Heterometal doping on nickel selenide corrugations for solar-assisted electrocatalytic hydrogen evolution

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Experimental

Materials

Ni foam (thickness: 1.6 mm), selenium powder (Se, ≥99.5%, Sigma-Aldrich), manganese acetate tetrahydrate ($C_4H_6MnO_4 \cdot 4H_2O$, ≥99%, Sigma-Aldrich), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, ≥98%, Sigma-Aldrich), iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, ≥98%, Sigma-Aldrich), potassium hydroxide (KOH, 50% w/v, Alfa Aesar), graphite foil (Alfa Aesar), and Pt wire (CH Instrument) were used. Deionized water (resistivity: 18.2 MΩ cm) was used for all of the aqueous solutions.

Characterization

X-ray diffraction (XRD, PANalytical X'pert PRO diffractometer with a Cu Ka radiation source), X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM scanning X-ray microprobe), scanning electron microscopy (SEM, LEO 1525) coupled with energy-dispersive X-ray spectroscopy (EDS), and transmission electron microscopy (TEM, JEOL 2010F) coupled with EDS were employed.

Electrochemical measurements

All electrochemical performance parameters were tested in an alkaline solution of 1 M KOH using a three-electrode electrochemical station. Graphite foil and a Hg/HgO electrode served as the counter electrode and the reference electrode, respectively. All potentials were converted to a reversible hydrogen electrode (RHE) by the Nernst equation ($E_{RHE} = E_{Hg/HgO} + 0.0591\ pH + 0.098$) and all measurements were conducted with iR compensation. The polarization curves were tested by sweeping the potential

from 0.065 to -0.325 V *vs.* RHE at a rate of 2 mV s^{-1}. The cyclic voltammetry (CV) curves were conducted from 0.1 to 0.2 V *vs.* RHE at different rates. Electrochemical impedance spectroscopy (EIS) was performed at -150 mV *vs.* RHE from 100 KHz to 10 mHz with an amplitude of 10 mV.

Supplementary Figures

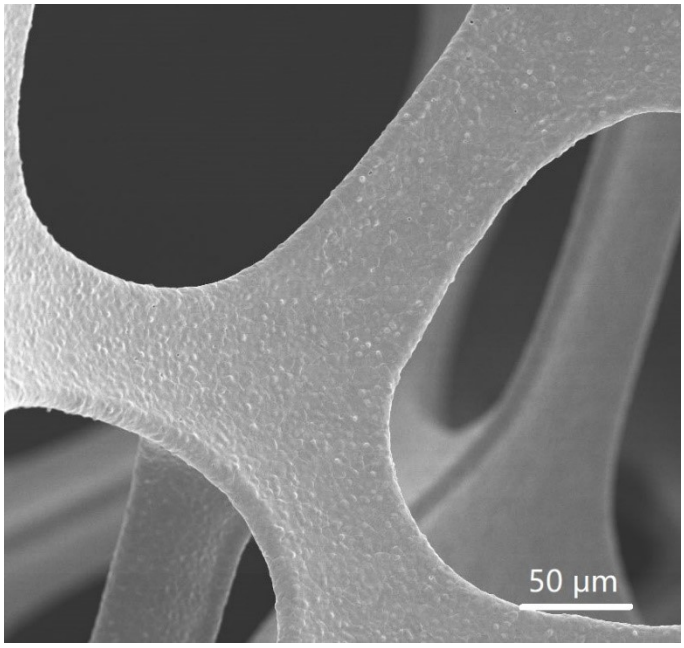

Fig. S1 SEM image of Ni foam.

