*Supporting Information*

# MOF-Derived Co-Doped Nickel Selenide/C Electrocatalysts Supported on Ni Foam for Overall Water Splitting

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**Experimental Section**

***Preparation of ZIF-67/NF*:** The Ni foam (1 cm × 2 cm) was pretreated with 30 mL of HCl solution (1 M) for 30 minutes to clean the surface oxides. After that, the NF was washed with deionized water and methanol carefully and then used as substrate. In a typical synthesis, 0.328 g of 2-methylimidazole was dissolved in 25 mL methanol to form a clean solution, which was then poured into a 25 mL methanol solution containing 0.291 g of $Co(NO_3)_2 \cdot 6H_2O$ under stirring. After that, NF was immersed into the above solution, which was then aged for 24 h. After the reaction completed, the NF was taken out and washed with methanol and dried at 50 °C for 6 h in an electric oven to get the purple ZIF-67/NF product.

***Preparation of NiCo LDH/C/NF*:** A piece of the as-prepared ZIF-67/NF and 38 mg ZIF-67 were transferred into a round bottomed flask containing 90 mg $Ni(NO_3)_2 \cdot 6H_2O$ and 25 mL ethanol. Then the mixture was refluxed at 90 °C for 1 h under stirring. After the reaction, the NF was washed with ethanol for 3 times and dried at 50 °C for 6 h to get the NiCo LDH/C/NF.

***Preparation of Co-Ni-Se/C/NF:*** The as-synthesized NiCo LDH/C/NF was converted into Co-Ni-Se/C/NF using a horizontal alundum tube furnace. The NiCo LDH/C/NF and 0.5 g of Se powder were placed at the downstream and upstream sides of the tube furnace, respectively. The furnace was heated to 400 °C for 2 h with a heating ramp of 2 °C $min^{-1}$ in $N_2$ atmosphere. During the whole process, the flow of $N_2$ was maintained

at a rate of 100 sccm.

***Preparation of Pt/C/NF and $RuO_2$/NF***: The commercial 20 wt.% Pt/C and $RuO_2$ samples were prepared by ultrasonically mixing 4 mg of the catalyst powder with the mixture of 40 μL 5% Nafion solution, 560 μL ethanol and 400 μL $H_2O$ for 15 min to form homogeneous catalyst ink. Next, a certain volume of the ink was carefully dropped onto the clean NF, leading to a desirable catalyst loading. The catalyst loading was about 1.5 mg $cm^{-2}$.

***Characterizations.*** The characterizations of Co-Ni-Se/C/NF were carried out by X-ray diffraction (XRD, Rigaku) with Cu Kα radiation (λ = 1.54056 Å), filed emission scanning electron microscopy (SEM, ZEISS, SIGMA), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM, Tecnai-F20). X-ray photoelectron spectroscopy (XPS) measurement was performed on PHI Quantum-2000 XPS (US). Raman spectra were recorded using a Horiba XploRA Confocal Raman microscope fitted with 532 nm excitation laser. The amount of different elements was determined by inductively couple plasma mass spectrometry (ICP-MS) (Thermo Fisher, U.S.). It should be noted that the samples were put in concentrated HCl to dissolve the NF for ICP-MS measurement.

***Electrochemical measurements.*** All electrochemical measurements were conducted at room temperature in a typical three-electrode or two-electrode configuration using an

electrochemical workstation (CHI 660E, CH Instruments, Inc.). The HER and OER performance was evaluated in 1 M KOH (pH = 13.6) solution using the as-fabricated Co-Ni-Se/C/NF as the working electrode, a platinum plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode, respectively. The overall water splitting performance was evaluated in 1 M KOH solution using the Co-Ni-Se/C/NF as both the anode and the cathode. For comparison, the HER and OER performance of the NiCo LDH/C/NF and the bare NF were also measured. The overall water splitting performance of bare NF was evaluated as well. All polarization curves are *iR*-corrected according to: $E_{corr} = E_{mea} - iR_s$

Where $E_{corr}$ is *iR*-corrected potential, $E_{mea}$ is experimentally measured potential, and $R_s$ is the equivalent series resistance extracted from the electrochemical impedance spectroscopy measurement. Unless otherwise specified, all potentials reported are on the reversible hydrogen electrode (RHE) scale by converting the potentials measured versus SCE according to: $E_{(RHE)} = E_{(SCE)} + 0.241 + 0.059pH$

