

Supporting Information

Interfacial engineering of CoSe@NiFe heterostructure electrocatalyst for high-efficiency water and urea oxidation

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References

Experimental Section

S1. Chemicals and reagents

Analytical grade chemicals including selenium dioxide (SeO_2 , ≥ 99 wt.%), cobalt(II) chloride (CoCl_2 , ≥ 99 wt.%), potassium chloride (KCl , ≥ 99.5 wt.%), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, ≥ 98.5 wt.%), nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ≥ 98.5 wt.%), ethanol ($\text{C}_2\text{H}_6\text{O}$, ≥ 99.7 wt.%), acetone ($\text{C}_3\text{H}_6\text{O}$, ≥ 99.5 wt.%), hydrochloric acid (HCl , 36 ~ 38 wt.%) and potassium hydroxide (KOH , ≥ 85.0 wt.%) were ordered from Shanghai Aladdin Industrial Corporation and directly used in the experiments without further purification. Ni foam (NF, porosity, 97.2%; thickness, 1 mm) was purchased from KunShan Kunag Xun Electronics Co., Ltd. Platinum on carbon (Pt/C, 20 wt.%), ruthenium (IV) oxide (RuO_2 , ≥ 99.9 wt.%), and Nafion (5

wt.%) were obtained from Shanghai Macklin Biochemical Industrial Co., Ltd. The deionized water ($18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$) used in all experiments was purified by a Millipore system.

S2.Synthesis of catalysts

S2.1. Treatment of Ni foam

Prior to usage, the NF ($1 \text{ cm} \times 2 \text{ cm}$) was cleaned by ultrasonication in acetone and 3 M HCl for 15 min each to remove the surface oxide layer, then rinsed several times in water and ethanol, and finally dry in a vacuum oven at 60°C for 2 h.

S2.2. Synthesis of the CoSe/NF

All electrochemical deposition was conducted using a three-electrode setup of the electrochemical workstation (CHI 760E, Chenhua Instruments, China). CoSe/NF was prepared by the in-situ electrodeposition method. The cleaned NF served as the working electrode; a mercury oxide electrode (Hg/HgO) and a graphite rod were used as the reference and counter electrode, respectively. The electrolyte was attained by dissolving 1.8 mmol SeO_2 , 1.6 mmol CoCl_2 , and 9.0 mmol KCl in 60 mL DI water. The electrodeposition process was performed at a constant potential of -0.56 V versus the Hg/HgO for 30 min. After deposition, the above sample was carefully washed several times with water and ethanol before drying in an oven at 60°C . In addition, CoSe-15/NF and CoSe-45/NF were prepared in the same way, except the different electrodeposition time (15 and 45 min).

S2.3. Synthesis of CoSe@NiFe/NF and NiFe/NF electrodes

The CoSe@NiFe/NF and NiFe/NF were fabricated using a facile hydrothermal method. First, 0.75 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 30 mL H_2O and stirred at room temperature until form a transparent light-yellow solution. Then, the homogeneous solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave with the prepared CoSe/NF as a template and heated to 180 °C and maintain for 1 hour. Finally, the obtained product was picked out and washed several times with deionized water and ethanol before drying in a vacuum oven for 6 h. In addition, time-dependent experiments were carried out. Several CoSe@NiFe-X/NF ($x = 30$ and 90) products were obtained using a similar synthetic method with reaction time of 30 and 90 min, and the prepared samples were denoted as CoSe@NiFe-30/NF and CoSe@NiFe-90/NF, respectively. As for NiFe/NF, the identical procedure as for CoSe@NiFe/NF is applied, except that freshly treated NF is used as a template in the hydrothermal reaction.

S2.4. Synthesis of $\text{Ni}(\text{OH})_2/\text{NF}$ and CoSe@ $\text{Ni}(\text{OH})_2/\text{NF}$ electrodes

The $\text{Ni}(\text{OH})_2/\text{NF}$ and CoSe@ $\text{Ni}(\text{OH})_2/\text{NF}$ electrodes were synthesized similarly to NiFe/NF and CoSe@NiFe/NF, except the added transition metal precursors, i.e., using 0.75 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ instead of 0.75 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to prepare NiFe/NF and CoSe@NiFe/NF.

S2.5. Synthesis of Fe₂O₃/NF and CoSe@Fe₂O₃/NF electrodes

Fe₂O₃/NF was synthesized via two steps, similar to what was reported by Cheng et al [1]. Specifically, a piece of fresh NF was immersed in a solution of iron nitrate nonahydrate (0.15 M) and dried at room temperature. It was then thermally treated in a sealed vacuum quartz tube at 300 °C for 1 hour to obtain Fe₂O₃/NF. Furthermore, we prepared other catalysts with different templates, replacing the freshly treated NF with CoSe/NF as the template which was designated as CoSe@Fe₂O₃/NF.

S2.6. Synthesis of RuO₂/NF and Pt/C/NF electrodes

The RuO₂/NF and Pt/C/NF electrodes were fabricated by casting powder on a nickel foam support, which is then protected with a polymer binder (Nafion). Briefly, 14 mg of RuO₂ (or Pt/C) was dispersed under sonication in the 20 µL of 5.0 wt.% Nafion and 480 µL of anhydrous ethanol to form a homogeneous catalyst ink. Then 50 µL of the above ink was drop-cast onto a geometrical surface area of 0.2 cm² NF support with an average mass loading of 7 mg cm⁻².

S3.Characterization

The chemical compositions and microstructures of the catalysts were characterized with different analytical methods. The X-ray diffraction (XRD) was carried out on Bruker Eco D8-Advance X-ray diffractometer with Cu K α radiation source ($\lambda = 1.5418 \text{ \AA}$) to analyze the crystal phases of as-obtained samples. The Raman spectroscopy was recorded on a confocal micro-Raman spectrometer (LabRAM HR

Evolution, Horiba Jobin Yvon) with a 532 nm wavelength laser excitation. The morphology and structure of the electrocatalysts were characterized via the field-emission scanning electron microscopy (FESEM) (Hitachi SU8010), Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy images (HRTEM) and corresponding selected area electron diffraction (SAED) images were performed using the FEI Talos F200X instrument. X-ray photoelectron spectroscopy (XPS; Thermo Scientific K-Alpha) was conducted to identify the surface chemical compositions and electronic interactions. The specific surface area of catalysts was measured by utilizing the Brunauer-Emmett-Teller (BET) method. The hydrophilic characterization of the samples was tested on the JY-82B KRUSS DSA contact angle measuring instrument. Liquid products were characterized via IC (Thermo Fisher Scientific ICS-5000+).

S4. Electrochemical measurements

All electrochemical performance parameters were acquired by a CHI 660E electrochemistry workstation (Chenhua Instruments, China) using a three-electrode system at room temperature. In our case, an as-synthesized sample ($1 \times 2 \text{ cm}^2$) was used as the working electrode, a mercury oxide electrode (Hg/HgO) was used as the reference electrode, and the counter electrode was a graphite rod electrode. The overpotentials of OER, UOR, MOR, and EOR were obtained by cyclic voltammogram (CV) curves and linear sweep voltammetry (LSV) measurements at a scan rate of 5

$\text{mV} \cdot \text{s}^{-1}$. The electrolytes for OER, UOR, MOR, and EOR tests were 1 M KOH, 1 M KOH with 0.5 M urea, 1 M KOH with 0.5 M methanol, and 1 M KOH with 0.5 M ethanol, respectively. All potentials measured vs. Hg/HgO were converted into the reversible hydrogen electrode (RHE) as: $E \text{ vs. RHE} = E \text{ vs. Hg/HgO} + 0.098 + 0.059 \times \text{pH}$. All the LSV polarization curves were corrected during the test by manual iR compensation using current and electrolyte resistance. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 100 kHz to 1 Hz with an amplitude potential of 5 mV. The Tafel slope was obtained according to the Tafel equation: $\eta = b \log j + a$, where η is the overpotential. b , j , and a represent the Tafel slope, the corresponding current density, and the intercept, respectively. The long-term stability test was implemented by the chrono-potentiometric method (i-t) at certain potentials.

S4.1. Calculation of ECSA

Cyclic voltammetry (CV) was employed to probe the electrochemical double layer capacitance (C_{dl}) of different samples in 1 M KOH solution at non-Faraday overpotentials to evaluate the effective electrode surface area. The working electrode was subjected to 20 cyclic voltammetry cycles until the current was stabilized and then data collection was performed. CV curves were performed at seven various scan rates (20, 40, 60, 80, 100, 120, and 140 $\text{mV} \cdot \text{s}^{-1}$) over a voltage range of 0.56 - 0.78 V vs. RHE, and then form the resulting $|j_{\text{anodic}} - j_{\text{cathodic}}|/2$ vs. RHE plots by extracting the

slope. Accordingly, the C_{dl} of the various samples can be determined, which is expected to be linearly proportional to the effective surface area. The electrochemically active surface area (ECSA) can be further estimated based on the C_{dl} value. The specific capacitance is $40 \mu\text{F} \cdot \text{cm}^{-2}$ and the ECSA of the catalyst was following the equations:

$$ECSA = \frac{C_{dl}}{40}$$

S4.2. Calculation of the turnover frequency (TOF)

The turnover frequency (TOF) was evaluated by using the following equation:

$$TOF = \frac{|j| \times N_A}{m \times F \times n}$$

where j stands for current density at defined overpotential; N_A denotes the Avogadro number; F is Faraday constant ($96500 \text{ C} \cdot \text{mol}^{-1}$). A $1/m$ factor is introduced to take into account the different values of the electrons consumed to produce a gas molecule from water (i.e., OER-4 electrons and UOR-6 electrons). The number of surface active sites (n) can be calculated with the formula: $n = Q/(1 \times 1.602 \times 10^{-19})$, and assume a one-electron transfer process for both reduction and oxidation herein. While charge (Q) can be derived from the reductive negative scan peak areas of cyclic voltammetry (CV) curves at a specific scan rate.

S4.3. Calculation of specific activity and mass activity

The specific activities ($\text{mA} \cdot \text{cm}^{-2}$) of the catalysts for the OER can be assessed by normalizing the measured kinetic currents by ECSA (or BET surface area). In addition,

the mass activity ($\text{mA} \cdot \text{mg}^{-1}$) of the electrode catalyst can be calculated from the catalyst loading amount (m , $\text{mg} \cdot \text{cm}^{-2}$) obtained by the differential weight method (i.e., weighing the mass of NF before and after the synthesis reaction) and the measured current density (j , $\text{mA} \cdot \text{cm}^{-2}$) at a given potential. The equation used is as follows:

$$\text{specific activity} = \frac{j}{\text{ECSA}}$$

$$\text{specific activity} = \frac{j}{10mS_{\text{BET}}}$$

$$\text{mass activity} = \frac{j}{m}$$

S5. Potential-dependent in situ Raman spectroscopy

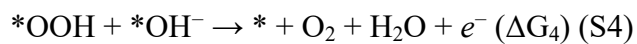
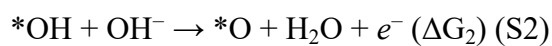
In situ Surface Enhanced Raman Spectroscopy (SERS) was performed with a confocal Raman microscope (Horiba Jobin Yvon HR evolution system) with $50 \times$ Olympus microscope objective. The excitation source used was a 10 mW (532 nm). All in situ Raman measurements were adjusted potentials by an electrochemical workstation. The integration time is 10 s. The working electrode was perpendicular to the laser. Using Pt tablet served as the counter electrode. A Hg/HgO electrode served as the reference electrode. To study the surface reconstruction process, all samples would not be subjected to CV activation as for LSV measurement.

S6. Theoretical calculation details

In this study, all calculations were performed by using density functional theory (DFT) with the Vienna ab-initio simulation package (VASP). The projector augmented wave (PAW) potentials were adopted to treat the electron-ion interaction. We applied

the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) function to characterize the exchange and correlation potential. The DFT-D3 method of Grimme was employed to correct the intermolecular van der Waals (vdW) interaction. A heterogeneous interface model of the CoSe (101) @ NiFeOOH (101) for OER was established. The plane wave energy cutoff was set as 450 eV. The first Brillouin zone was sampled in the Monkhorst-Pack grid. The $8 \times 5 \times 1$ k-point mesh is used for the calculations. The energy (converged to 1.0×10^{-3} eV/atom) and force (converged to 0.05 eV/Å) were set as the convergence criterion for geometry optimization. To avoid interaction between the adjacent layers, a vacuum layer of approximately 25 Å was set along the z axis.

The OER performance of the electrocatalysts was determined by the adsorption free energy change (ΔG_{ads}) of the intermediates OH, O, OOH and O₂ in alkaline media. Eq. (S1) – (S4) were employed to represent the mechanism of OER, as the four-electron transfer reaction pathway in the calculation:



Here, the * denotes the catalytic active sites on the surface of the samples, and the oxygen-containing groups (*OH, *O, and *OOH) represent the adsorbed intermediates on the active sites. The free energy of the adsorbed intermediates was calculated based on the standard hydrogen electrode, defined as Eq. (S2), where E, ZPE, ΔH_t , T, and S represented the total energy, zero-point energy, the change in the heat capacity, thermal

correction energy (298.15 K), and entropy, respectively. The Gibbs free energy in the OER process were obtained according to the formulas Eq. (S5) - S(12).

$$G = E + \text{ZPE} + \Delta H_t - T \cdot S \quad (\text{S5})$$

$$\text{ZPE} = \frac{h}{2} \sum_{i=1}^{3N} V_i \quad (\text{S6})$$

$$\Delta H_t = \sum_{i=1}^{3N} \frac{hV_i}{e^{\frac{hV_i}{k_B T} - 1}} \quad (\text{S7})$$

$$T \cdot S = \sum_{i=1}^{3N} \left[\frac{hV_i}{e^{\frac{hV_i}{k_B T} - 1}} - k_B T \ln \left(1 - e^{-\frac{hV_i}{k_B T}} \right) \right] \quad (\text{S8})$$

$$\Delta G_1 = G(*\text{OH}) + \frac{1}{2} G(\text{H}_2) - G(\text{H}_2\text{O}) - G(*) - eU - k_B T \ln(10) \times \text{pH} \quad (\text{S9})$$

$$\Delta G_2 = G(*\text{O}) + \frac{1}{2} G(\text{H}_2) - G(*\text{OH}) - eU - k_B T \ln(10) \times \text{pH} \quad (\text{S10})$$

$$\Delta G_3 = G(*\text{OOH}) + \frac{1}{2} G(\text{H}_2) - G(\text{H}_2\text{O}) - G(*\text{O}) - eU - k_B T \ln(10) \times \text{pH} \quad (\text{S11})$$

$$\Delta G_4 = 4.92 - \sum_{i=1}^3 \Delta G_i(0,0) - eU - k_B T \ln(10) \times \text{pH} \quad (\text{S12})$$

where U, e, and k_B are the applied electrode potential, the transferred charge and the Boltzmann constant, respectively. The theoretical overpotential (η) was defined as below:

$$\eta = \max\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\} / e - 1.23 \text{V} \quad (\text{S13})$$

Here, 1.23 V represents the balanced potential.

