

Supporting Information

In Situ Crystallization of Active NiOOH/CoOOH Heterostructures with Hydroxide Ion-Adsorption Sites on Velutipes-like CoSe/NiSe-nanorods as Catalysts for Oxygen Evolution and Co-catalysts for Methanol Oxidation

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1. Experimental section

Synthesis of Pt-CoSe-x/NiSe-nrs/NF and Pt-NiSe-nrs/NF composites. Pt-CoSe-x/NiSe-nrs/NF and Pt-NiSe-nrs/NF composites with a nominal Pt loading of 0.5 wt.% are prepared by using the microwave-assisted polyol process. 5 mL of chloroplatinic acid ethylene glycol solution ($\text{H}_2\text{PtCl}_6\text{-EG}$) with Pt^{2+} concentration of 0.2 mM is added in a 10 mL beaker, and then the pH of the solution is adjusted by 1 mol L^{-1} NaOH-EG solution until the pH is maintained at around 12 under vigorous stirring. Subsequently, a piece of CoSe-x/NiSe-nrs/NF is immersed in the above solution and then the beaker is placed at the center of a microwave oven (2450 MHz, 800 W) with a consecutive heating for 15 s for the completed reduction of Pt compound. Before the heating, nitrogen gas was fed into the ink for 15 min to expel oxygen. After standing overnight, the obtained Pt-CoSe-x/NiSe-nrs/NF is thoroughly washed with DI water and ethanol three times to remove residual impurities. Finally, the Pt-CoSe-x/NiSe-nrs/NF catalysts are dried in a vacuum oven at 60 °C for 8 h. Pt-NiSe-nrs/NF is also synthesized as the reference sample under the same condition. Commercial Pt/C (10 wt.%) is also used as the reference sample.¹

Materials characterization: X-ray diffraction (XRD) analysis was performed on a Rigaku D/max 2500 diffractometer equipped with Cu-K α radiation ($k=1.5406 \text{ \AA}$, 40 kV, 20mA). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos-ULTRA AXIS DLD with Al K α X-ray source to determine the surface components of the catalysts. Morphologies of these samples and element mapping were observed on a field emission scanning electron microscope (FE-SEM, Hitachi S-4800). Transmission electron microscope (TEM) was conducted on a JEOL JEM-2010 at an accelerating voltage of 200 kV to record the electron micrographs of the samples.¹

Electrochemical tests: Both MOR and OER measurements were performed on an electrochemical workstation (CHI760E, Chenhua, shanghai) using a standard three-electrode system at room

temperature (25 °C). The Pt-CoSe-x/NiSe-nrs/NF and CoSe/NiSe-nrs/NF was held by electrode holder used as a working electrode directly for MOR and OER tests, respectively. Pt/C catalyst ink was prepared by ultrasonically dispersing 5 mg of catalyst in a mixture containing 100 μL of ethanol and 50 μL of Nafion (5 wt.%, Dupont) solution. The catalyst ink was loaded on a glassy-carbon electrode (GCE) (diameter of 3 mm and area of 0.07065 cm^2) as the working electrode. RuO_2 electrode was prepared according to the following steps: 20 mg of commercial RuO_2 was ultrasonically dispersed in the mixture of deionized water, ethanol and 0.5 wt% of Nafion in a volume ratio of 0.75 : 0.2 : 0.05 for 15 min, and then drop-cast onto the cleaned Ni foam to obtain a mass loading of 9 mg cm^{-2} .² The saturated calomel electrode was used as the reference electrode, and the counter electrode was a polished platinum sheet (1 cm^2) electrode.^{1,2}

Before the OER measurements, 1.0 M KOH was purged with high-pure O_2 for 30 min to saturate the electrolyte. All of the potentials were converted to the potentials versus the reversible hydrogen electrode (RHE) according to the following equation: $E(\text{RHE}) = E(\text{SCE}) + 0.24 + 0.059\text{pH}$. The polarization curves were corrected against the ohmic potential drop. The linear sweep voltammetry (LSV) and cyclic voltammetric (CV) tests were conducted in the potential range from 0 to 0.8 V (vs SCE) at a scan rate of 2 mV s^{-1} . chronopotentiometry (CP) tests were performed for 10h to investigate long-term durability of the catalysts in 1.0 M KOH solution at a constant current of 100mA. The electrochemically active surface areas (ECSAs) were evaluated from CV data at the potential range from -0.4 to -0.3 V (vs SCE) at scanning rates between 30 and 120 mV s^{-1} . EIS tests were conducted in the frequency range of 100 kHz to 100 mHz at a 5 mV voltage amplitude.³ Turnover frequencies (TOF) value was calculated by assuming that the surface active Ni and Co atoms had undergone the redox reaction just before the onset of OER only involved in OER electrocatalysis.⁴ The corresponding equations are shown as follows:

