# Supporting Information

# Bionic carbon framework activating oxygen lattice sites of NiFe<sub>2</sub>O<sub>4</sub> to

# enhance electrochemical water splitting

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#### **1. Experimental Section**

**Materials:** N-methylpyrrolidone (NMP, 99.9%), Metanilic acid (MA, 98%), p-Toluenesulfonic acid (PA, 99%) were from Shanghai Macklin Biochemical Co., Ltd. Potassium hydroxide (KOH, 90%), Urea(99%), Ammonia solution (NH<sub>3</sub>.H<sub>2</sub>O, 25.0%-28.0%), Diatomite(Pure De), Ethanol(C<sub>2</sub>H<sub>5</sub>OH, 95%), Nickel(II) chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O, 98%), Iron(III) chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O, 99%) were from Chengdu Kelong Chemical Co., Ltd.

All the reagents were used as received without any further purification and deionized water (18  $M\Omega$ ·cm resistivity) was used for preparing all aqueous solutions.

**1.1 Preparation of Poly@De:** The original Poly@De was prepared by putting 50 mmol of methacrylic acid (MA), 50 mmol of p-toluenesulfonic acid (PA), and 100 mg of diatomite into the inner liner of a 100 mL polytetrafluoroethylene reaction kettle. The pH was adjusted to 7 by using ammonia solution, and then a hydrothermal reaction was carried out at 120 °C for 3 hours. After cooling to room temperature, the mixture was centrifuged at a rotational speed of 6000 rpm for 3 minutes. Subsequently, it was washed three times with distilled water (DO) and ethanol (EO), and then dried at 120 °C for 6 hours to obtain Poly@De in a dry oven.

**1.2 Preparation of NiFe-LDH/Poly@De and NiFe<sub>2</sub>O<sub>4</sub>/SNC@De: In order to obtain NiFe-LDH/Poly, firstly, 162 mg of ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), 142 mg of nickel chloride hexahydrate(NiCl<sub>2</sub>·6H<sub>2</sub>O), and 100 mg of Poly@De were added to the inner liner of a 100 mL polytetrafluoroethylene reaction kettle. Then, 80 mL of N-methylpyrrolidone (NMP) was added, and the mixture was ultrasonicated at a rotational speed of 700 rpm for 10 minutes. After that, 150 mg of urea was added. The reaction was carried out in a rotating oven at 120 °C for 24 hours. After cooling to room temperature, it was dried at 120 °C for 6 hours. Subsequently, the temperature was raised to 900 °C at a heating rate of 5 °C min<sup>-1</sup> under a nitrogen atmosphere and maintained for 2 hours to obtain NiFe<sub>2</sub>O<sub>4</sub>/SNC@De.** 

**1.3 Preparation of NiFe<sub>2</sub>O<sub>4</sub>/SNC:** 100 mg of NiFe<sub>2</sub>O<sub>4</sub>/SNC@De was added to the inner liner of a 100 mL polytetrafluoroethylene reaction kettle, and then 70 mL of a 6 M potassium hydroxide solution (deionized water:ethanol=1:1) was added. Subsequently, a hydrothermal reaction was carried out at 160 °C for 24 hours to etch the diatomite. After cooling to room temperature, centrifugation and washing were performed using distilled water and ethanol. Finally, it was dried at 120 °C for 6 hours to obtain NiFe<sub>2</sub>O<sub>4</sub>/SNC.

**1.4 Preparation of RF@De:** 0.36 g of resorcinol and 100 mg of diatomite were added to 30 mL of ethanol. Then, it was ultrasonically stirred at a rotation speed of 600 rpm for 2 to 3 minutes. Subsequently, 30 mL of deionized water and 1 mL of aqueous ammonia monohydrate were slowly

added to this solution respectively, and the mixture was stirred for 30 minutes. Then, 0.39 mL of formaldehyde was added, and the reaction was carried out at room temperature for 8 to 12 hours. After that, centrifugal washing was performed, and drying was carried out to obtain RF@De.

**1.5** Preparation of NiFe-LDH/RF@De and NiFe<sub>2</sub>O<sub>4</sub>/C@De: Add 162 mg of FeCl<sub>3</sub>·6H<sub>2</sub>O and 142 mg of NiCl<sub>2</sub>·6H<sub>2</sub>O into the inner lining of a 100 mL polytetrafluoroethylene reaction kettle, and then add 100 mg of RF@De into it. Next, add 80 mL of N-methylpyrrolidone (NMP), and ultrasonically treat the mixture at a rotation speed of 700 rpm for 10 minutes. Then, add 150 mg of urea. Conduct a hydrothermal reaction in a rotating oven at 120 °C for 24 hours. After cooling to room temperature, dry it in a drying oven at 120 °C for 6 hours. Subsequently, raise the temperature to 900 °C at a heating rate of 5°C/min under a nitrogen atmosphere and maintain it for 2 hours to obtain NiFe<sub>2</sub>O<sub>4</sub>/C@De.