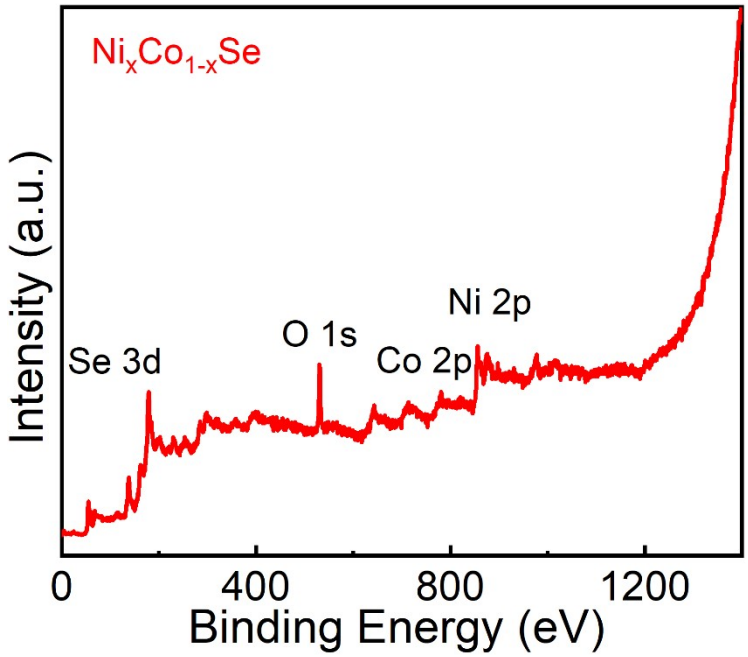

Fig. S2 XPS spectra of $Ni_{1-x}Co_xSe$.

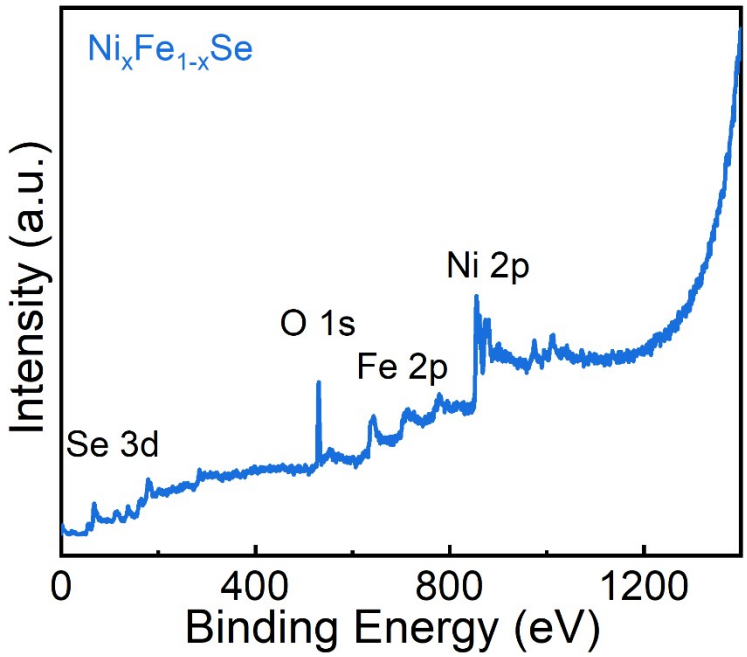

Fig. S3 XPS spectra of $Ni_{1-x}Fe_xSe$.

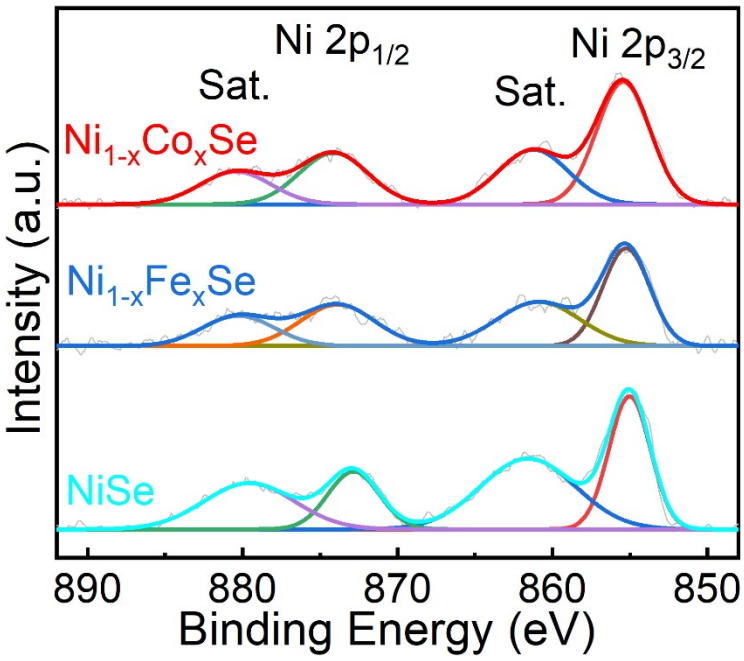

Fig. S4 High-resolution XPS spectra of Ni 2p in $Ni_{1-x}Co_xSe$, $Ni_{1-x}Fe_xSe$ and NiSe.