**Additional Figures and Data**

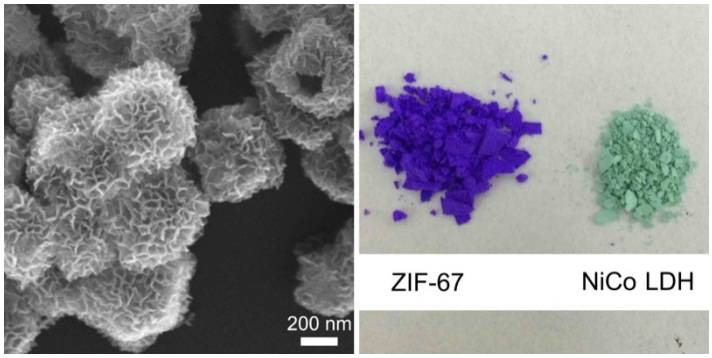


**Fig. S1** (a) SEM image of NiCo LDH powder. (b) Digital photograph of ZIF-67 and NiCo LDH powder.

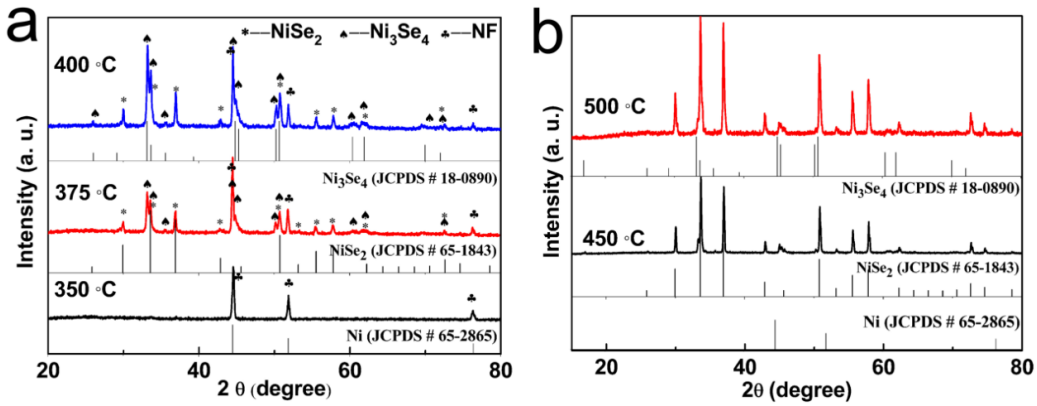


**Fig. S2** XRD patterns of Co-Ni-Se/C/NF-*x* samples, where *x* represents the thermal selenization temperature. (a) *x* = 350, 375, and 400°C. (b) *x* = 450 and 500 °C.

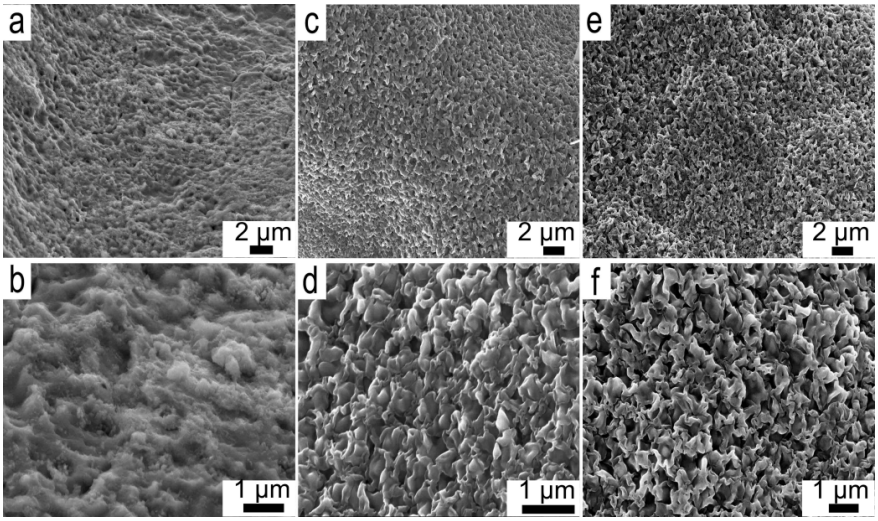


**Fig. S3** SEM images of Co-Ni-Se/C/NF samples obtained at different temperatures: (a,b) 350°C, (c,d) 375°C, and (e,f) 400°C.

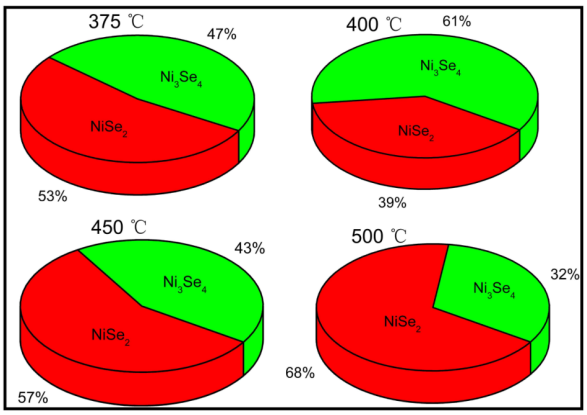


**Fig. S4** Semi-quantitative analysis of phase composition of different Co-Ni-Se/C/NF samples. The analysis is made using HighScore software after background subtraction.

