Highly Active and Dual-Functional Self-Supported Multiphase NiS-NiS_2-Ni_3S_2/NF Electrode for Overall Water Splitting

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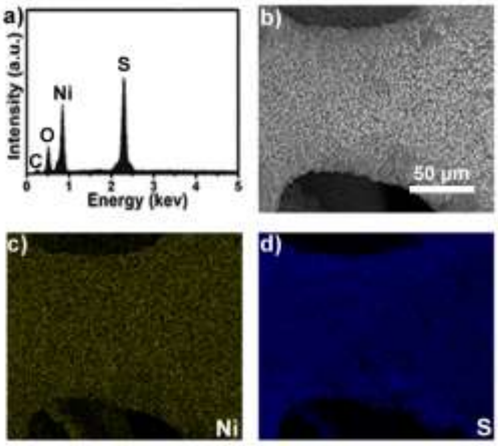

Fig. S1 Morphology of the sample. **a**, EDS spectrum. **b**, SEM image of the m-NiS_x-0.5/NF electrode. **c-d**, elemental mapping of the m-NiS_x-0.5/NF electrode, respectively.

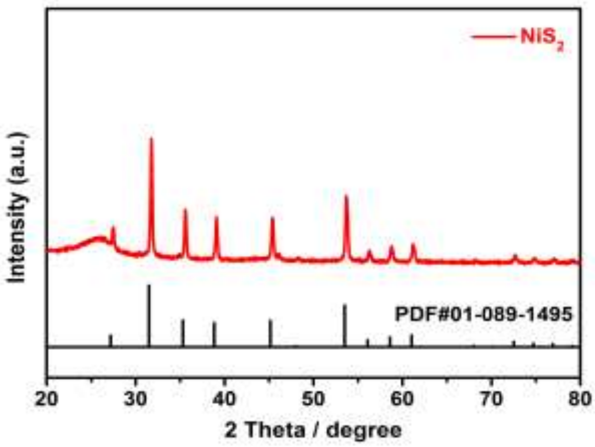

Fig. S2 XRD diffraction pattern of the as-prepared NiS_2 supported on carbon cloth.

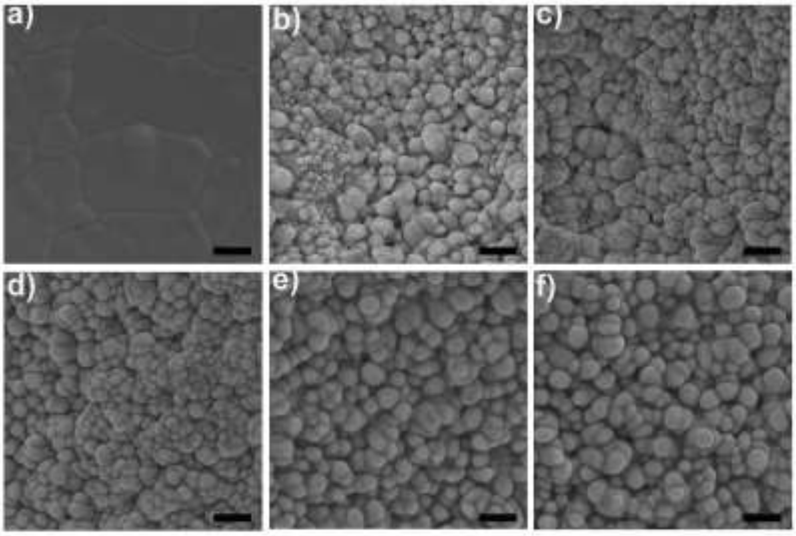

Fig. S3 Morphologies of the samples. SEM images of (**a**) NF, (**b**) m-NiS_x-0.1/NF, (**c**) m-NiS_x-0.2/NF, (**d**) m-NiS_x-0.5/NF, (**e**) m-NiS_x-1.0/NF, and (**f**) m-NiS_x-U/NF, respectively. Each scale bar is 5 µm.