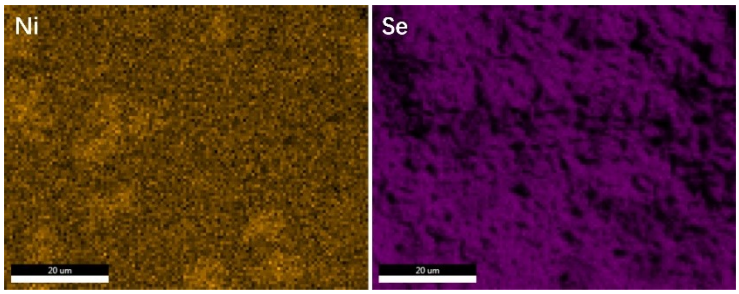

Fig. S5 EDS mapping images of Ni and Se in $Ni_{1-x}Co_xSe$ from SEM.

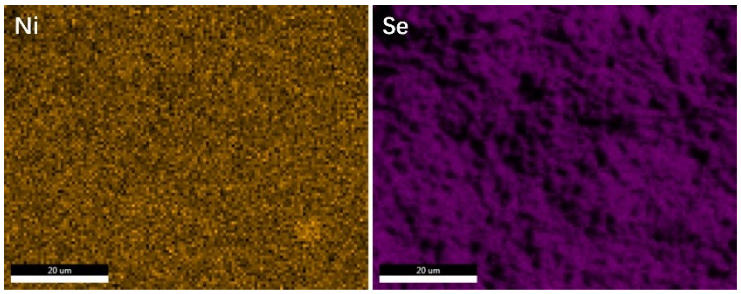

Fig. S6 EDS mapping images of Ni and Se in $Ni_{1-x}Fe_xSe$ from SEM.

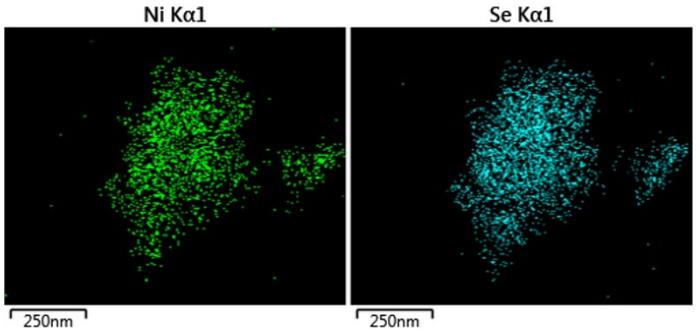

Fig. S7 EDS mapping images of Ni and Se in $Ni_{1-x}Co_xSe$ from TEM.

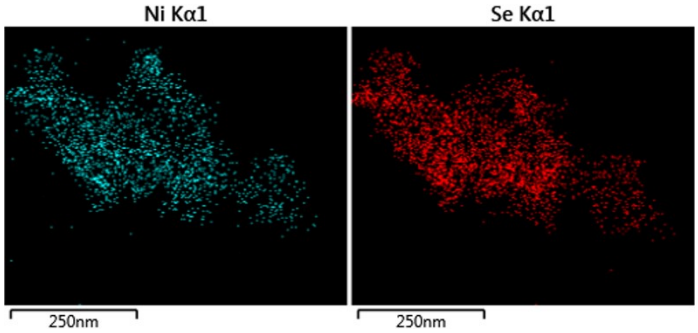

Fig. S8 EDS mapping images of Ni and Se in $Ni_{1-x}Fe_xSe$ from TEM.

