Supporting Information

2D Fe-doped NiO nanosheets with Grain Boundary Defect for Advanced Oxygen Evolution Reaction

Yin Dong[a], *Juntao Yang*[a], *Yujie Liu*[a], *Yao Wang*[a], *Zhun Dong*[a], *Meilin Cui*[a], *Mingxuan Li*[a], *Xiaolin Yuan*[a], *Xin Zhang*[a]*, *Xiaoping Dai*[a]

[a]*State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering, China University of Petroleum, Beijing 102249, China.*

E-mail: zhangxin@cup.edu.cn. (X. Zhang).

1. Experimental Section

1.1. Reagents and Chemicals

Nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), iron nitrate nonahydrate ($Fe(NO_3)_3$ $9H_2O$), anhydrous sodium acetate ($NaCH_3COO$) and polyethylene glycol 200 (PEG200) are analysis reagent (A.R.) and purchased from Sinopharm Chemical Reagent Co. Ltd. Ethanol is A.R. and purchased from Beijing Chemical Reagent Company. All reagents were used as received without further purification.

1.2. Synthesis of the Fe-containing NiO

In a typical synthesis process, 1 mmol $Ni(NO_3)_2{\cdot}6H_2O$ (0.291 g), 0.1 mmol $Fe(NO_3)_2{\cdot}9H_2O$ (0.040 g) and 4 mmol (0.328 g) anhydrous sodium acetate ($NaCH_3COO$) were dissolved in 35 ml polyethylene glycol 200 (PEG-200) to form a clear solution. After being stirred vigorously for 1 h, the mixture was put into a 50 ml Teflon-lined stainless steel autoclave. The autoclave was treated at 200 °C and maintained for 16 h before cooled in air. The resulting precipitates were filtered and washed thoroughly with deionized water (DI) and ethanol three times and then dried in air at 80 °C for 12 h. The precursor was calcined at 350 °C in air for 2 h with a slow heating rate of 2 °C min^{-1} to obtain Fe-containing NiO.

For varied Fe containing content, the amount of $Fe(NO_3)_2{\cdot}9H_2O$ was added from 0, 0.05, 0.2 and 0.5 mmoL while keeping other parameters constant. The product was noted as $NiFe_xO$ (x: the Fe molar ratio).

1.3. Characterizations

Electrode preparation and electrochemical tests

All of the electrochemical experiments were performed on the CHI 760E electrochemistry workstation at room temperature. A conventional three-electrode system was used, including a mercuric oxide electrode (SME) as the reference electrode, a carbon rod as the counter electrode and a glassy carbon (GC) electrode (3 mm in diameter) as the working electrode. All potentials measured were converted to the potential versus reversible hydrogen electrode (RHE) according to the following equations: ERHE = $E_{SME} + E^{\theta}_{SME} + 0.059 * pH$. Before the experiments, the GC electrode was polished by Al_2O_3 powder and washed with deionized water. The working electrode was made using the following method: typically, 2 mg of catalyst was suspended in a mixture of 200 μL of ethanol and 800 μL of deionized water with 10 μL of Nafion (5 wt %) solution to form a homogeneous catalyst ink by sonication for 40 min. Subsequently, 5 μL of catalyst ink was dropped onto the surface of electrode by a micropipette followed by drying at room temperature. The loading amount of the catalyst is about 0.14 mg cm^{-2}. All electrochemical tests, including cyclic voltammograms (CVs), linear sweep voltammograms (LSVs), chronoamperometry were performed in an O_2-saturated 1.0 M KOH aqueous solution at room temperature, corrected by 80% IR-compensation. The CV tests were conducted from 0 to 0.6 V (vs. Hg/HgO) at a sweep rate of 50 mV·s^{-1} . The CVs were obtained after 20 cycles. LSVs were obtained by sweeping the potential from 0 to 0.7 V (vs. Hg/HgO) at a scan rate of 50 mV·s^{-1}. The stability tests were then performed by CVs scanning from 0 to 0.6 V (vs. Hg/HgO) for 2000 cycles at a scan rate of 50 mV·s^{-1}. The long-term durability of 2D $NiFe_{0.1}O$ nanosheets was also investigated through chronoamperometry in 1.0 M KOH. EIS measurements were conducted from 100 kHz to 0.01 Hz. The electrochemically active surface area (ECSA) was calculated based on the capacitance of the double layer (C_{dl}) measurements. A series of CVs was performed in non-Faradaic region at scan rates of 20-100 mV·s^{-1}. C_{dl} was estimated by plotting the $\Delta J = (Ja - Jc)/2$ against the scan rate, and then the slope of the curve is twice C_{dl}.

