Electronic Supplementary Information

Co/CoO Nanoparticles Immobilized on Co-N-doped Carbon as a Trifunctional Electrocatalyst for Oxygen Reduction, Oxygen Evolution and Hydrogen Evolution Reactions

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Experimental section

Preparation of N-doped carbon nanodots (N-CNs): N-doped carbon nanodots (N-CNs) were synthesized by one-step hydrothermal method using shrimp shells (River Shrimps, Hefei City, Anhui Province, China) as starting material without any synthetic chemicals. The shrimp shells were first dried at 80 °C for 12 h, and then ground into powder form as reaction precursor. Subsequently, 6.0 g shrimp shell powder was added to 60 mL of deionized water, and then transferred into a 100 mL of Teflon-lined autoclave and kept at 180 °C for 15 h. After hydrothermal reaction, the obtained mixture was adequately filtrated to remove large size residues by simple filtration approach (two times using 0.45 μm Millipore filter; one time using 0.22 μm Millipore filter). The obtained solution was further treated by centrifugation at 14,000 rpm for 15 min to collect supernate, and then the supernate was further dialyzed for two days to remove all kinds of inorganic ions. The product yield of N-CNs is ~15% and the concentration of N-CNs solution is ~15 mg mL^{-1}.

Preparation of Co^{2+}/N-CNs@PPy and Co/CoO (or Co)@Co-N-C samples: In a typical synthesis, 45 mL of 15 mg mL^{-1} N-CNs solution and 0.6 mL of pyrrole were first mixed under stirring for 10 min, and then added to 25 mL of 0.25 M $Co(NO_3)_2$ solution followed by ultrasonication for 15 min and vigorous stirring for 30 min. Subsequently, 200 μL of 36% HCl and 4.0 mL of 30% H_2O_2 solution were dropwise added to the above solution under continuous stirring at room temperature. After continuous stirring of 4 h for complete polymerization, the obtained polymerized product (Co^{2+}/N-CNs@PPy) was separated by filtration and washed adequately with ethanol and water. The resultant product (Co^{2+}/N-CNs@PPy) was dried at 80 °C for overnight in N_2 atmosphere for further use.

The Co/CoO (or Co)@Co-N-C composites were fabricated by pyrolysis of the polymerized product (Co^{2+}/N-CNs@PPy) at different temperatures (700, 800, 900, 1000 °C) for 2 h with a heating rate of 5 °C min^{-1} in N_2 atmosphere. The pyrolytic product was denoted as Co/CoO (or Co)@Co-N-C-*X* (*X* represents pyrolysis temperature of 700, 800, 900, 1000 °C, respectively).

Preparation of N-CNs-800, PPy/N-CNs-800 and Co-PPy-800 samples: For comparison, the N-CNs-800 was simply obtained by pyrolysis of the dried N-

CNs (obtained by freeze drying the N-CNs solution for 24 h) at 800 ^{o}C for 2 h with a heating rate of 5 ^{o}C min^{-1} in N_2 atmosphere. To obtain the PPy/N-CNs-800 sample, 0.6 mL of pyrrole and 45 mL of 15 mg mL^{-1} N-CNs solution were added into 25 mL of deionized water solution. Subsequently, 200 μL of 36% HCl and 4.0 mL of 30% H_2O_2 were quickly added into the above solution under vigorous stirring. After constant stirring of 4 h for complete polymerization, the product was separated by filtration and washed with ethanol and water. The hybrids were heated to 800 ^{o}C at a heating rate of 5 ^{o}C min^{-1} and kept at the temperature for 2 h in N_2 atmosphere. It should be noted that pyrrole in this work not only acts as polymerizer to trigger polymerization reaction, but also provides additional nitrogen doping source to improve the nitrogen doping content in carbon structure compared to only N-doped carbon nanodots as C and N sources. Moreover, the content of graphitic-N in resulting carbon structure enhances also after the introduction of pyrrole in comparison with the pyrolytic product made from only shrimp-shell derived N-doped carbon nanodots (see Table S1). The enhanced N doping content and suitable doping type (*e.g.*, graphitic-N) in resulting pyrolytic product are favourable for improving its electrocatalytic activity. The Co-PPy-800 sample was synthesized by the same process as Co/CoO (or Co)@Co-N-C-800 sample except for using 45 mL of deionized water solution to replace 45 mL of N-CNs.

