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Electronic Supplementary Information (ESI)

Combinational modulations of $NiSe_2$ nanodendrites by phase engineering and iron-doping towards efficient oxygen evolution reaction

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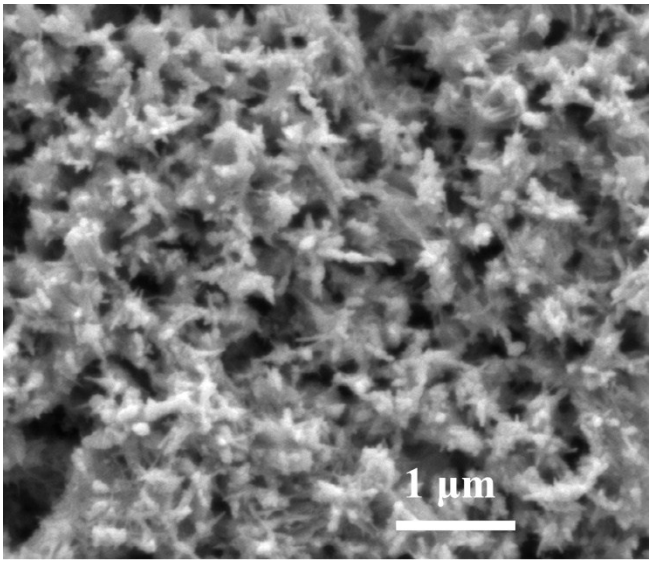

Fig. S1 SEM image of the p-$NiSe_2$ sample.

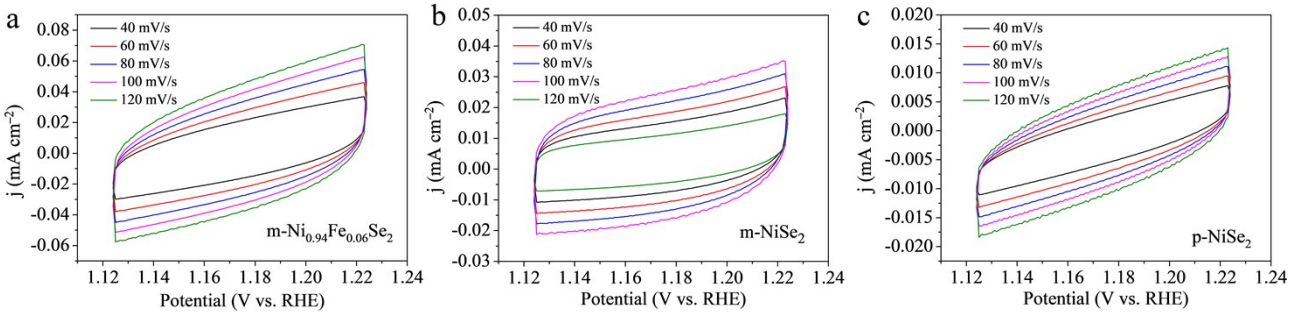

Fig. S2 CV curves of (a) m-$Ni_{0.94}Fe_{0.06}Se_2$, (b) m-$NiSe_2$, (c) p-$NiSe_2$ at various scan rates.