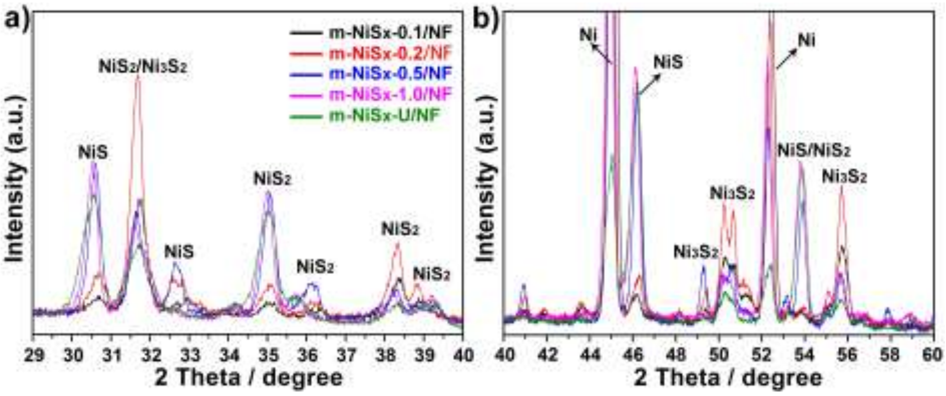

Fig. S4 XRD diffraction pattern of the as-prepared m-NiS_x/NF electrodes. The variation of grain sizes as the amount of sulfur powder increases.

Table S1 The approximate grain sizes of each phase in different quantity of sulfur powder[a, b]

Samples		2θ (degree)→D (nm)								
		22.3°	27.8°	30.7°	35.1°	38.4°	46.2°	50.2°	53.8°	55.7°
m-NiS$_x$-0.1/NF	NiS			21.1			35.6		22.0	
	NiS_2		22.1		20.4	41.3			22.0	
	Ni_3S_2	40.1						22.5		61.2
m-NiS$_x$-0.2/NF	NiS			32.9			36.8		23.2	
	NiS_2		36.2		33.9	48.2			23.2	
	Ni_3S_2	46.3						66.7		64.9
m-NiS$_x$-0.5/NF	NiS			47.0			79.0		51.8	
	NiS_2		23.4		65.3	36.1			51.8	
	Ni_3S_2	35.6						32.1		32.9
m-NiS$_x$-1.0/NF	NiS			48.2			80.7		52.9	
	NiS_2		23.4		35.1° 63.5 35.7° 35.8	36.1			52.9	
	Ni_3S_2	35.7						36.1		32.6
m-NiS$_x$-U/NF	NiS			47.8			80.4		53.4	
	NiS_2		23.4		35.2° 49.7 35.9° 34.7	31.3			53.4	
	Ni_3S_2	34.8						30.9		29.5

[a] All the data are the raw data. [b] Calculated with Scherrer formula $D = k\lambda/(\pi\times(\mathrm{FWHM}/180)\times\cos\vartheta)$, here, D is the grain size of particles (nm); k is the constant (0.89), ϑ is the half of the diffraction angle, and λ is the wavelength of Cu Kα radiation (1.5406 Å).

