Electronic Supplementary Information

Hierarchical Hetero-Ni_3Se_4@NiFe LDH Micro/nanosheets as Efficient Bifunctional Electrocatalysts with Superior Stability for Overall Water Splitting

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EXPERIMENTAL SECTION

Materials.

Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), urea (CON_2H_4), potassium hydroxide (KOH), ammonium fluoride (NH_4F), and hydrochloric acid (HCl) were all purchased from Sinopharm Chemical Reagent Corp. Selenium (Se) powder, sodium borohydride ($NaBH_4$), commercial Pt/C (20 wt %), and ruthenium oxide (RuO_2) were purchased from Sigma-Aldrich. Carbon fiber cloth (CFC) with a thickness of 1 mm (ROCKTEC, Ltd., Hubei, China) was served as the substrate. Deionized water was produced by a Milli-Q water purification system. All chemicals were used without further purification.

Synthesis of $Ni(OH)_2$ and Ni_3Se_4 microsized sheets.

In a typical synthesis of $Ni(OH)_2$ nanosheets, $NiCl_2 \cdot 6H_2O$ (1.5 mmol), NH_4F (2.5 mmol), and CON_2H_4 (5 mmol) were dispersed in 17 mL deionized water. The resulting solution was stirred for 5 min to form a homogeneous solution and then transferred into a 20 mL Teflon autoclave with the cleaned CFC (1 cm × 4 cm). The autoclave was heated at 180 °C for 6 h in an oven. After cooling, the CFC with the product was washed by deionized water several times and dried in a vacuum oven at 60 °C for 1 h.

For the fabrication of Ni_3Se_4 nanosheets, Se powder (100 mg) and $NaBH_4$ (96 mg) were dispersed in 17 mL deionized water in a Teflon autoclave. After ultrasonic dissolving for 5 min, a clear NaHSe solution was obtained. Subsequently, the as-obtained $Ni(OH)_2$ nanosheets were immersed in NaHSe solution and then placed in an oven at 180 °C for

4 h. After hydrothermal reaction, the resultant Ni_3Se_4 nanosheets on CFC were collected for further use.

Synthesis of NiFe LDH nanosheets on CFC

In a typical procedure of NiFe LDH on CFC, a piece of cleaned CFC (1 cm × 4 cm) was immersed in a 17.5 mL aqueous solution containing 0.25 mmol of $Fe(NO_3)_3 \cdot 9H_2O$, 0.75 mmol of $Ni(NO_3)_2 \cdot 6H_2O$, and 1.25 mmol of CON_2H_4 in a Teflon autoclave, which was hydrothermally treated at 120 °C for 10 h for the growth of NiFe LDH nanosheets on CFC.

Synthesis of hierarchical hetero-Ni_3Se_4@NiFe LDH micro/nanosheets.

Typically, the obtained Ni_3Se_4 micro-sized sheets on CFC was immersed in a 17.5 mL aqueous solution containing 0.25 mmol of $Fe(NO_3)_3 \cdot 9H_2O$, 0.75 mmol of $Ni(NO_3)_2 \cdot 6H_2O$, and 1.25 mmol of CON_2H_4 in a Teflon autoclave, which was hydrothermally treated at 120 °C for 10 h. After that, the autoclave was cooled naturally and the sample was washed by deionized water several times and dried in a vacuum oven at 60 °C for 6 h. Finally, the hierarchical hetero-Ni_3Se_4@NiFe LDH micro/nanosheets on CFC were formed.

Characterization.

Powder X-ray diffraction (XRD) data of all samples were performed via a Philips X'pert Pro X-ray diffractometer with Cu Kαradiation (λ= 0.15419 nm). The FESEM images of products were characterized by field emission scanning electron microscopy (FESEM, Sirion 200). Transmission electron microscopy (TEM), high-resolution TEM, energy-dispersive X-ray spectroscopy (EDS) elemental mapping images of final

products were recorded by transmission electron microscopy (FEI, Tecnai G2 F20). X-ray photoelectron spectroscopy (XPS) data were carried out with an ESCALABMK II X-ray photoelectron spectrometer equipped with Mg exciting source. The elements stoichiometry of products was further calculated from inductively coupled plasma mass spectrometry (ICP-MS). The Brunauer-Emmett-Teller (BET) surface areas of the samples were obtained with a N_2 porosimeter (TriStar II 3020, Micromeritics Instrument Corp.). All the Electrochemical measurements were conducted using a CHI 760e electrochemical workstation in a standard three-electrode cell.

Electrochemical Measurements.

