Electronic Supplementary Information (ESI)

NiMOF derived oxygen vacancies rich NiO with excellent capacitance and ORR/OER activities as cathode material for Zn based hybrid battery

Dandan Xu, Qianqian Huang, Xinxin Xu* and Xiaoguang Sang*

Department of Chemistry, College of Science, Northeastern University, Shenyang 110819, China

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 **NiMOF** 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 (CCDC 2020900). PXRD patterns were recorded on X-ray diffractometer with Cu Kα (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.

Charge-discharge property

The powder of **O-NiO@MCSN** 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 powder of **O-NiO@MCSN** was dispersed in aqueous solution of water (0.8 mL), ethanol (0.15 mL) and 50 µL Nafion (5 %). The ink (10 µL) was cast on rotating disk electrode (RDE). The obtained 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 $mV \cdot s^{-1}$. Different rotating speeds of RDE were employed for the ORR measurements. Cyclic voltammetry (CV) cycling was carried out with scanning rate of 10 $mV \cdot s^{-1}$. In OER, LSV curves were also measured at 5 $mV \cdot s^{-1}$. In ORR, the electron transfer number was determined by using the Koutechy-Levich (K-L) equation (Eq. 1). In this equation j is the measured current density, j_k is the kinetic current density, and ω is 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 n is the electron transfer number per oxygen molecule, F is the Faraday constant (F = 96485 $C \cdot mol^{-1}$), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH ($D_0 = 1.9 \times 10^{-5}$ $cm^2 \cdot s^{-1}$), *v* is the kinetic viscosity (*v* = 0.01 $cm^2 \cdot s^{-1}$), and C_0 is the bulk concentration of O_2 ($C_0 = 1.2 \times 10^{-6}$ $mol \cdot cm^{-3}$). 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 Ni-ZnHB hybrid battery

Hybrid battery was assembled with a home-made cell in the size $4.2 \times 4 \times 4$ cm^3. In

this battery, the Zn plate acts as anode with working area 3.2 cm^2. The ink of **Zn-NiHB** 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 **Zn-NiHB** 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.

Table S1. The comparison of **O-NiO@MCSN** with NiO based ORR, OER

electrocatalysts. The performances of Zn-air batteries with NiO based electrocatalyst as cathode materials.

Materials	Half wave potential of ORR (V)	Overoptential of OER (mV)	Specific Capacity of Zn-air battery (mAh/g_{Zn})	Ref
Ni@NiO@C	0.7	380	No	S1
Ni/NiO	0.76	260	830	S2
N-doped NiO	0.69	270	853	S3
Co-doped NiO	0.79	300	819	S4
O-NiO@MCSN	0.76	410	800.3	Our work

References

S1 D.Y. Xu, C.P. Mu, B.C. Wang, J.Y. Xiang, W.J. Ruan, F.S. Wen, X. Du, Z.Y. Liu, Y.J. Tian, *Sci China Mater* 2017, 60, 947-954.

S2 P.T. Liu, J.Q. Ran, B.R. Xia, S.B. Xi, D.Q. Gao, J. Wang, *Nano-Micro Lett*. 2020, 12, 68.

S3 J.M. Qian, XW. Bai, S.B. Xi, W. Xiao, D.Q Gao, J.L. Wang, *ACS Appl. Mater. Interfaces* 2019, 11, 30865-30871.

S4 J. M. Qian, X.S. Guo, T.T. Wang, P.T. Liu, Hong Zhang, D.Q. Gao, *Appl. Catal. B: Environ*. 250 (2019) 71-77.