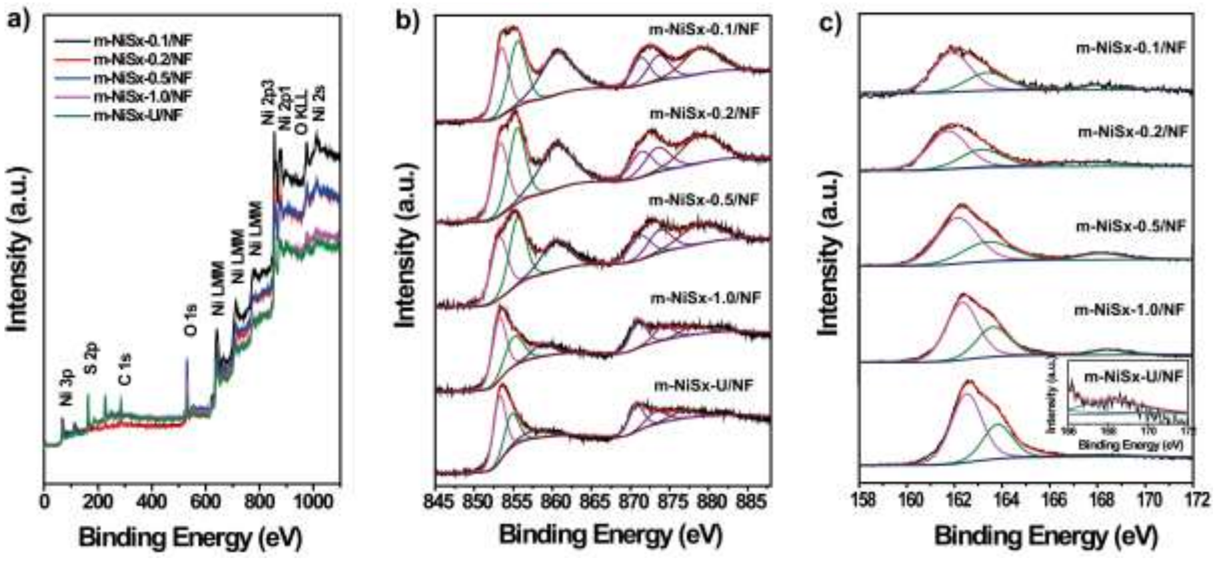

Fig. S5 XPS full spectra (**a**), the high-resolution spectra of Ni 2p (**b**), and S 2p (**c**) for the m-NiS$_x$-0.1/NF, m-NiS$_x$-0.2/NF, m-NiS$_x$-0.5/NF, m-NiS$_x$-1.0/NF, and m-NiS$_x$-U/NF, respectively.

Table S2 The area ratio summary of Ni $2P_{3/2}$ in Ni 2P

Samples	Area(855.5 eV)	Area(853.2 eV)	Area(855.5 eV)/Area(853.2 eV)
m-NiS_x-0.1/NF	67134.970	59107.040	1.14
m-NiS_x-0.2/NF	51422.200	45412.700	1.13
m-NiS_x-0.5/NF	41177.070	38245.680	1.07
m-NiS_x-1.0/NF	20086.780	31799.010	0.63
m-NiS_x-U/NF	19327.250	32582.770	0.59

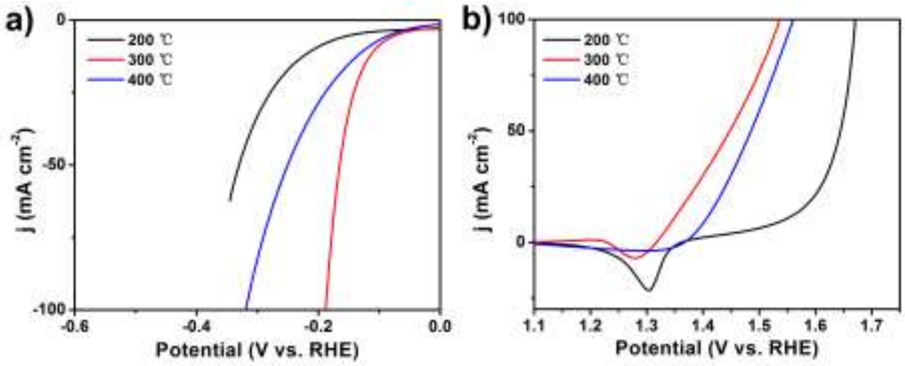

Fig. S6 LSV curves of the catalysts sulfidization with 200 °C, 300 °C and 400 °C in 1.0 M KOH toward (a) HER and (b) OER.

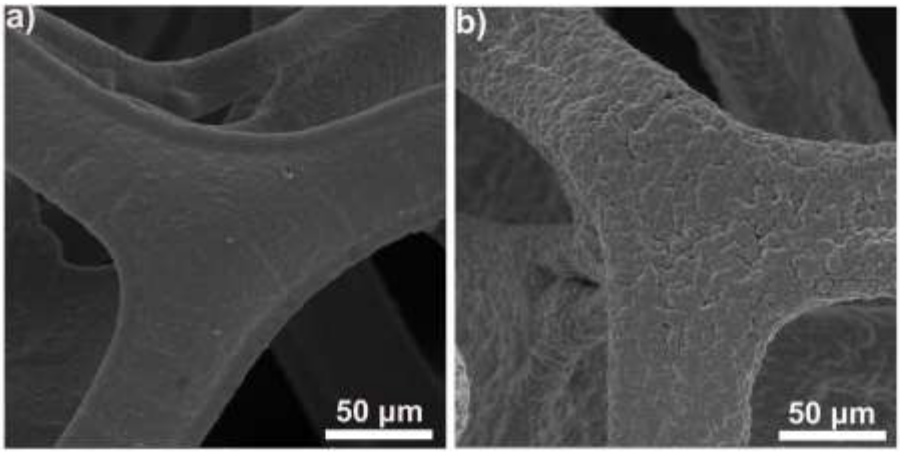

Fig. S7 SEM images of (**a**) m-NiS_x-0.5/NF prepared at 200 ℃ and (**b**) m-NiS_x-0.5/NF prepared at 400 ℃.

