## **Electronic Supplementary Information**

# 3D Hierarchical Porous Co<sub>3</sub>O<sub>4</sub> Nanotube Network as Efficient Cathode for Rechargeable Lithium-Oxygen Batteries

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### **Experimental Section**

#### **Preparation of PPy nanofibers**

PPy nanofibers were synthesized via an oxidative template assembly route. Pyrrole (Py) was distilled before use. In a typical process, 0.72 g cetrimonium bromide (CTAB) was dissolved in 200 mL of 1 M HCl solution by constant stirring in an ice bath (0-5 °C). Subsequently, 0.33 g distilled Py monomer was added into the above solution, and another 0.5 h stirring was carried out. Meanwhile, 1.13 g ammonium persulfate (APS) was dissolved in 20 mL distilled water which was then dropped into the Py monomer-containing solution and allowed to react for 24 h in an ice bath (0-5 °C). After that, the black product was suction filtered and washed several times with 1 M HCl solution and distilled water, followed by drying in a vacuum oven at 80 °C overnight. Finally, a black powder was yielded and denoted as PPy nanofiber.

#### Preparation of Co<sub>3</sub>O<sub>4</sub> nanotube (HPNT) network

In a typical synthesis <sup>1, 2</sup>, 0.4125 g cobalt (II) acetate was dissolved in 15 mL distilled water and 26 mL ethanol mixed solvent. Then, 50 mg of PPy nanofibers was added into the mixed solution, which was ultrasonically treated for 1 h. Secondly, 1.5 ml 25% ammonium was added under vigorous stirring. The mixture was stirred in air for about 10 min to form a homogeneous dark slurry. Then, the suspension was transferred into a 120 mL autoclave, sealed, and maintained at 150 °C for 3 h. Afterwards, the autoclave was cooled to room temperature naturally. The resulting black solid products were washed with water via centrifugation and re-dispersion and dried in a vacuum oven at 80 °C overnight, which was followed by a heat-treatment at 450 °C for 6 h in air atmosphere. Meanwhile, pristine  $Co_3O_4$  under the same hydrothermal conditions without PPy nanofiber as template was also prepared as a control sample, with the sample denoted as  $Co_3O_4$  NP.

#### **Physical characterizations**

X-ray diffraction (XRD) (GBC MMA) patterns were collected over a  $2\vartheta$  range of  $20^{\circ}$ -  $70^{\circ}$  with a scan rate of  $4^{\circ}$  min<sup>-1</sup> and analysed with Traces<sup>TM</sup> software in combination with the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction files. The morphologies of the samples were examined by field emission scanning electron microscopy (FE-SEM, JEOL 7500) and transmission electron microscopy (TEM, JEOL ARM-200F). The XPS data were analysed using CasaXPS software, and all the results were calibrated by C 1s at 284.6 eV for graphite. Thermogravimetric analysis (TGA) was carried out using a SETARAM Thermogravimetric Analyzer (France). Brunauer-Emmett-Teller (BET) surface area and pore size distribution (PSD) measurements were conducted by N<sub>2</sub> adsorption/desorption at 77 K on a Quantachrome Autosorb-IQ MP instrument.

#### Li-O<sub>2</sub> battery measurements

The electrochemical performance of lithium-oxygen batteries containing the samples as active materials was investigated using 2032 coin-type cells with air holes on the cathode side. For the preparation of the porous cathode electrode, 60 wt.% catalyst, 30 wt.% Ketjen Black (KB), and 10 wt.% poly(1,1,2,2-tetrafluoroethylene) (PTFE) (60% dispersion) were mixed in an isopropanol solution. The resulting homogeneous slurry was coated on carbon paper. The same procedure was applied to prepare pristine KB electrodes. After that, the electrodes were dried at 120 °C in a vacuum oven for 12 h. All the lithium-oxygen batteries were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany) with both water and oxygen contents below 0.1 ppm. They consisted of lithium metal foil as the counter electrode, a glass fiber separator (Whatman GF/D), non-carbonate electrolyte containing 1 M LiCF<sub>3</sub>SO<sub>3</sub> dissolved in tetraethylene glycol dimethyl ether (TEGDME), and the air cathode electrode. All the assembled coin cells were stored in an O<sub>2</sub>-purged chamber which was connected to a LAND CT 2001 instrument, a multi-channel battery tester, for 2 h before each test. The galvanostatic discharge-charge tests were then conducted on the battery testing system with the voltage between 2.35-4.35 V (*vs.* Li<sup>+</sup>/Li), and the capacities reported in this work were normalized by the mass of active material and carbon used in the cathodes. The loading amount in each cathode was approximately 1 mg cm<sup>-2</sup>. Cyclic voltammetry (CV) was conducted in O<sub>2</sub>-saturated 0.2 M lithium trifluoromethanesulfonate (LiCF<sub>3</sub>SO<sub>3</sub>) in tetraethylene glycol dimethyl ether (TEGDME) with a scan rate of 10 mV s<sup>-1</sup>.