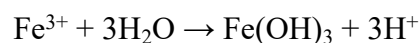
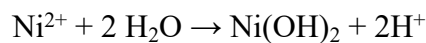
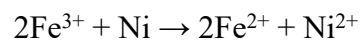
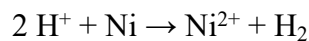
S7. Overall water splitting and urea-assisted water splitting

The overall water splitting and urea-assisted water splitting were evaluated in 1 M KOH or 1 M KOH containing 0.5 M urea using a two-electrode set-up. The synthetic CoSe@NiFe/NF and Pt/C/NF were used as an anode electrode and cathode electrode, respectively. The mass loading of the above two electrodes was approximately 7 mg·cm⁻². The polarization curves were obtained at a scan rate of 5 mV·s⁻¹.

Figures and Tables

Exploration of formation mechanism

A possible formation mechanism regarding the CoSe@NiFe/NF electrode is proposed, and the corresponding chemical formula are shown below:



Previous reports have demonstrated that metal hydroxide nanostructures can be spontaneously formed on NF substrates after immersing them in an acidic solution [2]. In our work, at the initial stage, the NF surface is etched to form Ni²⁺ ions, which are readily adsorbed on the electrodeposited CoSe/NF, under the combined effect of the acidity of Fe(NO₃)₃·9H₂O (Fig. S-PH paper) and the sufficient oxidative property of Fe³⁺. Then with the increase of temperature in the hydrothermal process, a lot of

oxygen-rich functional groups (-OH and -O) inevitably exist on the surface of CoSe nanosheets. Moreover, due to their analogous solubility product constants [3], Fe^{3+} ions and Ni^{2+} ions will undergo co-hydrolysis and start to combine with OH^- to form $\text{Ni}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$. $\text{Fe}(\text{OH})_3$ is susceptible to thermal decomposition by water loss at relatively high temperatures (180 °C) to form Fe_2O_3 . And ultimately, a self-supported multi-heterojunction interface electrocatalyst of CoSe@NiFe anchored on NF will form.

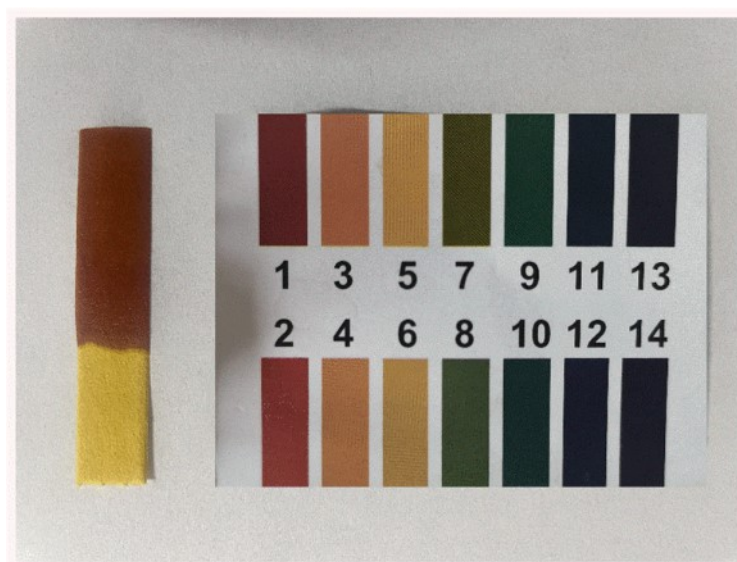


Fig. S1. Digital images of pH paper.

The solution containing $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ has a yellow color (Fig. S2a), subsequently, the homogeneous solution was transferred to a Teflon-steel autoclave heated to 180°C and kept for 1 h. At the end of the reaction, the residue turned red (Fig. S2b). Following the above analysis, we can infer that the red residue is constituted by aggregated Fe_2O_3 nanoparticles.

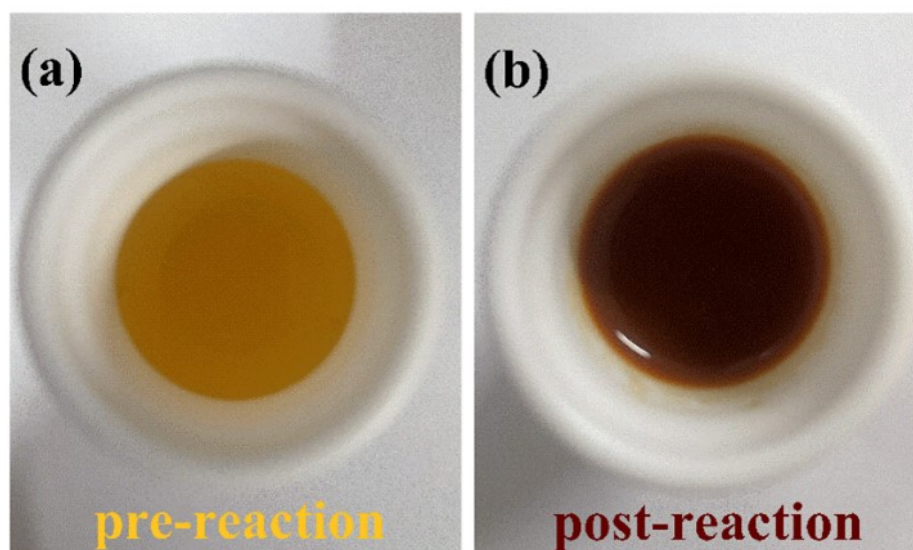


Fig. S2. Digital images of a homogeneous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (a) before and (b) after the hydrothermal reaction.

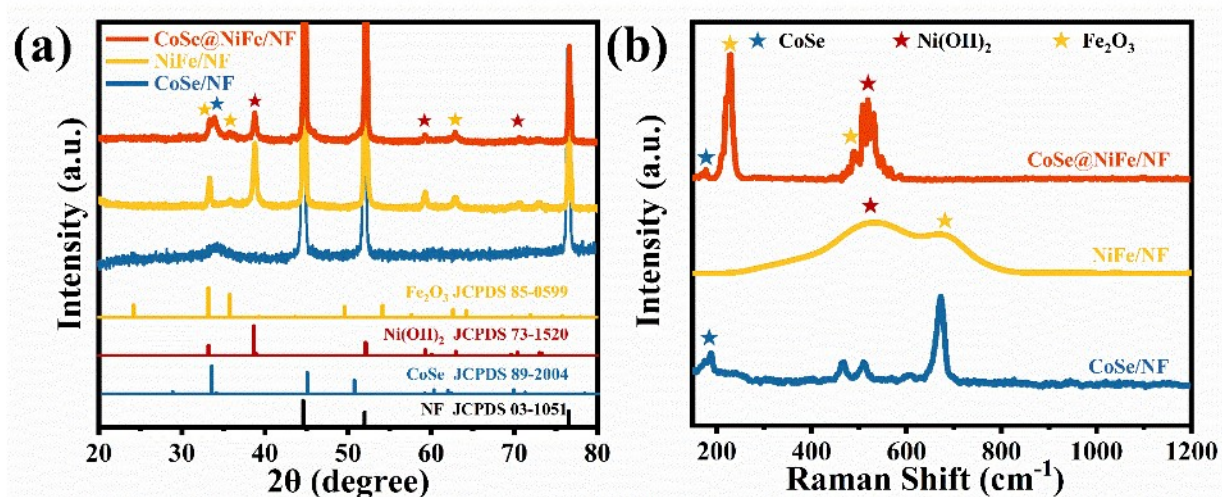


Fig. S3. (a) XRD pattern and (b) Raman spectra for CoSe@NiFe/NF and contrast samples.

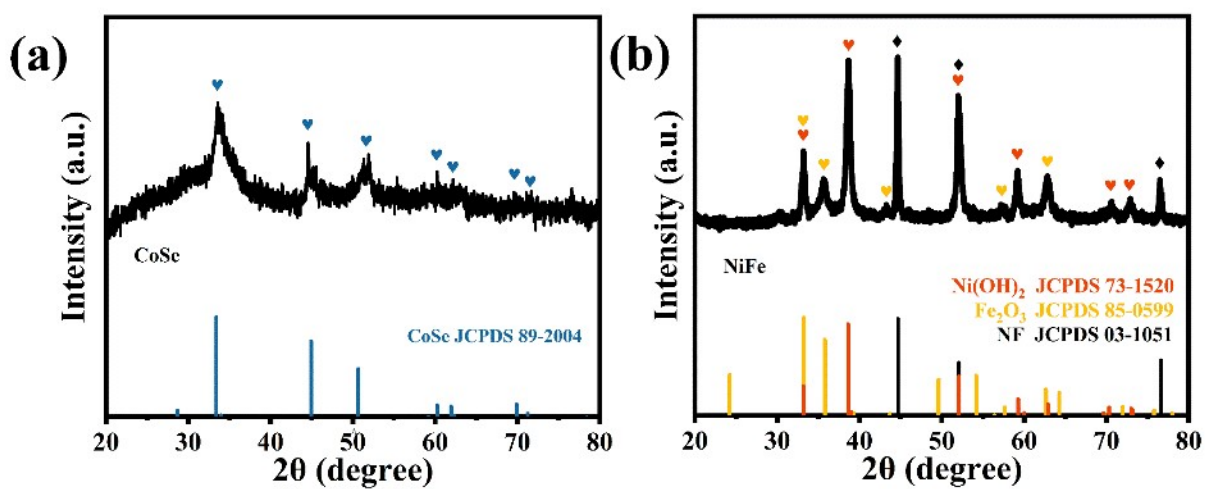


Fig. S4. XRD patterns of (a) CoSe and (b) NiFe peeled off from NF.

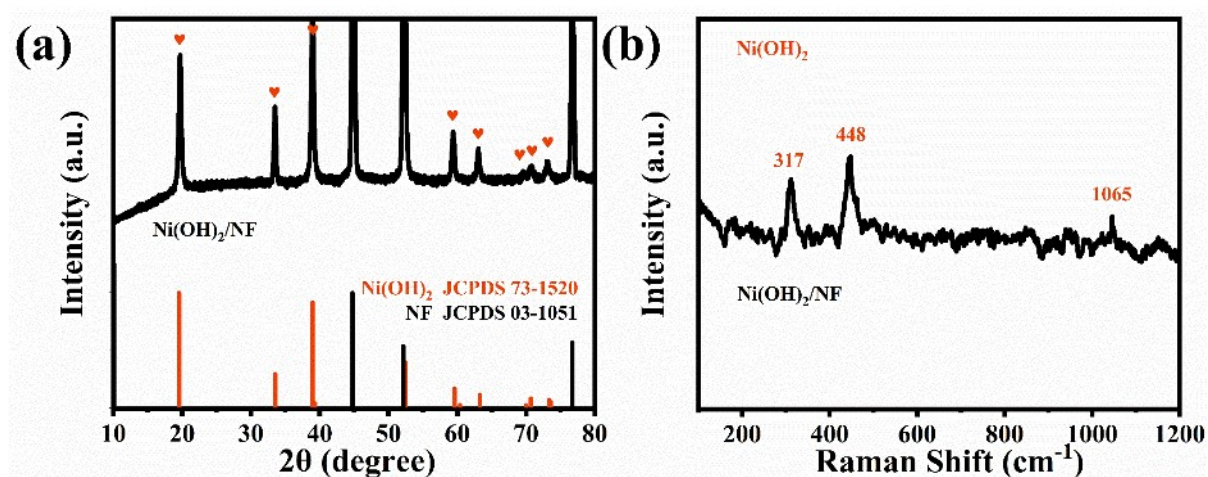


Fig. S5. (a) XRD pattern and (b) Raman spectra for $\text{Ni(OH)}_2/\text{NF}$.

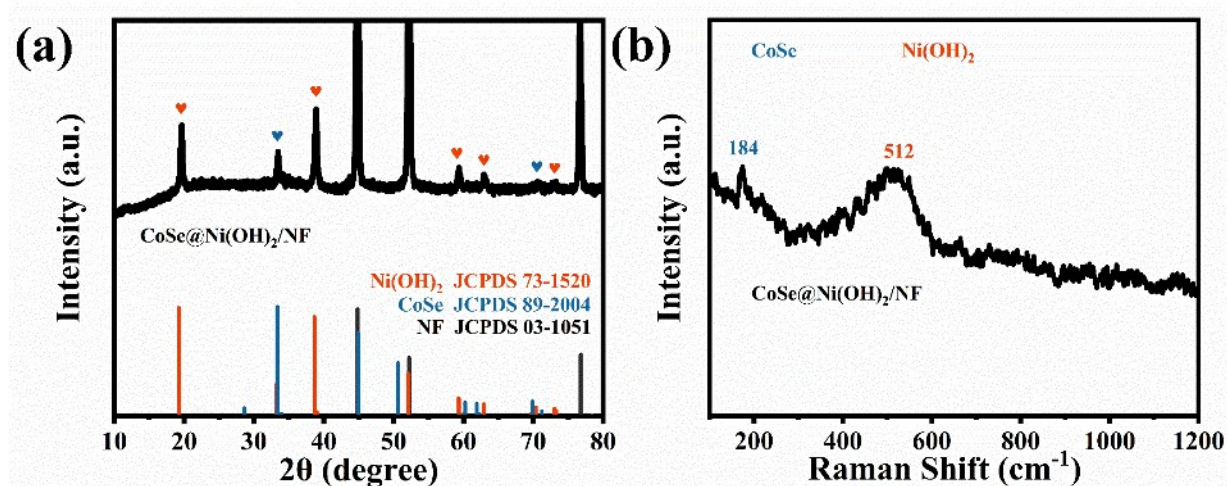


Fig. S6. (a) XRD pattern and (b) Raman spectra for $\text{CoSe@Ni(OH)}_2/\text{NF}$.

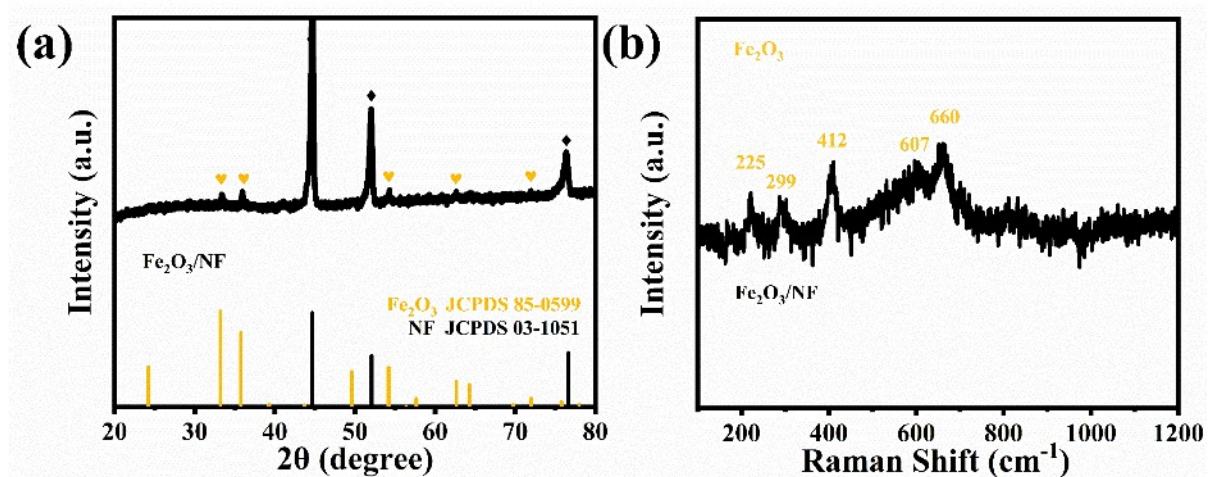


Fig. S7. (a) XRD pattern and (b) Raman spectra for $\text{Fe}_2\text{O}_3/\text{NF}$.