Characterizations

The crystalline structures of samples were identified by X-ray diffraction analysis (XRD, Philips X'pert PRO) using Nifiltered monochromatic CuKa radiation (λKα1 = 1.5418 Å) at 40 kV and 40 mA. The morphology and structure of samples were characterized by field emission scanning electron microscopy (FESEM, Quanta 200FEG) and transmission electron microscopy (TEM, JEOL 2010) with an energy dispersive X-ray spectrometer (EDS Oxford, Link ISIS). X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, America) equipped with Al Kα1, 2 monochromatized radiation at 1486.6 eV X-ray source. The surface area and porosity of samples were measured by a Surface Area and Porosity Analyzer (Tristar3020M). FT-IR spectra of the samples were performed on a Nexus FT-IR spectrophotometer.

Electrochemical measurements

Electrochemical measurements were performed on an electrochemical workstation (CHI 760D, CH Instruments, Inc., Shanghai, China) coupled with a PINE rotating disk electrode (RDE) system (Pine Instruments Co. Ltd. USA). A standard three-electrode electrochemical cell equipped with gas flow system was employed during measurements. Prior to measurements, rotating disk electrode (RDE, 5.0 mm in diameter) was first polished with 5.0, 3.0 and 0.05 μm alumina slurry sequentially and then washed ultrasonically in water and ethanol for 1 min, respectively. The cleaned electrode was dried with a high-purify nitrogen steam. The Co/CoO (or Co)@Co-N-C catalyst ink was prepared by dispersing catalyst powder (5.0 mg) into a mixture including 100 μL of Nafion solution (0.5 wt.%) and 900 μL of ethanol, followed by ultrasonic treatment for 2 min. After that, 12 μL of catalyst ink was then cast onto glassy carbon (GC) electrode surface, leading to a catalyst loading amount of 305 μg cm^{-2}. For comparison, commercial Pt/C and RuO_2 catalyst inks were also made as the same procedure as Co/CoO (or Co)@Co-N-C catalyst ink.

The ORR performance of catalysts was investigated by cyclic voltammogram (CV) and linear sweep voltammogram (LSV) measurements in O_2 (or N_2)-saturated 0.1 M KOH solution. CV curves were measured at a scan rate of 50 mV s^{-1}. LSV curves were measured at a scan rate of 10 mV s^{-1} under different disk rotation rates of 400, 625, 900, 1225, 1600 and 2025 rpm. All the potentials in this work were recorded with respect to the Ag/AgCl reference electrode. The electron transfer number (*n*) per oxygen molecule in an ORR process was calculated by the Koutecky-Levich (K-L) equation:

$$J^{-1} = J_k^{-1} + \left(B\omega^{1/2}\right)^{-1} \quad (1)$$

$$B = 0.62nF\left(D_0\right)^{2/3}v^{-1/6}C_0 \quad (2)$$

$$J_k = nFkC_0 \quad (3)$$

where J is the measured current density during ORR, J_k is the kinetic current density, ω is the electrode rotating angular velocity ($\omega = 2\pi N$, N is the linear rotation speed), B is the slope of K-L plots, n represents the electron transfer number per oxygen molecule, F is the Faraday constant ($F = 96485\ C\,mol^{-1}$), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH ($1.9 \times 10^{-5}\ cm^2\,s^{-1}$), v is the kinetic viscosity ($0.01\,cm^2\,s^{-1}$), C_0 is the bulk concentration of O_2 ($1.2 \times 10^{-3}\,mol\,L^{-1}$).