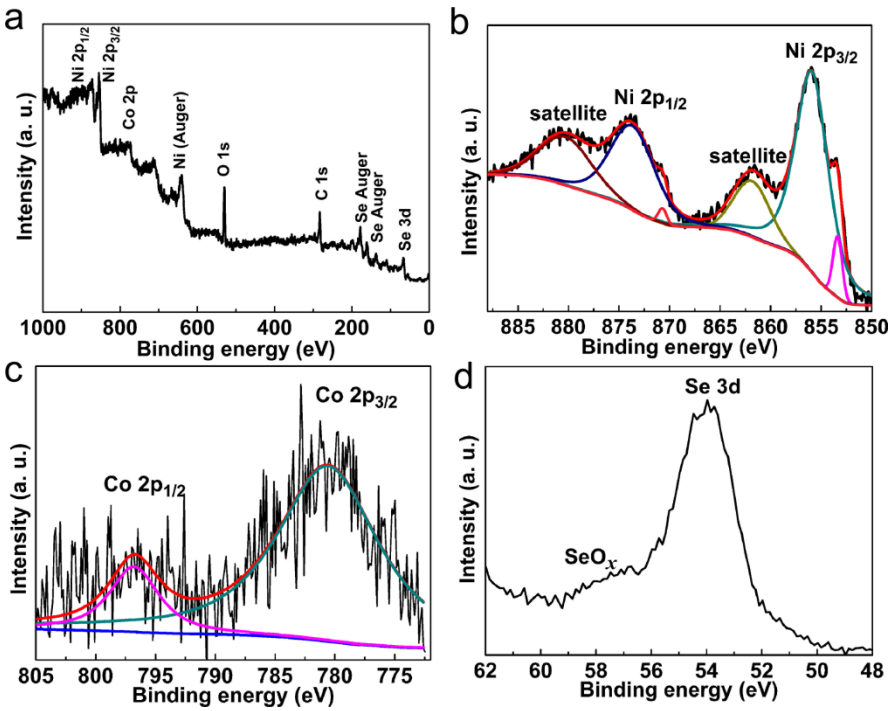


**Fig. S5** (a) XPS survey spectrum of the Co-Ni-Se/C/NF. High resolution XPS spectra of (b) Ni *2p*, (c) Co *2p*, and (d) Se *3d* regions.

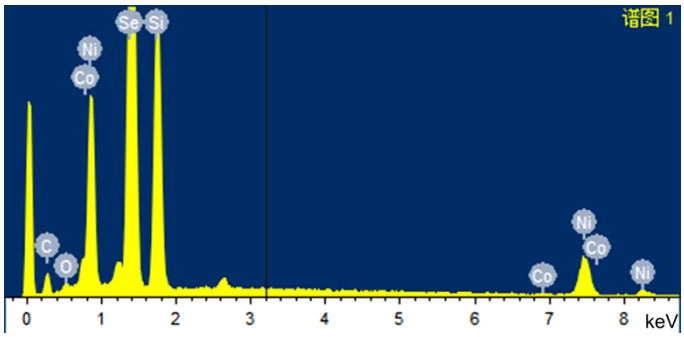


**Fig. S6** EDS pattern of the Co-Ni-Se/C/NF. Note that the sample has been pretreated with concentrated HCl to dissolve the Ni foam substrate.

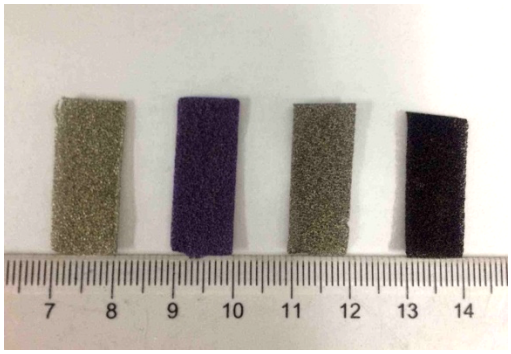


**Fig. S7** Digital photograph of the NF, ZIF-67/NF, NiCo LDH/C/NF, and Co-Ni-Se/C/NF (from left to right).

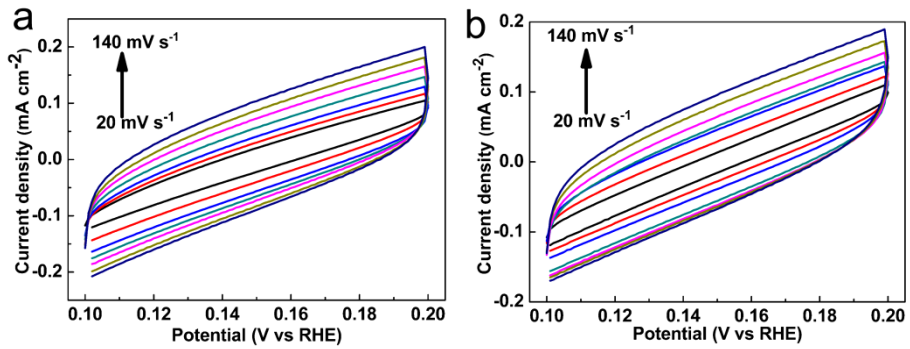


**Fig. S8** Electrochemical cyclic voltammetry curves at different scan rates for (a) NiCo LDH/C/NF and (b) NF.

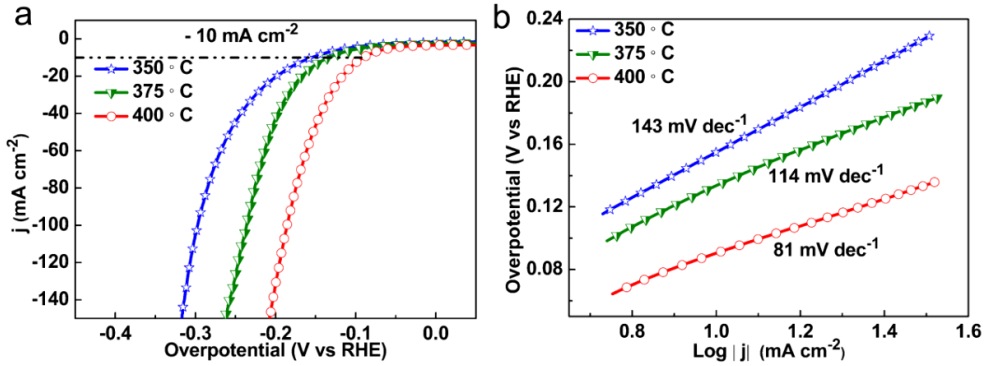


**Fig. S9** (a) Polarization curves of Co-Ni-Se/C/NF obtained at different temperatures for HER and (b) their corresponding Tafel plots.