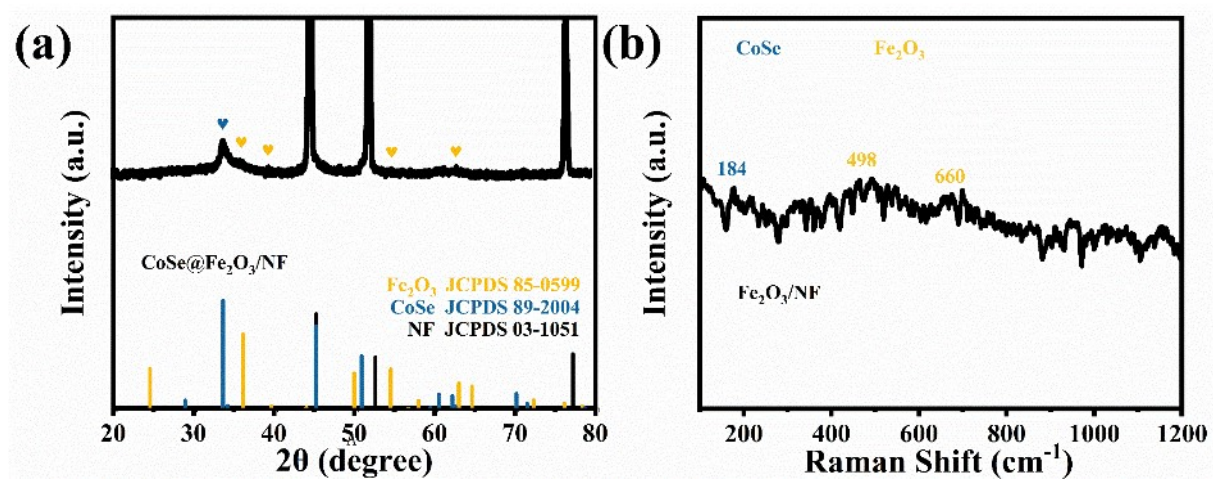


Fig. S8. (a) XRD pattern and (b) Raman spectra for $\text{CoSe@Fe}_2\text{O}_3/\text{NF}$.

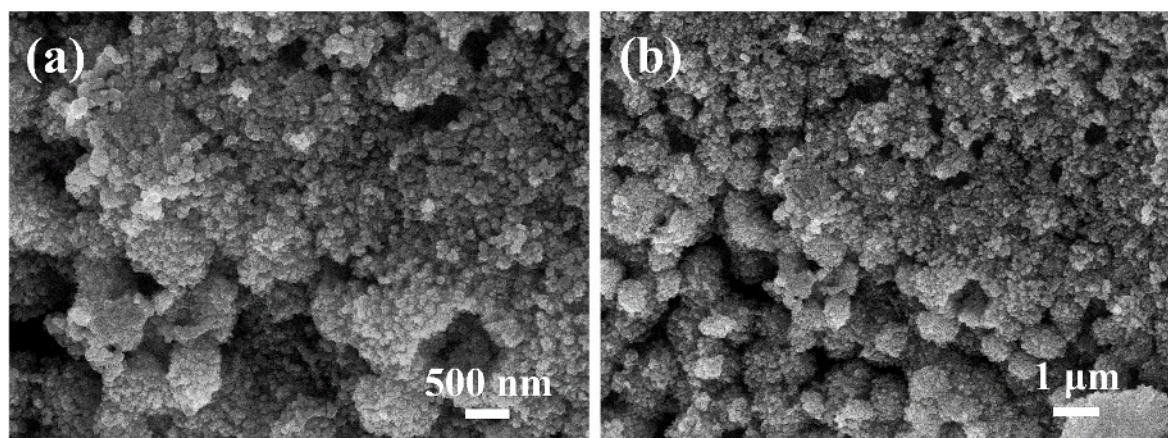


Fig. S9. (a-b) SEM images of CoSe@NiFe/NF at different magnifications.

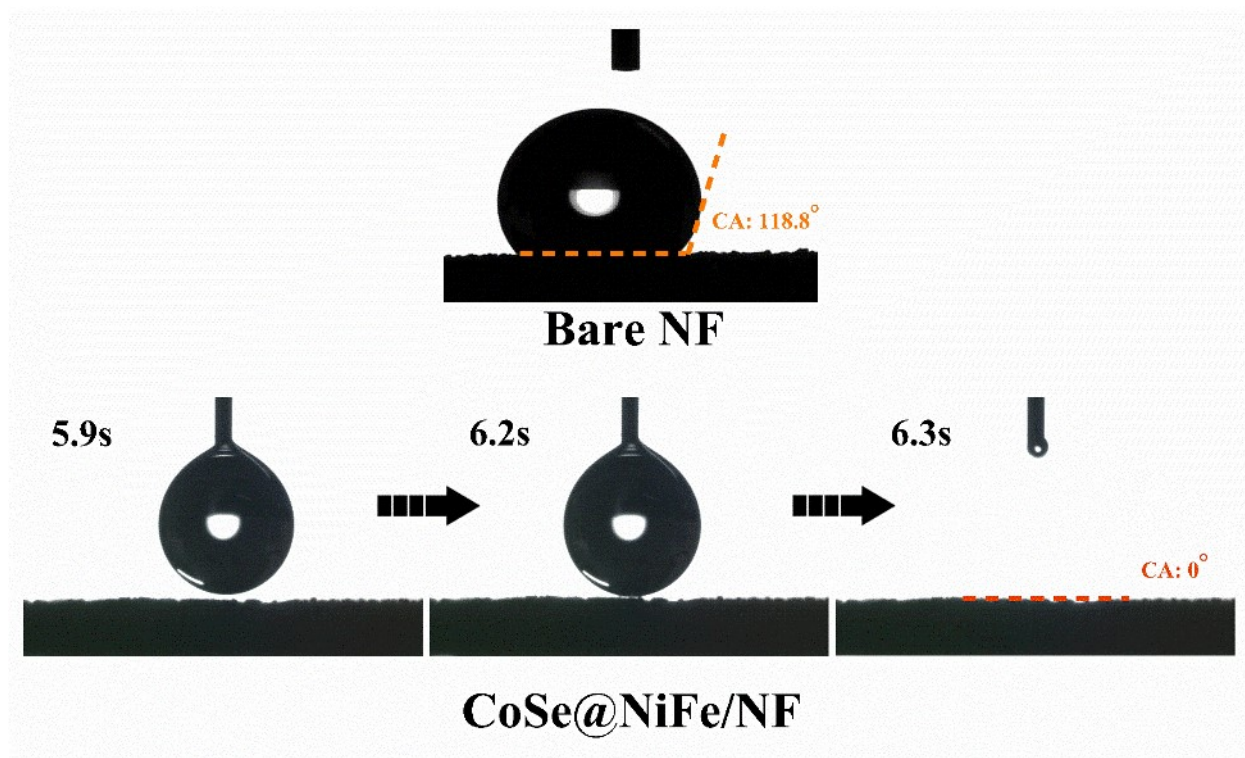


Fig. S10. The pictures of dynamic contact angle of CoSe@NiFe/NF.

The contact angle of bare NF is about 118.8° due to its hydrophobicity. When CoSe@NiFe was loaded onto the NF, the surface wettability is greatly improved, and the corresponding liquid-solid contact angle reduces to 0° . Remarkably, the water droplet immediately diffused and absorbed in the pores as soon as in contact with the CoSe@NiFe/NF surface, demonstrating that the electrode surface became superhydrophilic, which could effectively ameliorate the surface wettability and rapidly release gases to obtain excellent catalytic efficiency.

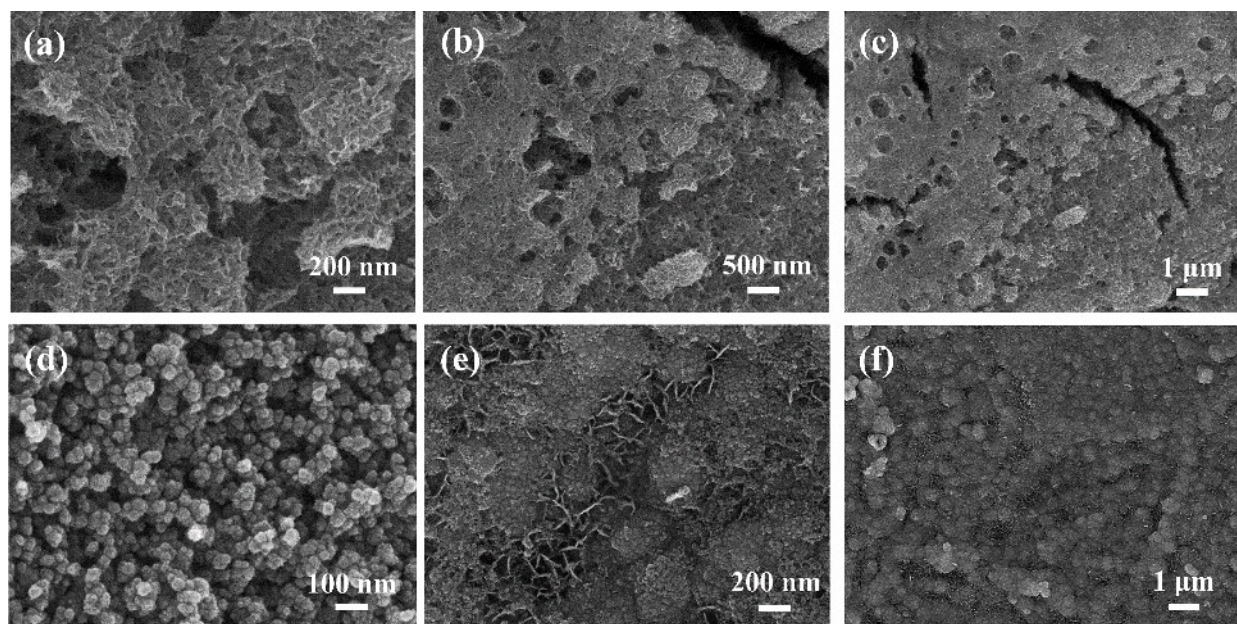


Fig. S11. (a-c) SEM images of CoSe on NF and (d-f) SEM images of NiFe on NF.

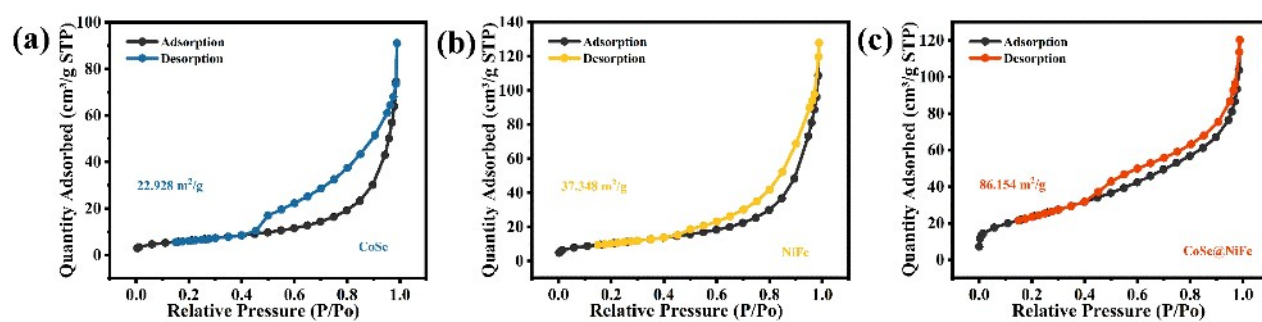


Fig. S12. The N_2 adsorption-desorption isotherms of (a) CoSe, (b) NiFe, and (c) CoSe@NiFe.

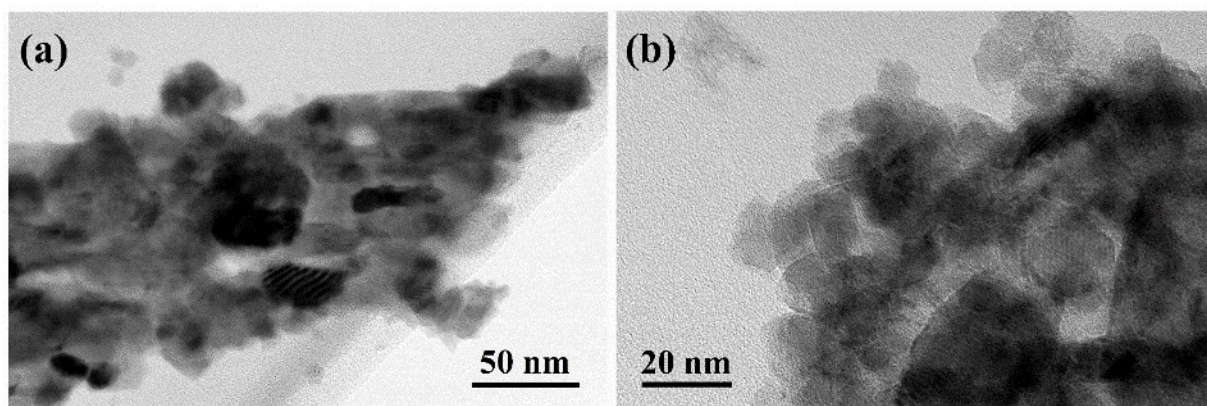


Fig. S13. TEM images of as-prepared CoSe@NiFe/NF.

