

Supporting Information

NiFe LDH nanodots anchored on 3D macro/mesoporous carbon as ORR/OER bifunctional electrocatalyst for rechargeable Zn-air battery

Wang Wang, Yucheng Liu, Jun Li, Jin Luo, Lei Fu* and Shengli Chen*

Experimental Section

Synthesis: Typically, 3D MPC was prepared according to the previously reported literature.¹⁸

The series of 3D MPC (H1, H2, H3, H4) was synthesized under the same first-pyrolysis condition, while for the second pyrolysis, the pyrolysis time and temperature for H1, H2, H3, H4 is 0 hour, 2 hours at 900 °C, 3.5 hours at 950 °C, 6 hours at 1000 °C, respectively. nNiFe LDH/3D MPC was prepared by a precipitation method. Firstly, disperse 20 mg 3D MPC, 22 mg Fe (NO₃)₃·9H₂O (Sinopharm Chemical Reagent Co., Ltd.) and 48 mg Ni (NO₃)₂·6H₂O (Sinopharm Chemical Reagent Co., Ltd.) in 30 mL deionized water with vigorous stirring at room temperature (about 24 °C). Then 6 mL of 0.1 M KOH solution was added into the solution dropwise. After stirring for 30 minutes, the solution was centrifuged at 10000 rpm and washed with deionized water and ethanol for 3 times. After drying for about 6 hours, the nNiFe LDH/3D MPC was obtained. bNiFe LDH+3D MPC was obtained through a two-step procedure. bNiFe LDH was first synthesized without adding 3D MPC. bNiFe LDH was further mixed and grinded thoroughly with 3D MPC at the same ratio with nNiFe LDH/3D MPC to obtain bNiFe LDH+3D MPC.

Characterization: The structure and morphology of the catalysts were characterized by Scanning Electron Microscope (HITACHI S-4800), Transmission Electron Microscope (TEM, JEM-2100F), Raman spectroscopy (Renishaw inVia, Renishaw, 532 nm excitation wavelength), and X-ray photoelectron spectroscopy (Kratos Ltd. XSAM-800). The N₂ adsorption isotherms were investigated by an ASAP2020 Surface Area and Porosity Analyzer

(Micromeritics, USA). XRD measurements were conducted on Rigaku Miniflex600 between 5° to 80° at a step of 6°/min. Thermogravimetric analysis (TGA) was conducted under O₂ atmosphere at a heating rate of 5 °C/min by a TGA Q500 (TA instrument , USA). The composition was analyzed through Atomic Absorption Spectrometer (ContrAA700, Germany).

Electrochemical Measurements: All electrochemical measurements were performed using a CHI 600 electrochemical workstation in a standard three-electrode cell with a graphite rod as the counter electrode, Hg/HgO electrode as the reference electrode for measurements in 0.1 M KOH, and a glassy carbon (GC) rotating-disk-electrode (RDE) electrode (5 mm in diameter) loaded with catalyst sample as the working electrode for ORR test (5 mm Au electrode for OER). To prepare the working electrode, 5 mg sample catalyst was dispersed in 1 mL Nafion/isopropyl alcohol solution (0.1%) to form the catalyst ink by sonicating for 30 min; 20 μL of the ink was then pipetted onto RDE electrode. The potentials were reported with respect to the reversible hydrogen electrode (RHE). To calibrate the equilibrium potential of the Hg/HgO electrode to RHE scale, the steady-state polarization curves of the hydrogen electrode reactions on Pt/C-loaded GC electrode in 0.1 M KOH saturated with H₂ was measured; the RHE zero potential was estimated with the potential at which the current crossed zero. RDE curves were recorded by under 900 rpm at a scan rate of 5 mV/s for ORR and 1mV/s for OER in 0.1 M KOH. The CV curves were recorded at a scan rate of 100 mV/s.