The electrocatalytic measurements were performed with a traditional three-electrode cell configuration by using a CHI 760e electrochemical workstation in 1 M KOH at ambient temperature. The hierarchical hetero-Ni_3Se_4@NiFe LDH micro/nanosheets on CFC (typically 1 cm × 2 cm) were directly used as the working electrode (WE), graphite rod was employed as the counter electrode (CE), and a saturated Ag/AgCl electrode (RE) was employed as the reference electrode. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronopotentiometric measurements were conducted and linear sweep voltammetry (LSV) curves were carried out at a scan rate of 2 mV s^{-1}. The double layer capacitance (C_{dl}) performed in a narrow potential window without faradaic processes were used to evaluate the active surface areas of catalysts. Briefly, the C_{dl} can be calculated by the half slope of the linearly fitted curve of the capacitive current ($\Delta j = j_{anodic} - j_{cathodic}$) plotted against the scan rate. The ECSA can be calculated by C_{dl} with using the specific capacitance value

for a standard with 1 cm^2 of real surface area. The specific capacitance of a flat surface is normally between 0.02 and 0.06 mF cm^{-2}. In this work, CFC was served as the substrate and its capacitance value is similar with that of a flat surface. Therefore, CFC was considered as the standard substrate and the ECSA of catalysts can be calculated by this equation:

$$A_{ECSA} = \frac{C_{dl\ catalyst}\ (mF\ cm^{-2})}{C_{dl\ CFC}\ (mF\ cm^{-2})\ per\ ECSA\ cm^2}$$

Thus, the C_{dl} values are proportional to ECSA.

The EIS measurements were recorded at -0.55 V versus Ag/AgCl for the HER and 0.5 V versus Ag/AgCl for the OER, with a frequency range from 100 kHz to 0.1 Hz and a 10 mV AC dither. For overall water splitting, the hierarchical hetero-Ni_3Se_4@NiFe LDH micro/nanosheets were directly used as cathode and anode in a two electrode configuration in 1 M KOH at ambient temperature. All the potentials reported in this study for OER and HER were converted to the corresponding potentials versus the reversible hydrogen electrode (RHE). All potentials and voltages were IR corrected.

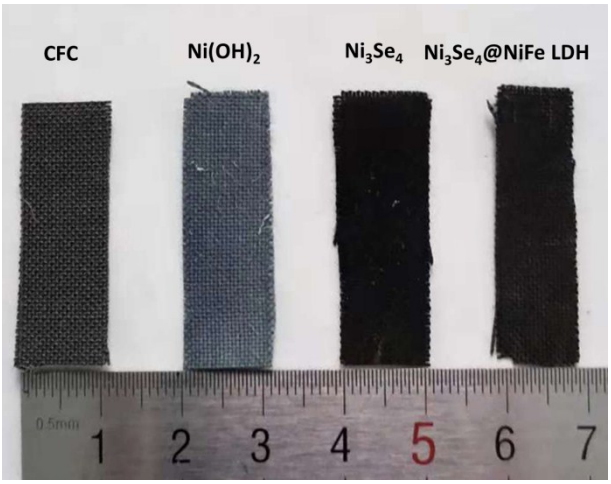


Figure S1. The digital photograph of the CFC, $Ni(OH)_2$, Ni_3Se_4, and hierarchical hetero-Ni_3Se_4@NiFe LDH micro/nanosheets, respectively.