$$\text{TOF} = (j \times N_A) / (F \times n \times \Gamma)$$

$$\Gamma = CV_{\text{area}}/(\text{Scan rate} \times e)$$

Where J is the current density, N_A is the values of Avogadro number (6.022×10^{23}), n is the electron transfer number (4), F is the Faraday constant (96485 C mol^{-1}), Γ is the Surface concentration, Scan rate is 0.3 V/s , e value is $1.602 \times 10^{-19} \text{ C}$. The CV tests for MOR were carried out in the potential range from -0.8 to $+0.4 \text{ V}$ (50 mV s^{-1}) in 1.0 M KOH alkaline electrolyte in the absence or presence of 1.0 M methanol. To evaluate the long-term durability of MOR, the amperometric (i-t) tests were performed for 3600 s in $1.0 \text{ M KOH} + 1.0 \text{ M CH}_3\text{OH}$ solution at a constant potential of 0.1 V . The electrochemical impedance spectroscopy (EIS) tests were conducted at 0.14 V over a frequency range of 10^5 to 10^{-2} Hz with a sinusoidal perturbation of 10 mV amplitude. The CO (99.99 %) stripping voltammetry was carried out in the potential range from -1.0 to $+0.4 \text{ V}$ at a scan rate of 10 mV s^{-1} in 1.0 M KOH solution. All of the used electrolytes were degassed with high-pure N_2 to remove the dissolved oxygen prior to each measurement.⁵

2. Results and discussion

Table S1. CoSe and Ni contents (wt.%) in the CoSe-x/NiSe-nrs/NF catalysts.

Components	CoSe-0.1/NiSe-nrs/NF	CoSe-0.2/NiSe-nrs/NF	CoSe-0.3/NiSe-nrs/NF
CoSe	8.3	16.3	25.1
Ni ²⁺	42.66	46.66	45.21

Table S2 The chemical compositions of Pt/CoSe-x/NiSe-nrs/NF electrocatalysts obtained from XPS analyses.

Catalysts	Pt (wt.%)	Ni (wt.%)	Co (wt.%)	O (wt.%)	Se (wt.%)
Pt-CoSe-0.1/NiSe-nrs/NF	0.55	43.72	15.34	19.95	20.44
Pt-CoSe-0.2/NiSe-nrs/NF	0.46	43.04	17.4	25.88	13.22
Pt-CoSe-0.3/NiSe-nrs/NF	0.52	34.27	18.91	31.85	14.45

Table S3 Electrochemical performances for methanol oxidation on the Pt/CoSe-0.2/NiSe-nrs/NF, Pt/NiSe-nrs/NF and 10 wt.% Pt/C catalysts.

Samples	Onset potentials (mV vs. SCE)	Specific activity (mA cm ⁻²)	Mass activity (mA mg _{Pt} ⁻¹)
Pt-CoSe-0.2/NiSe-nrs/NF	-633.3	256	1437.1
Pt-NiSe-nrs/NF	-475.7	160	917.9
Commerical Pt/C	-299.0	83.6	374.5

Table S4 Comparison of MOR activities and stabilities for Pt/CoSe-0.2/NiSe-nrs/NF catalyst and other reported catalysts.