Characterization

High-resolution transmission electron microscope (HRTEM) was observed on a Tecnai G2 F20 S-Twin at 200 kV. The scanning electron microscope (SEM) images were determined by an ULTRA 55 SEM at 20 kV. Power X-ray diffraction (XRD) was performed on a Brüker D8 Advance diffractometer at 40 kV and 40 mA for Cu Kα (λ= 0.15406). X-ray photoelectron spectrum (XPS) was measured on a PHI 5000 Versaprobe system using monochromatic Al Kα radiation (1486.6 eV), and all binding energies were calibrated by the C1s peak at 284.6 eV. Raman spectra were performed on a M-9836-3991-04-A inVia Raman spectrometer produced by Renishaw (UK) Ltd. with a 532 nm semiconductor laser as excitation source and the laser power of 0.15 mW.

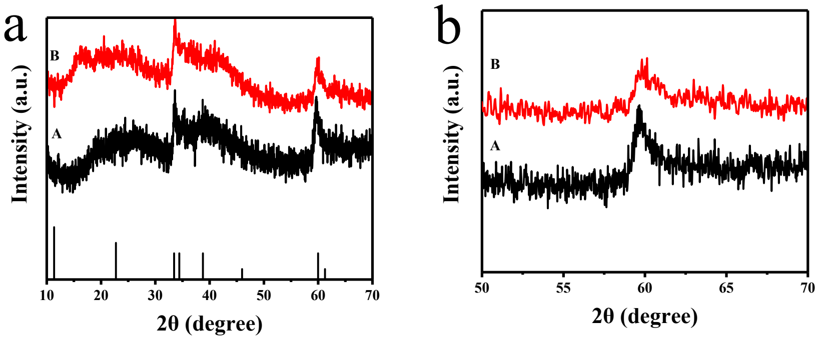

Figure S1 (a) The XRD patterns of the undoped precursor (A) and the Fe-doped precursor (B). (b) The magnified (110) peaks the undoped precursor (A) and the Fe-doped precursor (B).

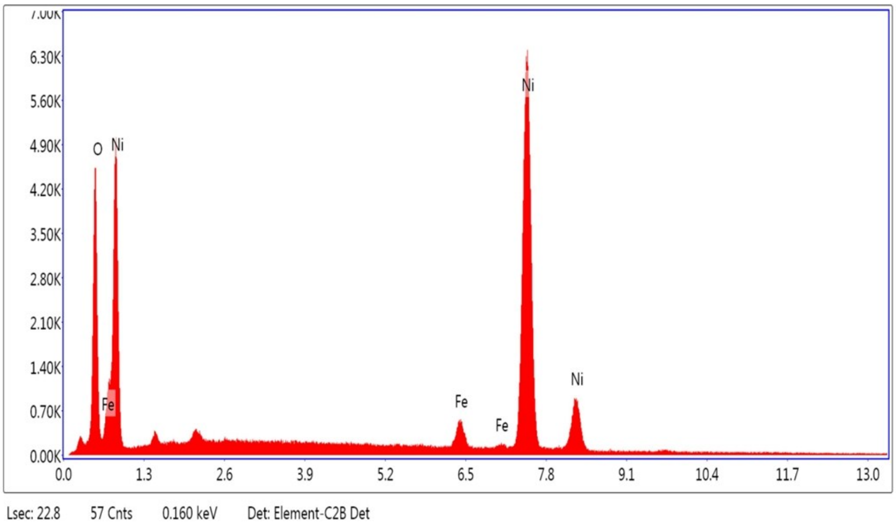

Figure S2 The EDX of $NiFe_{0.1}O$ nanosheet.