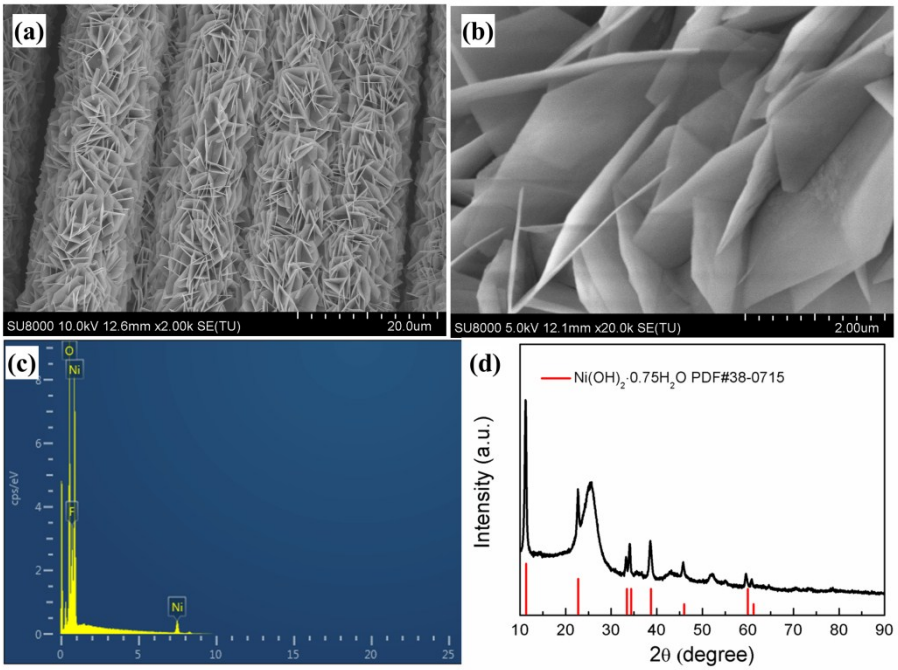


Figure S2. Low- and high-resolution FSEM images of the as-synthesized $Ni(OH)_2$ micro-sized sheets. (c and d) The corresponding EDS spectrum and XRD pattern.

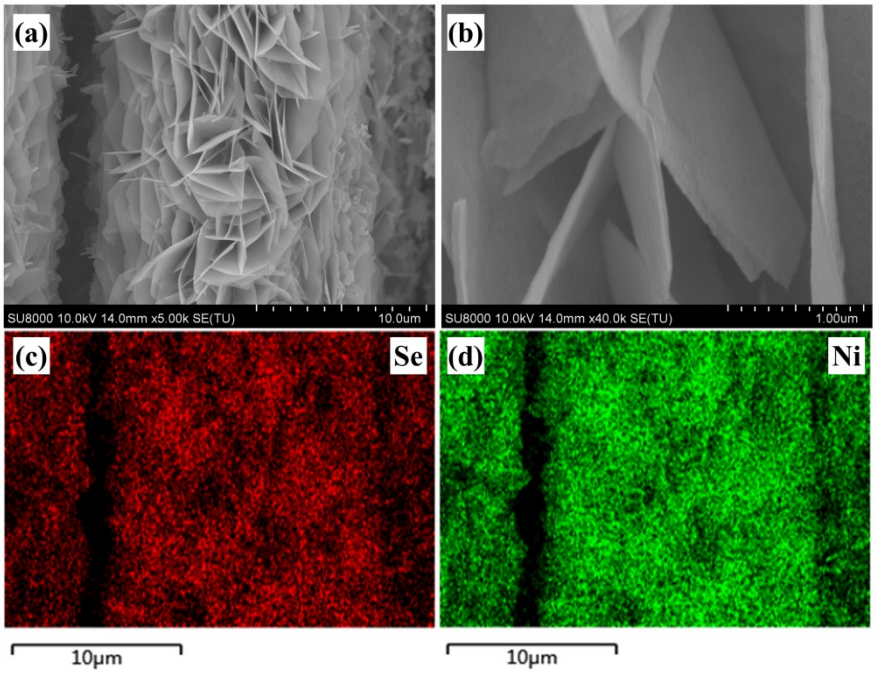


Figure S3. (a) Low- and (b) high-resolution FSEM images of the as-synthesized Ni_3Se_4 micro-sized sheets. (c and d) The corresponding EDS element mapping images of Se and Ni.

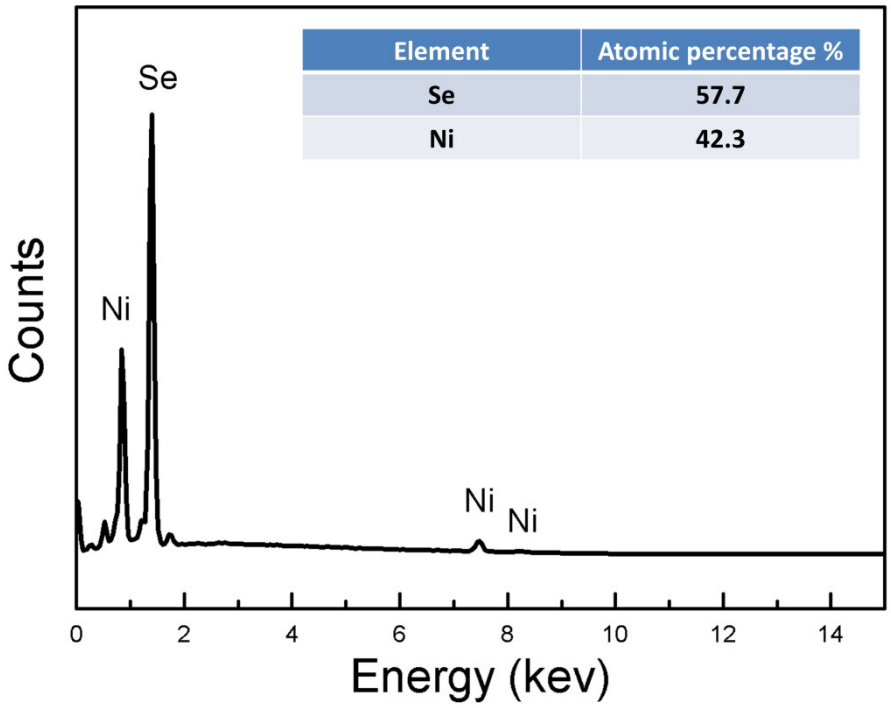
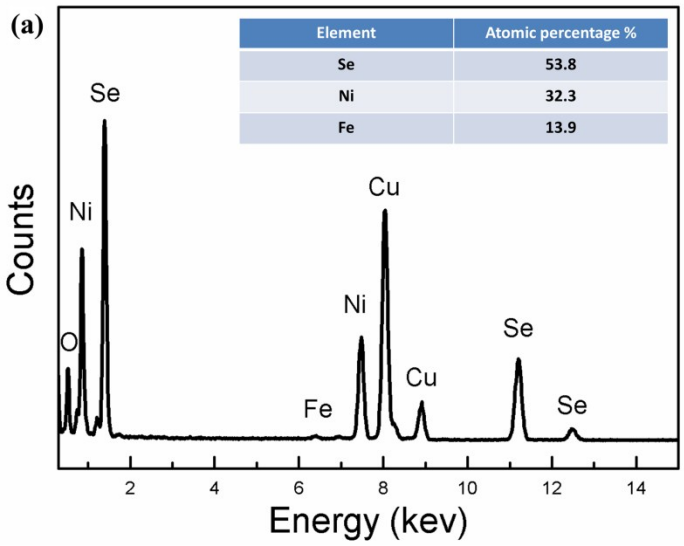