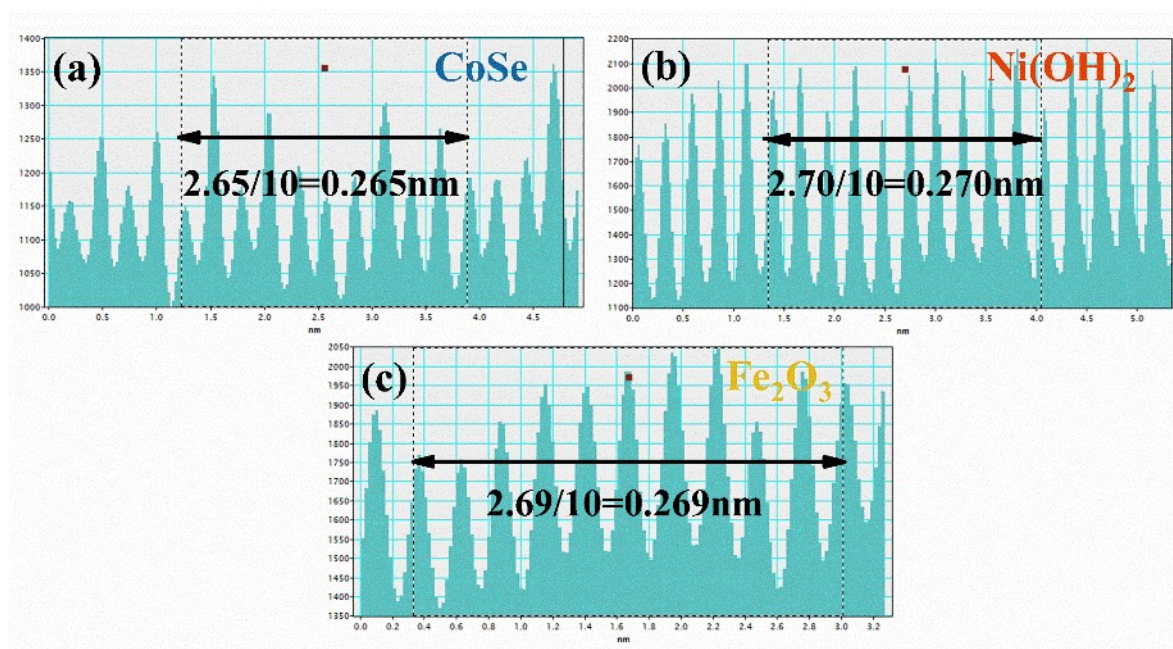


Fig. S14. (a-d) Corresponding intensity profile plots for measuring the lattice spacings in Fig. 2f-h.

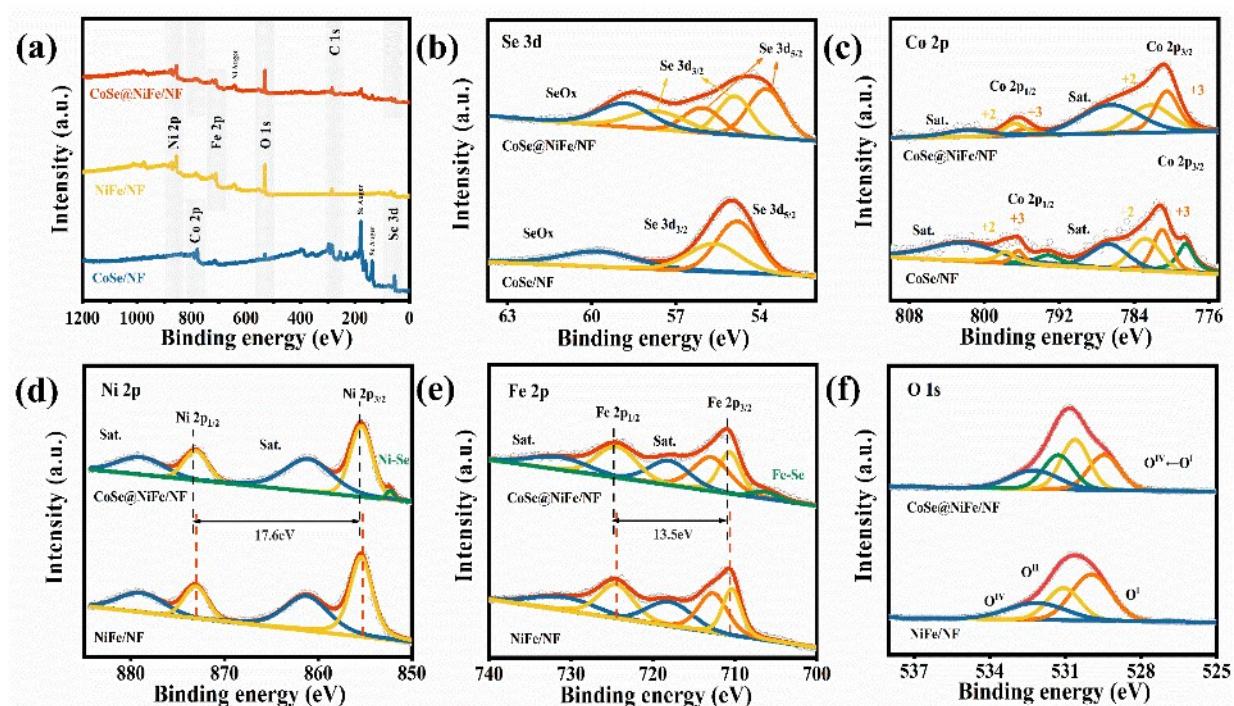


Fig. S15. Electronic structure recognition. (a) Full XPS spectra and high-resolution XPS spectra of (b) Se 3d, (c) Co 2p, (d) Ni 2p, (e) Fe 2p, and (f) O 1s of CoSe@NiFe/NF and contrast samples.

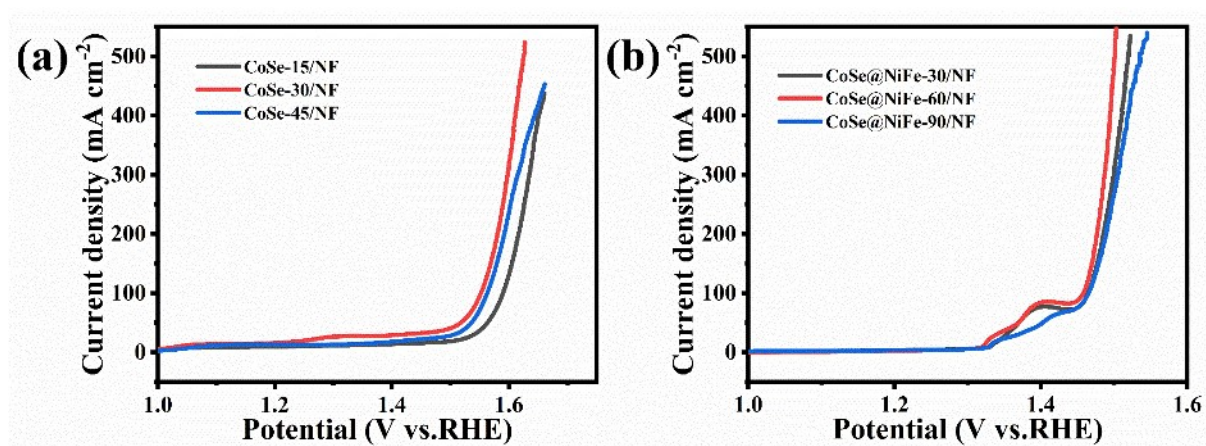


Fig. S16. Polarization curves of (a) CoSe/NF and (b) CoSe@NiFe/NF with different reaction time.

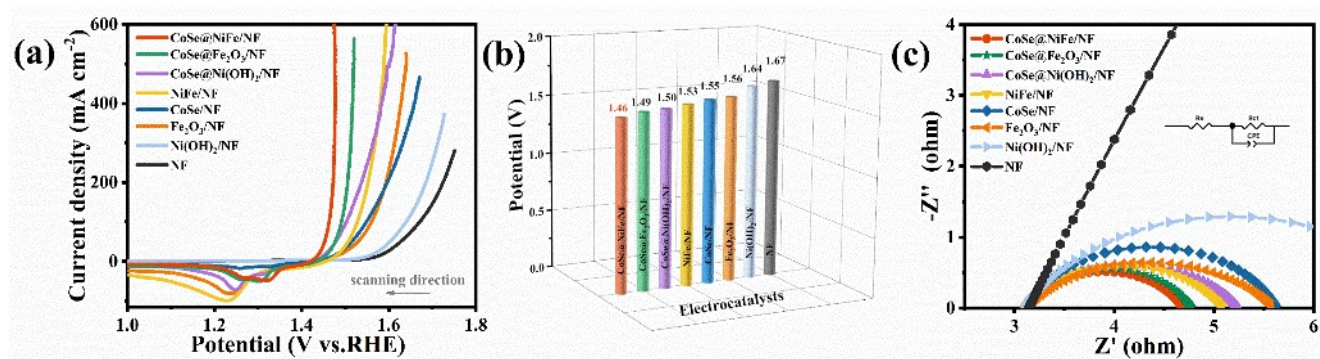


Fig. S17. OER property (a) LSV curves of CoSe@NiFe/NF and contrast catalysts. (b) Comparison of overpotentials at 100 mA·cm⁻² between CoSe@NiFe/NF and contrast catalysts. (c) Electrochemical impedance spectroscopy (EIS).

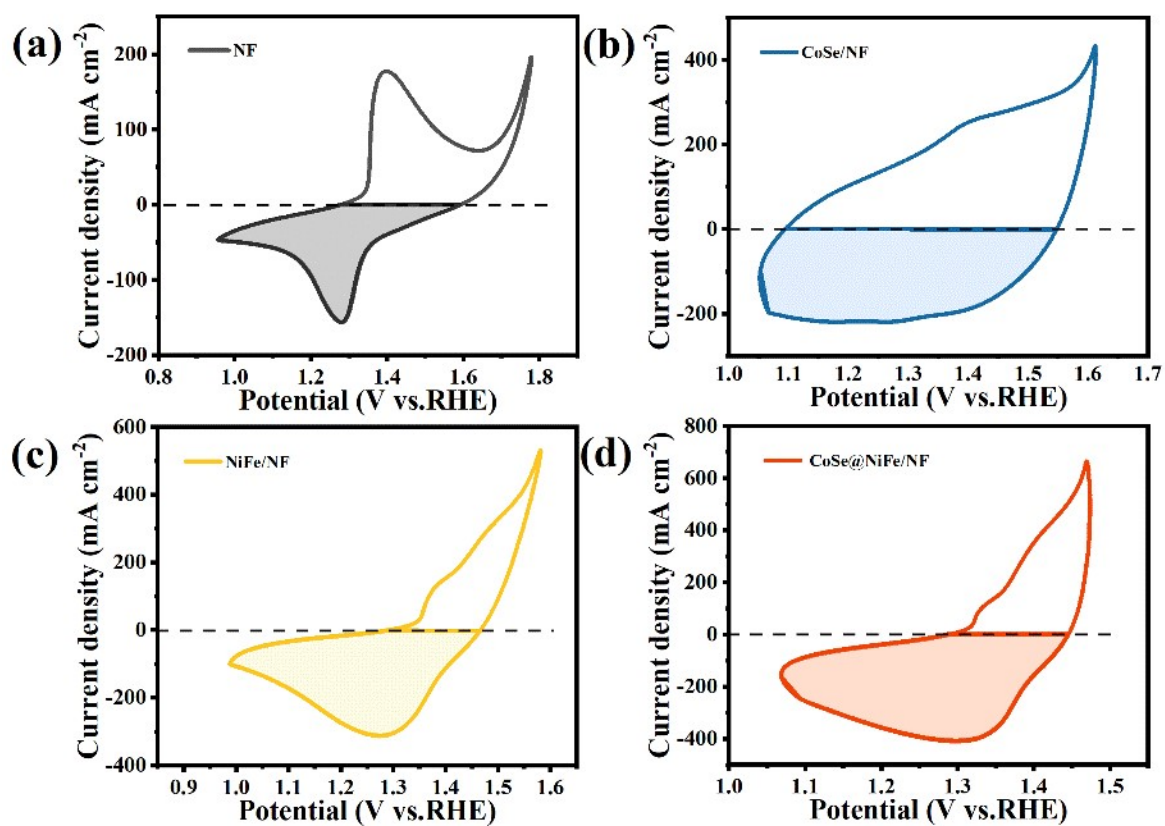


Fig. S18. Reduction peaks recorded at 0.2 V·s⁻¹. (a) NF, (b) CoSe/NF, (c) NiFe/NF, (d) CoSe@NiFe/NF.

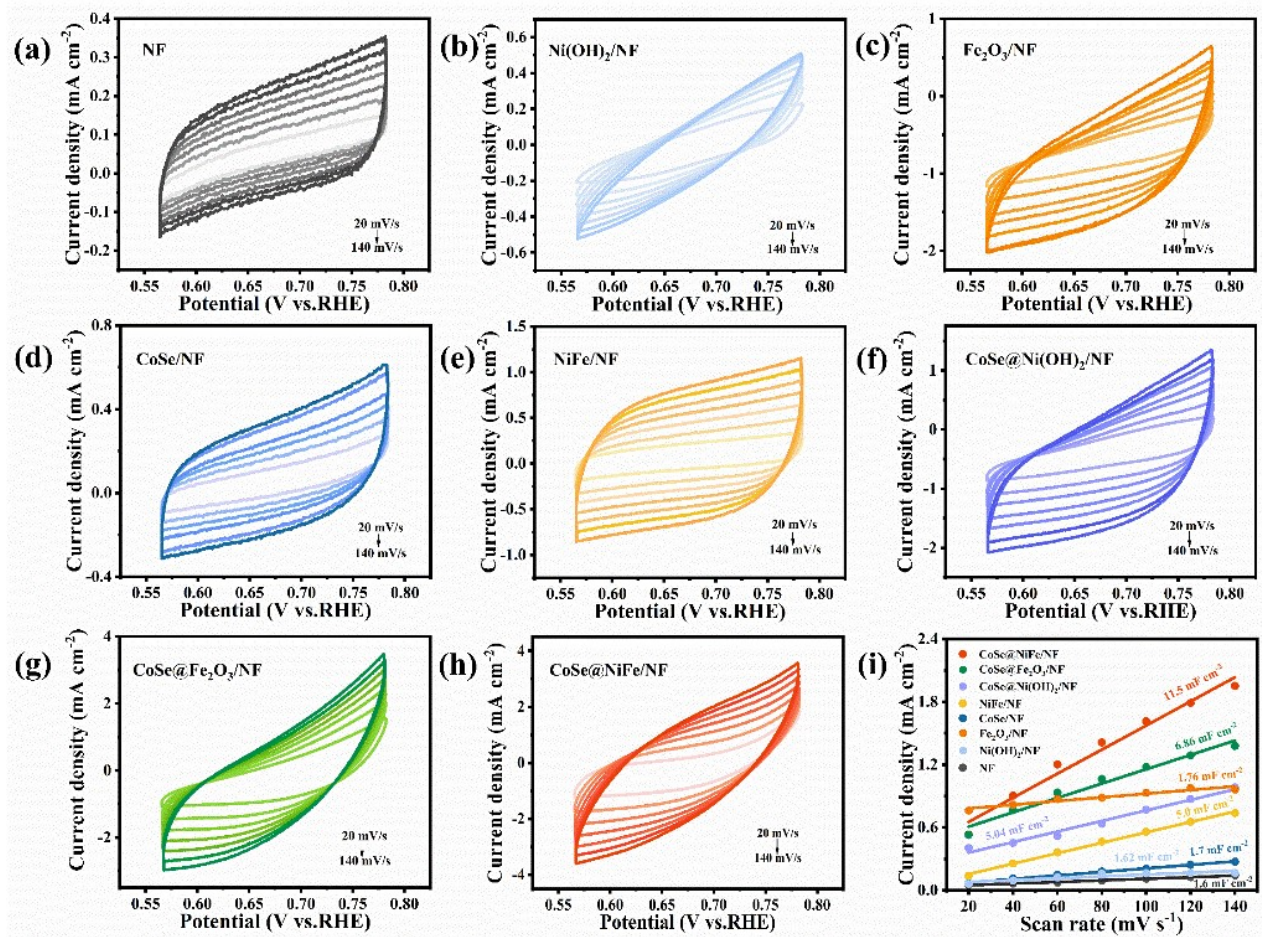


Fig. S19. Cyclic voltammetry (CV) curves of (a) NF, (b) $\text{Ni(OH)}_2/\text{NF}$, (c) $\text{Fe}_2\text{O}_3/\text{NF}$, (d) CoSe/NF , (e) NiFe/NF , (f) $\text{CoSe}@\text{Ni(OH)}_2/\text{NF}$, (g) $\text{CoSe}@\text{Fe}_2\text{O}_3/\text{NF}$, and (h) $\text{CoSe}@\text{NiFe}/\text{NF}$ measured with different scan rate from 20 to 140 $\text{mV} \cdot \text{s}^{-1}$ in 1.0 M KOH, and (i) double layer capacitance (C_{dl}) of all catalysts.