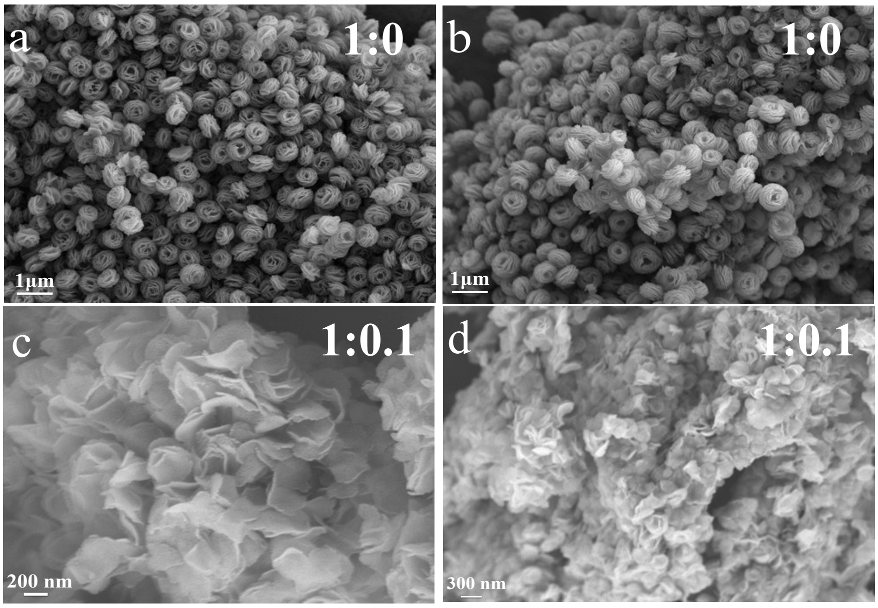

Figure S3 (a,c) SEM images of precursor, (b,d) SEM images of Fe-doped NiO.

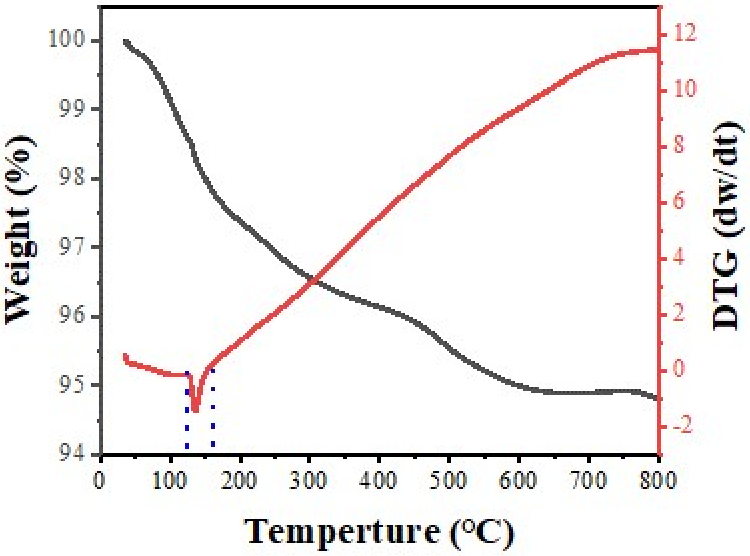

Figure S4 TG and DTG curves of as-prepared $NiFe_{0.1}O$ catalysts.

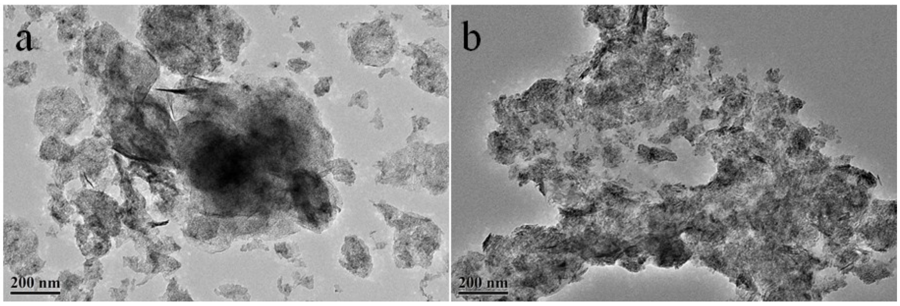

Figure S5 (a) SEM image of $NiFe_{0.1}O$ before OER test, (b) SEM image of $NiFe_{0.1}O$ after OER test.