Zn-air battery assembly and test: A home-made Zn-air battery was constructed. The air cathode was prepared by coating the catalyst on carbon paper with a loading of 2 mg cm⁻². A polished Zn plate (thickness : 1 mm, ≥ 99.9%, Sinopharm Chemical Reagent Co., Ltd.) was employed as an anode and the void between the two electrode was filled with 6 M KOH and 0.2 M Zn(AC)₂. The polarization curves were performed by linear sweep voltammetry (LSV)

(5 mV s⁻¹) at 25 °C with the electrochemical working station. The galvanostatic charge and discharge were carried out on a LAND testing system.

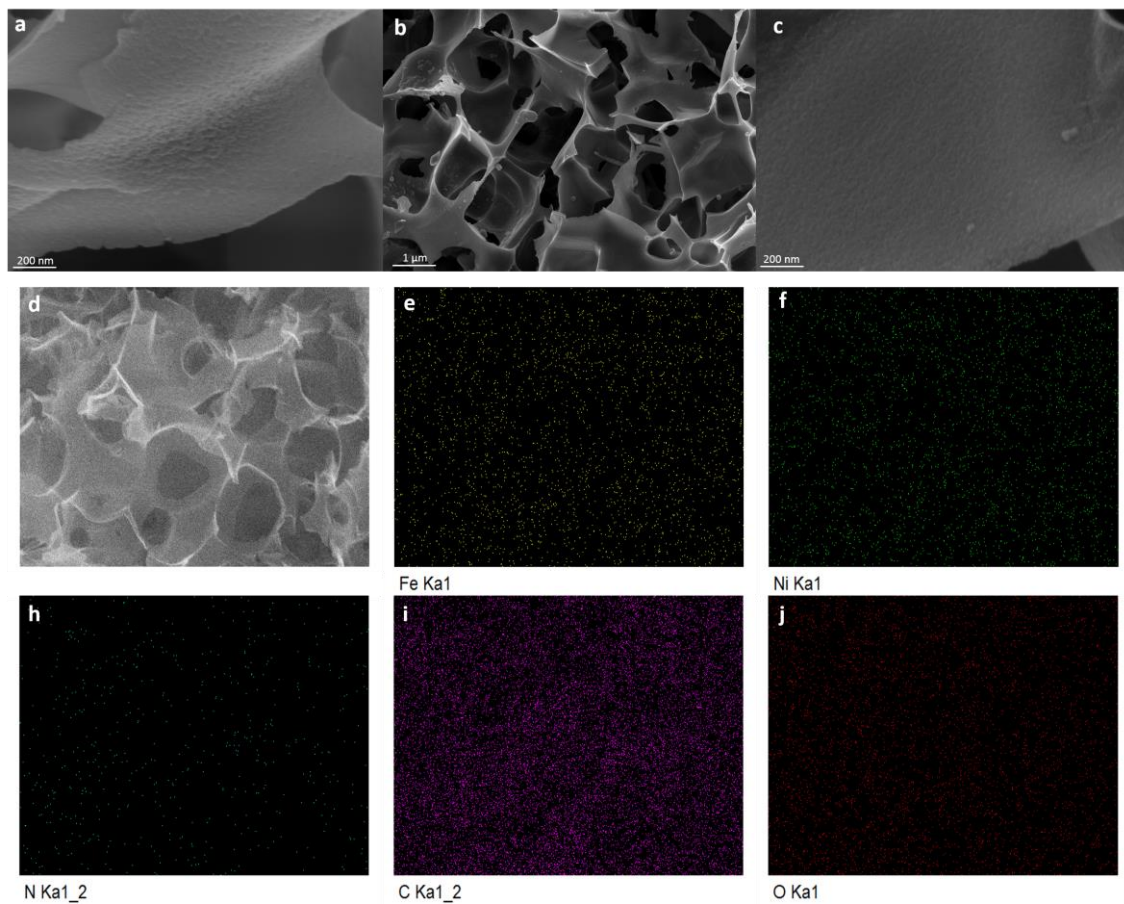


Figure S1. SEM images of 3D MPC (a), nNiFe LDH/3D MPC (b, c), elementary mapping of nNiFe LDH/3D MPC (d-j).