Figure S4. The corresponding EDS spectrum and atomic ratio of Se and Ni.

(a)



(b)

Element	Atomic percentage %
Se	53.7
Ni	32.5
Fe	13.8

Figure S5. The atomic ratio of Se, Ni, O, and Fe from EDS spectrum (a) and ICP-MS (b).

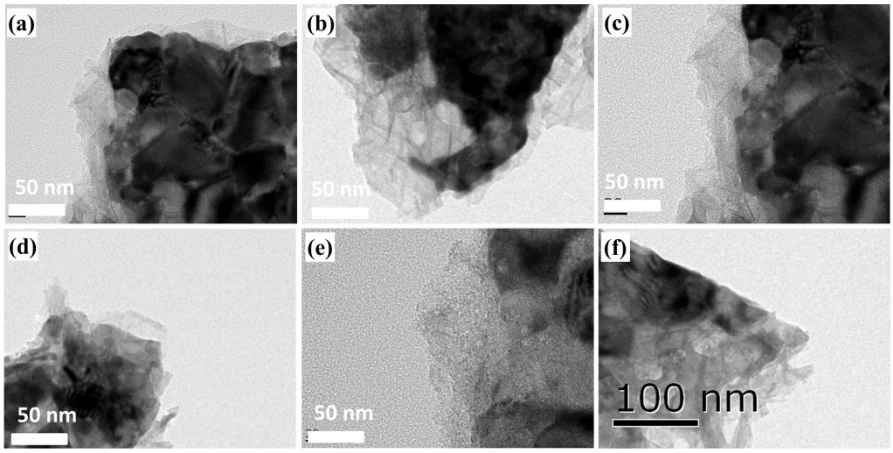


Figure S6.TEM images of the as-synthesized Ni_3Se_4/CFC micro/nanosheets.

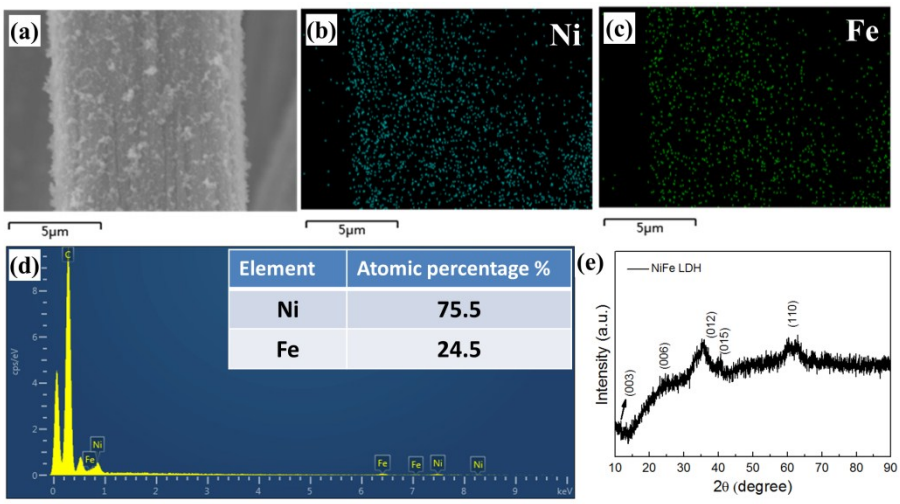


Figure S7. The FSEM image (a), EDS element mapping image (b,c), EDS pattern (d), and XRD spectrum (e) of NiFe LDH.

