Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information (ESI)

Co-MOF derived oxygen vacancies rich Co_3O_4 based composite as cathode material for hybrid Zn battery

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Materials and characterization

All chemicals were of analytical grade, commercially available from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China) and used as received without further purification. Suitable single crystal of **CoMOF** was carefully selected under an optical microscope and glued on a glass fiber. Structural measurement was performed on a Bruker AXS SMART APEX II CCD diffractometer at 293 K (1902269). PXRD patterns were recorded on X-ray diffractometer with Cu KR (λ=1.5418 Å) radiation (Philips X'Pert Pro Super, Philips). Raman spectroscopy was conducted with an excitation wavelength of 633 nm (LabRAMHR-800, HORIBA). N_2 sorption analysis was conducted using an ASAP 2020 accelerated surface area and a porosimetry instrument (Micromeritics, Norcross, GA), equipped with an automated surface area, at 77 K using Barrett-Emmett-Teller (BET) calculations for the surface area. The pore size distribution plot was based on the original density functional theory model. The morphology was observed on an ultra plus field emission scanning electron microscope (SEM, ultra plus, ZEISS) and a transmission electron microscopy (TEM, JEOL, JEM-2100F). XPS was performed with Mg Kα radiation (1253.6 eV) as an excitation source (ESCALab MKII, Thermo Scientific, Waltham, MA). Electrochemical experiments were conducted on CHI-660E electrochemical workstation. The LAND-CT2001A testing devices were used to analyze the battery charge-discharge performance.

Synthesis of $[Co(TPDC)(BIMB)(H_2O)]_n$ (CoMOF) and its nanoparticle

At first, TPDC (0.034 g, 0.2 mmol) and BIMB (0.042 g, 0.2 mmol) ligands were dispersed in 10 mL water. Then, $Co(OAc)_2{\cdot}4H_2O$ (0.049 g, 0.2 mmol) was added in this solution slowly. Finally the pH value of this solution was adjusted to 5.5 with 1.0

M KOH. After stirred for 15 min, the solution was poured into a Teflon-lined reactor (20 mL). The reactor was heated at 140 °C for 48 h and cooled to room temperature. A lot of red crystals were synthesized. To obtain the nanoparticle of CoMOF, the conditions kept unchanged, besides water was replaced by ethanol during reaction.

Synthesis of Co_3O_{4-x}@NSC

The nanoparticle of CoMOF was transferred into a tube furnace and heated with the rate 3 °C·min^{-1} to 400 °C. The calcination process was protected with N_2 gas flow for 4 h. The products were gathered and washed by water, ethanol for three times. Then transferred in the oven and dried for 12 h at 80 °C.

Charge-discharge property

The powder of **Co_3O_{4-x}@NSC** was dispersed in the mixed solution of ethanol and Nafion. The obtained ink was cast on Ni foam, which was served as working electrode in the following electrochemical tests. Carbon rod and Ag/AgCl electrode were used as counter and reference electrodes, respectively. Freshly prepared aqueous KOH solution (1 M) was used as the electrolyte.

ORR and OER activities study

The ink was obtained as above mentioned and cast on rotating disk electrode (RDE). The RDE served as working electrode. Carbon rod and Ag/AgCl electrode were used as counter and reference electrodes. ORR was performed in 0.1 M KOH. In ORR, linear sweep voltammetry (LSV) curves were recorded at 5 mV·s^{-1}. Different rotating speeds of RDE were employed for the ORR measurements. Cyclic voltammetry (CV) cycling was carried out from -0.1 to 1.5 V versus RHE a scanning rate of 10 mV·s^{-1}. In OER, LSV curves were also measured at 5 mV·s^{-1}. In ORR, the electron transfer number was determined by using the Koutechy-Levich (K-L) equation (Eq. 1). In this

equation jis the measured current density, j_k is the kinetic current density, and ωis the electrode rotating rate. The parameter B could be calculated from the slope of the K-L plots based on the following Levich equation (Eq. 2), in which nis the electron transfer number per oxygen molecule, Fis the Faraday constant (F= 96485 $C \cdot mol^{-1}$), D_0 is the diffusion coefficient of O_2 in0.1 M KOH (D_0 = 1.9 × 10^{-5} $cm^2 \cdot s^{-1}$), *v* is the kinetic viscosity (*v* = 0.01 $cm^2 \cdot s^{-1}$), and C_0 is the bulk concentration of O_2 (C_0 = 1.2 × 10^{-6} $mol \cdot cm^{-3}$). The value 0.2 is applied when the rotation speed is expressed in rpm.