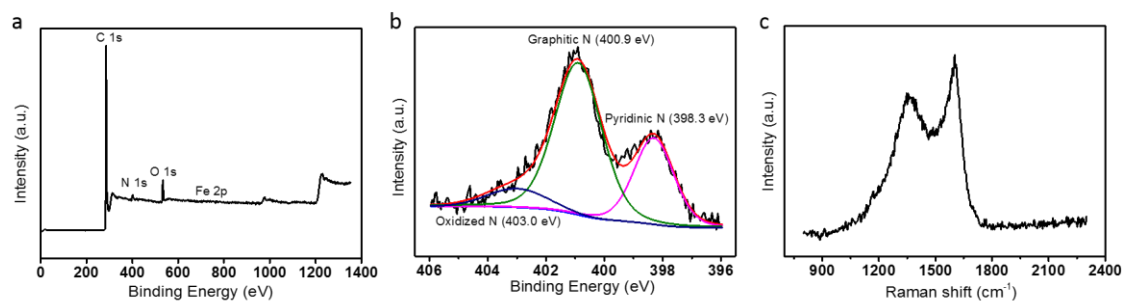


Figure S2. (a) XPS survey of 3D MPC. (b) High resolution of N 1s for 3D MPC. (c) Raman spectroscopy of 3D MPC.

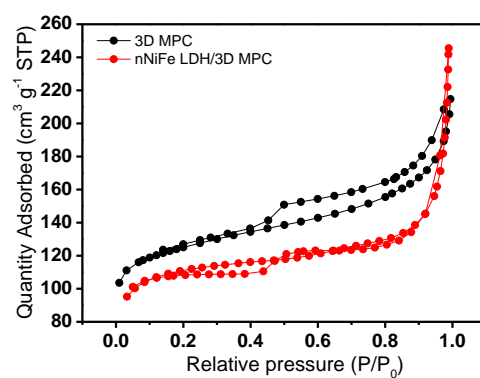


Figure S3. N₂ adsorption/desorption isotherm of 3D MPC and nNiFe LDH/3D MPC

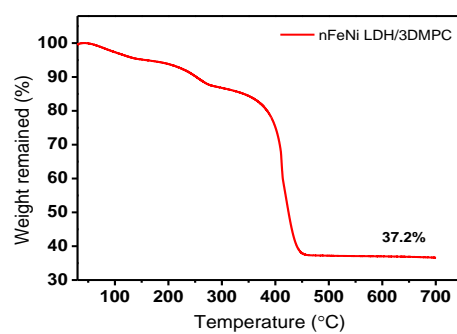


Figure S4. TGA measurement of nNiFe LDH/3D MPC conducted at air with a heating rate of 5 °C /min. It can be regarded that at 700 °C, only oxides were remained. The remaining mass of the oxides is 37.2% and it can be deduced that 47% of the mass is NiFe LDH.

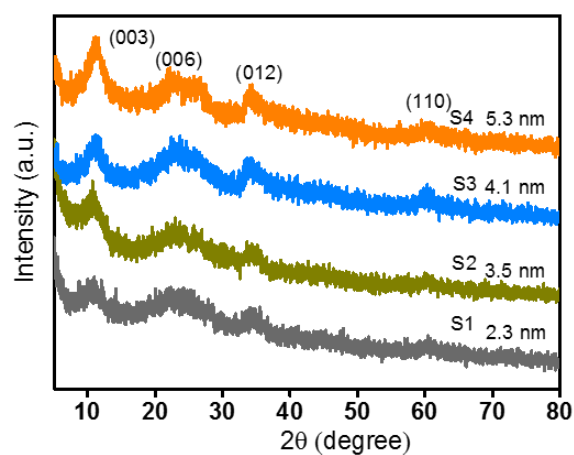


Figure S5. The XRD patterns of S1, S2, S3, S4. The average particle size was estimated through the Scherrer formula: $D = K\lambda/\beta\cos\theta$, $K=0.89$, λ is the wave length of the X-ray, $\lambda=0.15046$ nm, β is the peak width at half height, here peak of (003) is chosen.