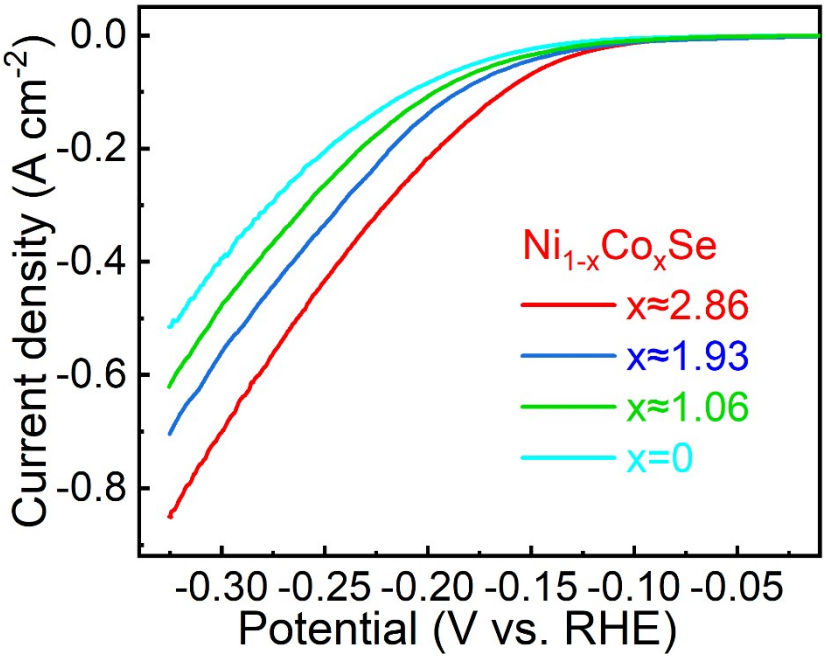

Fig. S9 Polarization curves of the $Ni_{1-x}Co_xSe$ samples with different content of Co in base.

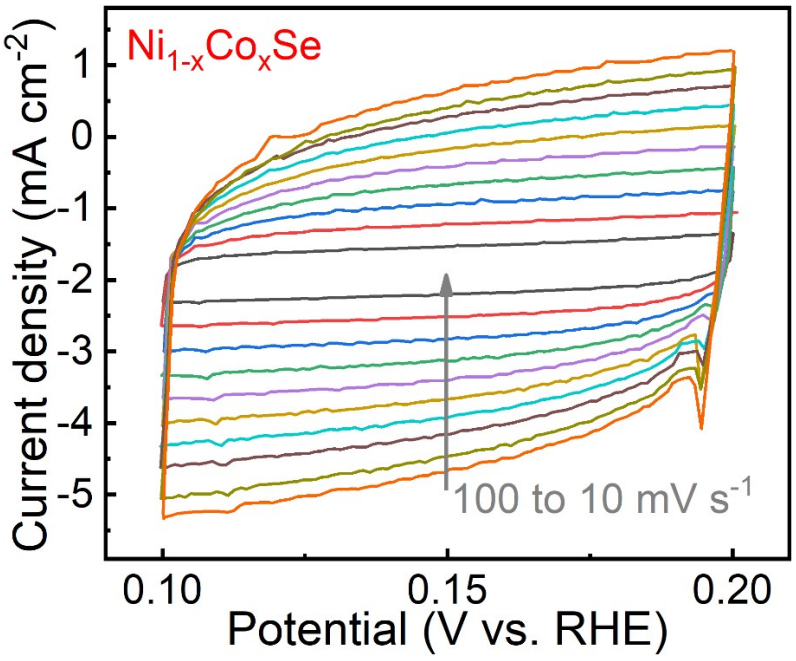

Fig. S10 CV curves recorded for $Ni_{1-x}Co_xSe$ electrodes over the potential range between 0.1 and 0.2 V *vs.* RHE at different rates in base.

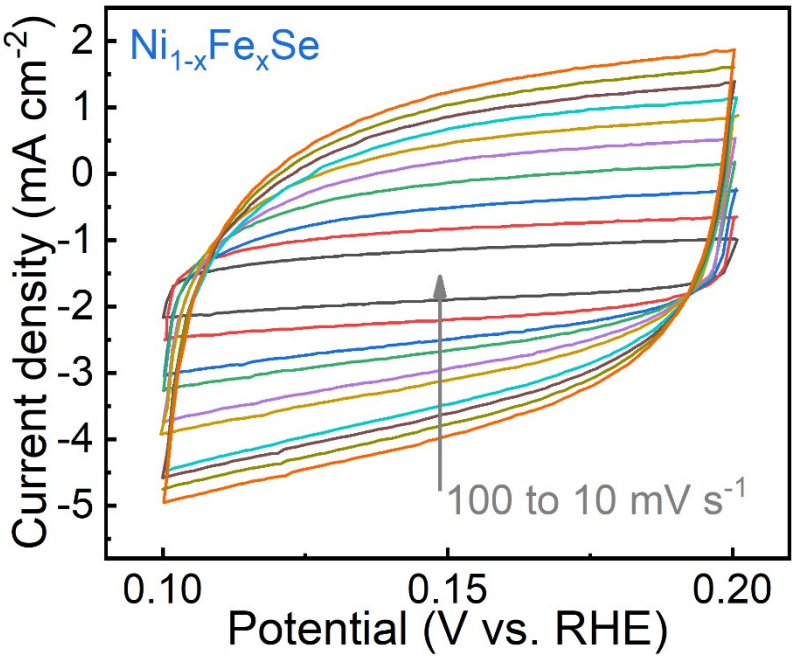

Fig. S11 CV curves recorded for $Ni_{1-x}Fe_xSe$ electrodes over the potential range between 0.1 and 0.2 V *vs.* RHE at different rates in base.