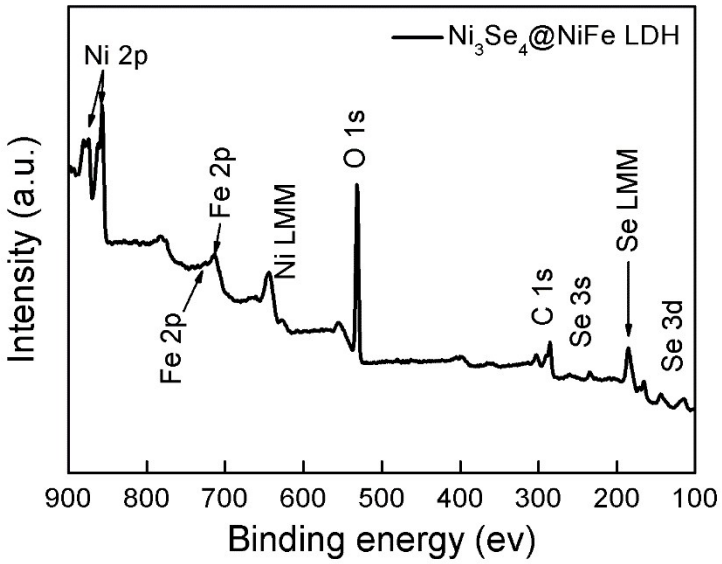


Figure S8. The survey XPS spectra of hierarchical hetero-Ni_3Se_4@NiFe LDH micro/nanosheets.

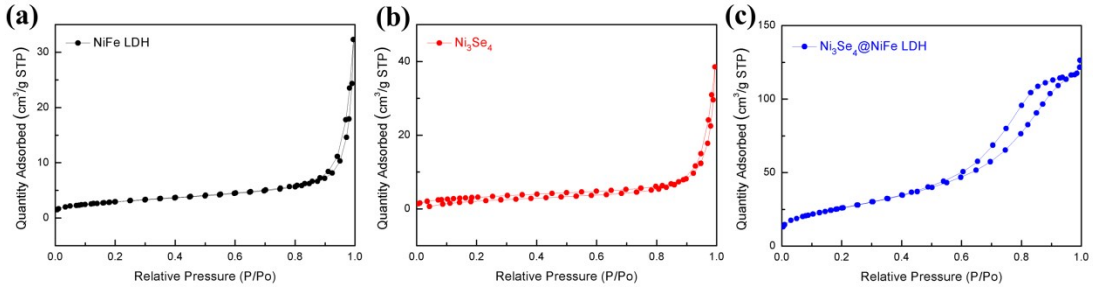


Figure S9. N_2 sorption isotherms of as-synthesized NiFe LDH, Ni_3Se_4, and hierarchical hetero-Ni_3Se_4@NiFe LDH micro/nanosheets. The BET surface areas of the NiFe LDH, Ni_3Se_4, and Ni_3Se_4@NiFe LDH are 10.7 m^2 g^{-1}, 11.5 m^2 g^{-1}, and 96.2 m^2 g^{-1}, respectively.

