Electronic Supplementary Information

Experimental section

Materials: $Ni(CH_3COO)_2 \cdot 4H_2O$, SeO_2, LiCl, HCl, $RuCl_3 \cdot 3H_2O$, H_2SO_4, and ethanol were purchased from Beijing Chemical Corp. KOH was purchased from Aladdin Ltd. (Shanghai, China). $Co(CH_3COO)_2 \cdot 4H_2O$ was purchased from Tianjin Chemical Corporation. Ti plate was provided by Hongshan District, Wuhan Instrument Surgical Instruments business. Pt/C (20 wt% Pt on Vulcan XC-72R) and Nafion (5 wt%) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Preparation of $Co_xNi_{1-x}Se_2$/Ti: $Co_{0.13}Ni_{0.87}Se_2$/Ti films were prepared on Ti substrates via electrodeposition. Prior to electrodeposition, Ti plate (~ 1 cm x 2 cm) was firstly washed with HCl, ethanol and water several times to remove the surface impurities. The electrodeposition was performed in a standard three-electrode glass cell consisting of the clean Ti plate as working electrode, a graphite plate as counter electrode and Ag/AgCl (3 M KCl) as the reference electrode at room temperature. The $Co_{0.13}Ni_{0.87}Se_2$ was electrodeposited on Ti plate in a 0.13 M $Ni(CH_3COO)_2 \cdot 4H_2O$, 0.007 M $Co(CH_3COO)_2 \cdot 4H_2O$, 0.035 M SeO_2 and 0.2 M LiCl aqueous electrolyte using a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai). The electrodeposition potential is -0.45 V vs. Ag/AgCl. After electrodeposition for 1 h, the black Ti plate was carefully rinsed several times with water and ethanol with the assistance of ultrasonication, and then dried at 60 °C for 8 h. The loading for $Co_{0.13}Ni_{0.87}Se_2$ nanoparticals on Ti plate was determined to be 1.67 mg cm^{-2} with the use of a high precision microbalance. Other catalytic electrodes of $NiSe_2$/Ti, $Co_{0.06}Ni_{0.94}Se_2$/Ti, $Co_{0.23}Ni_{0.77}Se_2$/Ti, and $Co_{0.29}Ni_{0.71}Se_2$/Ti were prepared through a similar method by simply adjusting the amount of $Co(CH_3COO)_2 \cdot 4H_2O$ to 0, 6.5, 7, and 16.25 mmol, respectively.

Preparation of Pt/C and RuO_2 loaded electrodes: RuO_2 catalyst was prepared according to reported method.[1] In brief, 0.01 mol of $RuCl_3 \cdot 3H_2O$ was dissolved in 100 mL deionized water and heated under air atmosphere at 100 °C for 10 min, followed by the addition of 1 mL KOH solution (1.0 M). The reaction mixture was maintained at this temperature under stirring for 45 min. After that, the solution was centrifuged for 10 minutes and filtered. The precipitate was washed several times with deionized water to remove the remaining chlorides. The resulting Ru-hydroxide was dried for 5 h at 80 °C and then calcined in air at 300 °C for 3 h to obtain RuO_2. To prepare Pt/C and RuO_2 loaded electrodes, 20 mg Pt/C or RuO_2 and 10 µL 5 wt% Nafion solution were dispersed in 1 mL 1:1 v water/ethanol solvent by 30-min sonication to form an ink finally. Then 83.5 µL catalyst ink was loaded on a Ti plant with a catalyst loading of 1.67 mg cm^{-2}.

Characterizations: Powder XRD data were acquired on a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). ICP-OES analysis was performed on ThermoScientific iCAP6300. XPS measurements were performed on an

ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. SEM measurements were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM measurements were performed on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. Raman spectra were collected with a Renishaw 2000 model confocal microscopy Raman spectrometer with a CCD detector and a holographic notch filter (Renishaw Ltd., Gloucestershire, U.K.) at ambient conditions. Radiation of 514.5 nm from an air-cooled argon ion laser was used for the SERS excitation. The laser beam was focused to a spot with a diameter of approximately 1 μm using a 20× microscope objective. The data acquisition time was 60 s for one accumulation. The Raman band of a silicon wafer at 520 cm^{-1} was used to calibrate the spectrometer. The generated gas was confirmed by gas chromatography (GC) analysis and measured quantitatively using a calibrated pressure sensor to monitor the pressure change in the anode and cathode compartment of a H-type electrolytic cell. The Faradaic efficiency for both processes was calculated by comparing the amount of experimentally quantified gas with theoretically calculated hydrogen (assuming 100% FE). GC analysis was carried out on GC–2014C (Shimadzu Co.) with thermal conductivity detector and nitrogen carrier gas. Pressure data during electrolysis were recorded using a CEM DT-8890 Differential Air Pressure Gauge Manometer Data Logger Meter Tester with a sampling interval of 1 point per second.