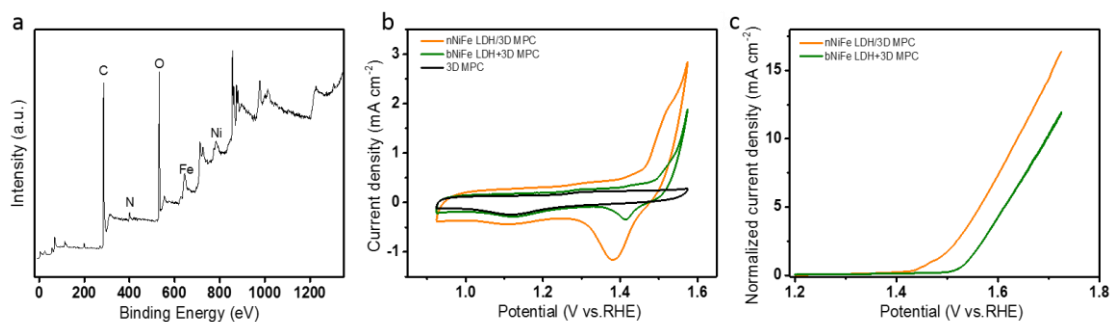


Figure S6. (a) XPS survey of nNiFe LDH/3D MPC. (b) CV curves of the catalysts at a scan rate of 100 mV s^{-1} . (c) Normalized polarization curves of the catalysts.

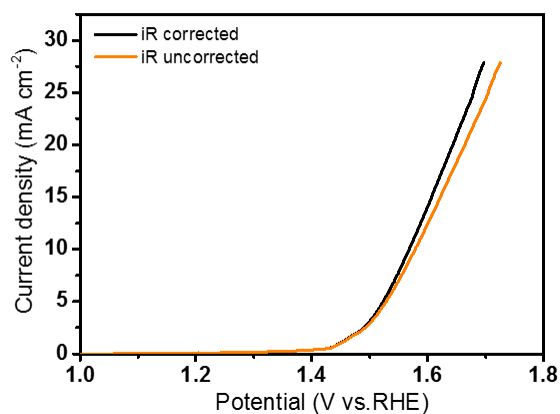


Figure S7. The iR drop corrected and uncorrected polarization curves of nNiFe LDH /3D MPC

Table S1 Comparison of the OER activity of the NiFe LDH powder catalysts

Electrocatalyst	Electrolyte	Overpotential at 10 mA cm ⁻²	Reference
NiFe-LDH/CNT	0.1 M KOH	~420 mV	<i>J. Am. Chem. Soc.</i> , 2013 , 135, 8452–8455
nNiFe LDH/NGF	0.1 M KOH	~337 mV (iR corrected)	<i>Adv. Mater.</i> 2015 , 27, 4516–4522
NiFe-LDH/Co,N-CNF	0.1 M KOH	312 mV (95 % iR corrected)	<i>Adv. Energy Mater.</i> 2017 , 1700467
Ni-Co LDH nano box	1 M KOH	420 mV	<i>Angew. Chem. Int. Ed.</i> 2017 , 56, 3897–3900
NiFe LDH	0.1 M KOH	399 mV	<i>Nano Energy</i> , 2017 , 39, 77–85
Ir/C	0.1 M KOH	410 mV	<i>Adv. Mater.</i> 2015 , 27, 4516–4522
IrO ₂ /C	0.1 M KOH	430 mV	<i>Chem. Commun.</i> , 2017 , 53, 11556–11559
RuO ₂ /C	0.1 M KOH	370 mV	<i>Adv. Mater.</i> 2018 , 30, 1704609
nNiFe LDH/3D MPC	0.1 M KOH	329 mV (iR corrected)	This work
nNiFe LDH/3D MPC	0.1 M KOH	340 mV	This work