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**Facile synthesis of cobalt and nitrogen co-doped graphene  
networks from polyaniline for oxygen reduction reaction in  
acidic solutions**

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## Experimental section

**Instrumentation and chemicals.** Electrochemical experiments were conducted on a CHI760E electrochemical workstation (CH Instrument Co., USA). The conventional three-electrode system was used, which contained a glassy carbon rotating disk electrode (RDE) or a rotating ring-disk electrode (RRDE) (Pine Research Instrumentation) coated with catalysts, a Pt auxiliary electrode and a saturated calomel reference electrode (SCE). All the potentials are reported with respect to the reversible hydrogen electrode (RHE) and all electrochemical data were obtained at room temperature. Scanning electron microscopy (SEM) studies were performed on a Hitachi S4800 scanning electron microscope. Transmission electron microscopy (TEM) studies were performed on a TECNAI F-30 high-resolution transmission electron microscope operating at 300 kV. X-ray diffraction (XRD) measurements were recorded on a PANalytical X'pert PRO diffractometer using Cu K $\alpha$  radiation, operating at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI QUANTUM 2000 X-ray photoelectron spectroscopic instrument. Surface area and pore size were determined by Surface Area and Porosity Analyzer (Micromeritics Instrument Corp. ASAP2020). The commercial Pt/C 20 wt% catalyst was purchased from Johnson-Matthey (JM). All chemicals were of analytical grade and used without further purification. Ultrapure water (Millipore,  $\geq 18\text{M}\Omega\text{ cm}$ ) was used throughout.

**Material preparations.** For the synthesis of polyaniline nanofibers, 10 mL aniline was dissolved in 1 M HCl aqueous solution under continuous stirring for about 20 min. Then 6.0 g of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  was added to the above solution, followed by continuous stirring about 6 h. The precipitates were collected by filtration, washed with deionized water, and finally dried at

60 °C. For the synthesis of Co-N-GNWs, the pre-synthesized polyaniline nanofibers were mixed with cobalt(II) nitrate powder in a weight ratio of 1:1 by a dry method using the mortar and pestle. The mixture was subjected to heat treatment at 200 °C for 2 h and then at 900 °C for 5 h under a N<sub>2</sub> atmosphere, with a heating ratio of 10 °C min<sup>-1</sup>. After cooling to room temperature, the resulting sample was etched in excessive 3 M HCl aqueous solution under continuous stirring. The precipitates were collected by filtration, washed with deionized water, and finally dried at 60 °C. Finally, the pre-leached catalyst underwent a second heat treatment at 900 °C for 2 h under N<sub>2</sub> atmosphere. For the synthesis of N-CNWs, the pre-synthesized polyaniline nanofibers was subjected to heat treatment at 200 °C for 2 h and then at 900 °C for 5 h under a N<sub>2</sub> atmosphere, with a heating ratio of 10 °C min<sup>-1</sup>.

**X-ray absorption spectroscopy measurements.** The X-ray absorption spectrum at the Co K-edge was recorded at the X-ray absorption spectroscopy station (BL14W1) of the Shanghai Synchrotron Radiation Facility. The electron storage ring was operated at 1.5 GeV, and a Si(111) double-crystal monochromator was used. The spectrum was collected in air at room temperature by using the third ionization chamber. The beam size was limited by the horizontal and vertical slits with the area of 1 × 4 mm<sup>2</sup> during X-ray absorption spectroscopy measurements. The as-obtained data was processed using WinXAS version 3.11. Reliable parameter values, such as bond distance, coordination number, *etc.*, were determined via single-shell *R*-space fitting of Co spectrum.

**Electrochemical Measurements.** The RDE and RRDE were polished with 1 and 0.05 μm alumina slurry sequentially and then washed ultrasonically in water and ethanol for 15 min, respectively. Then the RDE and RRDE were subjected to potential cycling (0 to 1.1 V vs.