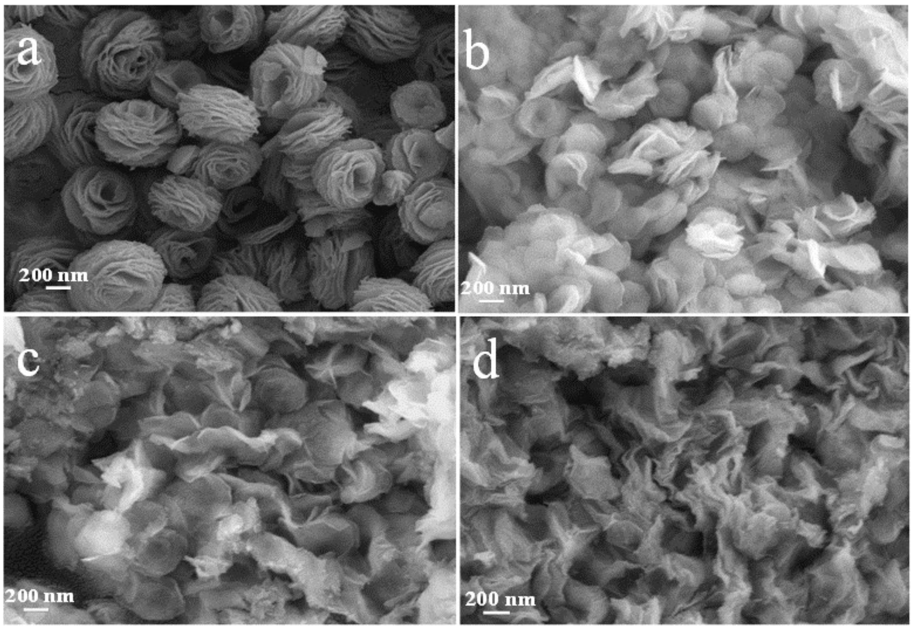

Figure S6 SEM images of of different Fe-doped NiO. (a) Ni/Fe=1/0, (b) Ni/Fe=1/0.05, (c) Ni/Fe=1/0.2, (d) Ni/Fe=1/0.5.

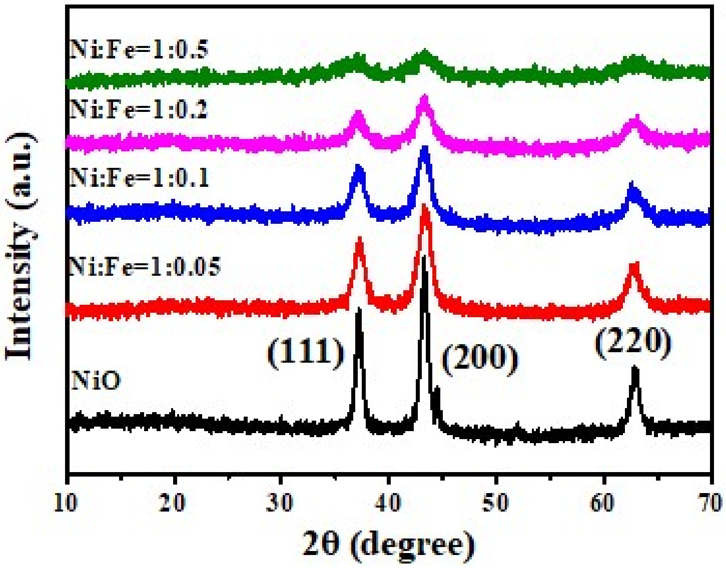

Figure S7 The XRD patterns of different Fe-doped NiO with different Fe content.

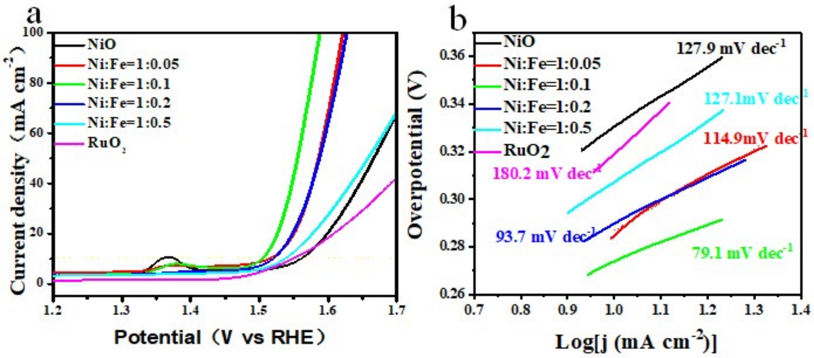

Figure S8 (a) OER polarization curves (b) Tafel slopes of Fe-doped NiO with different Ni/Fe molar ratios.