Catalysts	Pt (wt. %)	Mass Activity (mA mg ⁻¹ _{Pt})	Stability test	Scanning rate (mV s ⁻¹)	Conditions	Ref.
Pt-CoSe-0.2/NiSe-nrs/NF	0.5	1437.1	3600s loss of 28 %	50	1.0 M KOH + 1.0 M CH₃OH	This work
Pt NTs	—	2330.9	2000 s loss of 85.7 %	50	1.0 M KOH + 1.0 M CH ₃ OH	5
Pt-Pd-Cu nanodendrites	34.0	1447.0	200 cycles loss of 12 %	50	0.5 M KOH + 1.0 M CH ₃ OH	6
PdPt nanowires	20.0	1860	200 s loss of 38.5 %	50	1.0 M KOH + 1.0 M CH ₃ OH	7
Au/PtCu	—	1500	4000 s loss of 85.7 %	50	1.0 M KOH + 1.0 M CH ₃ OH	8
Pt /Ni (OH) ₂ /NF	1.5	1356	10 h loss of 30%	50	0.5 M KOH + 0.5 M CH ₃ OH	9
Pt-NiCo-LDH/NF	—	379.2	6000s loss of 73 %	50	1 M NaOH + 0.5 M CH ₃ OH	10
Pt/rGO	—	552.5	1000 cycles loss of 7.0 %	50	0.5 M KOH + 0.5 M CH ₃ OH	11
PtAuRu/RGO/GC	12.2	1605.5	500 cycles loss of 30.2 %	50	1.0 M KOH + 1.0 M CH ₃ OH	12

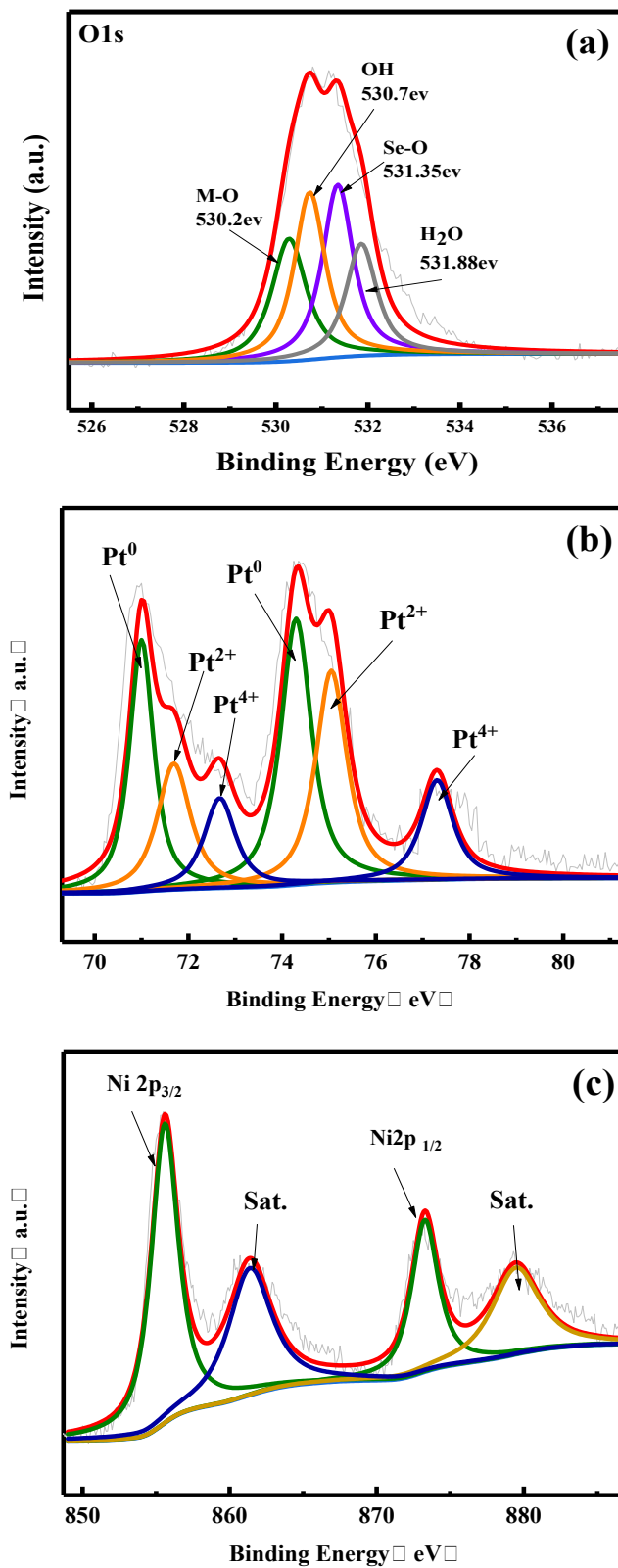


Figure S1. O 1s XPS spectra of Pt-CoSe-0.2/NiSe-nrs/NF(a), the Pt 4f (b) and Ni 2p (c) spectra of Pt-NiSe-nrs/NF.