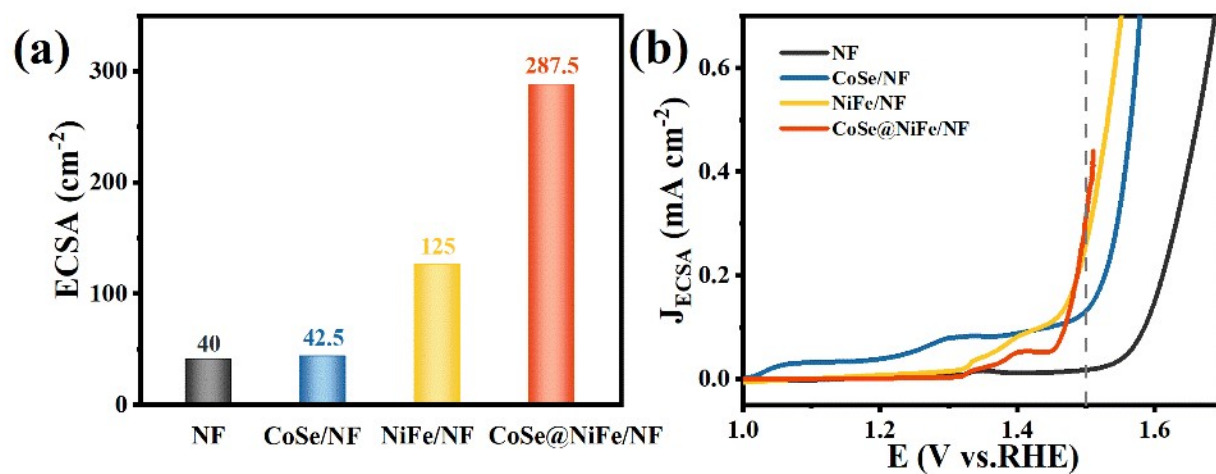


Fig. S20. (a) bar chart of the ECSA. (b) ECSA-normalized LSV curves.

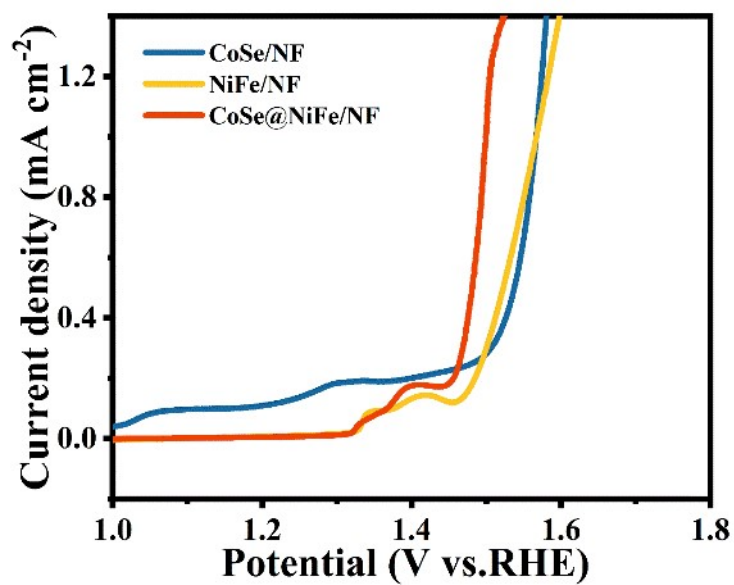


Fig. S21. The BET surface area-normalized current densities of catalysts.

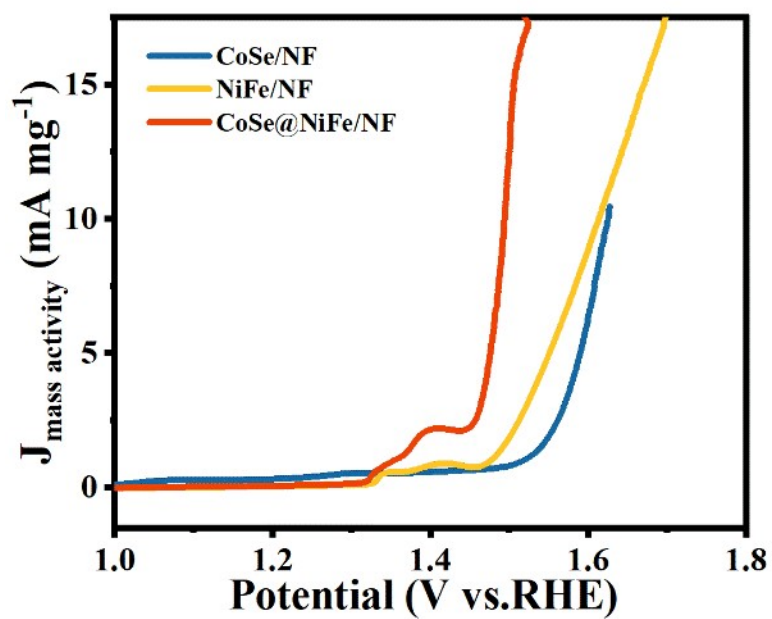


Fig. S22. The mass normalized current density of CoSe/NF, NiFe/NF and CoSe@NiFe/NF heterostructures.

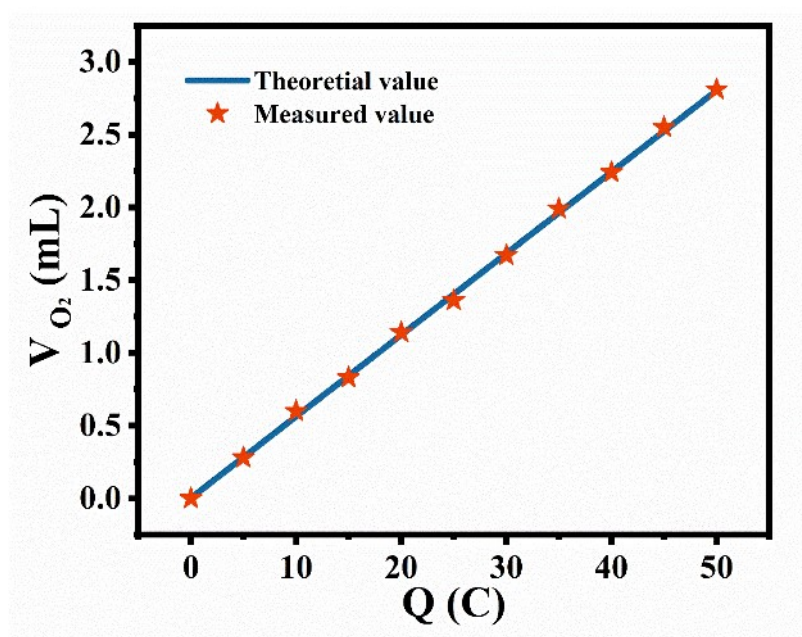


Fig. S23. Faradic efficiency for CoSe@NiFe/NF in 1 M KOH.



Fig. S24. The photograph of electrochemical in situ Raman spectroscopy.

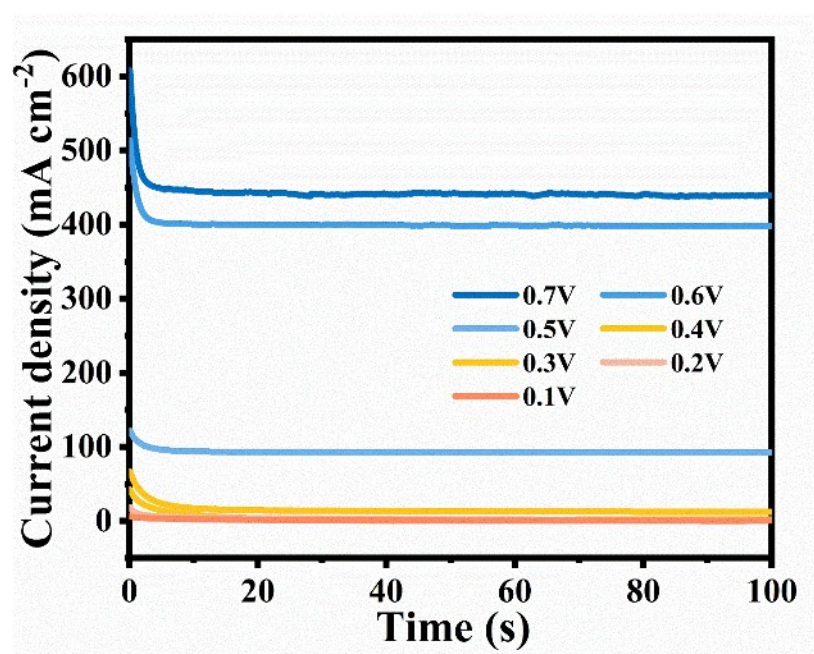


Fig. S25. The corresponding current densities at different applied potential during Raman measurements for CoSe@NiFe/NF electrode in 1 M KOH.

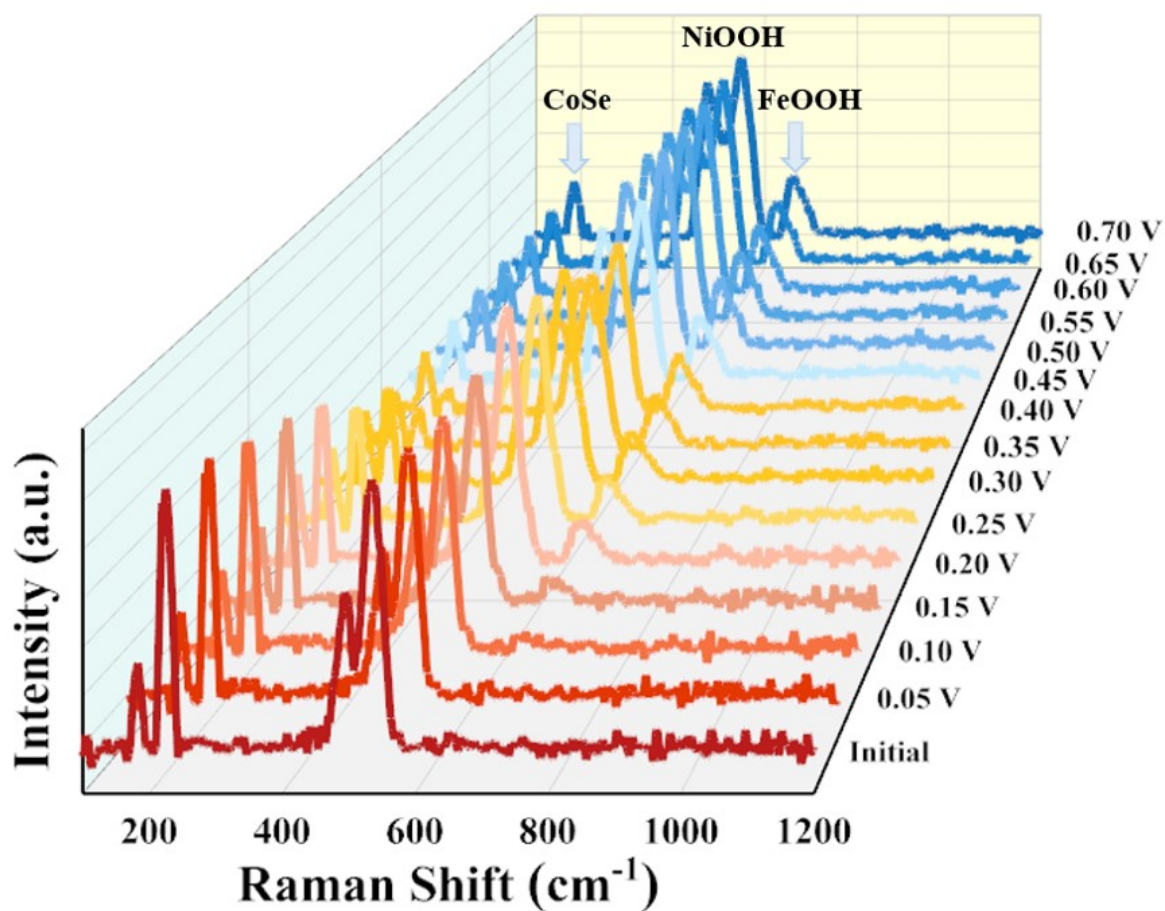


Fig. S26. Three-dimensional Raman spectra acquired at different potentials.

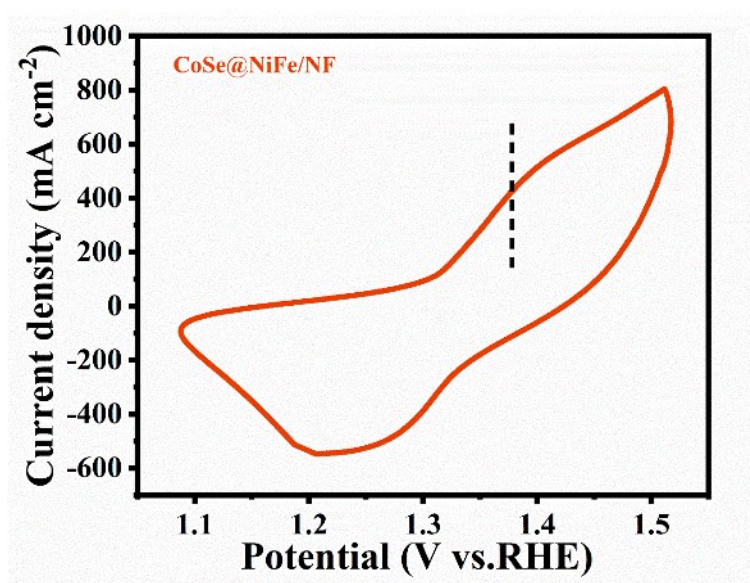


Fig. S27. The cyclic voltammograms of CoSe@NiFe/NF in 1

M KOH at a scan rate of $5 \text{ mV} \cdot \text{s}^{-1}$.