RHE, 50 mV s<sup>-1</sup>) in 0.10 M aqueous HClO<sub>4</sub> until reproducible cyclic voltammograms were obtained. 5 mg catalysts were dispersed in 5 ml ethanol, and then ultrasonicated to form a uniform black ink. The catalysts modified RDE and RRDE were prepared by cast-coating a designed volume of well-dispersed catalyst ink onto pre-polished RDE and RRDE. The catalyst loadings for Co-N-GNWs and N-CNWs are 500 μg cm<sup>-2</sup>, whereas the catalyst loadings for commercial Pt/C is 300 μg cm<sup>-2</sup>. After drying at room temperature, 5 μL of 0.1 wt% Nafion solution was further cast-coated to form a protection layer against catalyst detaching from the electrode surface. A 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution saturated with oxygen by bubbling O<sub>2</sub> for 30 min served as the supporting electrolyte. A flow of O<sub>2</sub> was maintained over the electrolyte solution for continued O<sub>2</sub> saturation during electrochemical experiments. Oxygen reduction reaction (ORR) polarization curves were recorded at room temperature in an O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution at a sweep rate of 10 mV s<sup>-1</sup> and a rotation rate of 900 rpm. The background capacitive current was recorded at the same scan rate, but in N<sub>2</sub>-saturated electrolyte. The current recorded in O<sub>2</sub>-saturated solution was corrected for the background current to yield net ORR current of the tested catalyst.

For the Tafel plot, the kinetic current was calculated from the mass-transport correction of RDE by:

$$j_k = \frac{j \times j_L}{j - j_L}$$

Koutecky-Levich plots were analyzed at various electrode potentials. The slopes of their linear fit lines are used to calculate the electron transfer number (*n*) on the basis of the Koutecky-Levich equation:

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

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

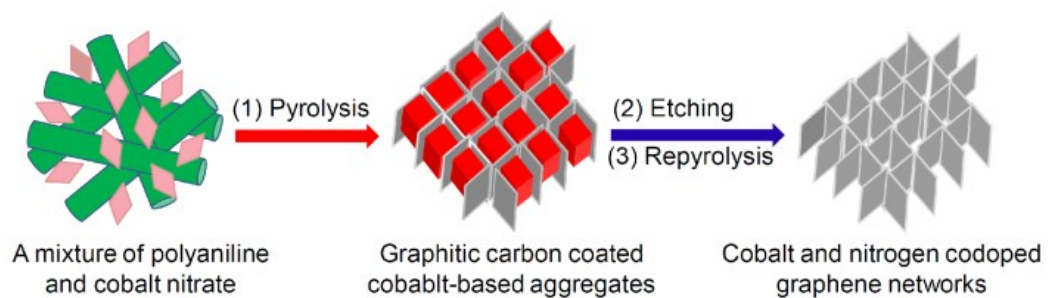
where  $j$  is the experimentally measured current,  $j_L$  is the diffusion-limiting current, and  $j_K$  is the kinetic current,  $\omega$  is the angular velocity,  $F$  is the Faraday constant,  $C_0$  is the bulk concentration of  $O_2$ , and  $\nu$  is the kinematic viscosity of the electrolyte.

For the RRDE measurements, the disk electrode was scanned cathodically at a rate of 10 mV s<sup>-1</sup> and the ring potential was kept at 1.2 V vs. RHE. The percentage of  $H_2O_2$  and the electron transfer number ( $n$ ) were determined by the followed equations:

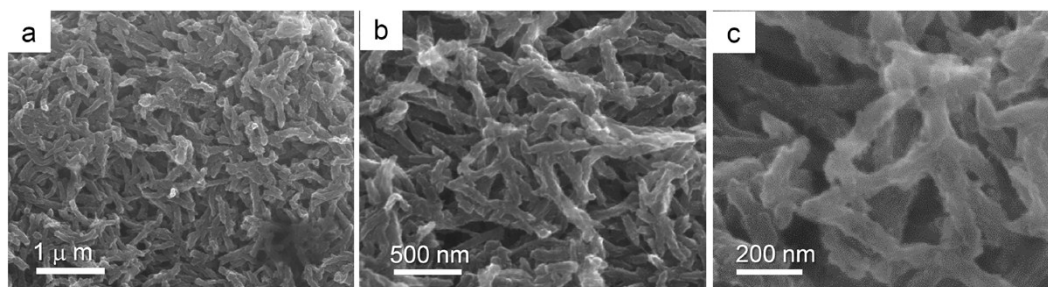
$$H_2O_2\% = 200 \times \frac{i_r / N}{i_d + i_r / N}$$