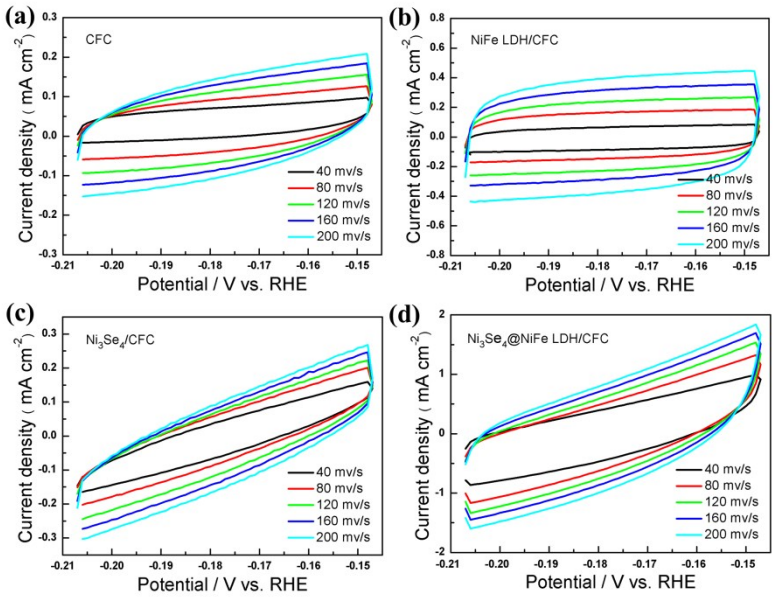


Figure S10. Cyclic voltammograms (CVs) for HER measured over (a) CFC, (b) NiFe LDH/CFC, (c) Ni_3Se_4/CFC, and hierarchical hetero-Ni_3Se_4@NiFe LDH/CFC modified electrodes in the double layer capacitance charging region at scan rates of 40, 80, 120, 160, and 200 mV/s in 1.0 M KOH solution.

Table S1. Comparison of the HER performance for hierarchical hetero-Ni_3Se_4@NiFe LDH/CFC catalyst with other reported electrocatalysts in 1 M alkaline electrolytes (KOH or NaOH). Here η-10 correspond to the overpotential at current densities of 10 mA cm^{-2} in the HER.

Catalyst	Support	η_{10} (mV)	Reference
Ni_3Se_4@NiFe LDH	CFC	85	This work
CoSe/NiFe LDH	Exfoliated grapheme foil	210	*Energy Environ. Sci.,* 2016, **9**, 478-483
NiFe LDH@NiCoP	Ni foam	120	Adv. Funct. Mater., 2018, 1706847
NiFe/$NiCo_2O_4$	Ni foam	105	Adv. Funct. Mater., 2016, 26, 3515
NiFe LDH@$NiCo_2S_4$	Ni foam	200	ACS Appl. Mater. Interfaces, 2017, 9, 15364
MoS_2-Ni_3S_2	Ni foam	98	ACS Catal., 2017, **7**, 2357-2366
MoS_2/Ni_3S_2	Ni foam	110	Angew. Chem. Int. Ed., 2016, **55**, 6702 - 6707
$NiCo_2O_4$@$CoMoO_4$	Ni foam	121	J. Mater. Chem. A, 2018, **6**, 16950-16958
Ni_3N-NiMoN	CFC	31	Nano Energy, 2018, **44**, 353-363

Table S2. Comparison of the OER performance for hierarchical hetero-Ni_3Se_4@NiFe LDH/CFC catalyst with other reported electrocatalysts in 1 M alkaline electrolytes. Here η_{10} and η_{100} correspond to the overpotentials at current densities of 10 and 100 mA cm^{-2} in the OER, respectively.

Catalyst	Support	η_{10} (mV)	Reference
Ni_3Se_4@NiFe LDH/CFC	CFC	223	This work
CoSe/NiFe LDH	Exfoliated grapheme foil	250	*Energy Environ. Sci.,* 2016, **9**, 478-483
NiFe LDH@NiCoP	Ni foam	220	*Adv. Funct. Mater.,* 2018, 1706847
NiFe/$NiCo_2O_4$	Ni foam	340	*Adv. Funct. Mater.,* 2016, **26**, 3515
NiFe LDH@$NiCo_2S_4$	Ni foam	201	*ACS Appl. Mater. Interfaces,* 2017, **9**, 15364
MoS_2-Ni_3S_2	Ni foam	249	*ACS Catal.,* 2017, **7**, 2357-2366
MoS_2/Ni_3S_2	Ni foam	218	*Angew. Chem. Int. Ed.,* 2016, **55**, 6702 -6707
$NiCo_2O_4$@$CoMoO_4$	Ni foam	265	*J. Mater. Chem. A*, 2018,**6**, 16950-16958
Ni_3N-NiMoN	CFC	277	*Nano Energy,* 2018, **44**, 353–363

Table S3. Comparison cell voltage of hierarchical hetero-Ni_3Se_4@NiFe LDH/CFC with other bifunctional electrocatalysts in 1 M alkaline electrolytes.

Catalyst	Support	Cell voltage at 10 m A cm^{-2}	Reference
Ni_3Se_4@NiFe LDH/CFC	CFC	1.54	This work
CoSe/NiFe LDH	Exfoliated grapheme foil	1.67	*Energy Environ. Sci.,* 2016, **9**, 478-483
NiFe LDH@NiCoP	Ni foam	1.57	*Adv. Funct. Mater.,* 2018, 1706847
NiFe/$NiCo_2O_4$	Ni foam	1.67	*Adv. Funct. Mater.,* 2016, **26**, 3515
NiFe LDH@$NiCo_2S_4$	Ni foam	1.6	*ACS Appl. Mater. Interfaces,* 2017, **9**, 15364
MoS_2-Ni_3S_2	Ni foam	1.5	*ACS Catal.,* 2017, **7**, 2357-2366
MoS_2/Ni_3S_2	Ni foam	1.56	*Angew. Chem. Int. Ed.,* 2016, **55**, 6702 -6707
$NiCo_2O_4$@$CoMoO_4$	Ni foam	1.55	*J. Mater. Chem. A,* 2018, **6**, 16950-16958
Ni_3N-NiMoN	CFC	1.54	*Nano Energy,* 2018, **44**, 353-363