The OER polarization curves and HER polarization curves were also obtained with a scan rate of 5.0 mV s^{-1} at room temperature in O_2 and N_2-saturated 0.1 M KOH, respectively. All potentials were iR-compensated. And the presented current density was normalized to the geometric surface area. All the polarization curves are the steady-state ones after several cycles.

The measurements of rechargeable zinc-air batteries were performed on home-built electrochemical cells. All data were collected from the as-fabricated cell with a CHI 760D (CH Instruments, Inc., Shanghai, China) electrochemical workstation at room temperature. Briefly, zinc foil was used as anode and catalysts loaded on the gas diffusion layer (Teflon-coated carbon fiber paper with a geometric area of 1.0 cm^2, catalyst loading amount of 2.0 mg cm^{-2}) was used as the air cathode. For comparison, the rechargeable battery was also made from a mixture of Pt/C and RuO_2/C with a mass ratio of 1:1. The electrolyte was 6.0 M KOH and 0.2 M zinc acetate solution.

Table S1 The chemical compositions of Pyrrole, N-CNs, N-CNs-800, PPy/N-CNs-800, Co/CoO@Co-N-C-700, Co/CoO@Co-N-C-800, Co@Co-N-C-900 and Co@Co-N-C-1000 obtained by XPS characterization.

Sample	C (at.%)	N (at.%)	O (at.%)	Co (at.%)
Pyrrole	80	20	/	/
N-CNs	63.45	14.42	22.13	/
N-CNs-800	82.88	8.07	8.41	/
PPy/N-CNs-800	74.69	11.69	12.92	/
Co/CoO@Co-N-C-700	85.05	9.40	4.72	0.84
Co/CoO@Co-N-C-800	83.41	7.44	7.94	1.21
Co@ Co-N-C-900	86.43	4.65	7.56	1.36
Co@Co-N-C-1000	87.60	3.62	7.33	1.45

Table S2 The atomic percentage of Pyridinic N, Pyrrolic N, Graphitic N and Oxided N of N-CNs, N-CNs-800, PPy/N-CNs-800 and Co/CoO@Co-N-C-800 obtained by their corresponding high resolution N 1s XPS spectrum.

Sample	Pyridinic N (at.%)	Pyrrolic N (at.%)	Graphitic N (at.%)	Oxided N (at.%)
N-CNs	40.0	38.4	21.6	/
N-CNs-800	36.9	30.1	26. 1	6.6
PPy/N-CNs-800	25.1	25.9	37.4	11.6
Co/CoO@Co-N-C-800	28.1	26.4	33.6	11.9

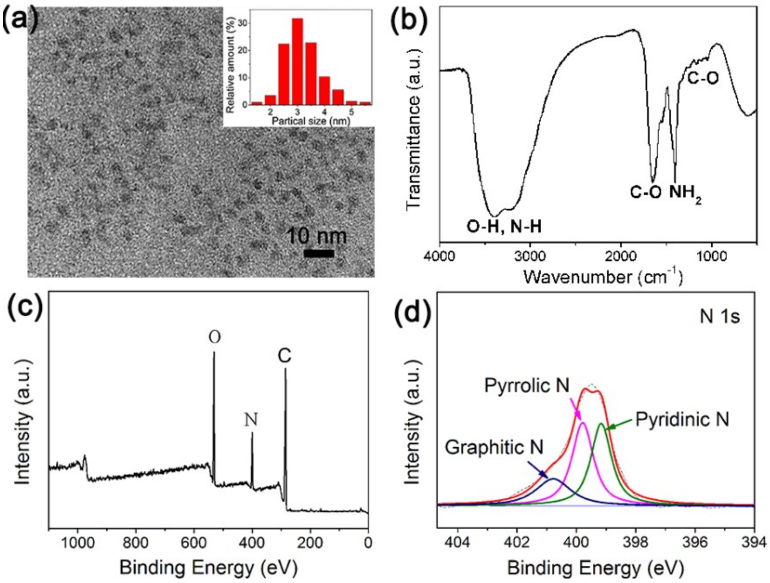

Fig. S1 (a) TEM image of shrimp-shell derived N-CNs (inset of nanodot size distribution). (b) FT-IR spectrum of shrimp-shell derived N-CNs. (c) Surface survey XPS spectra of shrimp-shell derived N-CNs. (d) High resolution N 1s XPS spectrum of shrimp-shell derived N-CNs.