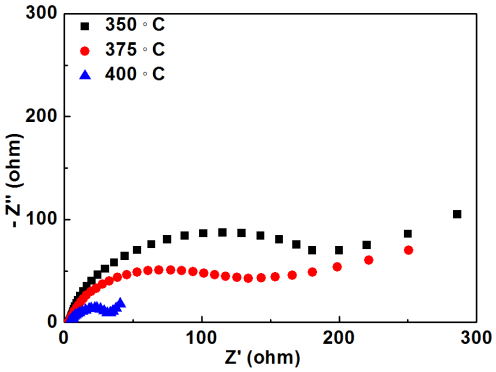


**Fig. S10** Nyquist plots of Co-Ni-Se/C/NF samples obtained at different temperature recorded in 1M KOH.

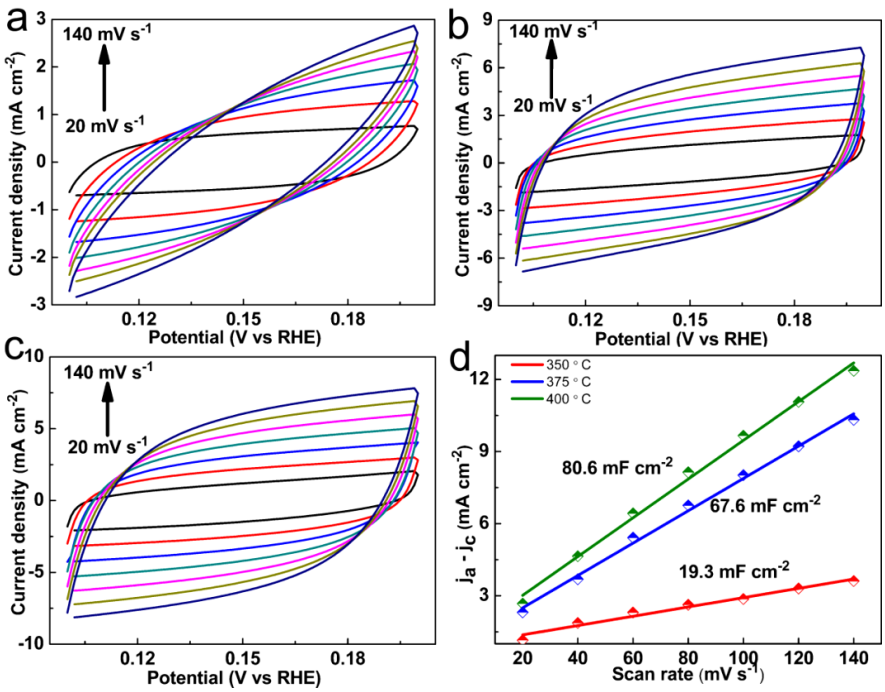


**Fig. S11** Electrochemical cyclic voltammetry curves at different scan rates for (a) Co-Ni-Se/C/NF-350, (b) Co-Ni-Se/C/NF-375, and (c) Co-Ni-Se/C/NF-400. (d) The difference in current density at 0.15 V vs RHE plotted against the scan rate.

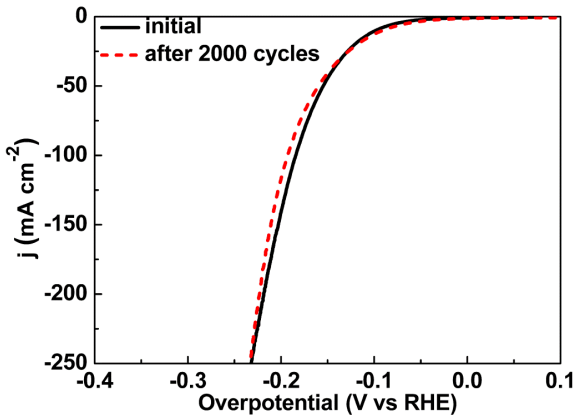


**Fig. S12** Polarization curves of Co-Ni-Se/C/NF before and after 2000 CV cycles at a scan rate of 3 mV $s^{-1}$ for HER.