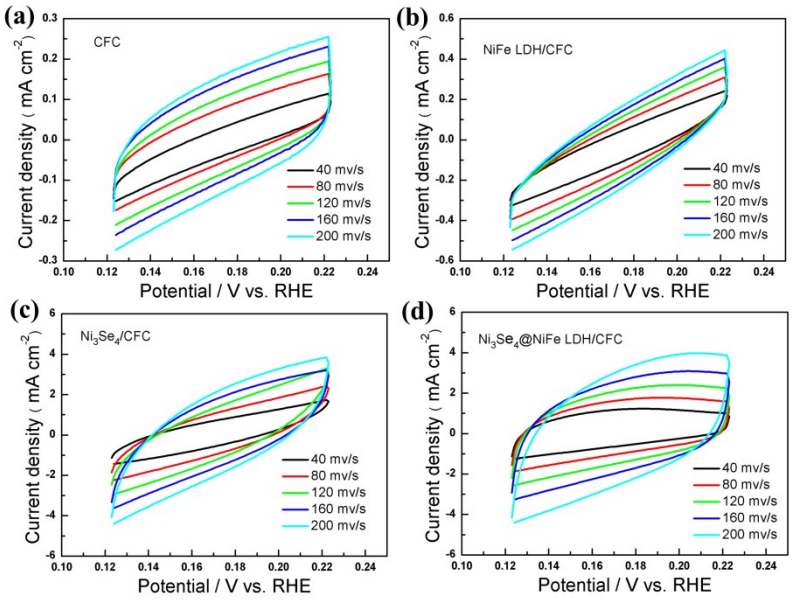


Figure S11. Cyclic voltammograms (CVs) for OER measured over (a) CFC, (b) NiFe LDH/CFC, (c) Ni_3Se_4/CFC, and hierarchical hetero-Ni_3Se_4@NiFe LDH/CFC modified electrodes in the double layer capacitance charging region at scan rates of 40, 80, 120, 160, and 200 mV/s in 1.0 M KOH solution.

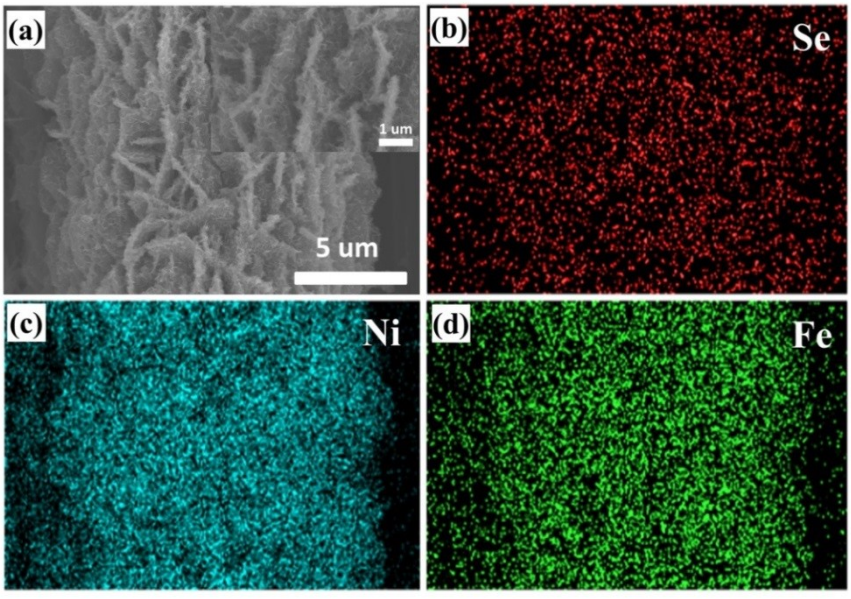


Figure S12. The FSEM image (a) and EDS element mapping image (b-d) of hierarchical hetero-Ni_3Se_4@NiFe LDH/CFC after OER stability test.