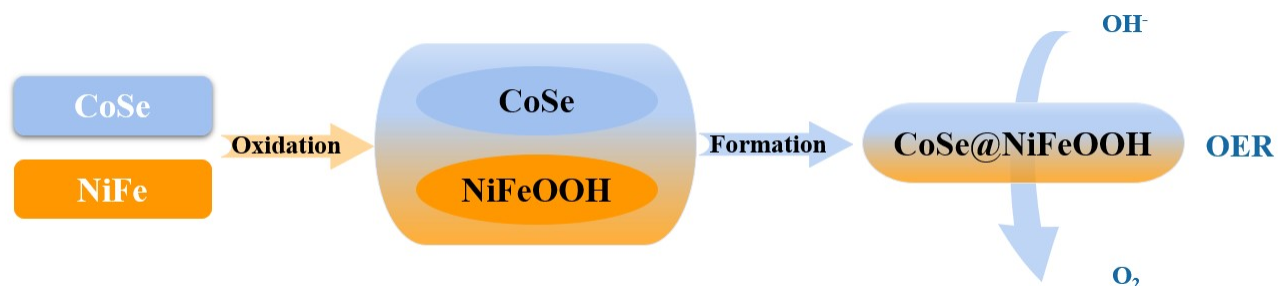


Fig. S28. Schematic illustration of the dynamic surface formation to form active CoSe@NiFeOOH at the CoSe@NiFe surface in alkaline water.

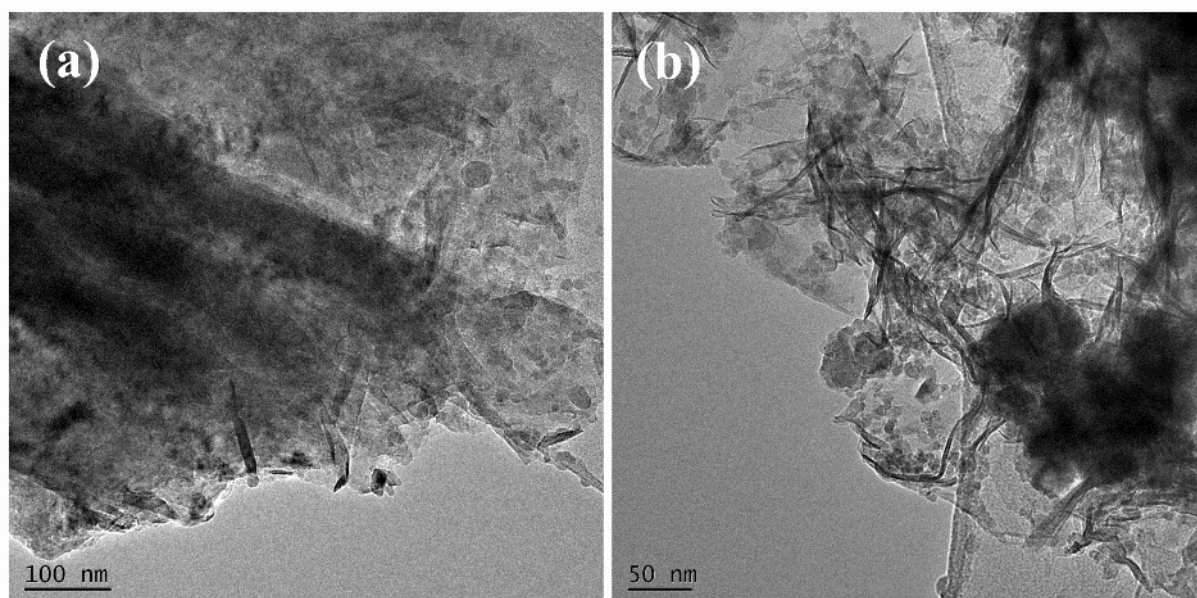


Fig. S29. TEM images of CoSe@NiFe/NF after OER chrono-potentiometry test at different magnifications.

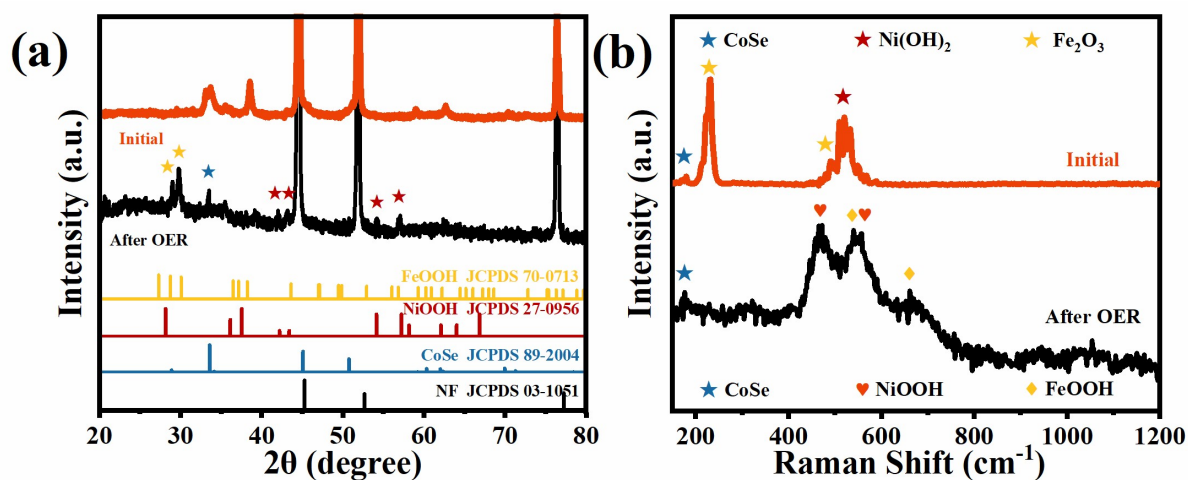


Fig. S30. (a) The XRD pattern and (b) the Raman spectra of CoSe@NiFe/NF initial and after OER chrono-potentiometry test.

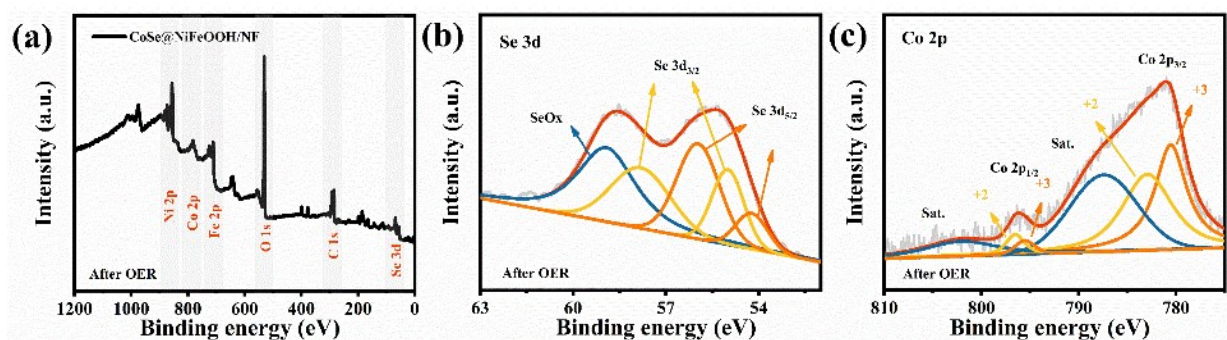


Fig. S31. (a) The full XPS spectra and high-resolution XPS spectra of (b) Se 3d, and (c) Co 2p of CoSe@NiFe/NF after OER chrono-potentiometry test.

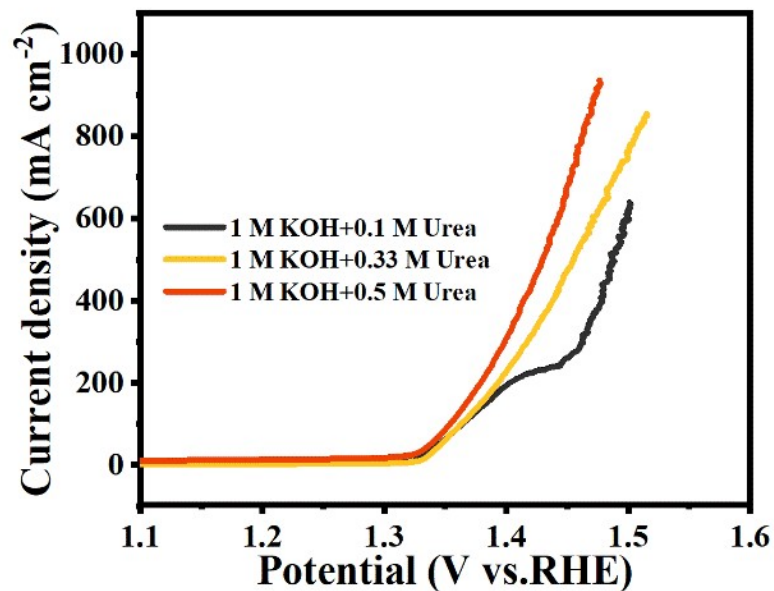


Fig. S32. (a) LSV curves of CoSe@NiFe/NF with different concentrations of urea.

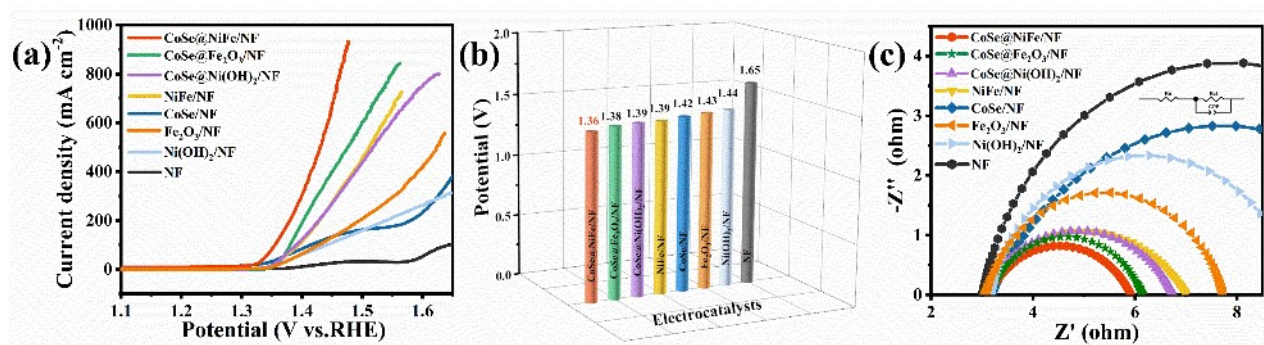


Fig. S33. UOR property (a) LSV curves of CoSe@NiFe/NF and contrast catalysts. (b)

Comparison of overpotentials at $100 \text{ mA} \cdot \text{cm}^{-2}$ between CoSe@NiFe/NF and contrast catalysts. (c) Electrochemical impedance spectroscopy (EIS).

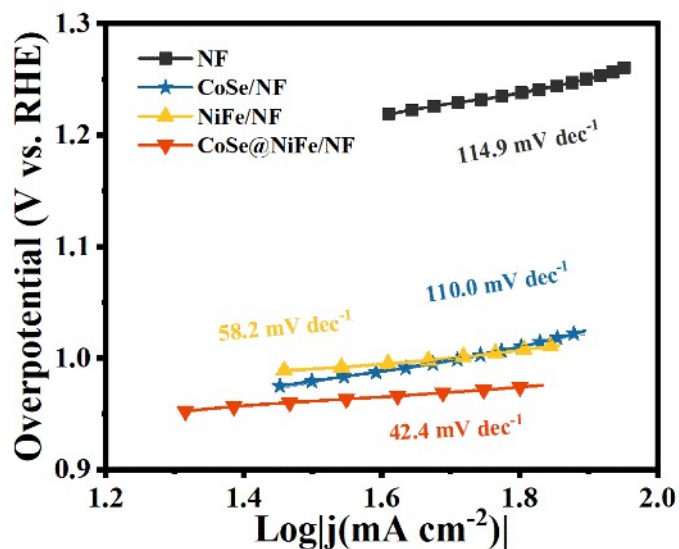


Fig. S34. Tafel plots of different samples.

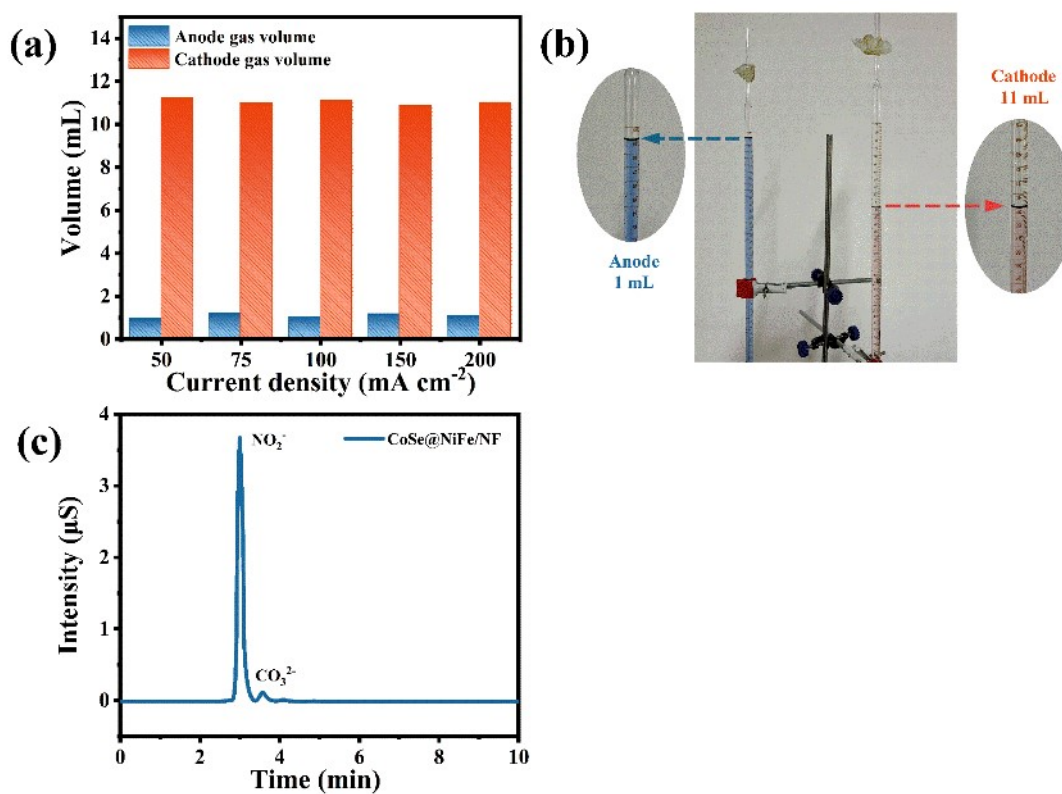


Fig. S35. (a) Plots of the volumes of different gas products produced by CoSe@NiFe/NF (anode) and Pt/C/NF (cathode) in 1 M KOH solution with 0.5 M urea. (b) The photo of the gas collector after electrolysis. (c) The IC curve of the electrolyte after UOR.