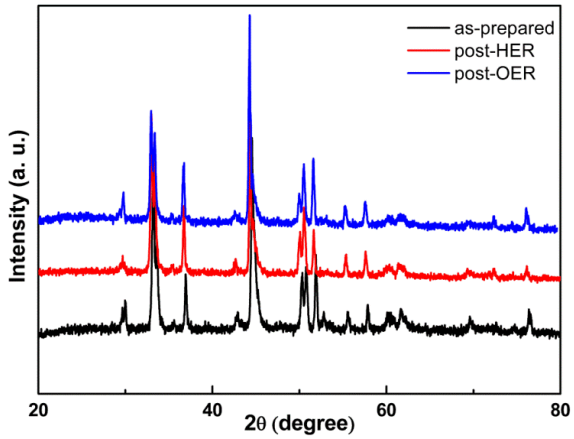


**Fig. S13** XRD patterns of the as-prepared, post-HER, and post-OER Co-Ni-Se/C/NF samples.

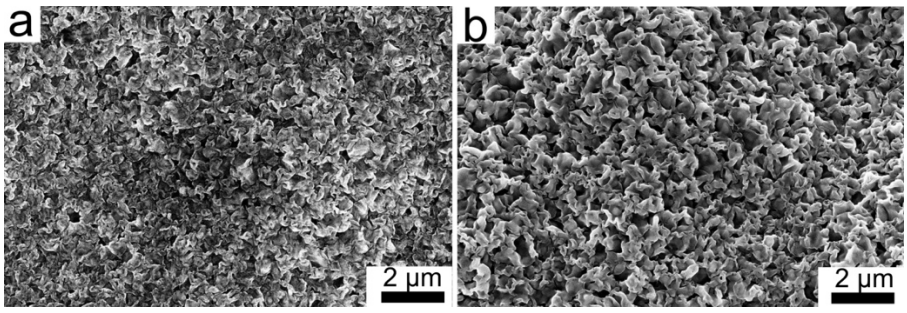


**Fig. S14** SEM images of the (a) post-HER and (b) post-OER Co-Ni-Se/C/NF samples.

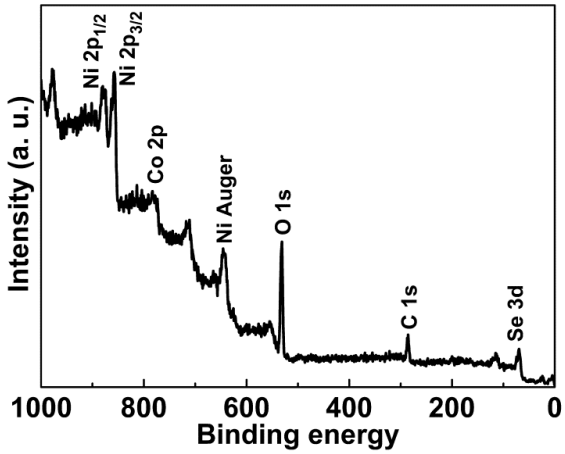


**Fig. S15** XPS survey spectrum of the Co-Ni-Se/C/NF after HER electrolysis.

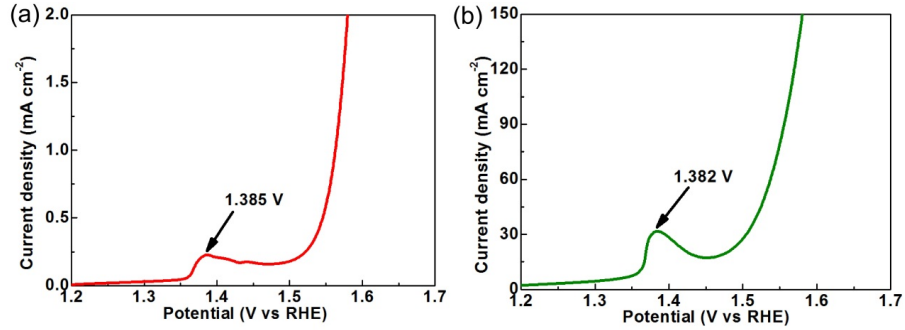


**Fig. S16** The polarization curves of (a) NF and (b) Co-Ni-Se/C/NF for OER.

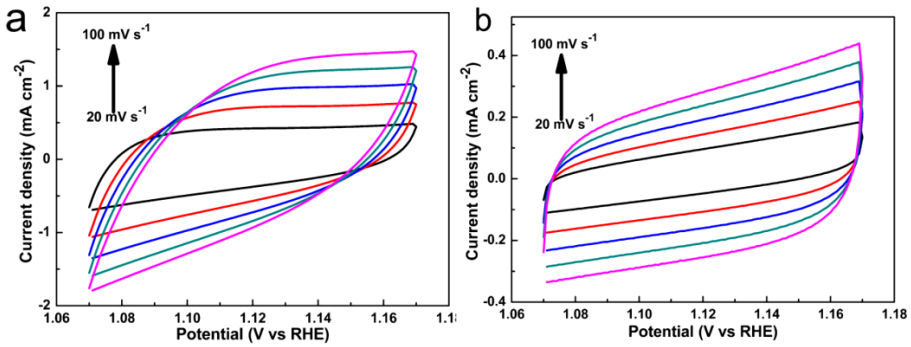


**Fig. S17** Electrochemical cyclic voltammetry curves at different scan rates for (a) NiCo-LDH/C/NF and (b) NF.

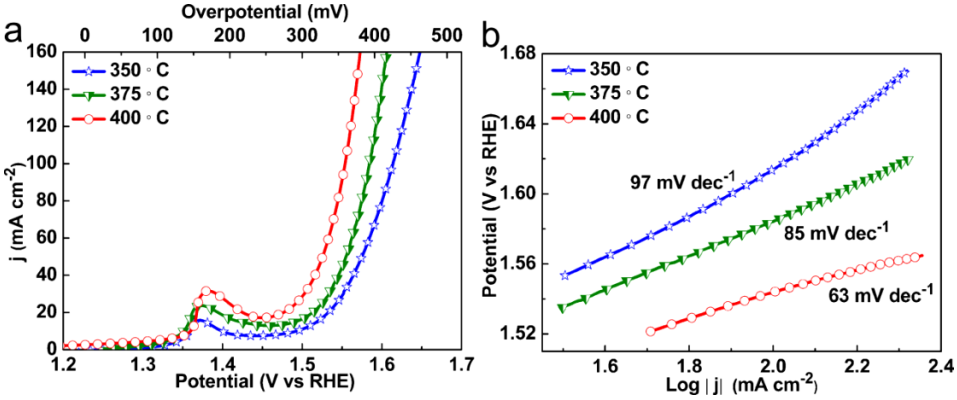


**Fig. S18** (a) Polarization curves of Co-Ni-Se/C/NF obtained at different temperatures for OER and (b) their corresponding Tafel plots.