As shown in Figure S1b and Figure 2f, the high Pt(0) integral areas of Pt-CoSe-x/NiSe-nrs/NF imply that it possesses a higher Pt(0) proportion than that of Pt-NiSe-nrs/NF, indicating that Pt-CoSe-x/NiSe-nrs/NF can supply more metallic Pt for MOR. Compared with Pt-NiSe-nrs/NF, the binding energies of metallic Pt of Pt-CoSe-x/NiSe-nrs/NF catalysts reveal slight positive shifts, meaning that the CoSe-x/NiSe-nrs heterostructures with specific electronic structure change the surface feature of Pt(0) and create a stable state of Pt(0) even in harsh environment, further enhancing the MOR activity and durability of Pt-CoSe-x/NiSe-nrs/NF.

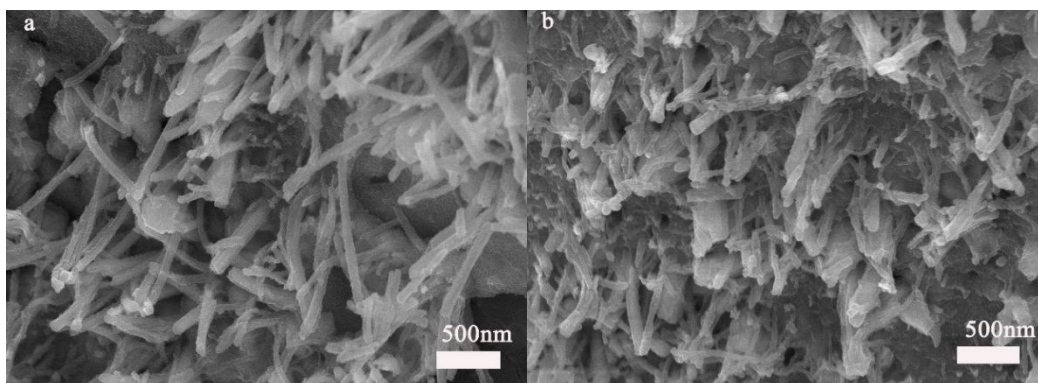


Figure S2. SEM images of CoSe-0.1/NiSe-nrs/NF (a) and CoSe-0.3/NiSe-nrs/NF (b).

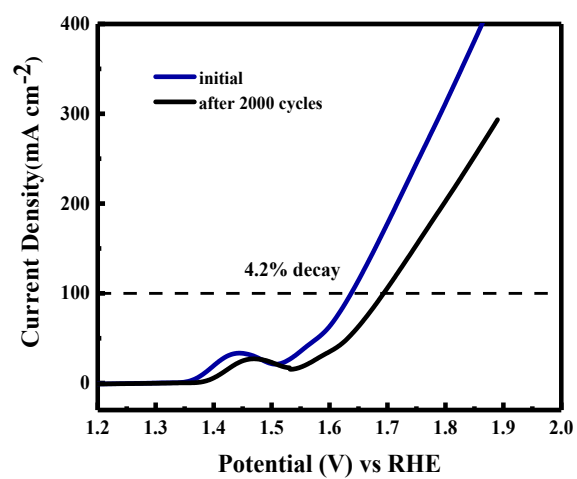


Figure S3. (left) Polarization curves at a scan rate of 2 mV s^{-1} for NiSe-nrs/NF before and after 1000 CV cycles.