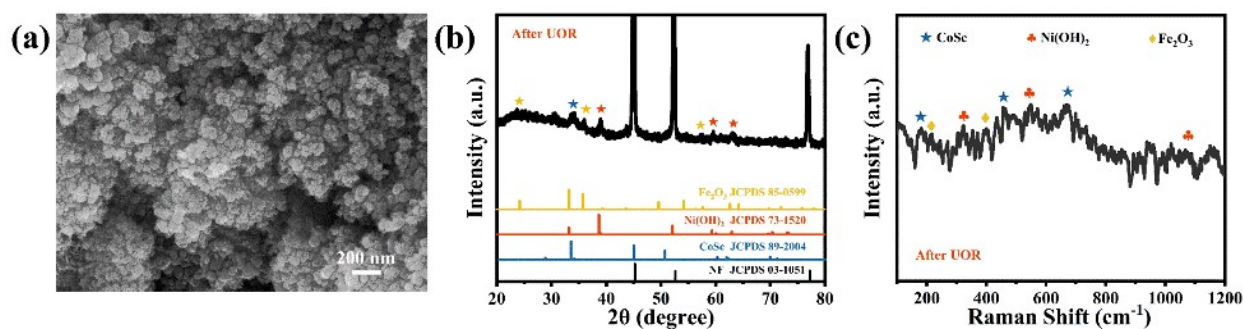


Fig. S36. (a) The SEM image, (b) the XRD pattern, and (c) the Raman spectra of CoSe@NiFe/NF after UOR chrono-potentiometry test.

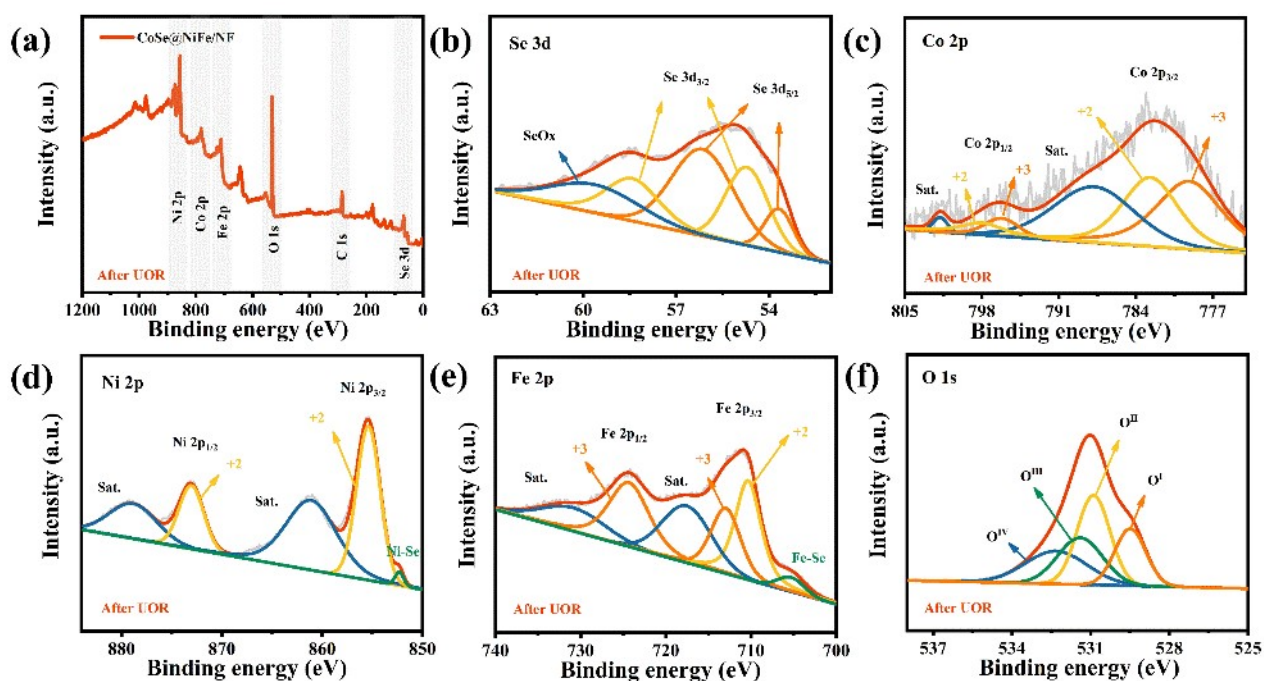


Fig. S37. (a) The full XPS spectra and high-resolution XPS spectra of (b) Se 3d, (c) Co 2p, (d) Ni 2p, (e) Fe 2p, and (f) O 1s of CoSe@NiFe/NF after UOR chrono-potentiometry test.

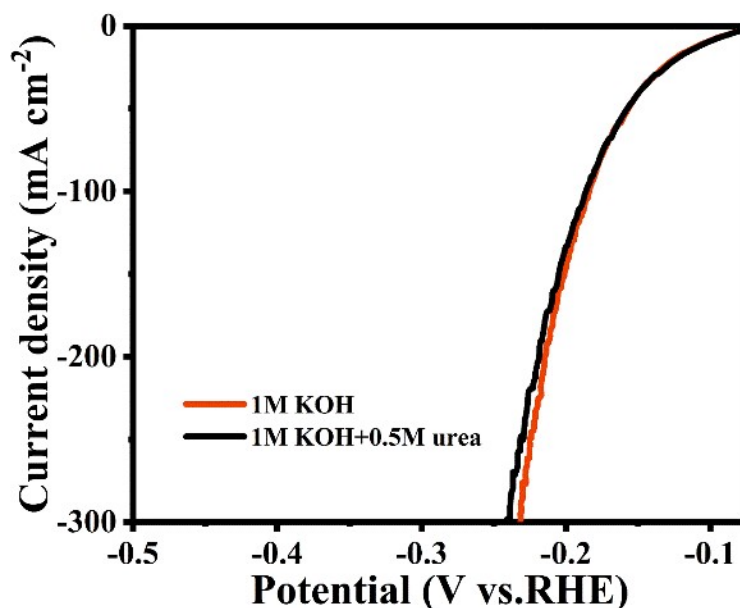


Fig. S38. HER electrocatalytic performance of the Pt/C/NF electrocatalysts of polarization curves in solutions of 1 M KOH and 1 M KOH with 0.5 M urea.

Electrocatalytic performance for MOR and EOR.

Typical MOR LSV curves of CoSe/NF, NiFe/NF, and CoSe@NiFe/NF were shown in Fig. S39a, and the designed CoSe@NiFe/NF exhibits superior MOR activity with a potential of only 1.40 V to drive $200 \text{ mA} \cdot \text{cm}^{-2}$, which is better than other reference samples. In addition, Fig. S39b shows the corresponding potentials at different current densities in the presence of 0.5 M methanol, lower than that demanded OER, indicating that the CoSe@NiFe/NF has a higher catalytic activity for the oxidation of methanol than OER. Similarly, the LSV polarization curves of EOR as shown in Fig. S39d are used to compare the catalytic activities of the various catalyst. To show the excellent catalytic activity of CoSe@NiFe/NF for methanol oxidation, bar graph (Fig. S39e) can be compared more visually with the potentials required for

various samples at different current densities (10, 50, 200 $\text{mA}\cdot\text{cm}^{-2}$). Interestingly, in addition to the excellent catalytic performance, CoSe@NiFe/NF was also tested for stability in a 1 M KOH solution containing 0.5 M methanol or ethanol, and the Chronopotentiometry curves were measured for 20 h, as well as its cycling durability by linear sweep voltammetry measurement, which collectively demonstrated the excellent stability (Fig. S39c and S39f).

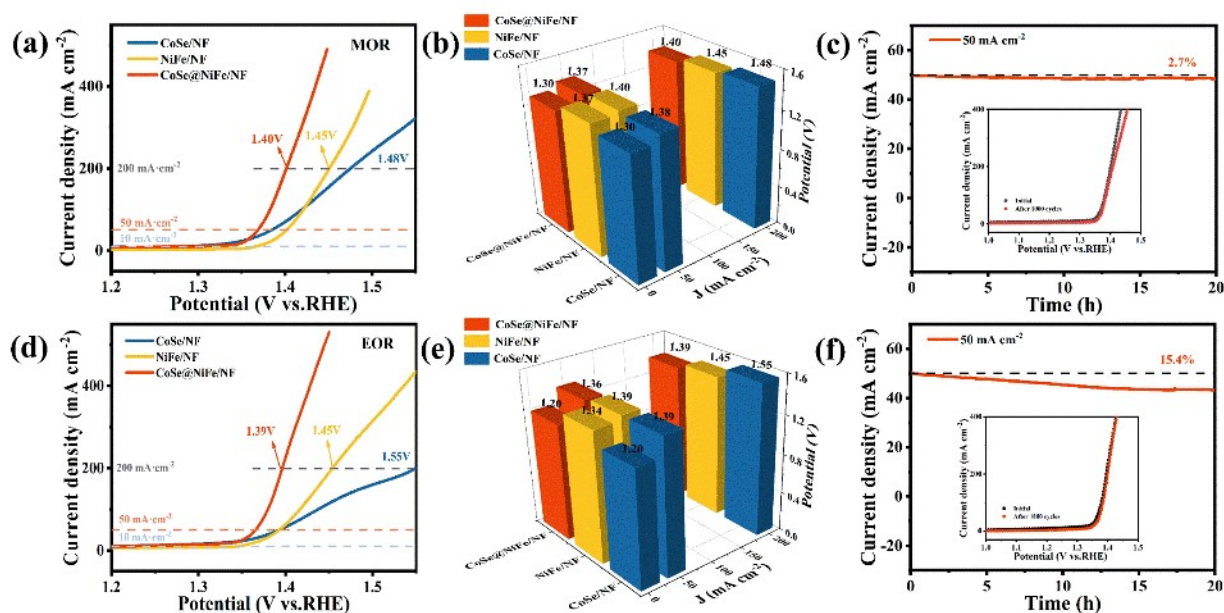


Fig. S39. (a) MOR polarization curves (b) corresponding potentials of electrocatalyst at 10, 50 and 200 $\text{mA}\cdot\text{cm}^{-2}$ in 1 M KOH with 0.5 M methanol. (c) Long-term stability test performed at a constant $j = 50 \text{ mA}\cdot\text{cm}^{-2}$. (d) EOR polarization curves (e) corresponding potentials of electrocatalyst at 10, 50 and 200 $\text{mA}\cdot\text{cm}^{-2}$ in 1 M KOH with 0.5 M ethanol. (f) Long-term stability test performed at a constant $j = 50 \text{ mA}\cdot\text{cm}^{-2}$.

Table S1. Corresponding structure of XRD peaks in CoSe@NiFe/NF.

2θ (degree)	Corresponding phase	PDF card
44.8	NF	03-1051
52.2		
76.8		
33.2	CoSe	89-2004
38.6	Ni(OH) ₂	73-1520
59.3		
70.4		
33.2	Fe ₂ O ₃	85-0599
35.8		
62.7		

Table S2. Comparison of OER performance with previous reported state-of-the-art non-noble metal OER catalysts.

OER catalysts	J (mA·cm⁻²)	Overpotential (mV) @ J	Reference
CoSe@NiFe	10/100	194/228	This work
Ni _{0.76} Fe _{0.24} Se	10/100	197/~260	[4]
NiFe/NiFe-OH	10/100	222/261	[5]
NiFe/NF	10/100	235/296	This work
Co _{0.7} Fe _{0.3} -Se/NF	10/100	237/~270	[6]
Co _{0.9} Fe _{0.1} -Se/NF	10/100	246/287	[6]
Co-Se/NF	10/100	275/326	[6]
CoFeNiO _x /NF	10/100	240/272	[7]
Sn-Ni(OH) ₂	10/100	250/312	[8]
CoSe _{1.26} P _{1.42}	10/100	255/~370	[9]
Fe-Se/NF	10	263	[10]
Ni-Fe LDH	10/100	280/~330	[11]

Fe ₂ O ₃ @CNT	10/100	270/~320	[12]
Ni ₁ Fe ₂ @Fe ₂ O ₃ @C	10/100	271/~370	[13]
CoSe/NF	10/100	278/322	This work
CoFe _{0.7} Se _{1.7}	10/100	279/~320	[14]
CoSe/CP	100	417	[14]
a-CoSe	10/100	292/~365	[15]
CoSe	10	295	[16]
CFO ₁	10	304	[17]
NrN@Ni	10/100	313/~360	[18]
NFP40	10/100	319/~361	[19]
NiOOH/Fe ₂ O ₃	10	325	[20]
β-Ni(OH) ₂ hexagonal NPs	10	444	[21]
α-Ni(OH) ₂ HSs	10	331	[21]
β-Ni(OH) ₂ NPs	10	340	[22]
Fe ₂ O ₃ @CuO NTs	100	398	[23]

Table S3. Quantitative analysis of Ni³⁺/Ni²⁺+Ni³⁺ ratio in CoSe@NiFe/NF and CoSe@NiFeOOH/NF obtained from the XPS result in Fig. S15d and 4f.

	CoSe@NiFe/NF (area CPS. eV)	CoSe@NiFeOOH/NF (area CPS. eV)
Ni ²⁺	151665.61	91744.96
Ni ³⁺	0	66354.13
Ni ³⁺ /Ni ²⁺ +Ni ³⁺	ca. 0	ca. 0.42

Table S4. Quantitative analysis of Fe³⁺/Fe²⁺+Fe³⁺ ratio in CoSe@NiFe/NF and CoSe@NiFeOOH/NF obtained from the XPS result in Fig. S15e and 4g.

	CoSe@NiFe/NF (area CPS. eV)	CoSe@NiFeOOH/NF (area CPS. eV)
Fe ²⁺	115500.39	86012.83
Fe ³⁺	27339.43	134290.63
Fe ³⁺ /Fe ²⁺ +Fe ³⁺	ca. 0.19	ca. 0.61

Table S5. The electron gains and losses for CoSe@NiFeOOH.