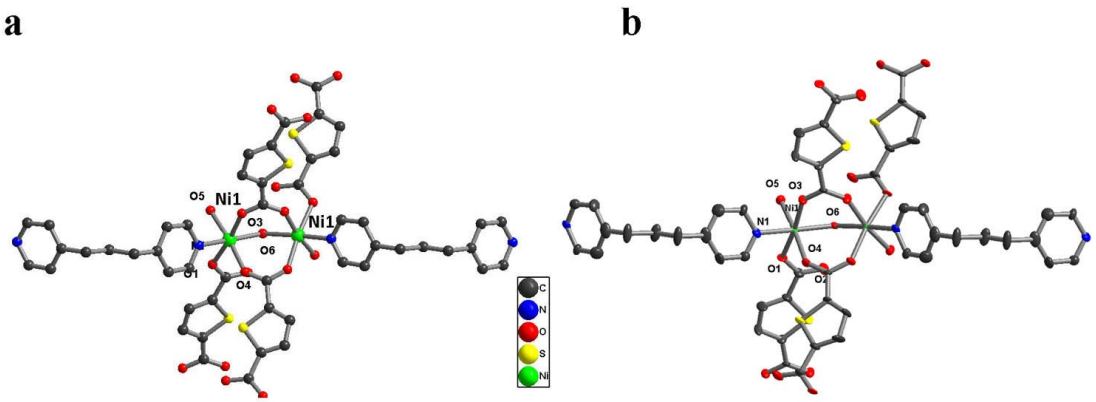

Fig. S1 the fundamental unit of **NiMOF**: (a) ball-stick mode; (b) ellipsoid mode.