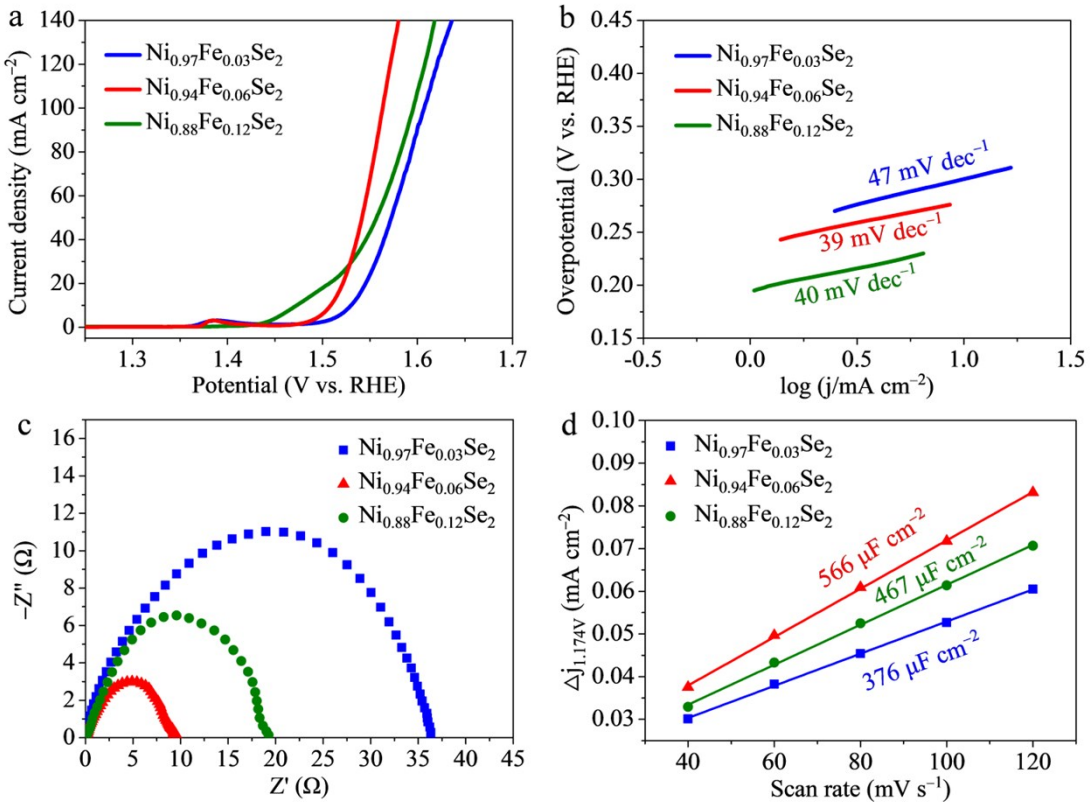

Fig. S3 (a) Linear sweep voltammetry curves of m-$Ni_{1-x}Fe_xSe_2$ (x=0.03, x=0.06, x=0.12) catalysts recorded at a scan rate of 5 mV s^{-1}. (b) The corresponding Tafel plots. (c) Nyquist plots of catalysts at 1.624 V (vs RHE) for the OER in 1M KOH. (d) Linear fitting of the capacitive current density of corresponding catalysts vs. scan rate.

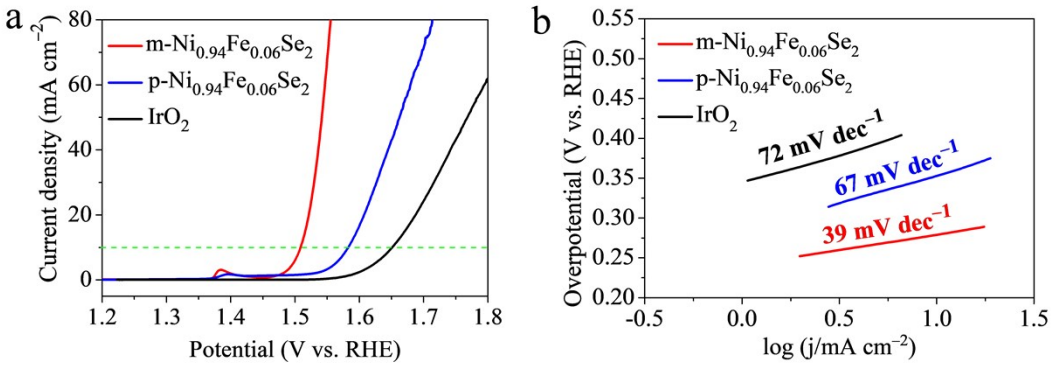

Fig. S4 LSV polarization curves (a) and corresponding Tafel plots (b) of the m-$Ni_{0.94}Fe_{0.06}Se_2$, p-$Ni_{0.94}Fe_{0.06}Se_2$ and the commercial IrO_2 catalysts.