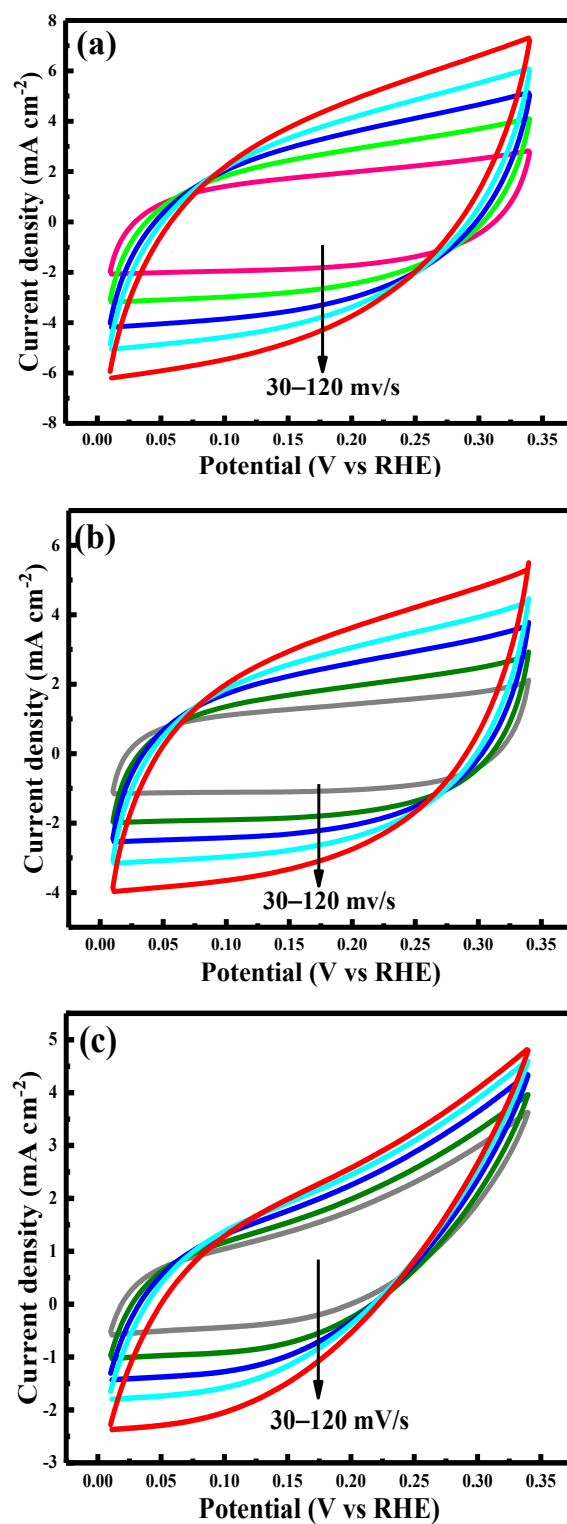


Figure S4. Cyclic voltammograms of CoSe-0.2/NiSe-nrs/NF (a), NiSe-nrs/NF (b), and bare NF (c).

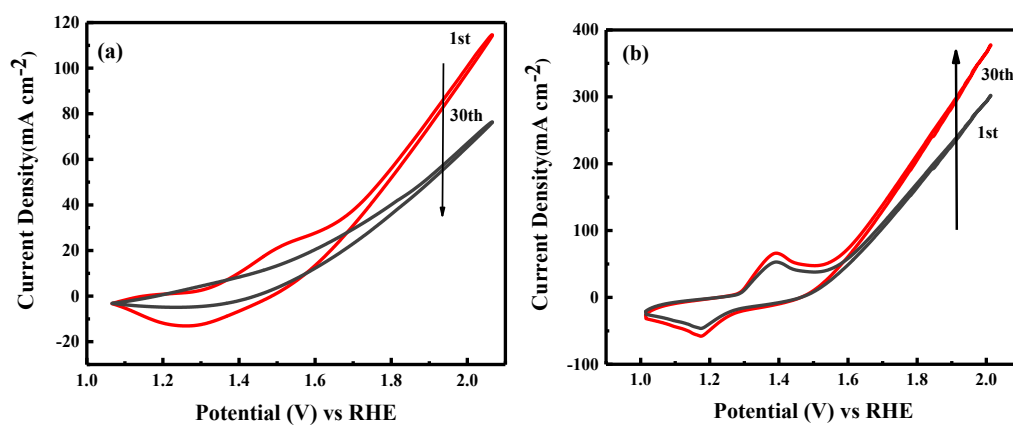


Figure S5. CV curves measured in 1 M PBS (a) and 1 M KOH (b).