Fig. S1a shows the TEM image of shrimp-shell derived N-CNs. As shown, the hydrothermally converted N-doped carbon nanodots possess a size distribution of 1.5~5.5 nm (inset in Fig. S1a). The FT-IR analysis (Fig. S1b) indicates that shrimp-shell derived carbon nanodots contain rich surface O and N functional groups such as O-H, N-H, C=O/C=N, and C-O/C-N.[1-3] Further, the XPS survey spectra of N-CNs confirm the presence of C, N and O elements with a nitrogen content of ~14.42% (Fig. S1c). The high resolution N 1s XPS spectrum (Fig. S1d) of N-CNs reveals the existence of three types of doped N atoms, namely, pyridinic-N (398.7 eV), pyrrolic-N (399.7 eV) and graphitic-N (400.8 eV).[1-3]

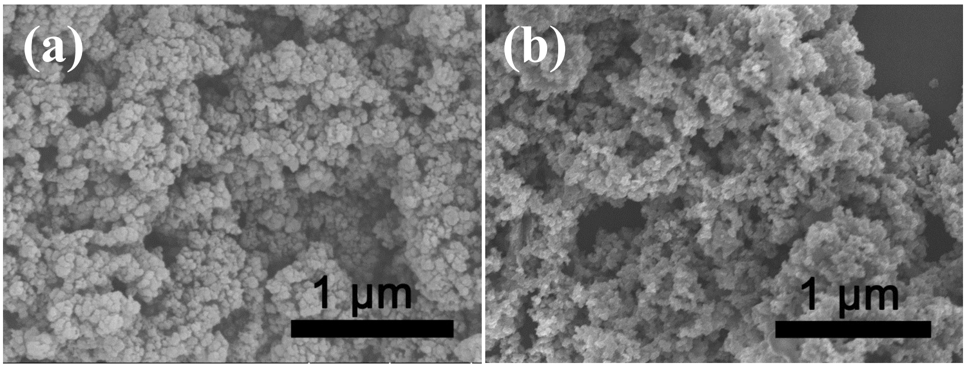

Fig. S2 (a) Surface SEM image of Co^{2+} contained composite by a polymerization reaction of pyrrole in the presence of Co^{2+} and N-CNs. (b) Surface SEM image of Co/CoO@Co-N-C-800.