$$n = 4 \times \frac{I_d}{i_d + i_r / N}$$

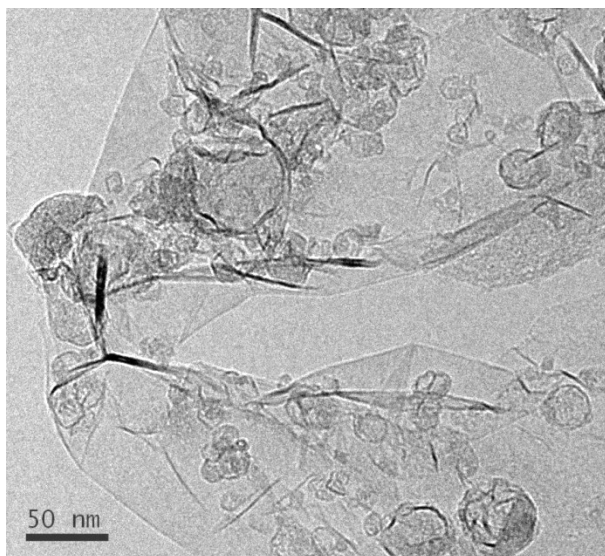
where  $I_d$  is the disk current,  $I_r$  is the ring current and  $N$  is the current collection efficiency of the Pt ring.  $N$  was determined to be 0.38 from the reduction of  $K_3Fe[CN]_6$ , well consistent with the manufacturer's value (0.37).



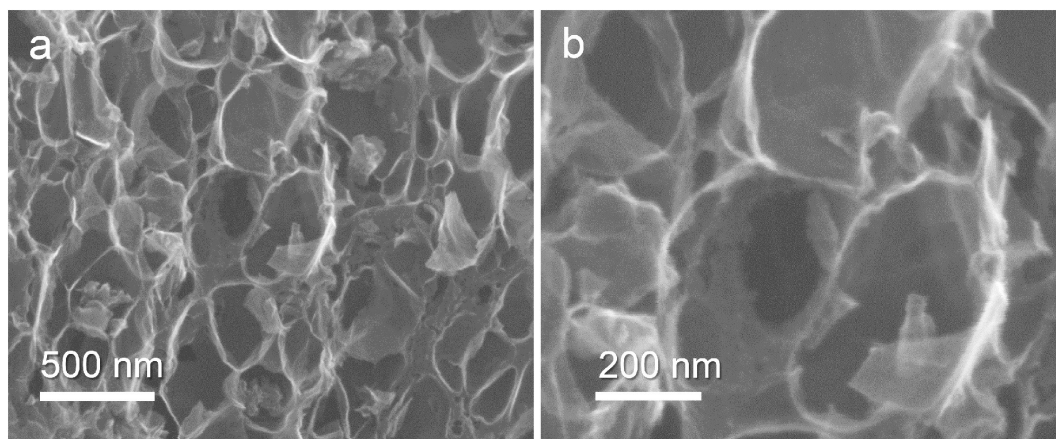
**Scheme S1** Illustration of the synthetic procedure for Co-N-GNWs.



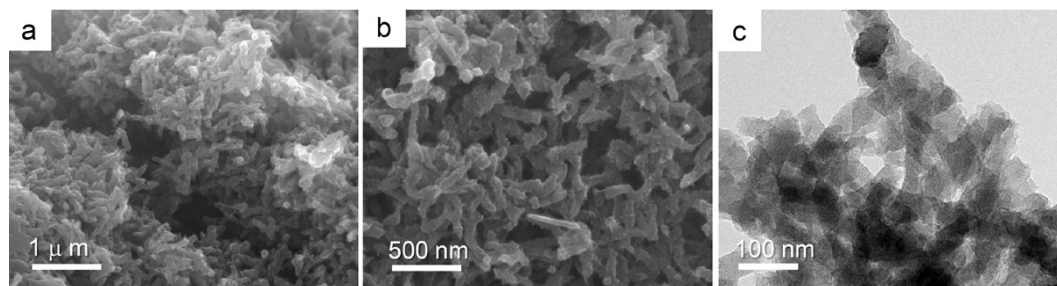
**Fig. S1** SEM images of polyaniline nanofibers.