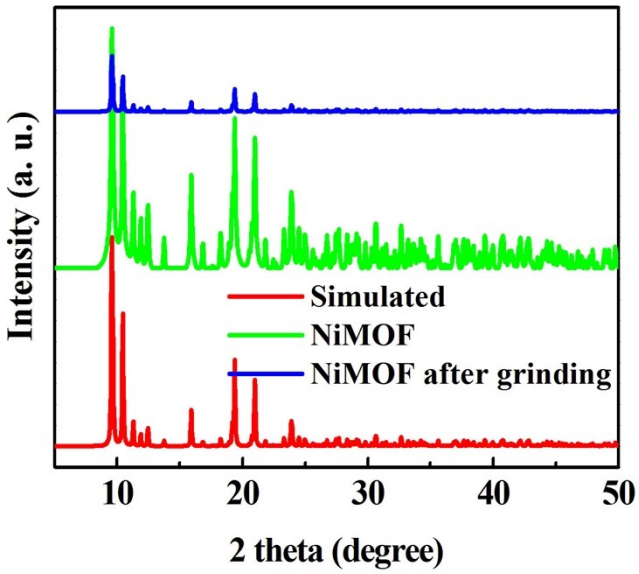

Fig. S2 PXRD of **NiMOF**

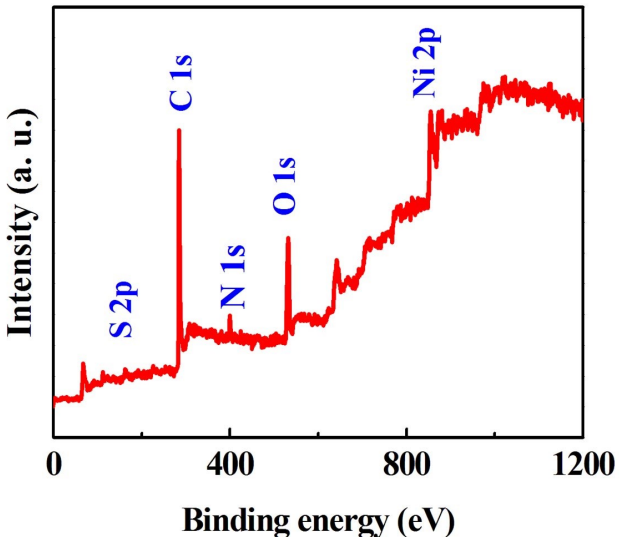

Fig. S3 XPS survey of **O-NiO@MCSN**

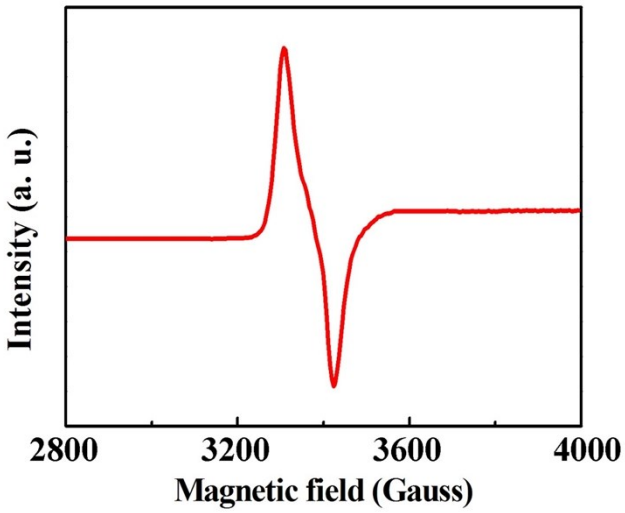

Fig. S4 EPR spectrum of **O-NiO@MCSN**

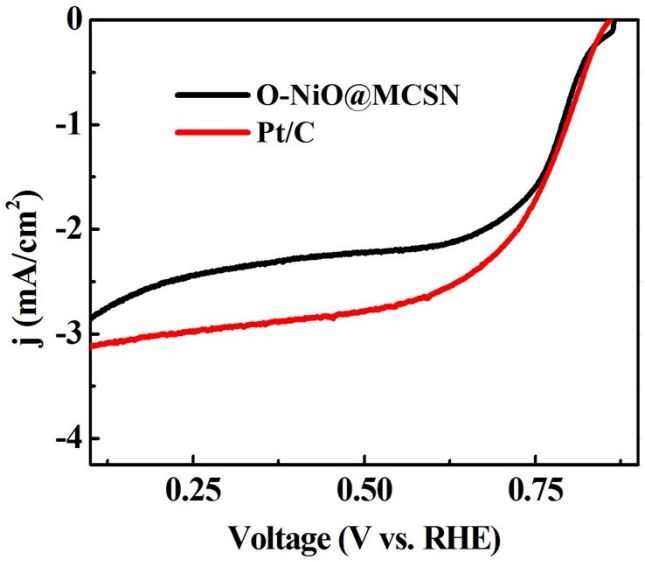

Fig. S5 LSV of **O-NiO@MCSN and Pt/C** at 1600 rpm

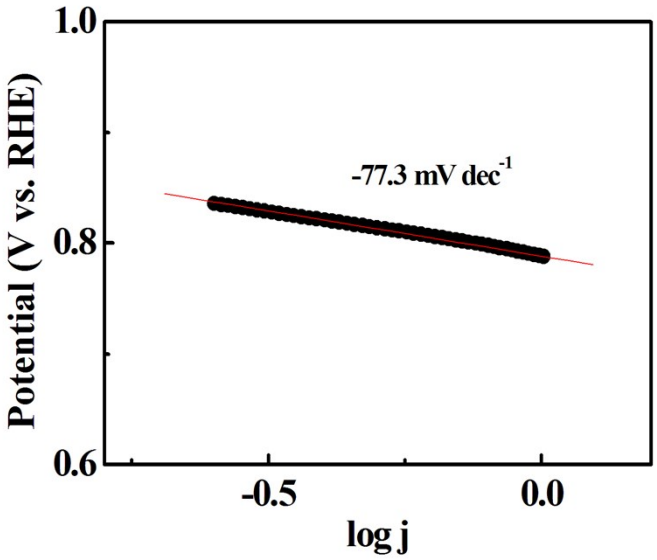

Fig. S6 Tafel slope of **O-NiO@MCSN** during ORR