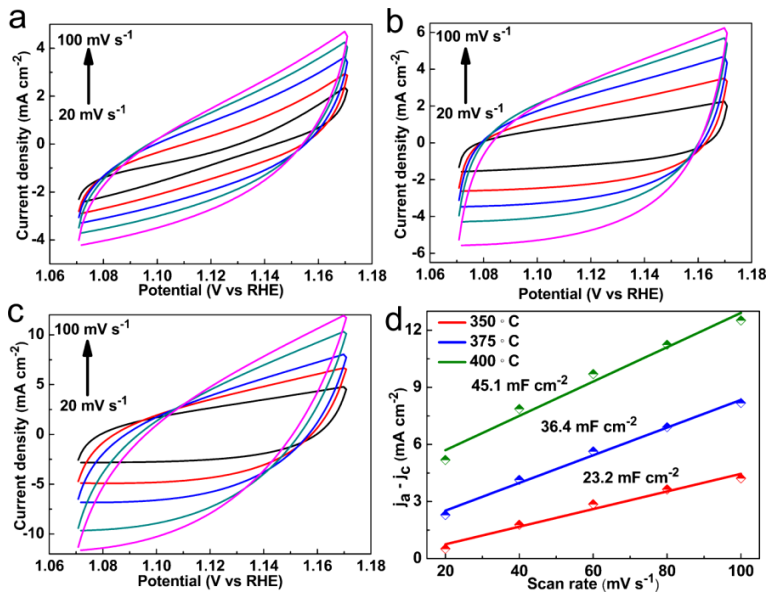


**Fig. S19** Electrochemical cyclic voltammetry curves at different scan rates of (a) Co-Ni-Se/C/NF-350, (b) Co-Ni-Se/C/NF-375, and (c) Co-Ni-Se/C/NF-400. (d) The difference in current density at 1.12 V vs RHE plotted against the scan rate.

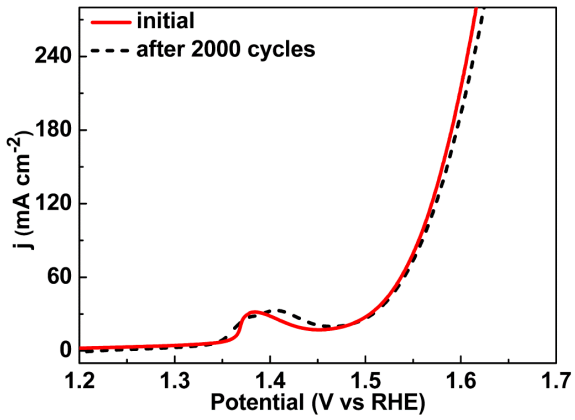


**Fig. S20** Polarization curves of Co-Ni-Se/C/NF before and after 2000 CV cycles at a scan rate of 0.5 mV $s^{-1}$ for OER.