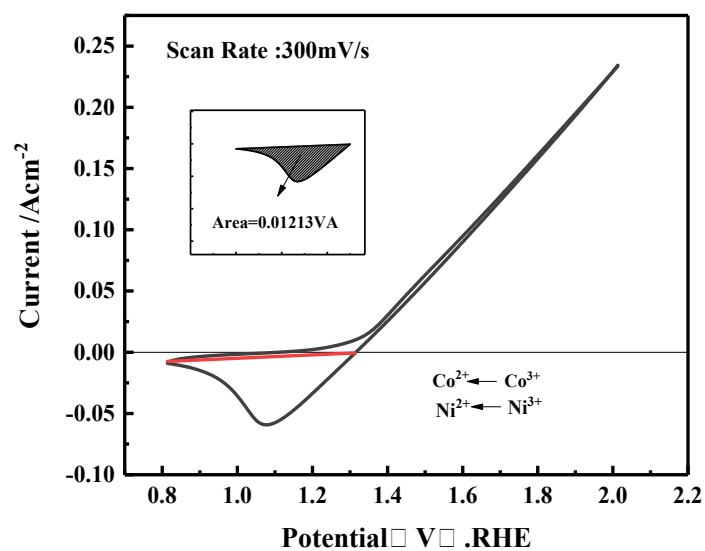


Figure S6. Area of redox features in CV curve of CoSe-0.2/NiSe-nrs/NF for calculation of the number of surface active sites.

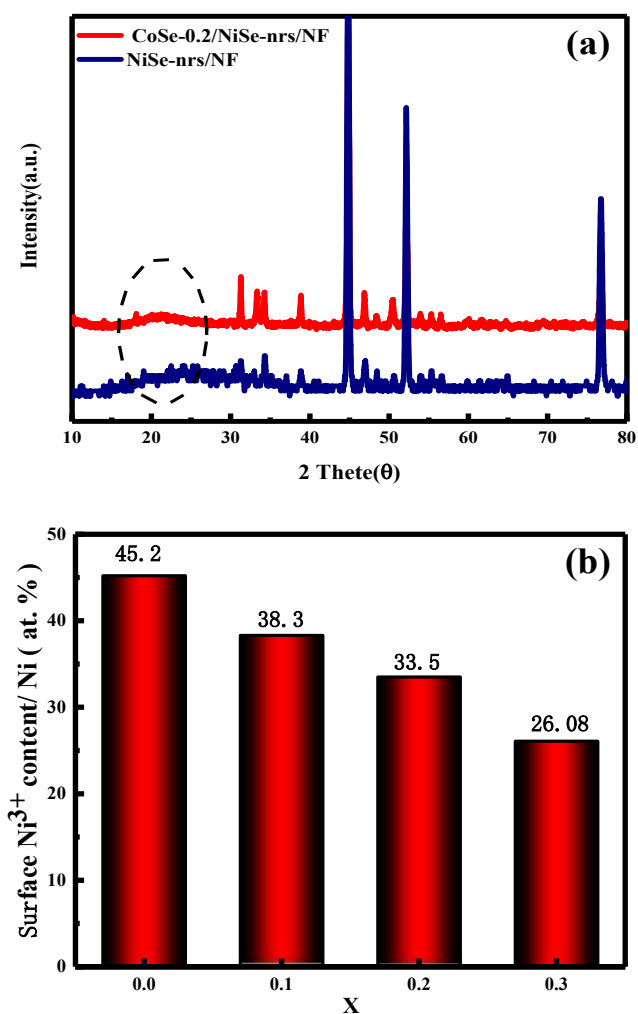


Figure S7. XRD patterns of NiSe-nrs/NF and CoSe-0.2/NiSe-nrs/NF after 30 CV cycles(a); the contents of Ni³⁺ in NiSe-nrs/NF and CoSe-x/NiSe-nrs/NF (x=0.1, 0.2 and 0.3) after 30 CV cycles (b).