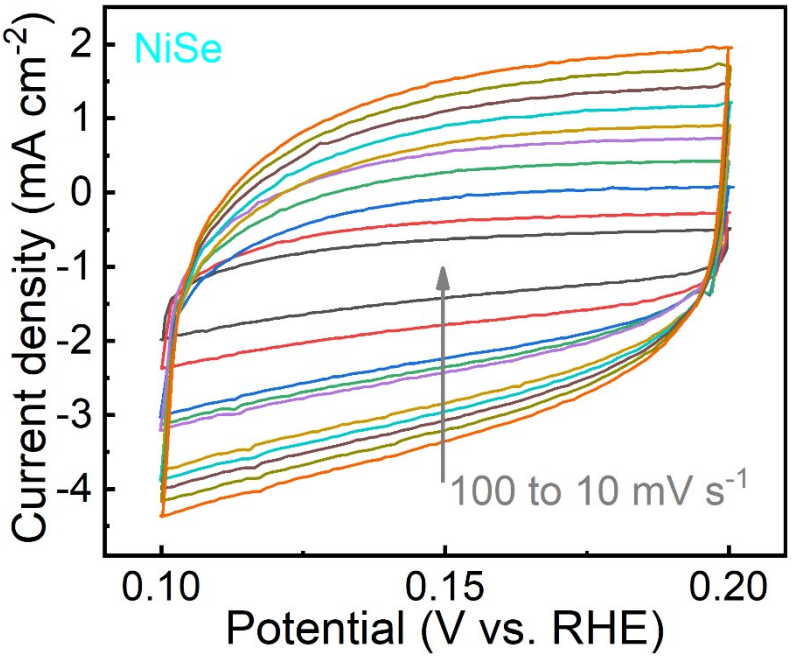

Fig. S12 CV curves recorded for NiSe electrodes over the potential range between 0.1 and 0.2 V *vs.* RHE at different rates in base.

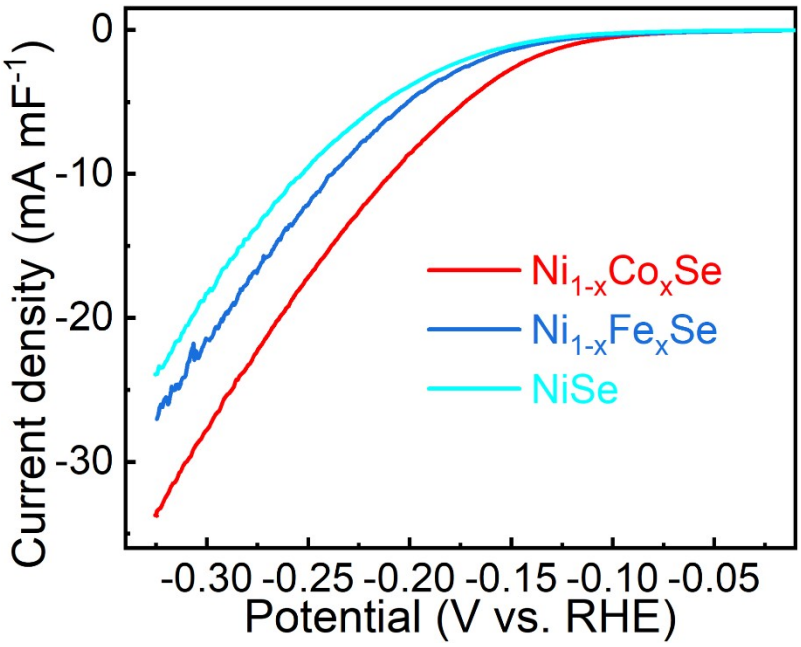

Fig. S13 Normalization of the current based on the linear sweep voltammetry (LSV) curves.