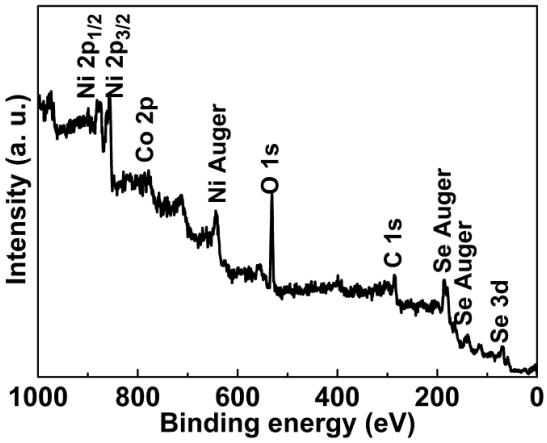


**Fig. S21** XPS survey spectrum of the Co-Ni-Se/C/NF after OER electrolysis.

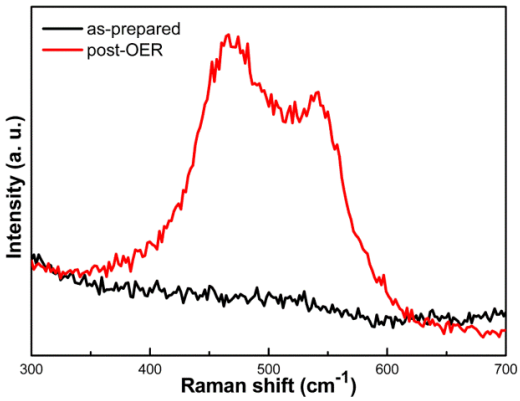


**Fig. S22** Raman spectra of the as-prepared Co-Ni-Se/C/NF and the post-OER sample.

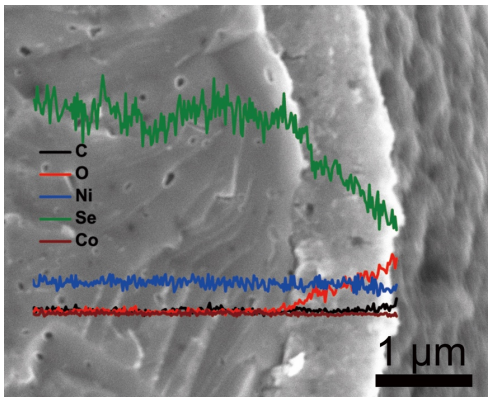


**Fig. S23** The cross-section SEM image of the post-OER electrode. The inset shows the EDS spectrum.

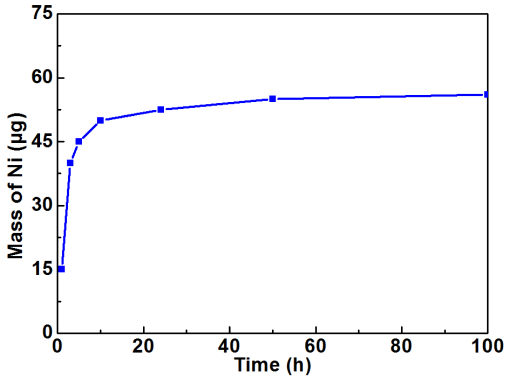


**Fig. S24** Corrosion rate of Ni detected from the electrolyte by ICP.

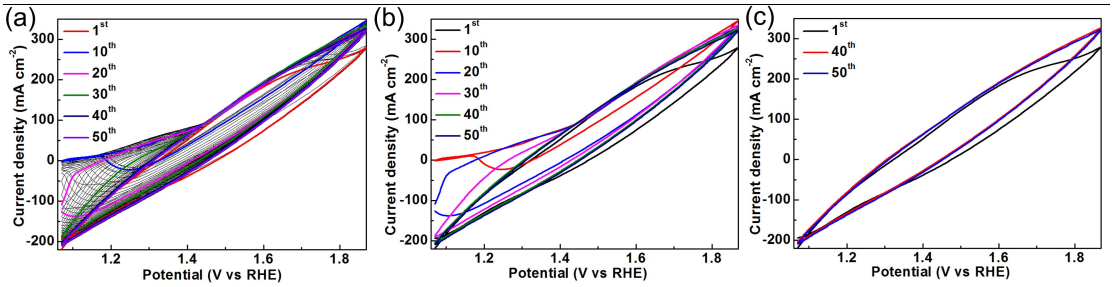


**Fig. S25** (a) The first 50 cyclic voltammetry curves and (b,c) the selected cycles at a scan rate of 50 mV $s^{-1}$.

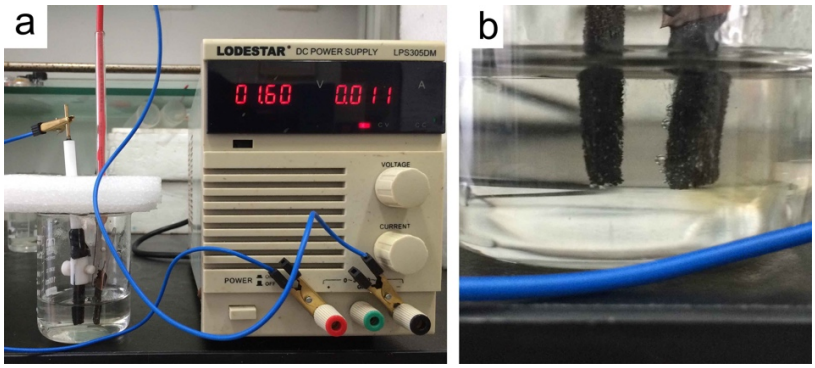


**Fig. S26** (a) Digital photograph showing the evolution of $H_2$ and $O_2$ gas from the electrodes at 1.6 V. (b) Enlarged view of the electrodes and obvious gas bubbles can be seen.

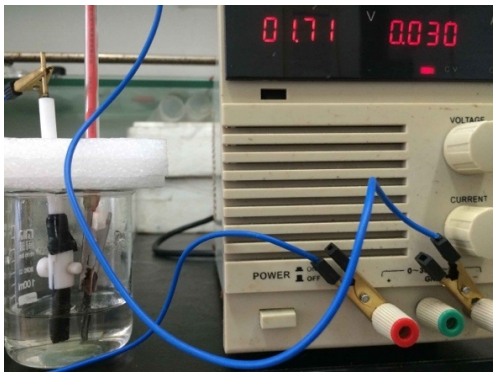


**Fig. S27** A digital photograph showing the evolution of $H_2$ and $O_2$ gas from the electrodes at 30 mA $cm^{-2}$.

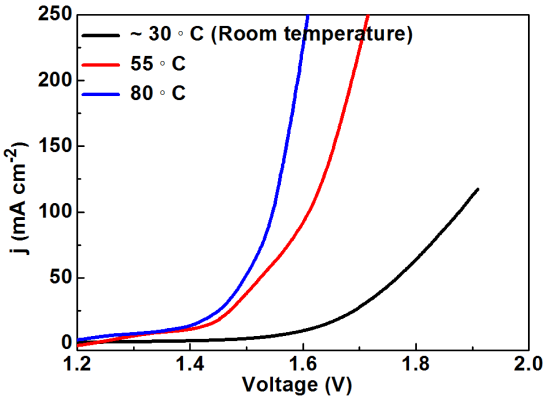


**Fig. S28** Polarization curves of Co-Ni-Se/C/NF at different temperatures for overall water-splitting.

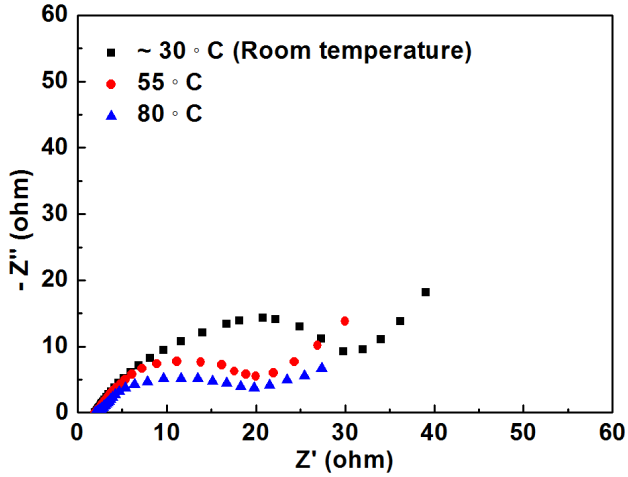


**Fig. S29** Nyquist plots of Co-Ni-Se/C/NF electrolyzer at different temperatures recorded in 1M KOH.

**Table S1.** ICP analysis on the composition of the samples obtained at different temperatures.

| Reaction temperature | Co:Ni:Se |
|---|---|
| 350 °C | 0.035 : 1 : 1.65 |
| 375 °C | 0.031 : 1 : 1.62 |
| 400 °C | 0.029 : 1 : 1.52 |
| 450 °C | 0.026 : 1 : 1.63 |
| 500 °C | 0.025 : 1 : 1.75 |

