

One-step conversion from metal-organic framework to $\text{Co}_3\text{O}_4@\text{N}$ -doped carbon nanocomposites towards high efficient oxygen reduction catalyst

(Supplementary Information)

Materials and General Methods

All materials were reagent grade obtained from commercial sources and used without further purification. The particle size and shape were analysed with TEM using a Philips/FEI Tecnai 12 BioTWIN TEM operating at 200 kV. The TEM samples were prepared by dropping the sample solution onto a copper grid covered with carbon and dried in air. The XPS spectra were obtained by using a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatised Mg $K\alpha$ X-ray ($h\nu = 1283.3$ eV). XPS samples were prepared by drying a dispersion of different products on a piece of Cu wafer. Powder X-ray diffraction (PXRD) data were collected on an X'Pert-ProMPD (Holand) D/max- γ A X-ray diffractometer with Cu $K\alpha$ radiation in a flat plate geometry.

Synthesis of Co-I-MOF

A mixture of $\text{Co}(\text{OAC})_2 \cdot 4\text{H}_2\text{O}$ (0.6 mmol), Hypoxanthine (0.6 mmol), NaOH aqueous solution (0.6 mL, 1 M) and distilled water (10 mL) was placed in an 18 mL Teflon-lined stainless steel vessel and stirred about 15 min in air. The vessel was sealed and heated at 130 °C for 4 d under autogenous pressure, and then cooled to room temperature naturally, purple block crystals were obtained.

Synthesis of $\text{Co}_3\text{O}_4@\text{N}$ -C nanocomposites

The obtained Co-I-MOF were calcined in nitrogen at 800 °C for 12 h, and $\text{Co}_3\text{O}_4@\text{N}$ -C doped carbon nanocomposites were prepared.

Sample preparation for TEM and XRD

TEM samples were prepared by drop-drying the samples from their diluted aqueous suspensions onto copper grids. XRD samples were prepared by drop-drying the samples from their aqueous suspensions onto glass substrates.

Electrochemical Measurements

Electrochemical measurements were performed at room temperature using a rotating disk working electrode made of glassy carbon (3 mm in diameter). The catalyst ink was fabricated as follows: 4 mg of powder was dispersed in 1 ml absolute ethanol by sonicating. 15 ml catalyst ink was dropped on the glassy carbon disk electrode and dried naturally. Finally, 10 ml Nafion (0.05 wt%) solution was pipetted onto the catalyst film, and dried at room temperature.

All the electrochemical measurements were performed using a CHI660C electrochemical workstation at a scanning rate of 10 mV s^{-1} at room temperature in a standard three-electrode cell at room temperature, in which a Pt wire was used as the counter electrode, a saturated calomel electrode (SCE) was used as the reference, and the modified glass carbon rotating disk electrode was used as the working electrode. Electrolyte was saturated with oxygen by bubbling O_2 prior to the start of each experiment. A flow of O_2 was maintained over the electrolyte during the recording of CVs in order to ensure its continued O_2 saturation. The working electrode was cycled at least 5 times before data were recorded at a scan rate of 5mVs^{-1} . In control

experiments, CV measurements were also performed in N_2 by switching to N_2 flow through the electrochemical cell. The electrochemical measurements for ORR were performed in O_2 -saturated 0.1 M KOH solution. The polarization curves were obtained by sweeping the potential from -1.0 to -0.2 V (vs. SCE) at the scan rate of 10 mV s^{-1} under different rotation rates.

N_2 adsorption–desorption measurement

To further confirm the confinement characteristics of the present $Co_3O_4@N-C$ core–shell nanostructures, N_2 adsorption–desorption measurement was carried out. The N_2 adsorption–desorption isotherm for $Co_3O_4@N-C$ core–shell nanostructures (Fig. S2) exhibits a type-IV isotherm, indicating a typical physisorption process of a mesoporous material. That is to say, the obtained $Co_3O_4@N-C$ core–shell nanostructures provide an ideal model for the nanocatalyst with the effect of synergetic confinement. A suitable optimization of the structures and composition can further enhance their catalytic property.