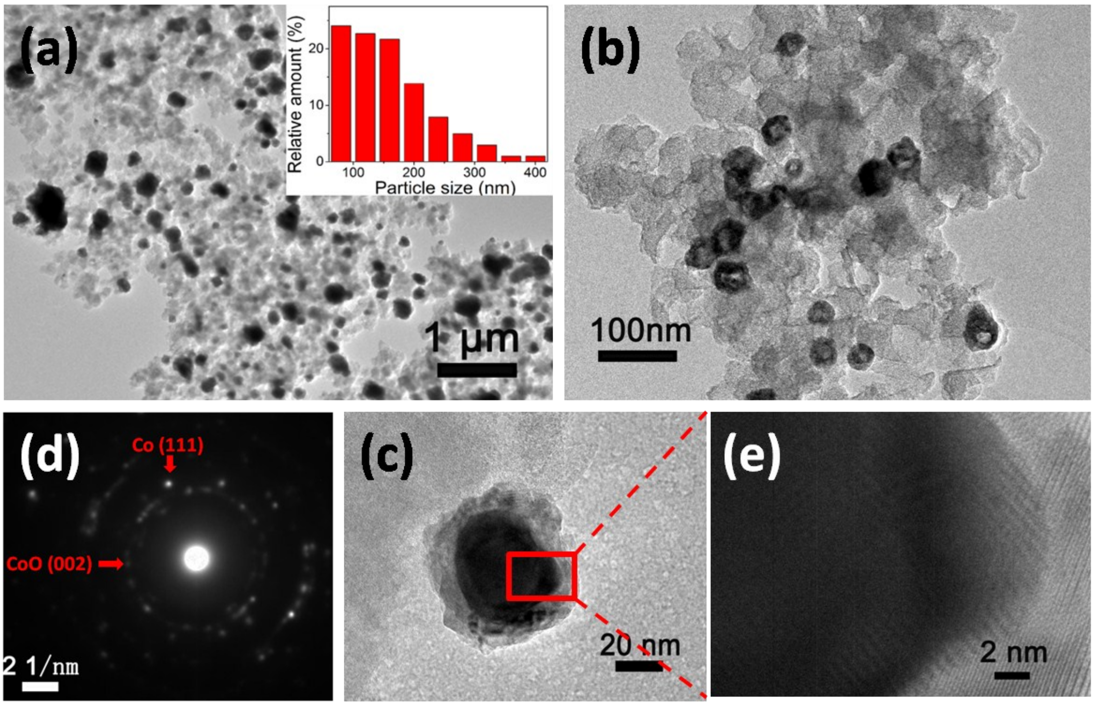

Fig. S3 (a), (b), (c) Low magnification TEM images of Co/CoO@Co-N-C-800 (inset in Fig. S3a of size distribution of Co/CoO nanoparticles. (d) Corresponding SAED patterns from (c). (e) HRTEM image of an individual Co/CoO particle.

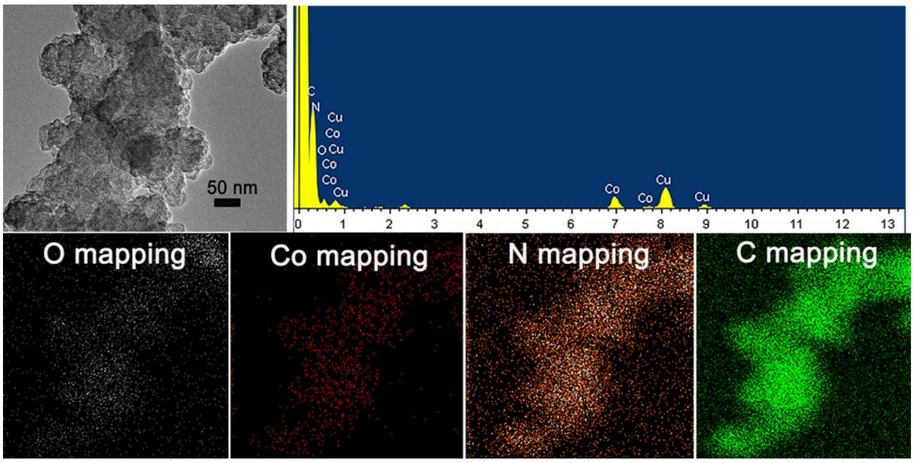

Fig. S4 The energy-filtered TEM spectrum analysis of Co/CoO@Co-N-C-800 in the area without Co/CoO nanoparticles.