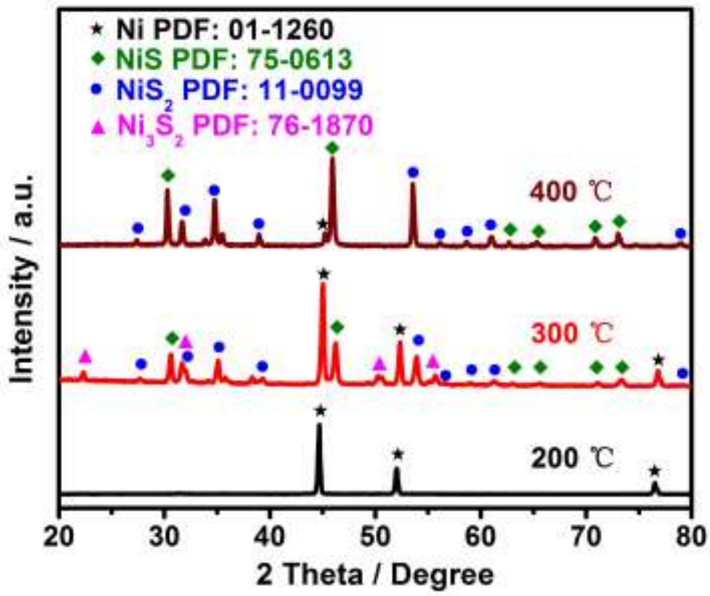

Fig. S8 XRD diffraction pattern of the as-prepared m-NiS_x-0.5/NF electrodes at different temperature.

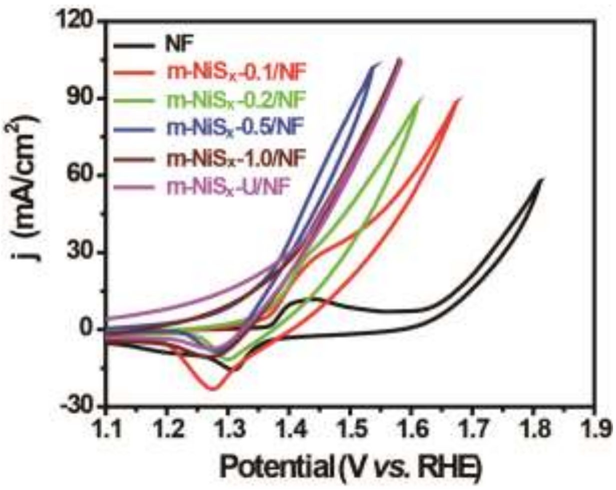

Fig. S9 Cyclic voltammograms of the fresh m-NiS_x/NF electrodes in 1.0 M KOH at a scan rate of 5 mV/s.

Table S3 Comparison of OER performance of m-NiS_x-0.5/NF electrode with various well-developed electrocatalysts in 1.0 M KOH

Samples	Overpotential@ 10 mA cm^{-2}(mV)	Substrate	Reference
m-NiS_x/NF	116	Ni foam	**This work**
h-NiS_x	180	Ni foam	Adv. Energy Mater. 2016, 6, 1502333
Ni_3S_2 NSs	260	Ni foam	J. Am. Chem. Soc.2015, 137, 14023
Fe-Ni_3S_2	282	Ni foil	Small 2017, 1604161
NiFe	215	Ni foam	Nat. Commun.2015, 6, 6616
$CoNi_2Se_4$	160	CF paper	Chem. Commun. 2017, 53, 5412
NiCoP	280	Ni foam	Nano Lett. 2016, 16, 7718
NiSe	270	Ni foam	Angew. Chem. Int. Ed. 2015, 54, 9351
Cu@CoS_x	160	Copper foam	Adv. Mater. 2017, 29, 1606200
MoO_2	260	Ni foam	Adv. Mater. 2016, 28, 3785
NiFe LDH	240	Ni foam	Science 2014, 345, 1593
NiFe HNSs	220	GCE	J. Mater. Chem. A. 2017, 5, 7769
FeCoW	223	GCE	Science 2016, 352, 333
Ni_2P	290	GCE	Energy. Environ. Sci. 2015, 8, 2347