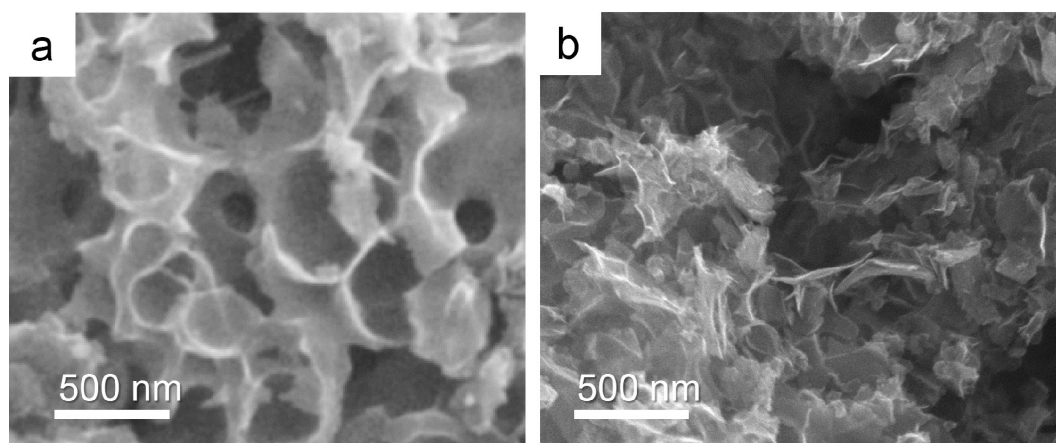
**Fig. S2** additional TEM image of Co-N-GNWs.



**Fig. S3** TEM images of products prepared under reaction conditions similar to those in Figure 1, except the absence of a second pyrolysis.

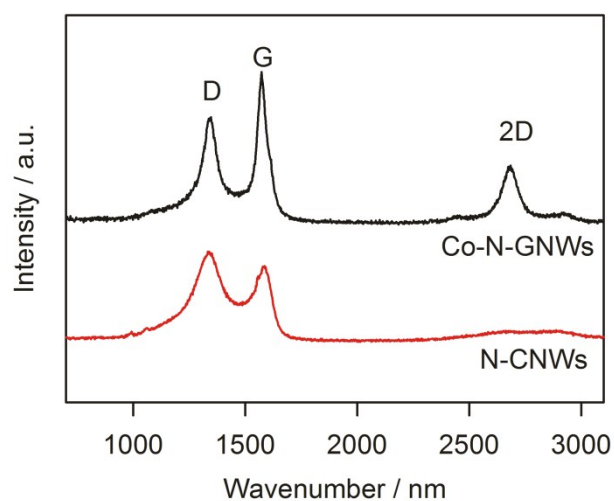


**Fig. S4** SEM (a,b) and TEM (c) images of N-CNWs.

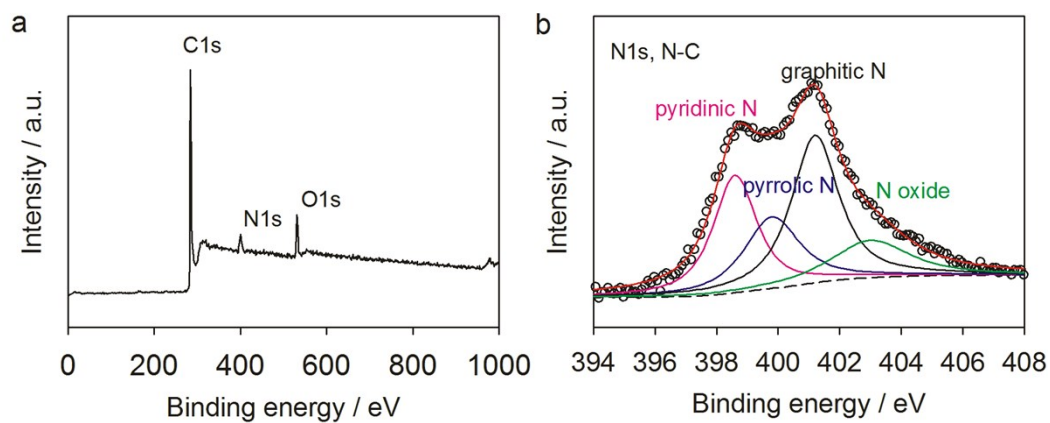


**Fig. S5** TEM images of products prepared under reaction conditions similar to those in Figure 1, except that the weight ratios of polyaniline nanofibers to cobalt(II) nitrate is changed to 2:1 (a) and 1:2 (b).