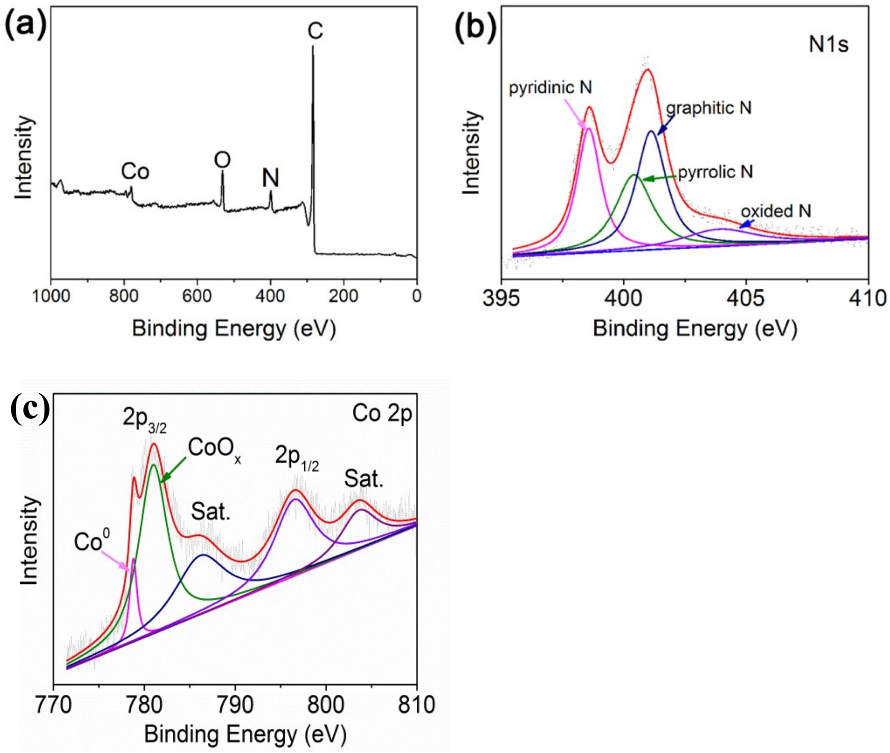

Fig. S5 (a) Surface survey XPS spectra of Co/CoO@Co-N-C-800. (b) High resolution N 1s XPS spectrum of Co/CoO@Co-N-C-800. (c) High resolution of Co 2p XPS spectrum of Co/CoO@Co-N-C-800.

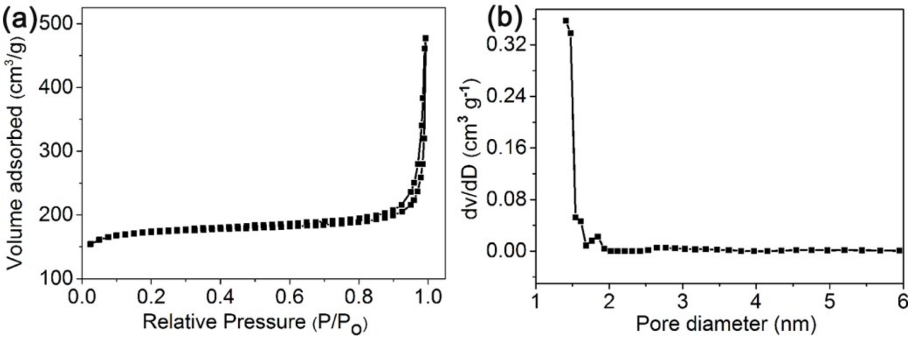

Fig. S6 (a) N_2 adsorption-desorption isotherm of Co/CoO@Co-N-C-800 and (b) corresponding pore size distribution.

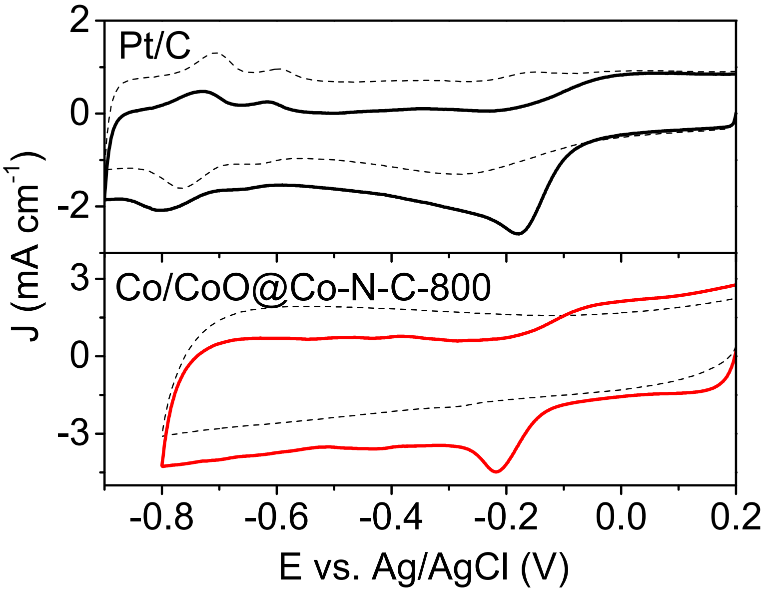

Fig. S7 Cyclic voltammetry (CV) curves of Co/CoO@Co-N-C-800 and commercial Pt/C catalysts in N_2- or O_2-saturated 0.1 M KOH solution; the scan rate of 50 mV s^{-1}.