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

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

Assemble of Zn-Co_3O_4HB hybrid battery

The hybrid battery was assembled with a home-made cell in the size 4.2 × 4 × 4 cm^3. In this battery, the Zn plate acts as anode with working area 3.2 cm^2. The ink of **Co_3O_{4-x}@NSC** was cast on carbon paper at first. Its other side was covered by PTFE and used as air diffusion layer. After covered by PTFE, the carbon paper with **Co_3O_{4-x}@NSC**loaded on was employed as cathode. The working area of air cathode is also 3.2 cm^2. In this hybrid battery, mixture solution of KOH (4.0 M) and $Zn(OAc)_2 \cdot 2H_2O$ (20 mM) was used as electrolyte. In measurement, no additional oxygen was inlet into this battery.

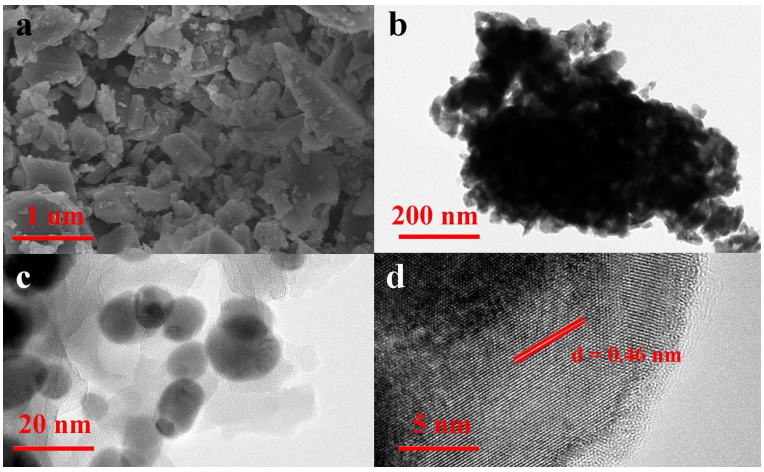

Fig. S1 (a) SEM of **CoMOF**; (b), (c) TEM of **Co_3O_{4-x}@NSC**; (d) High resolution TEM of **Co_3O_{4-x}@NSC**

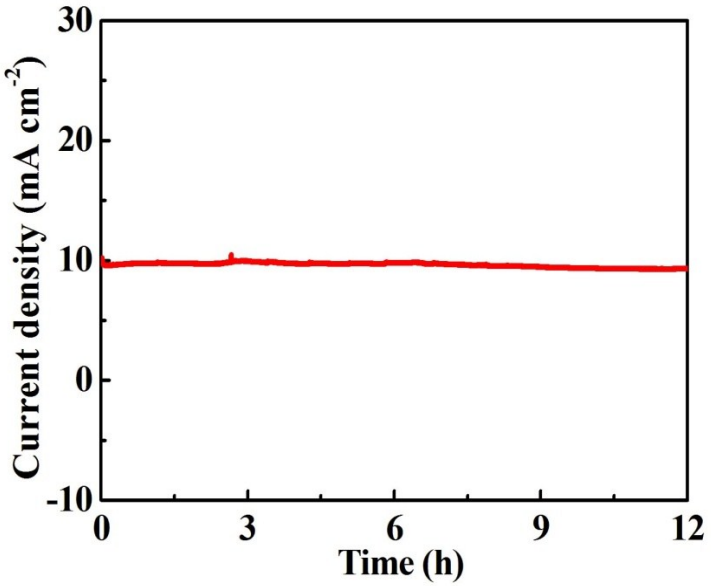

Fig. S2 I-t curve of **Co_3O_{4-x}@NSC**