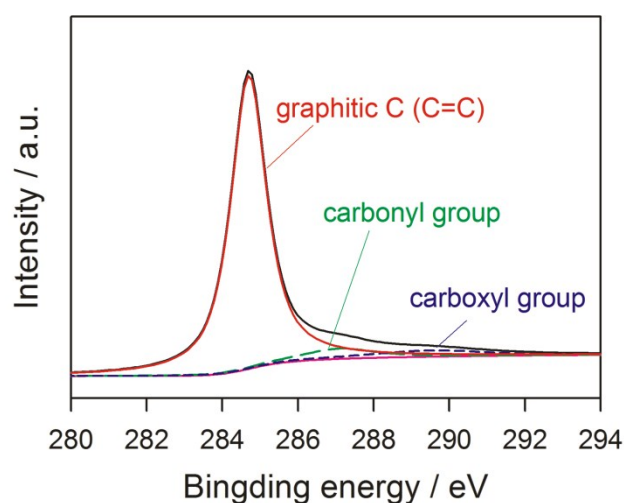




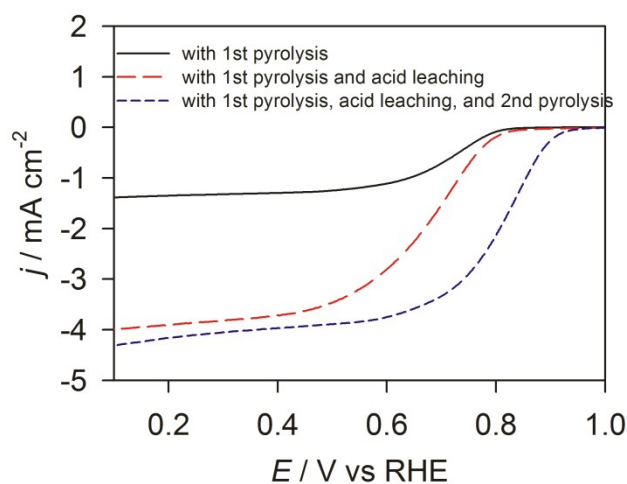
**Fig. S6** Raman spectra of Co-N-GNWs and N-CNWs.



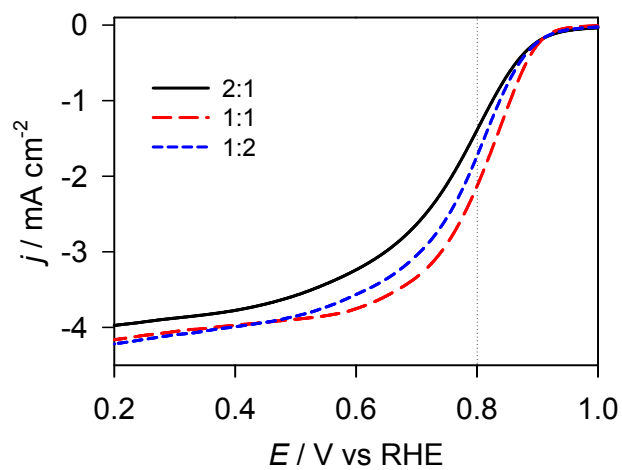
**Fig. S7** (a) XPS survey spectrum of N-CNWs. (b) High resolution XPS spectrum of N1s.



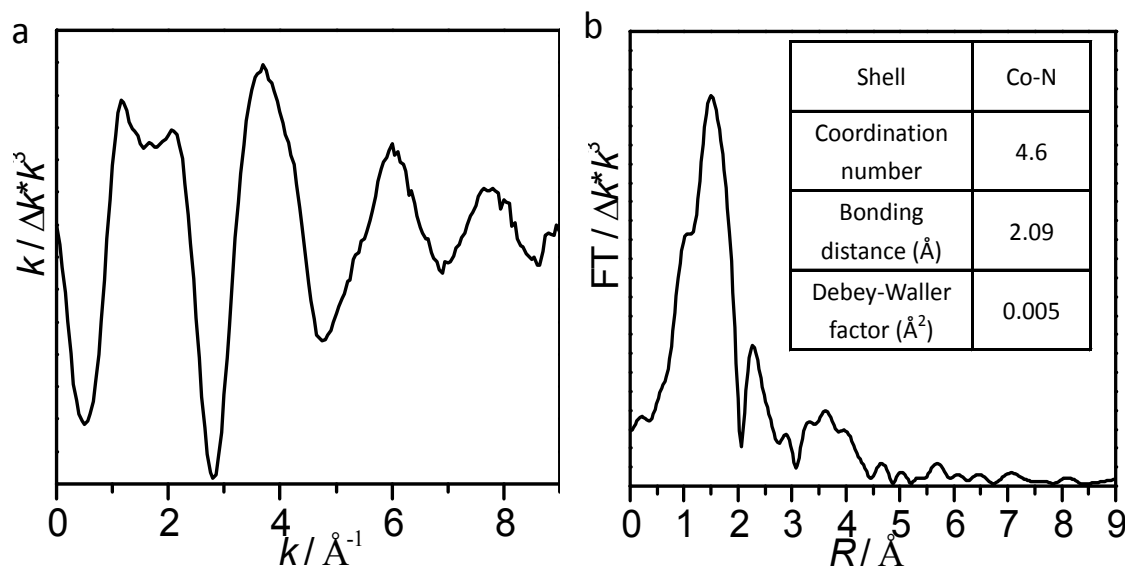
**Fig. S8** High resolution XPS spectrum of C1s for Co-N-GNWs.