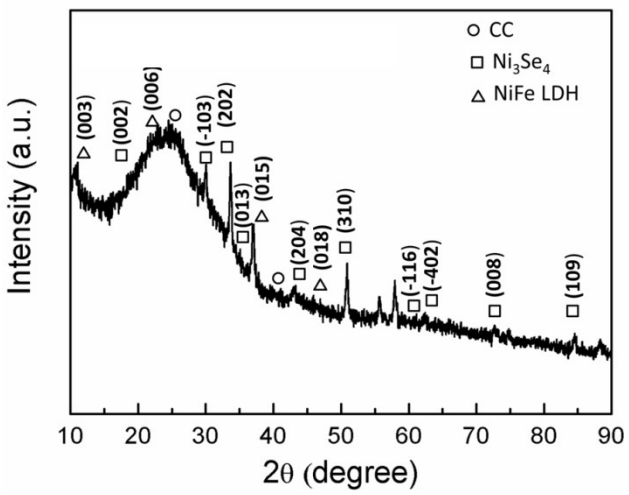


Figure S13. The XRD pattern of hierarchical hetero-Ni_3Se_4@NiFe LDH/CFC after OER stability test.

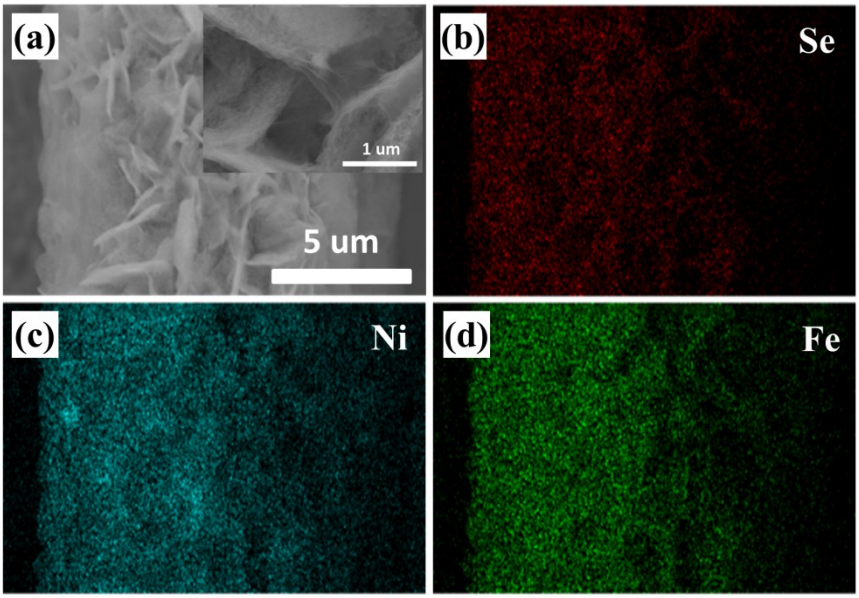


Figure S14. The FSEM image (a) and EDS element mapping image (b-d) of hierarchical hetero-Ni_3Se_4@NiFe LDH/CFC after HER stability test.

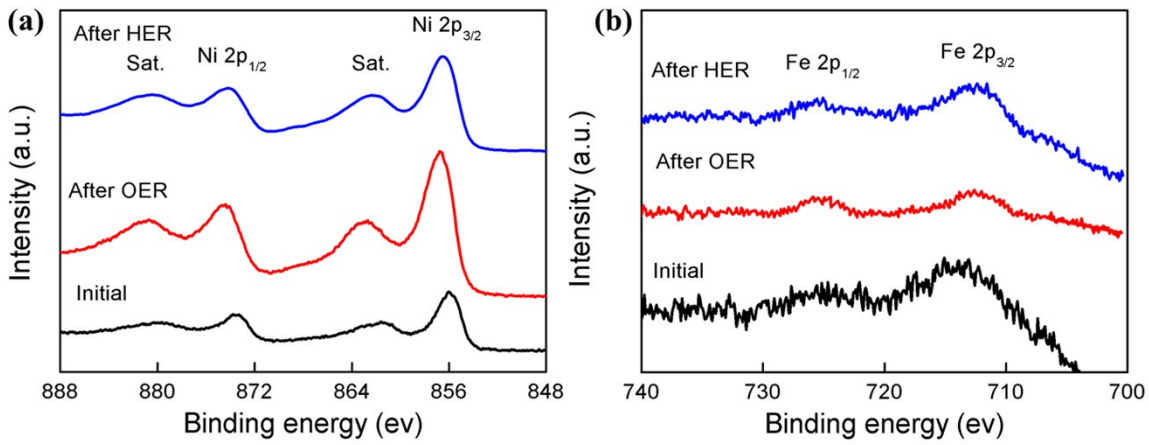


Figure S15. XPS spectra of the hierarchical hetero-Ni_3Se_4@NiFe LDH/CFC electrode before reaction, after OER, and after HER. (a) Ni 2p and (b) Fe 2p.