Atom	Original electron	Present electron	Gain electrons	Loss electrons
Ni	10	8.788081		1.211919
Ni	10	8.785106		1.214894
Fe	8	6.503508		1.496492
Fe	8	6.493066		1.506934
O	6	6.861786	-0.861786	
O	6	7.12771	-1.12771	
O	6	7.022445	-1.022445	
O	6	6.834641	-0.834641	
O	6	7.044318	-1.044318	
O	6	7.023636	-1.023636	
O	6	6.841235	-0.841235	
O	6	7.117768	-1.117768	
O	6	7.072629	-1.072629	
O	6	6.855938	-0.855938	

O	6	6.984077	-0.984077	
O	6	7.056174	-1.056174	
H	1	0.389085		0.610915
H	1	0.419647		0.580353
H	1	0.344558		0.655442
H	1	0.418692		0.581308
H	1	0.404312		0.595688
H	1	0.377725		0.622275
H	1	0.370104		0.629896
H	1	0.384088		0.615912
Co	9	8.698749		0.301251
Co	9	8.733407		0.266593
Co	9	8.70574		0.29426
Co	9	8.731128		0.268872
Co	9	8.265815		0.734185
Co	9	8.730826		0.269174
Co	9	8.705775		0.294225
Co	9	8.67172		0.32828
Co	9	8.713461		0.286539
Co	9	8.404593		0.595407

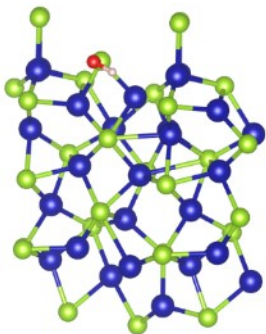
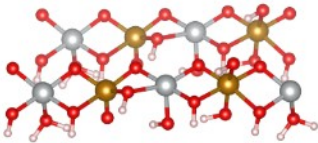
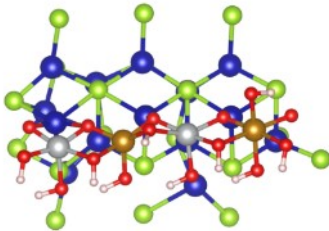
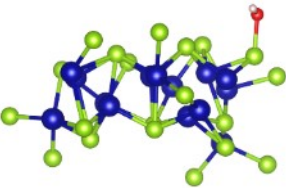
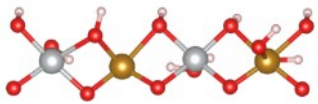
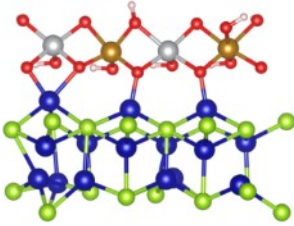
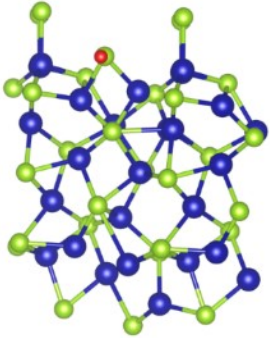
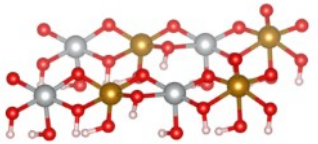
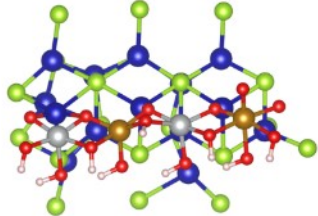
Co	9	8.734268		0.265732
Co	9	8.753738		0.246262
Co	9	8.733395		0.266605
Co	9	8.714268		0.285732
Co	9	8.418385		0.581615
Se	6	6.285154	-0.285154	
Se	6	6.413016	-0.413016	
Se	6	6.305607	-0.305607	
Se	6	6.234764	-0.234764	
Se	6	6.304753	-0.304753	
Se	6	6.404045	-0.404045	
Se	6	6.287602	-0.287602	
Se	6	6.193365	-0.193365	
Se	6	6.312069	-0.312069	
Se	6	6.341949	-0.341949	
Se	6	6.331552	-0.331552	
Se	6	6.292565	-0.292565	

PS: The electrons themselves are negatively valanced, i.e. those with a negative sign in the table should be positively valanced.

The above table displays the electron gains and losses in the CoSe@NiFeOOH heterostructure, from which we can see that the Ni, Fe, H, and Co atoms lose electrons,

while the O and Se atoms gains electrons. In order to investigate the electron transfer between NiFeOOH and CoSe, the overall electron gain/loss of NiFeOOH was calculated, and it was found that NiFeOOH should have 116 |e|, but in fact it has 117.520329 |e|, which means that about 1.52 electrons were transferred from CoSe to NiFeOOH.

Table S6. Top and side views of the theoretical models for CoSe, NiFeOOH and CoSe@NiFeOOH in the OER step involving *OH, *O, *OOH adsorption.

		CoSe	NiFeOOH	CoSe@NiFeOOH
*OH	Top view			
	Side view			
*O	Top view			

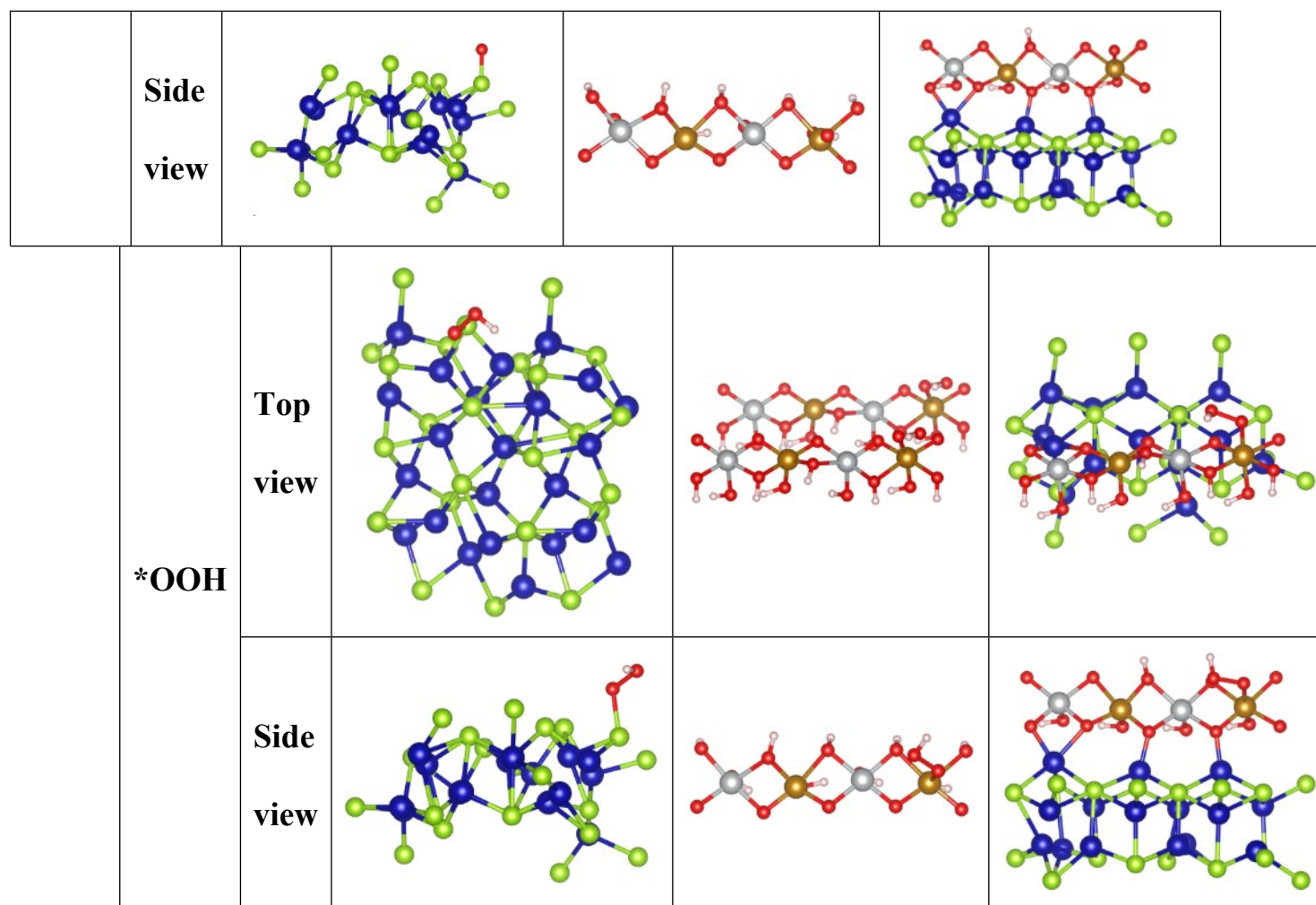


Table S7. OER and UOR bifunctional activity of catalysts in this work.

Catalysts	U_{OER} (V) @ J	U_{UOR} (V) @ J
CoSe@NiFe/NF	1.46@ 100 mA·cm ⁻²	1.36 @ 100 mA·cm ⁻²
CoSe@Fe ₂ O ₃ /NF	1.49@ 100 mA·cm ⁻²	1.38 @ 100 mA·cm ⁻²
CoSe@Ni(OH) ₂ /NF	1.50@ 100 mA·cm ⁻²	1.39 @ 100 mA·cm ⁻²
NiFe/NF	1.53@ 100 mA·cm ⁻²	1.39 @ 100 mA·cm ⁻²
CoSe/NF	1.55@ 100 mA·cm ⁻²	1.42 @ 100 mA·cm ⁻²
Fe ₂ O ₃ /NF	1.56@ 100 mA·cm ⁻²	1.43 @ 100 mA·cm ⁻²
Ni(OH) ₂ /NF	1.64@ 100 mA·cm ⁻²	1.44 @ 100 mA·cm ⁻²
NF	1.67@ 100 mA·cm ⁻²	1.65 @ 100 mA·cm ⁻²

Table S8. Comparison of UOR performance with previous reported state-of-the-art non-noble metal UOR catalysts.

UOR catalysts	Electrolytes	Potential (V) @ J	Reference
CoSe@NiFe	1 M KOH + 0.5 M urea	1.360 @ 100 mA·cm⁻²	This work
Fe ₇ Se ₈ @Fe ₂ O ₃	1 M KOH + 0.5 M urea	~1.400 @ 100 mA·cm ⁻²	[24]
FeCo-LDH	1 M KOH + 0.5 M urea	1.379 @ 100 mA·cm ⁻²	[25]
Fe-NiCoP	1 M KOH + 0.5 M urea	1.369 @ 100 mA·cm ⁻²	[26]
NiFe/N-C	1 M KOH + 1.0 M urea	1.370 @ 100 mA·cm ⁻²	[27]
Ni ₃ Se ₄	1 M KOH + 0.1 M urea	~1.450 @ 100 mA·cm ⁻²	[28]
Fe _{11.1%} -Ni ₃ S ₂	1 M KOH + 0.33 M urea	1.438 @ 100 mA·cm ⁻²	[29]
NiFe LDH	1 M KOH + 0.33 M urea	1.459 @ 100 mA·cm ⁻²	[30]
Cu-NiFe LDH	1 M KOH + 0.33 M urea	~1.520 @ 100 mA·cm ⁻²	[31]
NiCoSe ₂	1 M KOH + 0.33 M urea	1.520 @ 100 mA·cm ⁻²	[32]
CoFeSe ₂	1 M KOH + 0.33 M urea	1.460 @ 100 mA·cm ⁻²	[32]
NiFeCoSe ₂	1 M KOH + 0.33 M urea	1.440 @ 100 mA·cm ⁻²	[32]
Ni(OH) ₂	1 M KOH + 0.33 M urea	1.580 @ 100 mA·cm ⁻²	[33]

Table S9. Comparison of the overall water splitting CoSe@NiFe||Pt/C cell and other reported systems.

Catalysts	J (mA·cm ⁻²)	Voltage (V) @ J	Reference
CoSe@NiFe Pt/C	100	1.44	This work
NiCo/NiCo-OH NiFe/NiFe-OH	10/100	1.48/1.64	[5]
Co _{0.9} Fe _{0.1} -Se Co _{0.9} Fe _{0.1} -Se	10/100	1.55/~1.69	[6]
Sn-Ni(OH) ₂ Sn-Ni(OH) ₂	10/100	1.58/~1.87	[8]
Ni ₁ Fe ₂ @Fe ₂ O ₃ @C Pt/C	60/100	1.81/~1.88	[13]
a-CoSe/Ti a-CoSe/Ti	10/100	1.65/~1.90	[15]

NiFe/N-C Pt	10	1.64	[27]
Fe ₂ O ₃ /NiFe-LDHs Pt/C	10/100	1.47/~1.56	[34]
F(V)OOH-1.5 Pt/C	10/100	1.51/~1.59	[35]
FeCoNi Pt/C	10	1.523	[36]
FeNiS Pt/C	10/100	1.535/~1.70	[37]
F-Ni(OH) ₂ RuCo-OH	10	1.55	[38]
CoB ₂ O ₄ @FeOOH Pt/C	100	1.576	[39]
NiSe-Ni _{0.85} Se NiSe-Ni _{0.85} Se	10/100	1.62/1.89	[40]

Table S10. Comparison of the overall urea splitting CoSe@NiFe||Pt/C cell and other reported systems.

Catalysts	Electrolytes	Voltage (V) @ J	Reference
		(mA·cm ⁻²)	
CoSe@NiFe Pt/C	1 M KOH + 0.5 M urea	1.40 @ 100 mA·cm⁻²	This work
Fe ₇ Se ₈ @Fe ₂ O ₃ Fe ₇ Se ₈ @Fe ₂ O ₃	1 M KOH + 0.5 M urea	1.55 @ 10 mA·cm ⁻²	[24]
FeCo-LDH Pt/C	1 M KOH + 0.5 M urea	1.409 @ 10 mA·cm ⁻²	[25]
FeCo-LDH Pt/C	1 M KOH + 0.5 M urea	~1.84 @ 100 mA·cm ⁻²	[25]
Fe-NiCoP Fe-NiCoP	1 M KOH + 0.5 M urea	1.50 @ 10 mA·cm ⁻²	[26]
Fe-NiCoP Fe-NiCoP	1 M KOH + 0.5 M urea	~1.76 @ 100 mA·cm ⁻²	[26]
NiFe/N-C Pt	1 M KOH + 1.0 M urea	1.50 @ 10 mA·cm ⁻²	[27]
Fe _{11.1%} -Ni ₃ S ₂ Fe _{11.1%} -Ni ₃ S ₂	1 M KOH + 0.33 M urea	1.46 @ 10 mA·cm ⁻²	[29]
Fe _{11.1%} -Ni ₃ S ₂ Fe _{11.1%} -Ni ₃ S ₂	1 M KOH + 0.33 M urea	~1.76 @ 100 mA·cm ⁻²	[29]
F-Ni(OH) ₂ RuCo-OH	1 M KOH + 0.33 M urea	1.37 @ 10 mA·cm ⁻²	[38]

Ni-S-Se/NF Ni-S-Se/NF	1 M KOH + 0.5 M urea	1.47 @ 10 mA·cm ⁻²	[41]
Ni-S-Se/NF Ni-S-Se/NF	1 M KOH + 0.5 M urea	1.60 @ 100 mA·cm ⁻²	[41]
1% Cu:α-Ni(OH) ₂ 1% Cu:α-Ni(OH) ₂	1 M KOH + 0.33 M urea	1.60 @ 10 mA·cm ⁻²	[42]
1% Cu:α-Ni(OH) ₂ 1% Cu:α-Ni(OH) ₂	1 M KOH + 0.33 M urea	~1.82 @ 100 mA·cm ⁻²	[42]
1% Ce:α-Ni(OH) ₂ 1% Ce:α-Ni(OH) ₂	1 M KOH + 0.33 M urea	1.44 @ 10 mA·cm ⁻²	[43]
1% Ce:α-Ni(OH) ₂ 1% Ce:α-Ni(OH) ₂	1 M KOH + 0.33 M urea	1.73 @ 100 mA·cm ⁻²	[43]

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