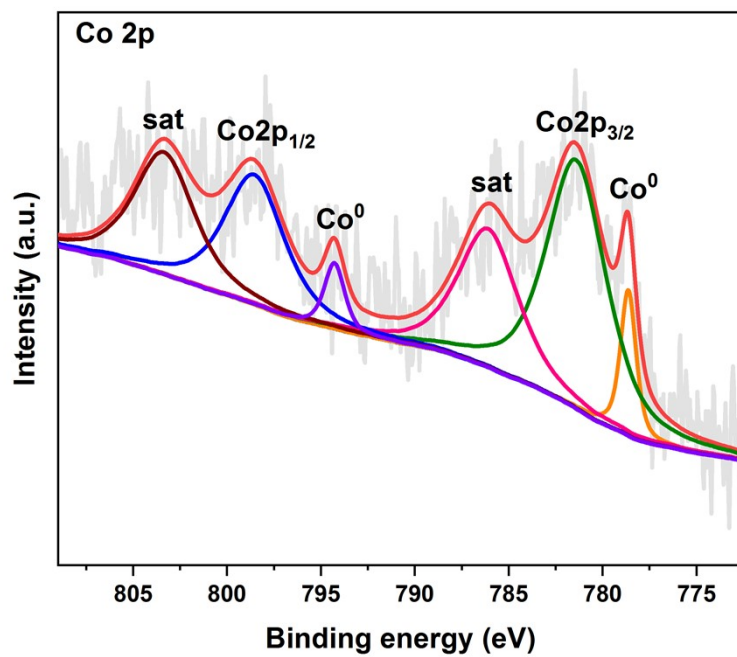
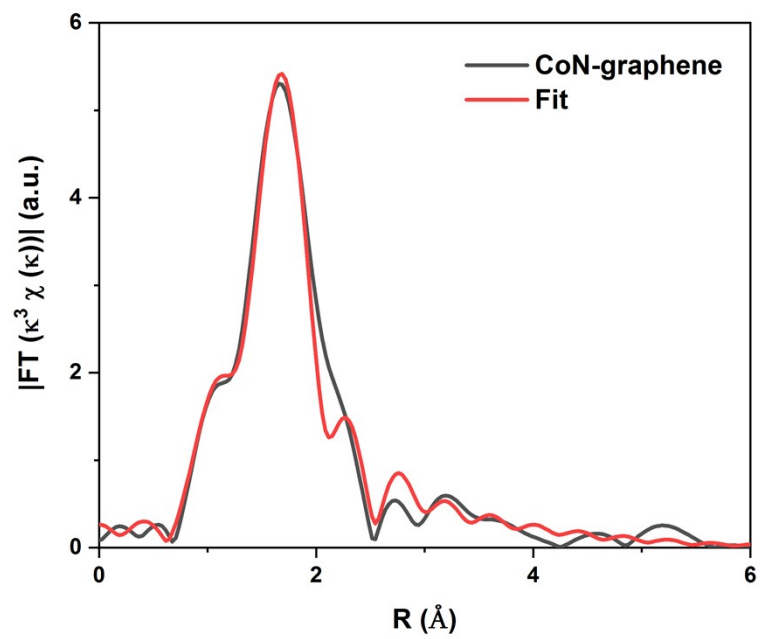


Fig. S15. Co 2p XPS spectrum of CoN-C.



**Fig. S16.** Co K-edge EXAFS fitting curves of CoN-graphene.

**Table S1.** BET surface area and total pore volume of CoN-graphene and CoN-C.

<b>Sample</b>	<b>BET surface area (m<sup>2</sup> g<sup>-1</sup>)</b>	<b>Total pore volume (cm<sup>3</sup> g<sup>-1</sup>)</b>
CoN-graphene	343.8	0.166
CoN-C	89.1	0.119



**Table S2.** Comparison of ORR catalytic activity of CoN-graphene with other reported Co-based carbon electrocatalysts.

<b>Catalysts</b>	<b>E<sub>onset</sub></b> <b>(V vs. RHE)</b>	<b>E<sub>1/2</sub></b> <b>(V vs. RHE)</b>	<b>J<sub>L</sub></b> <b>(mA cm<sup>-2</sup>)</b>	<b>n</b>	<b>Refs</b>
Co/CoP-HNC	0.94	0.83	4.75	4	1
Co,N-PCL[4]	-	0.846	5.22	3.97	2
Co-HNCS-0.2	0.94	0.82	5.8	3.96	3
MOFs-800	0.9	0.8	3.84	3.8	4
FeN <sub>4</sub> -O-NCR	1.050	0.942	-	-	5
Fe-N-C	0.96	0.75	5.2	-	6
Fe-N-C	0.8	0.805	-	-	7
Co@NC-PC(3-1)	0.88	0.8	5.93	3.97	8
Co-N/PC@CNT-700	0.92	0.79	4.5	3.85	9
Co@BNCNTs-900	0.93	0.82	5.3	3.96	10
Co-SAs@NC	0.96	0.82	4.96	3.97	11
Co <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> C-N/rGOA	0.962	0.837	5.58	4	12
CoNC-CNF-1000	-	0.8	5.9	3.96	13
Co-N-C	0.95	0.85	5.2	3.45	14
Co/NC	0.945	0.824	-	-	15
Co-NCNTs//CCM	0.86	0.79	-	-	16
<b>CoN-graphene</b>	<b>0.95</b>	<b>0.87</b>	<b>4.50</b>	<b>3.94- 3.96</b>	<b>this work</b>

**Table S3.** Co K-edge EXAFS curves Fitting Parameters.

<b>Sample</b>	<b>Path</b>	<b>N</b>	<b>R(Å)</b>	<b><math>\sigma^2(10^{-3} \text{ \AA}^2)</math></b>
<b>Co foil</b>	<b>Co-Co</b>	<b>12</b>	<b>2.491</b>	<b>6.00</b>

N, coordination number; R, distance between absorber and backscatter atoms;  $\sigma^2$ , Debye-Waller factor (account for both thermal and structural disorders).

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