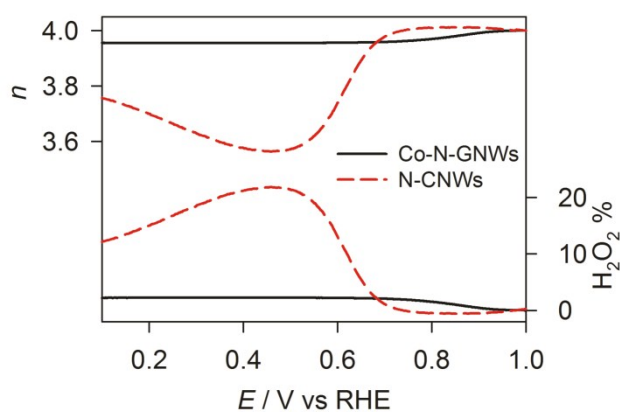
**Fig. S9** ORR polarization curves for catalysts prepared at different steps in an O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution at a sweep rate of 10 mV s<sup>-1</sup> and a rotation rate of 900 rpm. The catalyst prepared with only 1st pyrolysis without acid leaching show poor ORR activity, probably due to its small surface area. The half-wave potential of the catalyst prepared without a 2nd pyrolysis is ~ 120 mV negative shift compared that of the catalyst prepared with a 2nd pyrolysis, indicating that the 2nd pyrolysis is important to achieve high ORR activity.



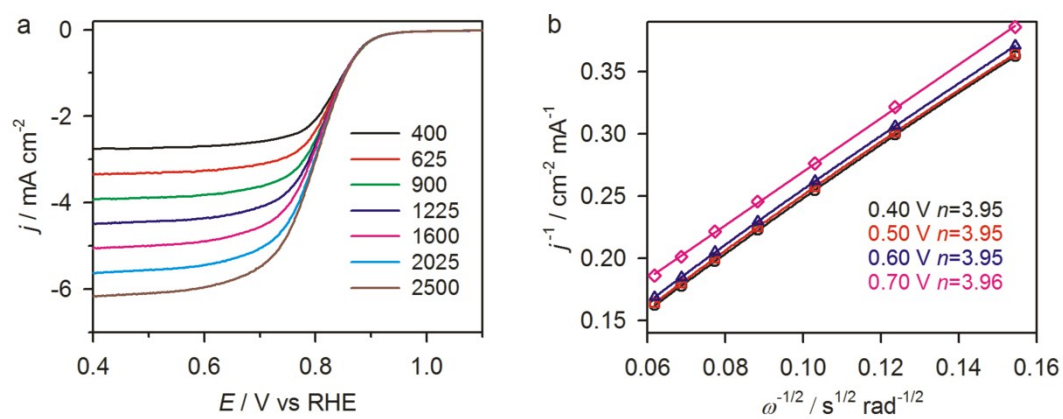
**Fig. S10** ORR polarization curves for various catalysts prepared with different weigh ratios of polyaniline nanofibers to cobalt nitrate.