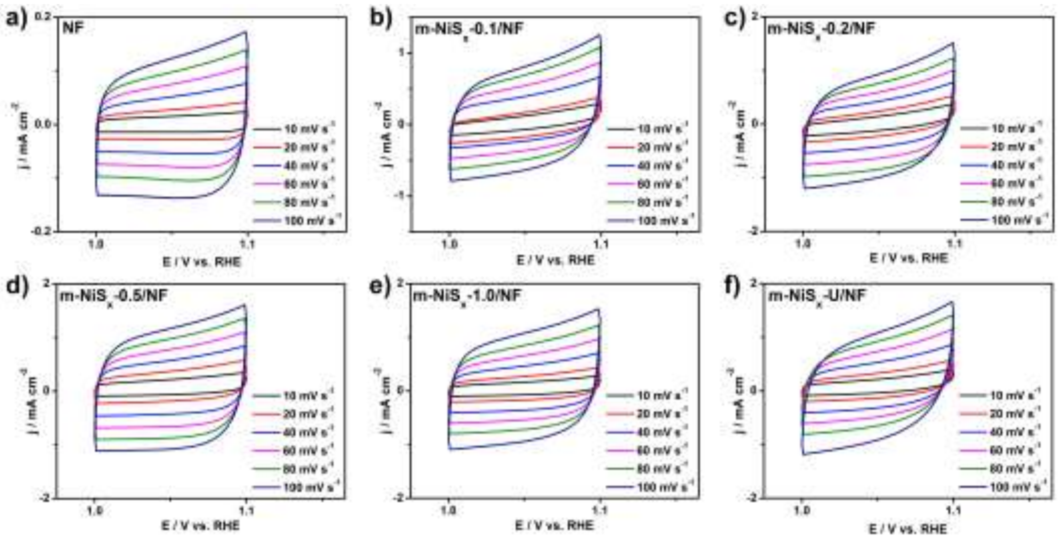

Fig. S10 Electrochemical double-layer capacitances of the NF (**a**), m-NiS_x-0.1/NF (**b**), m-NiS_x-0.2/NF (**c**), m-NiS_x-0.5/NF (**d**), m-NiS_x-1.0/NF (**e**), and m-NiS_x-U/NF (f) electrodes electrocatalysis for OER, respectively.

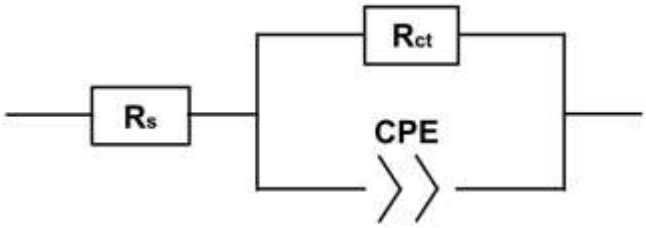

Fig. S11 Equivalent circuit diagram of the electrochemical double-layer capacitance measurements.

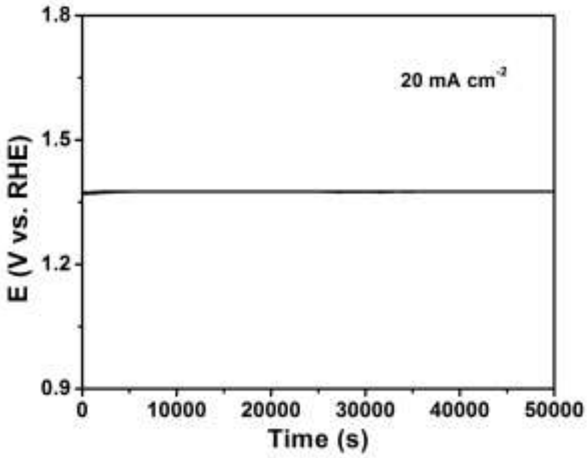

Fig. S12 Chronopotentiometric curve of the m-NiS_x-0.5/NF electrode electrocatalysis for OER at j = 20 mA cm^{-2}.