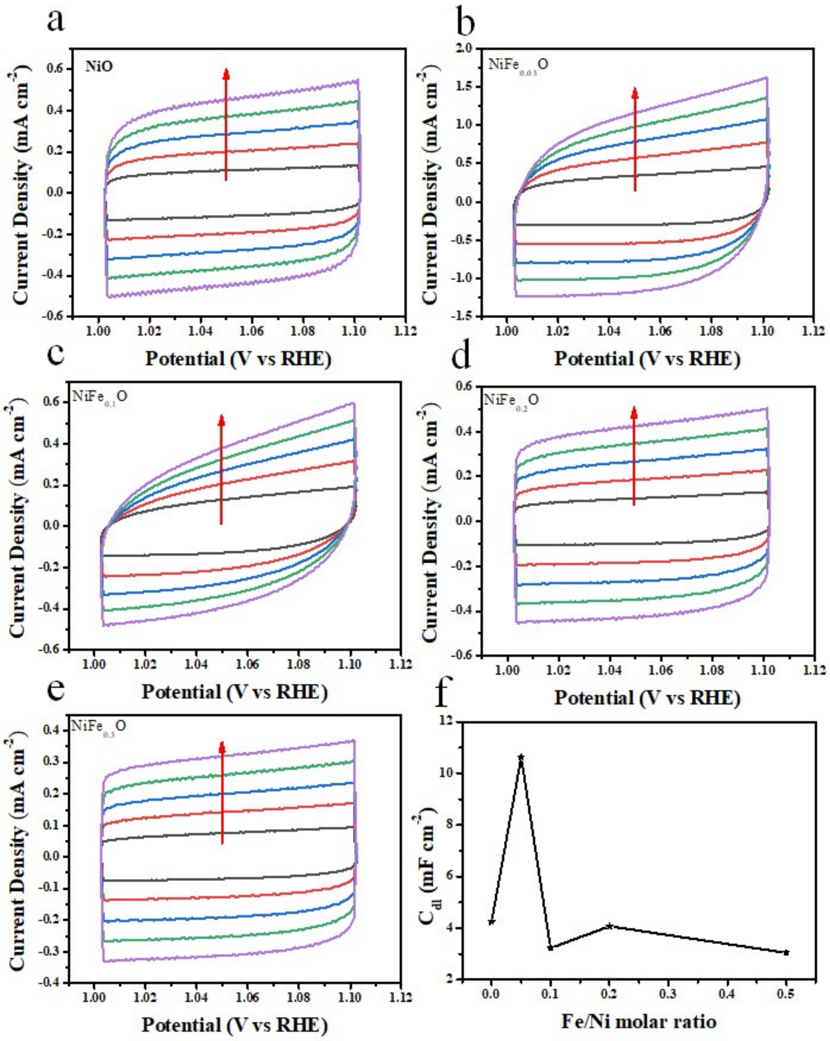

Figure S9 Cyclic voltammograms of the NiO (a) and Fe-containing NiO with different Fe content (b-e) at various scan rates of 20, 40, 60, 80 and 100 mV s^{-1}. (f) C$_{dl}$ of the NiO and Fe-containing NiO with different Fe content.

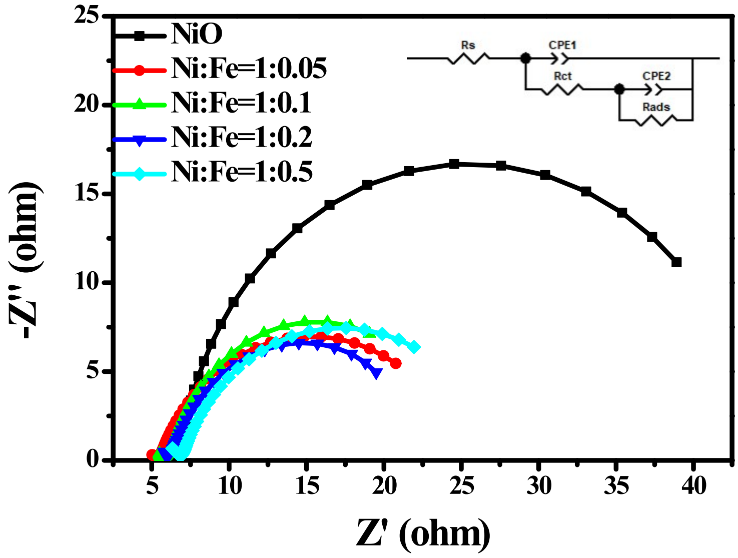

Figure S10 Nyquist plots of Fe-containing NiO with different Fe content. Z′ is realimpedance and Z″ is imaginary impedance.

Table S1 The element mapping results of $NiFe_{0.1}O$

Element	Ni	Fe	O
%	64	7	30

Table S2 The average grain size of different samples.

Samples	NiO	$NiFe_{0.05}O$	$NiFe_{0.1}O$	$NiFe_{0.2}O$	$NiFe_{0.5}O$
Grain size (nm)	125±35	66±17	59±22	55±25	34±26

Table S3 The ICP-OES results of different samples.

Samples	Molar Ratio (Ni:Fe)
NiO	49.07:0
$NiFe_{0.05}O$	49.07:2.15
$NiFe_{0.1}O$	44.98:4.30
$NiFe_{0.2}O$	40.89:8.60
$NiFe_{0.5}O$	34.76:17.19