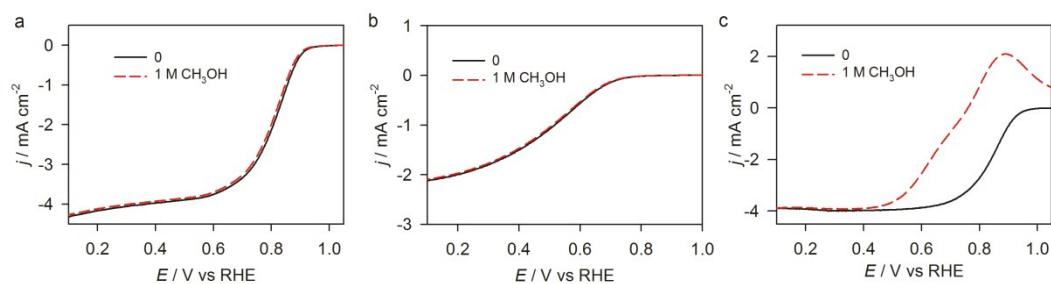
**Fig. S11** (a) XAFS spectrum at the Co K-edge of t Co-N-GNWs. (b) Fourier transforms (FT) of  $k^2$ -weighted Co K-edge EXAFS experimental data. The  $\chi(k)$  data weighted by  $k^1$  for the Co K-edge was Fourier transformed to  $R$ -space (the  $k$ -space ranging from 2.5 to 10  $\text{\AA}^{-1}$ ) to isolate the EXAFS contributions from the coordination shell.



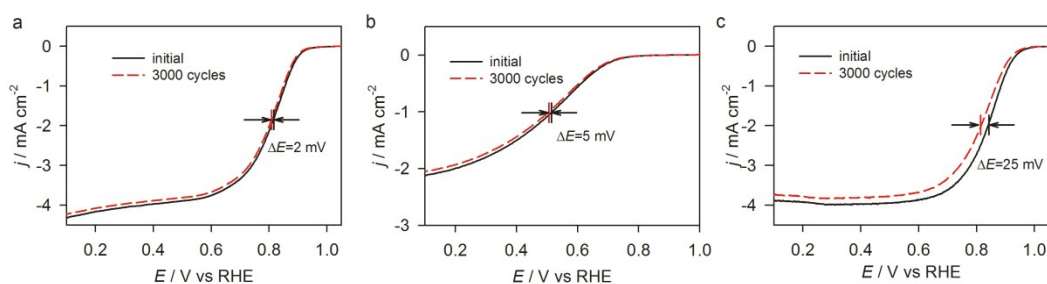
**Fig. S12** Percentage of peroxide and the electron transfer number of Co-N-GNWs and N-CNWs catalysts at various potentials.



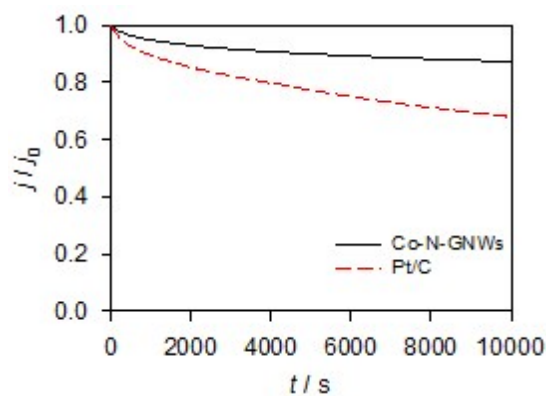
**Fig. S13** (a) Polarization curves for Co-N-GNWs catalyst at the different rotation rates indicated. (b) Koutecky-Levich plots for Co-N-GNWs catalyst at different potentials.



**Fig. S14** ORR polarization curves for Co-N-GNWs (a), N-CNWs (b), and Pt/C (c) catalysts in the absence and presence of 1 M  $\text{CH}_3\text{OH}$ . Scan rate:  $10 \text{ mV s}^{-1}$ . Rotation rate: 900 rpm.



**Fig. S15** ORR polarization curves for Co-N-GNWs (a), N-CNWs (b), and Pt/C (c) catalysts after 3000 potential cycles. Scan rate:  $10 \text{ mV s}^{-1}$ . Rotation rate: 900 rpm. The potential cycles were from 0.6 to 1.0 V in an  $\text{O}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$  solution at room temperature at a sweep rate of  $50 \text{ mV s}^{-1}$ .



**Fig. S16** Chronoamperometric responses of Co-N-GNWs and Pt/C catalysts at 0.70 V in an  $O_2$ -saturated 0.5 M  $H_2SO_4$  aqueous solution, which are normalized to the initial current responses.