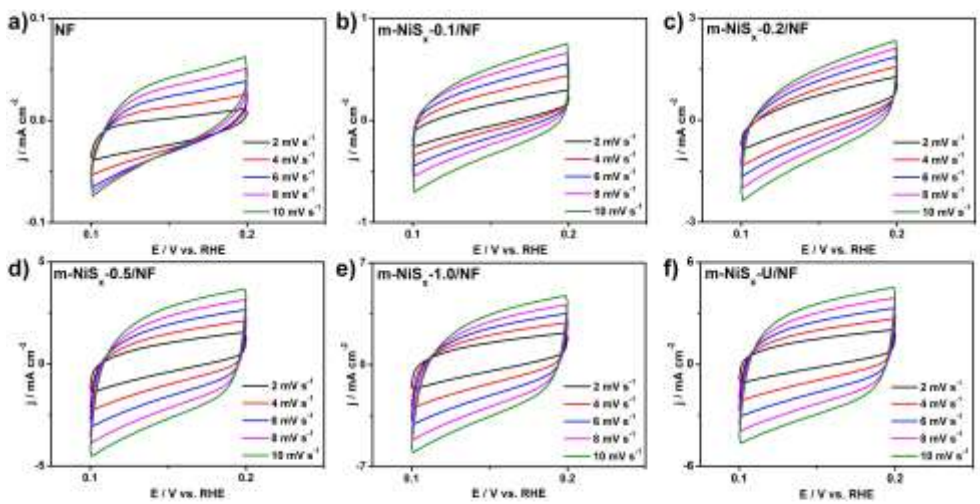

Fig. S13 Electrochemical double-layer capacitances of the NF (**a**), m-NiS_x-0.1/NF (**b**), m-NiS_x-0.2/NF (**c**), m-NiS_x-0.5/NF (**d**), m-NiS_x-1.0/NF (**e**), and m-NiS_x-U/NF (**f**) electrodes electrocatalysis for HER, respectively.

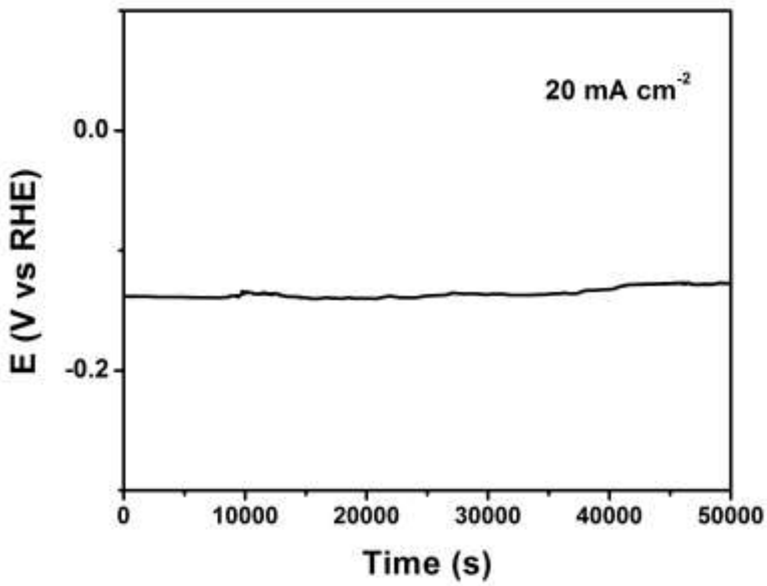

Fig. S14 Chronopotentiometric curve of the m-NiS_x-0.5/NF electrode electrocatalysis for HER at j = 20 mA cm^{-2}.

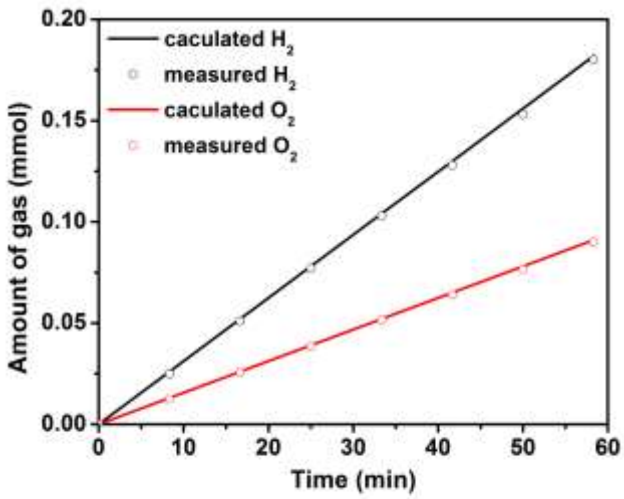

Fig. S15 Amount of gas theoretically calculated and experimentally measured versus time for m-NiS_x-0.5/NF in 1.0 M KOH.