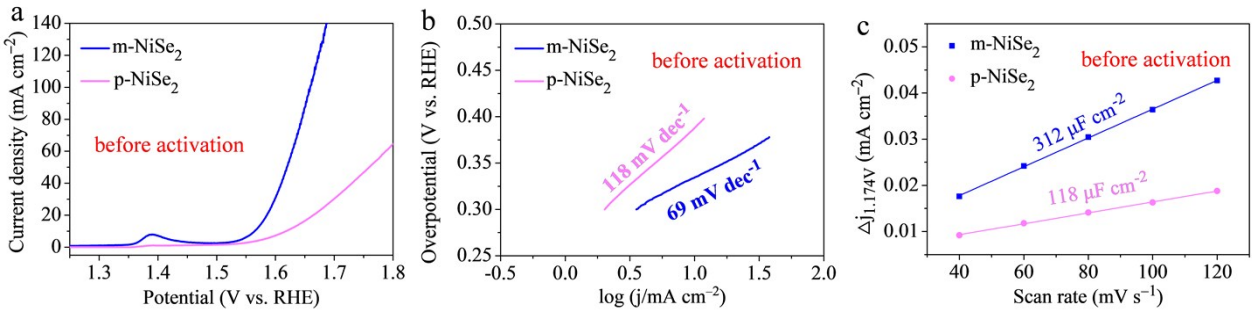

Fig. S5 LSV polarization curves (a), Tafel plots (b), and C_{dl} estimation of the m-$NiSe_2$ and p-$NiSe_2$ catalysts before activation

The m-$NiSe_2$ is a better pre-electrocatalyst for OER than the p-$NiSe_2$. LSV curves of the two catalysts before activation (i.e., initial CV cycling in the electrolyte) were obtained and shown in **Fig. S5a**. No amorphous NiOOH shells were formed on the surfaces of the m-$NiSe_2$ and p-$NiSe_2$ samples at this stage. It is observed that the p-$NiSe_2$ catalyst requires an overpotential of 388 mV to drive the current density of 10 mA cm^{-2}. This overpotential is dramatically reduced to 335 mV for the m-$NiSe_2$. **Fig. S5b** shows the corresponding Tafel slopes. It is obvious that the m-$NiSe_2$ catalyst has a Tafel slope of 69 mV dec^{-1}, which is much smaller than that of the p-$NiSe_2$ (118 mV dec^{-1}). In **Fig. S5c**, the C_{dl} value is 118 μF cm^{-2} for the p-$NiSe_2$, and increases to 312 μF cm^{-2} for the m-$NiSe_2$. The lower overpotential, smaller Tafel slope and larger C_{dl} value reveal that the m-$NiSe_2$ is a better pre-electrocatalyst for OER than the p-$NiSe_2$.

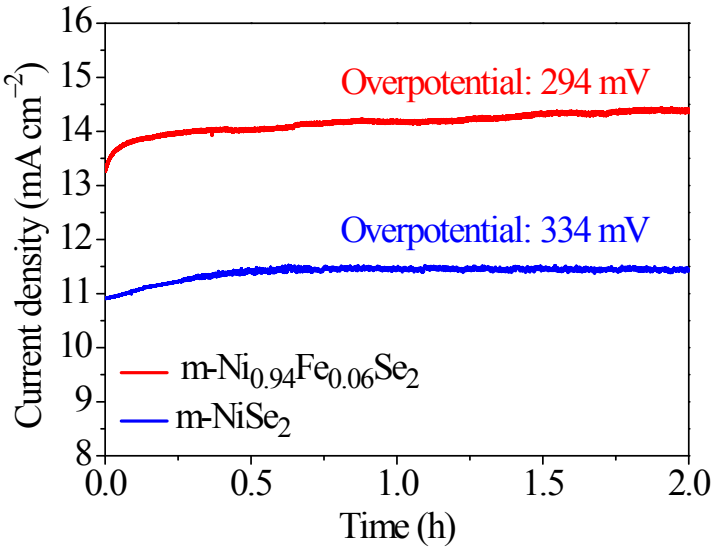

Fig. S6 Time-dependent current density curves of the catalysts in the initial 2 h.

Table S1 Recent advance of OER activity of Ni-based eletrocatalysts.