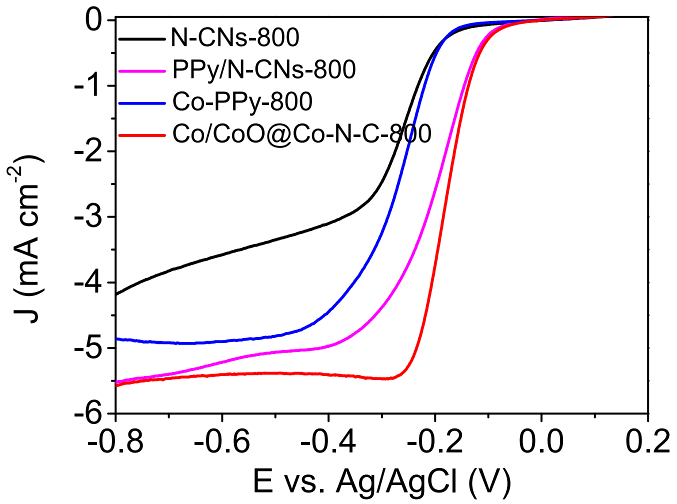

Fig. S8 LSV curves of N-CNs, PPy/N-CNs-800, Co-PPy-800 and Co/CoO@Co-N-C-800 in O_2-saturated 0.1 M KOH solution at a scan rate of 10 mV s^{-1} and a rotation speed of 1600 rpm.

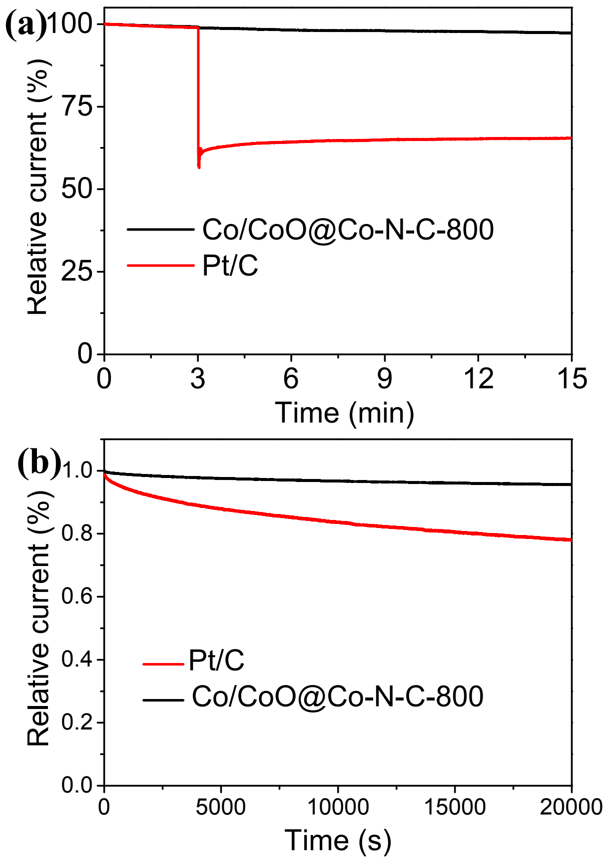

Fig. S9 Crossover effect (a) and durability (b) measurements of Co/CoO@Co-N-C-800 and commercial Pt/C catalysts.