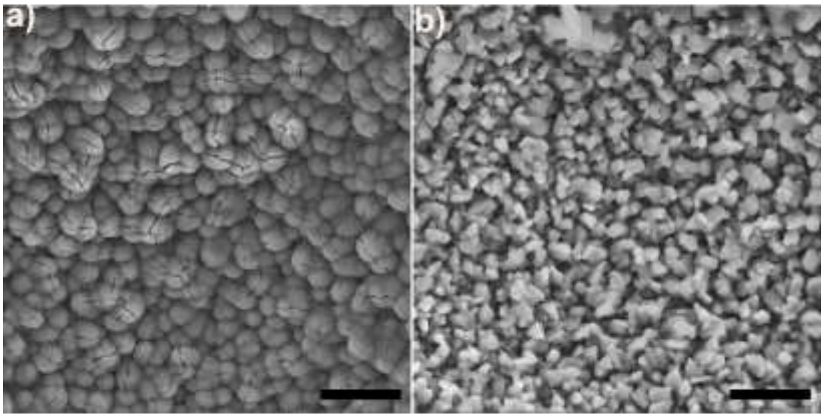

Fig. S16 The morphologies of m-NiSx-0.5/NF after long-term HER (a) and OER (b) tests. Each scale bar is 10 μm.

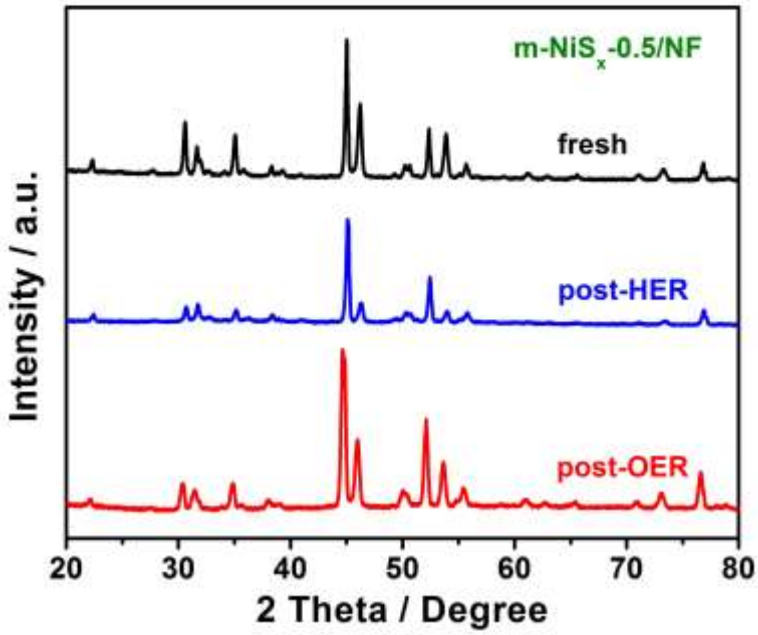

Fig. S17 XRD patterns of fresh, post-HER, and post-OER m-NiSx-0.5/NF samples.

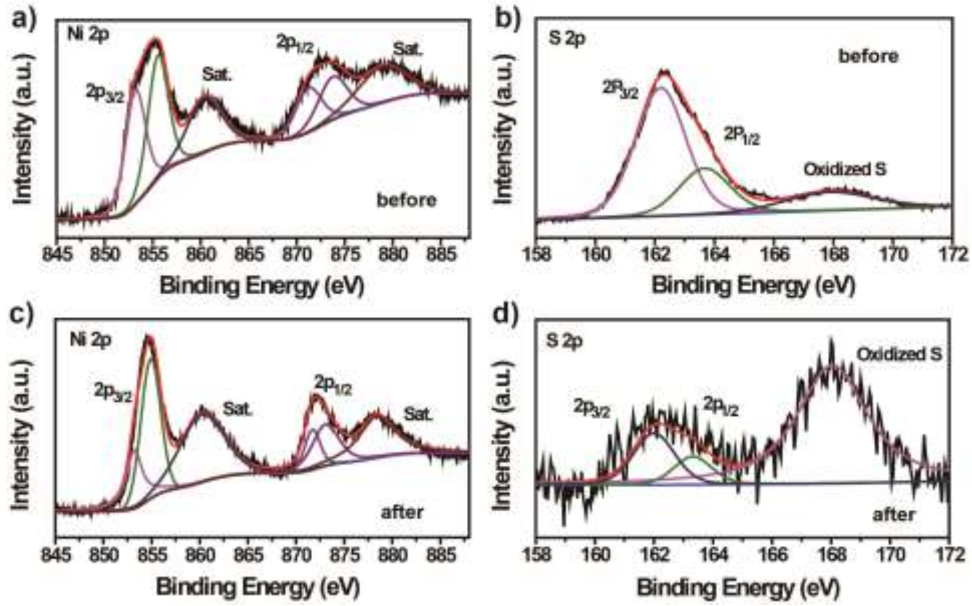

Fig. S18 XPS spectra of m-NiSx-0.5/NF (cathode) before and after water splitting.