Examination of the discharged and recharged electrodes involved disassembling the cell in the glove box, rinsing the cathode with tetraethylene glycol dimethyl ether, and removing the solvent under vacuum. For ex-situ XRD, SEM, and XPS tests, the electrodes were covered by a layer of Kapton film before moving them from the glove box to the outside instruments.

#### **Rotating disk electrode tests**

Rotating disk electrode (RDE) tests were performed using a computer-controlled potentiostat (Princeton 2273 and 616, Princeton Applied Research) in a conventional three-electrode cell at room temperature. The glassy carbon (GC) working electrode (0.196 cm<sup>-1</sup>) was first polished with alumina powder, rinsed with deionized water, and sonicated, first in ethanol and then in double-distilled water. A platinum wire and Ag/AgCl (filled with saturated KCl aqueous solution) were used as the counter and reference electrodes, respectively. Typically, the catalyst was redispersed in deionized water + isopropanol + 5% Nafion<sup>\*</sup> (v/v/v = 4/1/0.05) to form a homogeneous catalyst ink with a concentration of 2 mg mL<sup>-1</sup>. Then, 30 µL of this dispersion was pipetted onto the surface of the GC working electrode and dried under ambient conditions. For comparison, commercial Pt/C (20 wt. % Pt on Vulcan XC-72) catalyst ink was also obtained by the same method described above. Linear sweep voltammograms (LSVs) to measure the ORR performance were collected in  $O_2$  saturated 0.1 M KOH solution with different rotation speeds from 400 to 1600 rpm from -0.9 - 0.1 V with a scan rate of 10 mV s<sup>-1</sup>, while OER plots were obtained in Ar atmosphere from 0.1 - 0.9 V with a scan rate of 10 mV s<sup>-1</sup> and a rotation speed of 1600 rpm.

Koutecky-Levich (K-L) plots show the inverse current density ( $j^{-1}$ ) as a function of the inverse of the square root of the rotation speed ( $\omega^{-1/2}$ ) at different potentials. The number of electrons involved per O<sub>2</sub> in the ORR was determined by the Koutecky-Levich equation: <sup>3, 4</sup>

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_k}$$
(1)

where j,  $j_k$ , and  $j_d$  are the measured, the kinetically controlled, and the diffusion controlled current densities, respectively, and  $\omega$  is the electrode rotation rate. *B* is determined from the slope of the K-L plot based on the Levich equation:

$$B = 0.2nF(Do_2)^{2/3} v^{-1/6} Co_2$$
 (2)

where *n* represents the number of electrons gained per O<sub>2</sub>, *F* is the Faraday constant (F = 96485 C mol<sup>-1</sup>),  $Do_2$  is the diffusion coefficient of O<sub>2</sub> in 0.1 M KOH (1.9 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>), *v* is the kinetic viscosity (0.01 cm<sup>2</sup> s<sup>-1</sup>), and  $Co_2$  is the bulk concentration of O<sub>2</sub> (1.2 × 10<sup>-6</sup> mol cm<sup>-3</sup>).

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**Fig.S1.** SEM image of  $Co_3O_4$  nanoparticles ( $Co_3O_4$  NP).



Fig. S2. a)  $N_2$  adsorption-desorption isotherms and b) pore size distribution of the as-prepared  $Co_3O_4$  HPNT network, with the inset showing an enlargement of the indicated range.



Fig. S3. TGA plots of the  $Co_3O_4/PPy$  precursor and the as-prepared  $Co_3O_4$  HPNT network.



**Fig. S4.** Linear sweep voltammetry (LSV) curves at various rotation speeds in  $O_2$ -saturated 0.1 M KOH aqueous solution at a scan rate of 10 mV s<sup>-1</sup> in the potential range of -0.9-0.1 V (vs. AgCl/Ag) for (a) commercial 20 wt.% Pt/C, (b) the  $Co_3O_4$  HPNT network, and (c)  $Co_3O_4$  NP. (d) Calculated electron transfer numbers of the  $Co_3O_4$  HPNT,  $Co_3O_4$  NP and 20% Pt/C from the LSV curves.



**Fig. S5** Electrochemical impedance spectroscopy (EIS) plots of the as-prepared  $Co_3O_4$  HPNT network in fresh, 1<sup>st</sup> cycle discharged, 1<sup>st</sup> cycle recharged, and 40<sup>th</sup> cycle recharged states.