Supporting Figures

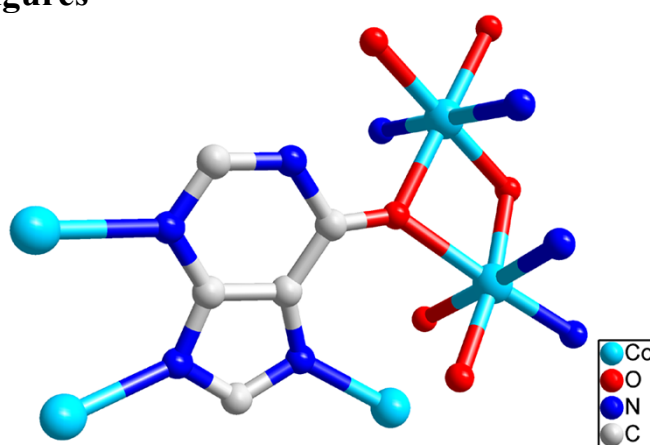


Fig. S1 Ball-stick view of the asymmetric unit of Co-I-MOF. For clarity, the hydrogen atoms and lattice water molecules are omitted.

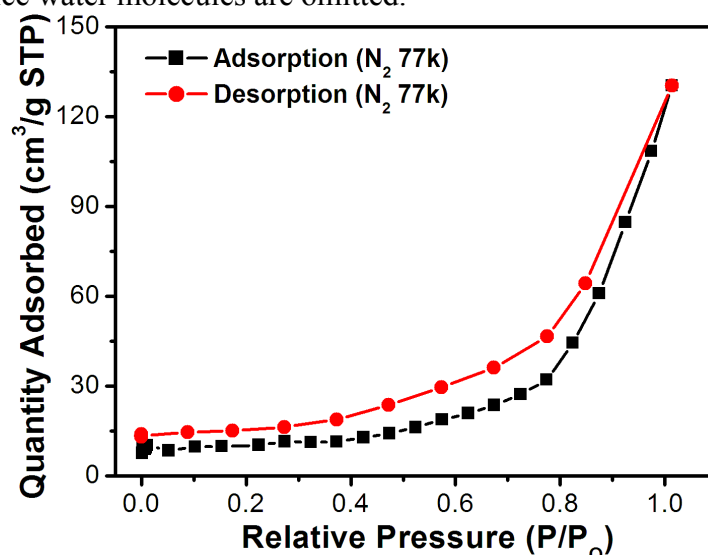


Fig.S2 Nitrogen adsorption–desorption isotherms of $Co_3O_4@N-C$ at 77 K.

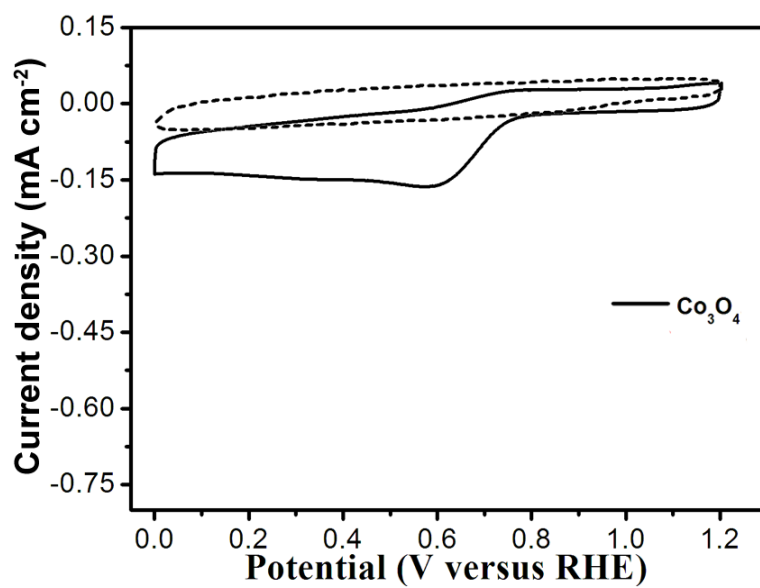


Fig.S3 (a) Cyclicvoltammograms of ORR on Co₃O₄ catalyst in O₂-saturated (solid line) or N₂-saturated 0.1M KOH (dash line) (scan rate: 50 mVs⁻¹).