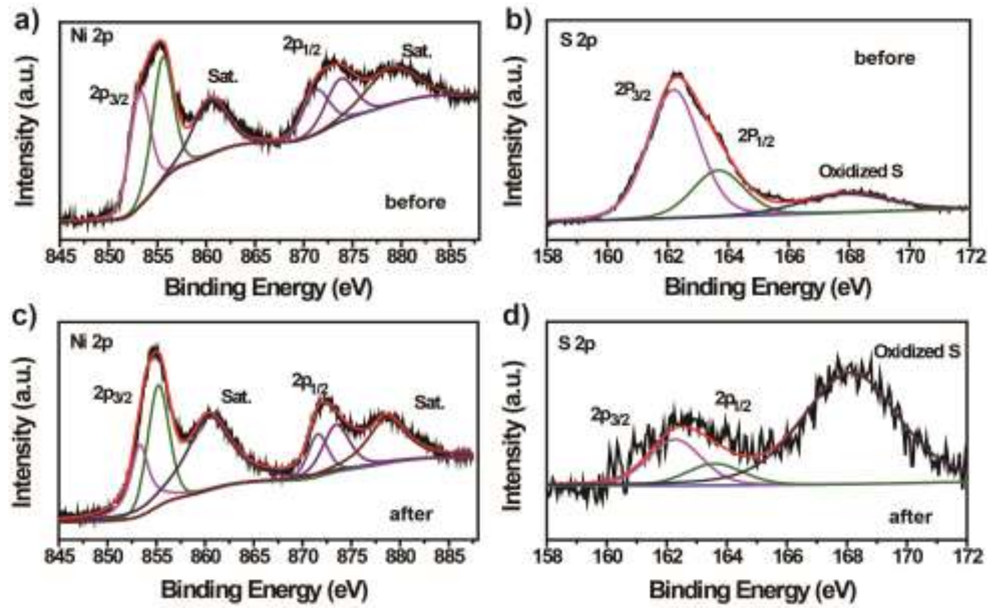

Fig. S19 XPS spectra of m-NiSx-0.5/NF (anode) before and after water splitting.

Table S4 Comparison of water-splitting performance of as-obtained m-NiS_x-0.5/NF couple to recently well-developed electrocatalysts in 1.0 M KOH

Samples	water splitting cell voltage @ j (mA cm^{-2})		Substrate	Reference
m-NiS_x	10	1.46 V	Ni foam	**This work**
N-S_3Ni_2	10	1.48 V	Ni foam	Adv. Mater. 2017, 1701584
h-NiS_x	20	1.53 V	Ni foam	Adv. Energy Mater. 2016, 6, 1502333
NiS	10	1.64 V	Ni foam	Chem. Commun. 2016, 52, 1486
Ni_3S_2 NSs	10	1.76 V	Ni foam	J. Am. Chem. Soc. 2015, 137, 14023
Cu@CoS_x	10	1.50 V	Copper foam	Adv. Mater. 2017, 29, 1606200
NiFe LDH	10	1.70 V	Ni foam	Science 2014, 345, 1593
NiFe HNSs	10	1.68 V	GCD	J. Mater. Chem. A. 2017, 5, 7769
NiFe LDH	10	1.54 V	Copper foam	Energy. Environ. Sci. 2017, 10, 1820
FeB_2	10	1.57 V	Ni foam	Adv. Energy Mater. 2017, 7, 1700513
Co_3Se_4	20	1.63 V	Cobalt foam	Adv. Energy Mater. 2017, 7, 1602579
CoO_x@CN	~20	1.55 V	GCE	J. Am. Chem. Soc. 2015, 137, 2688
MoS_2/Ni_3S_2	10	1.56 V	Ni foam	Angew. Chem. Int. Ed. 2016, 55, 6702
MoS_2-Ni_3S_2	10	1.50 V	Ni foam	ACS. Catal. **2017**, 7, 2357