**1.6 Preparation of NiFe<sub>2</sub>O<sub>4</sub>/C:** Weigh 100 mg of NiFe<sub>2</sub>O<sub>4</sub>/C@De, and then add 70 mL of 6 M potassium hydroxide solution (deionized water: ethanol = 1:1). Subsequently, conduct a hydrothermal reaction at 160 °C for 24 hours. After cooling to room temperature, perform centrifugation and washing using deionized water and ethanol. Finally, dry it at 120 °C for 6 hours to obtain NiFe<sub>2</sub>O<sub>4</sub>/C.

**1.7 Preparation of PDA@De:** Disperse 100 mg of diatomite in a mixed solution of 20 mL of water and 20 mL of ethanol. Then, add 300 mg of DA powder and stir for 30 minutes. Next, add 1 mL of ammonia water and stir at room temperature, and let the reaction proceed for 24 hours. Then, carry out centrifugal washing and drying to obtain PDA@De.

**1.8 Preparation of NiFe-LDH/PDA@De and NiFe<sub>2</sub>O<sub>4</sub>/NC@De:** 162 mg of FeCl<sub>3</sub>·6H<sub>2</sub>O, 142 mg of NiCl<sub>2</sub>·6H<sub>2</sub>O and 100 mg of PDA@De were added into a 100 mL polytetrafluoroethylene reaction kettle. NiFe-LDH/PDA@De was obtained by using the above-mentioned method. Subsequently, raise the temperature to 900°C at a heating rate of 5°C/min under a nitrogen atmosphere and maintain this temperature for 2 hours to obtain NiFe<sub>2</sub>O<sub>4</sub>/NC@De.

**1.9 Preparation of NiFe<sub>2</sub>O<sub>4</sub>/NC:** Add 100 mg of NiFe<sub>2</sub>O<sub>4</sub>/NC@De into a 100 mL polytetrafluoroethylene reaction kettle, and then add 70 mL of 6 M potassium hydroxide solution (deionized water: ethanol = 1:1). Subsequently, let the reaction proceed at 160 °C for 24 hours. After cooling to room temperature, carry out centrifugation and washing with deionized water and ethanol. Finally, dry it at 120 °C for 6 hours.

### 2. Materials characterizations

Further fine structure characterization could be obtained by using a Transmission Electron Microscope (Talos F200S, Thermo Fisher). The surface morphology was performed on FEI Nova 400 field emission scanning electron microscope. Fourier Transform Infrared Spectroscopy (FTIR, Thermo Fisher Nicolet iS5) was used to analyze the chemical bonds in the material. The surface chemical state of the material was collected by X-ray Photoelectron Spectroscopy (Thermo Scientific ESCALAB Xi+). The crystal structure of the sample was determined by X-ray Diffraction (Rigaku Ultima IV, Rigaku Corporation, Japan). The specific surface area and pore structure parameters were examined by the Brunauer-Emmett-Teller method (Quantachrome 4000 and Micromeritics 3020). The types and contents of elements whereas measured by Energy Dispersive X-ray Spectroscopy (EDS, FEI Nova 400 field emission scanning electron microscope).

#### 3. Electrochemical characterization

All electrochemical measurements were carried out at room temperature using a CHI 660E electrochemical workstation in a 1M potassium hydroxide (KOH) solution with a three-electrode system. A piece of nickel foam loaded with catalysts, with an area of 1 cm<sup>2</sup>, was used as the working electrode, while a platinum mesh and a mercury oxide/mercury electrode were used as the counter electrode and the reference electrode, respectively. All potentials can be converted to the reversible hydrogen electrode (RHE) scale, which is expressed by the formula:

#### $E(RHE) = E(Hg/HgO) + 0.059 \times pH + 0.098$

Before conducting the measurement, the working electrode was activated at a constant current density of 20 mA cm<sup>-2</sup> for 10 minutes. Linear sweep voltammetry (LSV) test was performed at a scan rate of 5 mV s<sup>-1</sup> without ohmic drop (iR) compensation. At a potential of 1.6 V relative to the reversible hydrogen electrode (RHE), the functional relationship between the current density and the pH value was obtained. The Tafel slope was derived by plotting the relationship between the overpotential and the logarithm of the low current density. Within the potential range of 1.125-1.145 V relative to the reversible hydrogen electrode, the electrochemical active surface area (ECSA) was measured by using cyclic voltammetry curves (CV) at different scan rates (from 0.01 to 0.1 V s<sup>-1</sup>). Electrochemical impedance spectroscopy (EIS) test was conducted within the frequency range of 0.01 to 10<sup>6</sup> Hz, and the opening voltage is 0.266 V, 0.240 V and 0.100 V for NiFe<sub>2</sub>O<sub>4</sub>/C, NiFe<sub>2</sub>O<sub>4</sub>/NC and NiFe<sub>2</sub>O<sub>4</sub>/SNC, respectively.

In addition, linear sweep voltammetry (LSV) tests were respectively carried out in 1.0 mol L<sup>-1</sup> potassium hydroxide and tetramethylammonium hydroxide (TMAOH) solutions. A constant voltage test was conducted at a potential of 1.6 V relative to the reversible hydrogen electrode for 2 hours in both 1 mol L<sup>-1</sup> potassium hydroxide and tetramethylammonium hydroxide solutions. Apart from that, We controlled the pH values of the potassium hydroxide electrolyte at 12, 12.5, 13, 13.5 and 14 respectively, and conducted electrochemical tests to further explore the lattice oxygen mechanism. The capacitive current ( $\Delta J$ ) was obtained at different scan rates. The capacitive current ( $\Delta J$ ) of the catalyst can be expressed by the following equation :

$$\Delta J = J_a - J_c$$

where  $\triangle J$  represents the capacitive current,  $J_a$  is the anodic current, and  $J_c$  is the cathodic current.

4. Supplementary Figures and Tables



Fig. S1 SEM of Poly@De (a), RF@De (b) and PDA@De (c).



Fig. S2 SEM of NiFe LDH/Poly@De (a), NiFe LDH/RF@De (b) and NiFe LDH/PDA@De (c).



Fig. S3 SEM of NiFe<sub>2</sub>O<sub>4</sub>/C (a), NiFe<sub>2</sub>O<sub>4</sub>/NC (b) and NiFe<sub>2</sub>O<sub>4</sub>/SNC (c).



Fig. S4 Brunauer-Emmett-Teller of NiFeO<sub>x</sub>/SNC.



Fig. S5 FTIR of NiFe<sub>2</sub>O<sub>4</sub>/SNC.



Fig. S6 EIS plots and the equivalent circuit diagram of the NiFe<sub>2</sub>O<sub>4</sub>/SNC, NiFe<sub>2</sub>O<sub>4</sub>/NC and NiFe<sub>2</sub>O<sub>4</sub>/C electrodes.



Fig. S7 ECSA of NiFe2O4/SNC, NiFe2O4/NC, NiFe2O4/C and RuO2



Fig. S8 OER stability of NiFe<sub>2</sub>O<sub>4</sub>/SNC. Electrolyte was refreshed at the time of black arrow.



Fig. S9 pH independence of  $NiFe_2O_4/NC$  and  $NiFe_2O_4/C$ .

Electrode	Overpotential	Tafel slope	Ref.
	(mV)	(mV dec <sup>-1</sup> )	
NiFe <sub>2</sub> O <sub>4</sub> /SNC	242	91.42	This work
Ni/NiFeO	284	84.93	1
NiFeIr-LDH	246	46.70	2
LCO-NiFe-C <sub>3</sub> N <sub>4</sub>	251.4	60.8	3
NiFe@LDH	260	76	4
NiFe/NiO	245	27.6	5
Ni <sub>0.5</sub> Fe <sub>0.5</sub> -THQ	272	47.9	6
NiFe-LDH/Ti <sub>3</sub> C <sub>2</sub>	334	55	7
NiFeCe-LDH/Fe-ZIF8@Nd-ZIF67	300	150	8
NiFe/WC@NC	290	57	9
P-NiFe <sub>2</sub> O <sub>4</sub>	231	49	10
NiFe <sub>2</sub> O <sub>4</sub> -NTs	331	51.8	11
NiFe <sub>2</sub> O <sub>4</sub> /KB	258	43.01	12
NiFe <sub>2</sub> O <sub>4</sub> /Ti3C2	266	73.6	13
NiO- NiFe <sub>2</sub> O <sub>4</sub> /rGO	296	43	14
AT NiFe2O4 QDs	262	37	15

Table S1 OER performance of NiFe<sub>2</sub>O<sub>4</sub>/SNC, comparing with other OER catalysts in 1.0 M KOH at 10 mA cm<sup>-2</sup>.

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