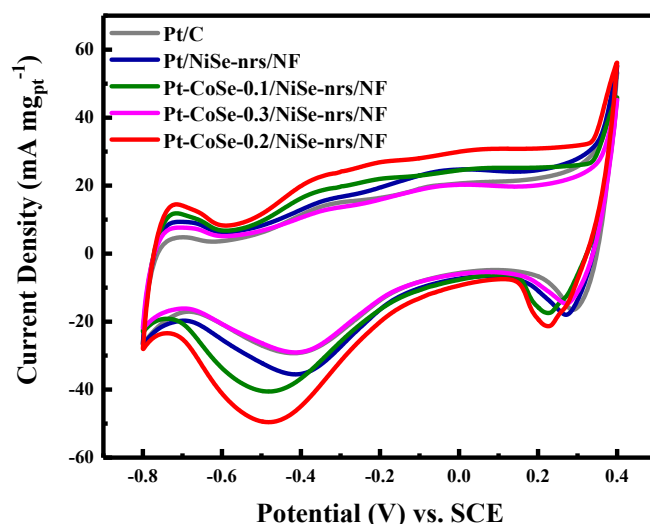


Figure S8. ECSAs (a) of CoSe-x/NiSe-nrs/NF, NiSe-nrs/NF and Pt/C

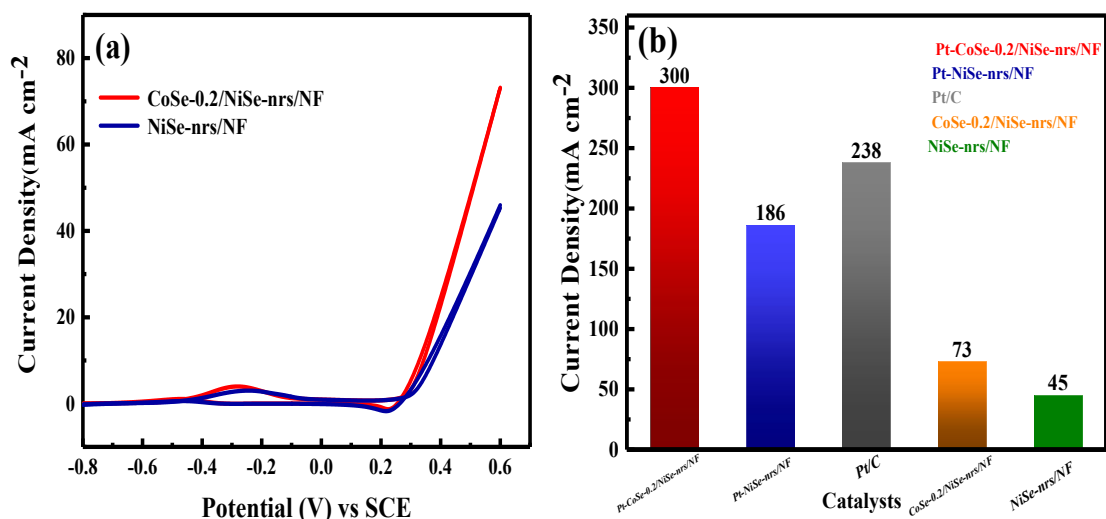


Figure S9. (a) CVs of CoSe-0.2/NiSe-nrs/NF and NiSe-nrs/NF electrodes in 1 M KOH electrolyte with 1 M methanol at a scan rate of 50 mV s⁻¹ and (b) area specific activities of the prepared electrodes.

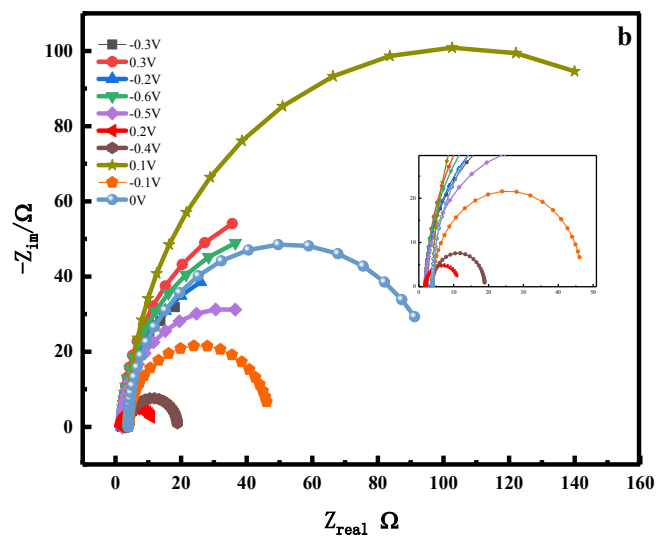


Figure S10. Nyquist plots of Pt/CoSe-0.2/NiSe-nrs/NF measured in 1 M KOH + 1 M CH₃OH.

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