**Table S2.** Comparison of electrocatalytic HER activity of various nonprecious catalysts in 1.0 M KOH.

| Catalysts | *J* (mA $cm^{-2}$) | *η* (mV vs RHE) | Tafel slope (mV $dec^{-1}$) | reference |
|---|---|---|---|---|
| Co-Ni-Se/C/NF | -10<br>-20<br>-100 | 90<br>116<br>183 | 81 | This work |
| NiFe LDH/NF | -10<br>-20 | 210<br>250 | | *Science*, 2014, **345**, 1593-1596. |
| Co-P | -10<br>-20 | 94<br>115 | 42 | *Angew. Chem., Int. Ed.*, 2015, **54**, 6251-6254. |
| $Ni_5P_4$ film | -10 | 150 | 53 | *Angew. Chem.*, 2015, **127**, 12538-12542. |
| NiSe/NF | -10 | 96 | 120 | *Angew. Chem., Int. Ed.*, 2015, **54**, 9351-9355. |
| CoP/CC | -10<br>-100 | 209<br>>500 | 129 | *J. Am. Chem. Soc.*, 2014, **136**, 7587-7590. |
| *a*-CoSe/Ti | -10 | 121 | 84 | *Chem. Commun.*, 2015, **51**, 16683-16686. |
| $NiCo_2O_4$ hollow microcuboids | -10<br>-100 | 110<br>245 | 49.7 | *Angew. Chem., Int. Ed.*, 2016, **55**, 1-6. |
| $Ni_3Se_2$/CF | -10 | 100 | 98 | *Catal. Sci. Technol.*, 2015, **5**, 4954-4958. |
| $Ni_3Se_2$ nanoforest/NF | -10<br>-100 | 203<br>279 | 79 | *Nano Energy*, 2016, **24**, 103-110. |

Note: NF = Ni foam, CC = carbon cloth, *a* = amorphous.

**Table S3.** Comparison of electrocatalytic OER activity of various nonprecious catalysts in 1.0 M KOH.

| Catalysts | $J$ (mA cm$^{-2}$) | $\eta$ (mV vs RHE) | Tafel slope (mV dec$^{-1}$) | reference |
|---|---|---|---|---|
| Co-Ni-Se/C/NF | 30<br>50 | 275<br>300 | 63 | This work |
| NiSe/NF | 20 | 270 | 64 | *Angew. Chem., Int. Ed.*, 2015, **54**, 9351-9355. |
| Ni-P nanoplate | 10 | 300 | 64 | *Energy Environ. Sci.*, 2016, **9**, 1246-1250. |
| Ni–$Co_2$–O hollow nanosponges | 10 | 362 | 64.4 | *Chem. Commun.*, 2015, **51**, 7851-7854. |
| Co-P films | 10 | 345 | 47 | *Angew. Chem., Int. Ed.*, 2015, **54**, 6251-6254. |
| $Ni_5P_4$ film | 10 | 290 | 40 | *Angew. Chem.*, 2015, **127**, 12538-12542. |
| $NiCo_2O_4$hollow microcuboids | 10 | 290 | 53 | *Angew. Chem., Int. Ed.*, 2016, **55**, 1-6. |
| Co-doped $NiSe_2$ | 100 | 320 | 94 | *Nanoscale*, 2016, **8**, 3911-3915. |
| $Ni_3Se_2$/CF | 50 | 340 | 80 | *Catal. Sci. Technol.*, 2015, **5**, 4954-4958. |

Note: NF = Ni foam, CF = Cu foam.

**Table S4.** Comparison of electrocatalytic activity for overall water splitting of various nonprecious catalysts in 1.0 M KOH.

| Catalysts | *J* (mA cm$^{-2}$) | Cell voltage (V) | reference |
|---|---|---|---|
| Co-Ni-Se/C/NF | 10<br>30 | 1.6<br>1.71 | This work |
| NiSe/NF | 10<br>20 | 1.63<br>1.74 | *Angew. Chem., Int. Ed.*, 2015, **54**, 9351-9355. |
| NiFe LDH/NF | 10 | 1.7 | *Science*, 2014, **345**, 1593-1596. |
| $NiCo_2O_4$ hollow microcuboids | 10<br>20 | 1.65<br>1.74 | *Angew. Chem., Int. Ed.*, 2016, **55**, 1-6. |
| Co-doped $NiSe_2$ | 10 | 1.62 | *Nanoscale*, 2016, **8**, 3911-3915. |
| $Ni_3Se_2$/CF | 10 | 1.65 | *Catal. Sci. Technol.*, 2015, **5**, 4954-4958. |
| $Ni_3Se_2$ nanoforest/NF | 10 | 1.612 | *Nano Energy*, 2016, **24**, 103-110. |

Note: NF = Ni foam, CF = Cu foam.