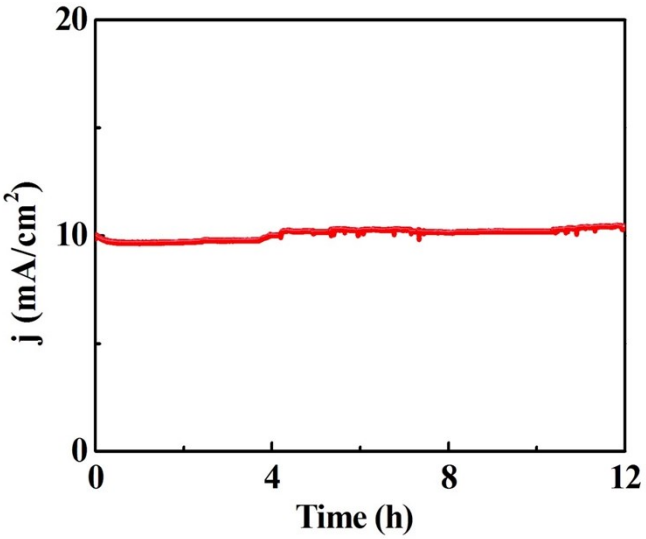

Fig. S7 Chronoamperometric i-t curve of **O-NiO@MCSN** during ORR

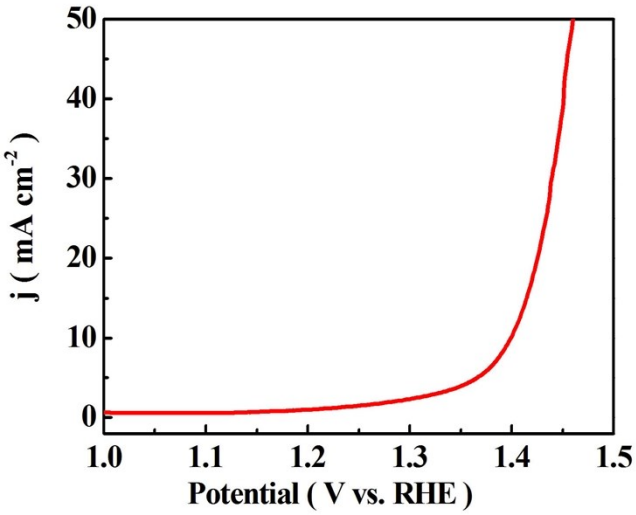

Fig. S8 LSV curve during OER for RuO_2

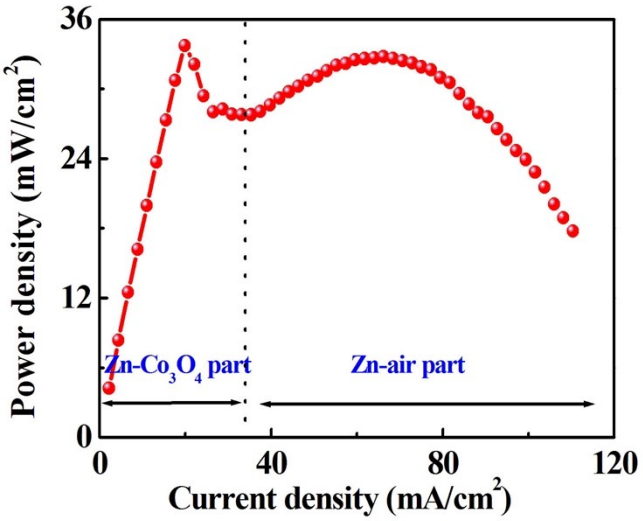

Fig. S9 Power density of **Ni-ZnHB**;

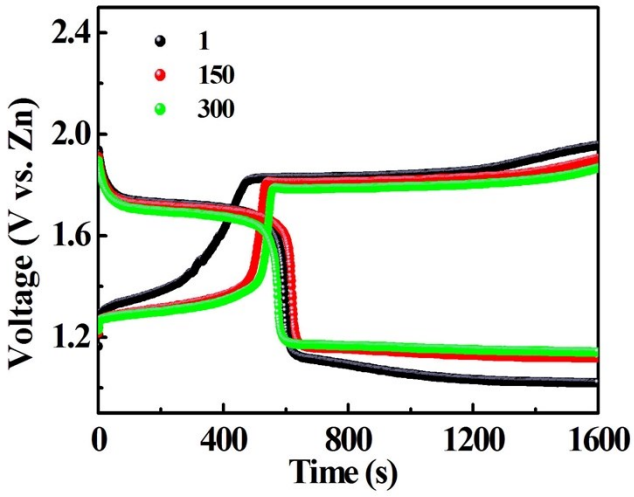

Fig. S10 Recycled charge-discharge property of **Ni-ZnHB**.