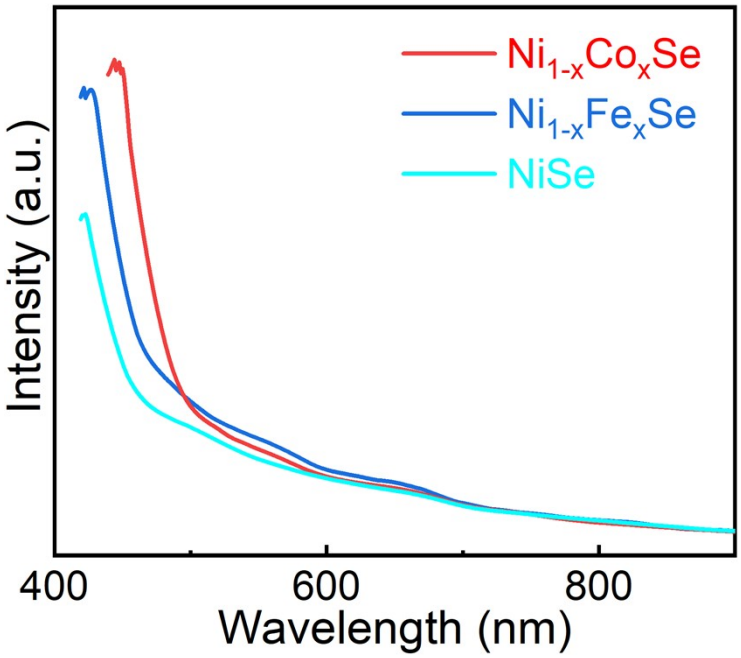

Fig. S14 Normalization of the current based on the linear sweep voltammetry (LSV) curves.

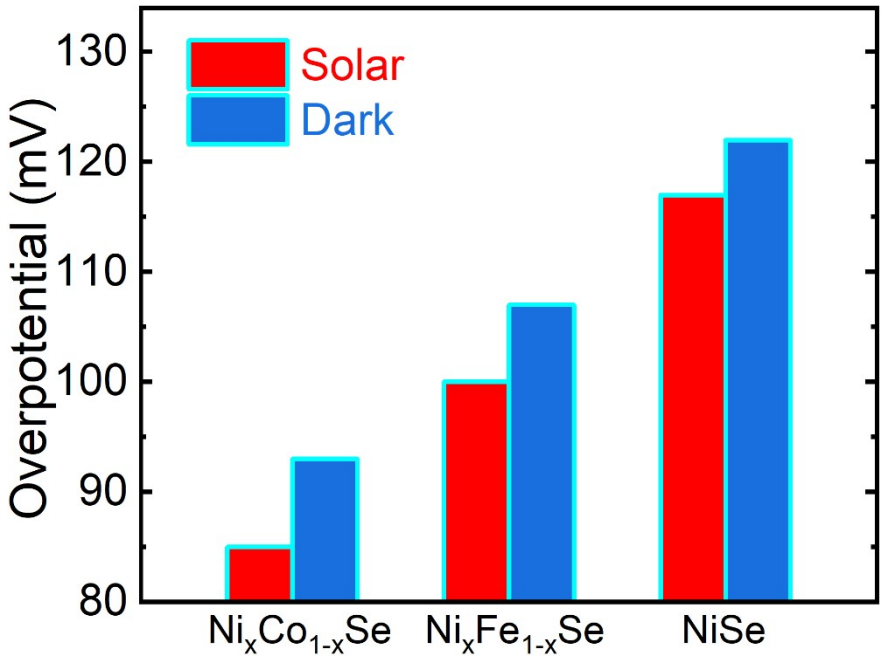

Fig. S15 Overpotentials of different catalysts with and without illumination at current densities of 10 mA cm^{-2}.

Supplementary Tables

Table S1 Comparison of the HER performance between $Ni_{1-x}Co_xSe$ and other previously reported NiSe-based catalysts in alkaline conditions. Here η_{10} is the overpotential at a current density of 10 mA cm^{-2}.

Catalyst	η_{10} (mV)	Tafel slope (mV dec^{-1})	Source
$Ni_{1-x}Co_xSe$	93	68.2	This work
NiSe/Ni foam	96	120	Angew. Chem. Int. Ed. 2015, 54, 9351
NiSe	~150	76.6	Electrochim. Acta 2017, 224, 412
NiSe-$Ni_{0.85}Se$/carbon paper	101	74	Small 2018, 14, 1800763
$MoSe_2$-NiSe/carbon nanosheets	180	80.6	Carbon 2018, 139, 1
Two-tiered NiSe	177	58.2	Adv. Energy Mater. 2018, 8, 1702704
NiSe/Ni_3Se_2/Ni foam	92	101.2	Adv. Mater. Interfaces 2018, 5, 1701507
$Fe_{7.4\%}$-NiSe	163	71.4	J. Mater. Chem. A 2019, 7, 2233