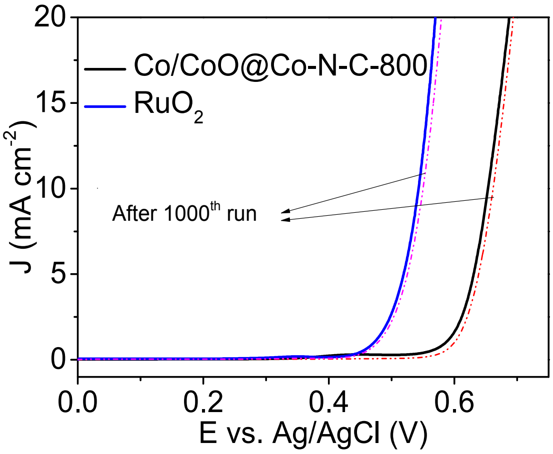

Fig. S10 LSV curves of Co/CoO@Co-N-C-800 and commercial RuO_2 in O_2-saturated 0.1 M KOH solution at a scan rate of 5.0 mV s^{-1} before and after 1000th run.

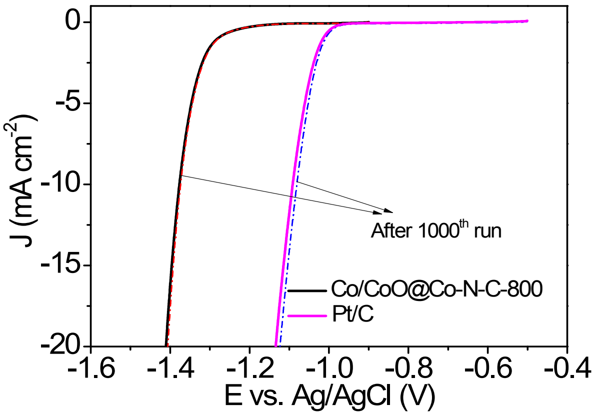

Fig. S11 LSV curves of Co/CoO@Co-N-C-800 and commercial Pt/C in N_2-saturated 0.1 M KOH solution at a scan rate of 5.0 mV s^{-1} before and after 1000th run.

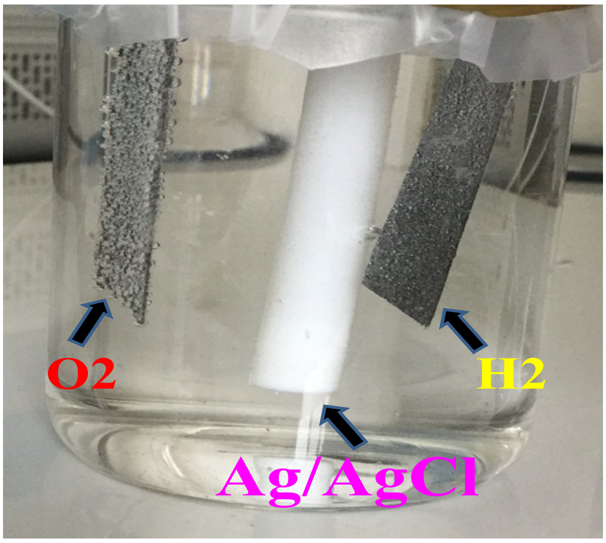

Fig. S12 Optical photo of water splitting measurement using Co/CoO@Co-N-C-800 loaded carbon fiber papers as cathode and anode. The applied potential of -0.9 V.

References:

1. S. Liu, J. Tian, L. Wang, Y. Zhang, X. Qin, Y. Luo, A. M. Asiri, A. O. Al-Youbi and X. Sun, *Adv. Mater.*, 2012, 24, 2037-2041.
2. H. Zhang, Y. Wang, D. Wang, Y. Li, X. Liu, P. Liu, H. Yang, T. An, Z. Tang and H. Zhao, *Small*, 2014, 10, 3371-3378.
3. R. Liu, H. Zhang, S. Liu, X. Zhang, T. Wu, X. Ge, Y. Zang, H. Zhao and G. Wang, *Phys. Chem. Chem. Phys.*, 2016, 18, 4095-4101.