Catalytsts	Electrolytes	ŋ (mV) @ j (mA cm^{-2})	Tafel slope (mV dec^{-1})	Working electrodes	References
marcasite $Fe_{1-x}Ni_xSe_2$ nanodendrites	1M KOH	279@10 333@100	39	Glassy carbon	This work
pyrite $Ni_{0.8}Fe_{0.2}Se_2$-drived oxide nanoplates	1M KOH	195@10	28	Ni foam	Nat. Commun., 2016, 7, 12324.
pyrite $Fe_{8.4\%}$-$NiSe_2$ ultrathin nanowires	0.1M KOH	268@10	41	Glassy carbon	Angew. Chem. Int. Ed., 2018, 57, 4020−4024.
pyrite $Fe_{0.09}Co_{0.13}$-$NiSe_2$ nanosheets	1M KOH	251@10	63	Carbon fiber	Adv. Mater., 2018, 30, 1802121.
pyrite $Fe_{0.2}NiSe_2$		280@10	88		
pyrite $Ni_{0.5}Fe_{0.5}Se_2$ octahedral crystalline	1M KOH	350@50	63	Carbon fiber	Appl. Surf. Sci., 2017, 401, 17.
pyrite $NiSe_2$ nanowires/XC72	1M KOH	287@10	65	Glassy carbon	Small, 2017, 13, 1701487.
pyrite $NiSe_2$/NiO_x/XC72		266@10	53		
pyrite $NiSe_2$ nanowrinkles	1M KOH	290@10	63	Ni foam	ACS Sustainable Chem. Eng., 2018, 6, 2231−2239.
NiSe@NiOOH Core/Shell Hyacinth-like Nanostructures	1M KOH	501@100	162	Ni foam	ACS Appl. Mater. Interfaces 2016, 8, 20057−20066
Ni_3Se_2 film/carbon fiber	1M KOH	284@10	80	Cu foam	Catal. Sci. Technol., 2015, 5, 4954−4958.
V-NiS_2 nanosheets	1M KOH	290@10	45	Glassy carbon	ACS Nano 2017, 11, 11574−11583
NiS/NiS_2 interwoven structure	1M KOH	416@100	156	Carbon cloth	J. Mater. Chem. A, 2018, 6, 8233-8237
NiFe LDH	1M KOH	350@10	40	Glassy carbon	Nat. Commun., 2014, 5, 4477.

FeCoNi /graphene spheres	1M KOH	325@10	60	Carbon paper	ACS Catal., 2017, 7, 469 479.
Holey $Ni(OH)_2$ nanosheets	1M KOH	293@10	65	Glassy carbon	Small 2017, 13, 1700334
$Ni(OH)_2$ nanosheets	1M KOH	330@50	150	Ni foam	ACS Appl. Mater. Interfaces, 2016, 8, 49, 33601-33607
α-NiOOH nanosheet arrays	1M KOH	266@10	76	Ni foam	ACS Sustainable Chem. Eng., 2017, 5, 3808−3818.
$Ni_{1-x}Fe_xOOH$ films	0.1M KOH	320@10	45	Au foil	J. Phys. Chem. C, 2015, 119, 32, 18303−18316.
Commercial RuO_2	1M KOH	344@10	65	Ni foam	ACS Appl. Mater. Interfaces, 2016, 8, 42, 28678-28688

Table S2 TOFs of the various catalysts.

Catalysts	TOF (s^{-1})
m-$NiSe_2$	0.97
m-$Ni_{0.97}Fe_{0.03}Se_2$	5.46
m-$Ni_{0.94}Fe_{0.06}Se_2$	10.82
m-$Ni_{0.88}Fe_{0.12}Se_2$	8.49
p-$NiSe_2$	0.17

TOF can be calculated using the below equation:

$$TOF = \frac{J \times S \times \mu}{4 \times F \times n},$$

where J (A cm^{-2}) is the current density at a given overpotential (η = 320 mV), S is the surface area of the electrode (0.071 cm^2), F is the Faraday constant (96485 C mol^{-1}), and n is the number of moles of reactive metal on the electrode. The μ is the Faradaic efficiency that was determined from the total amount of charge Q(C) passed through the cell and the total amount of the produced O_2 $n(O_2)$ (mol), as described by the equation $\mu = \frac{4 \times F \times n(O_2)}{Q}$, assuming the four electrons are needed to produce one oxygen molecule. Herein, we assume the μ values to be 100% when calculating the TOFs (*Nat. Commun.*, 2019, **10**, 2149). The Ni and Fe are supposed to be the active sites for the various samples.