Electrochemical characterization: Electrochemical measurements were performed with a CHI 660D electrochemical analyzer in a standard three-electrode system, using

$Co_xNi_{1-x}Se_2$/Ti (1 cm x 1 cm) as working electrode, a graphite plate as counter electrode and saturated calomel electrode (SCE) as reference electrode. RuO_2 or Pt/C was deposited on Ti plate using Nafion solution as immobilization agent. All the potentials reported in this work were vs. RHE in 1.0 M KOH. E (RHE) = E (SCE) + 1.068 V. In 0.5 M H_2SO_4, E (RHE) = E (SCE) + 0.281 V. The RHE scale was calibrated using two Pt electrodes in a H_2 purged electrolyte. All currents presented are corrected against the ohmic potential drop. To reflect the real catalytic currents, all polarization curves were extracted by subtracting the capacitive currents.[2]

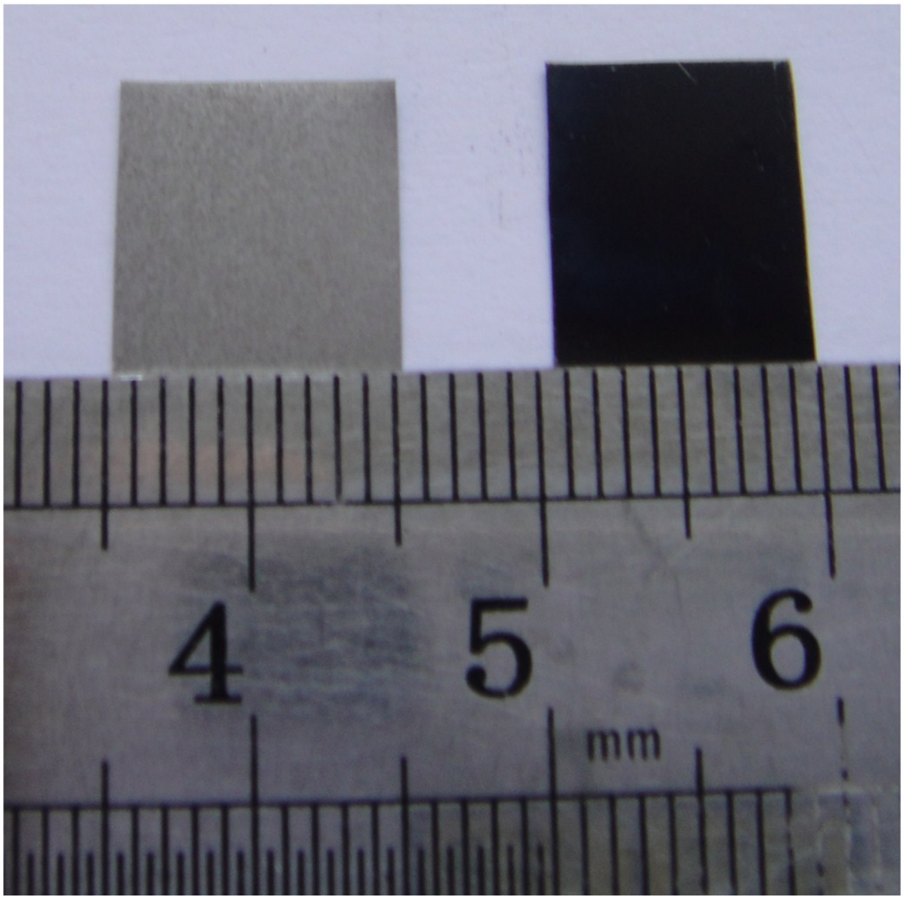

Fig. S1 Optical photograph of bare Ti plate (left) and $Co_{0.13}Ni_{0.87}Se_2$/Ti (right).

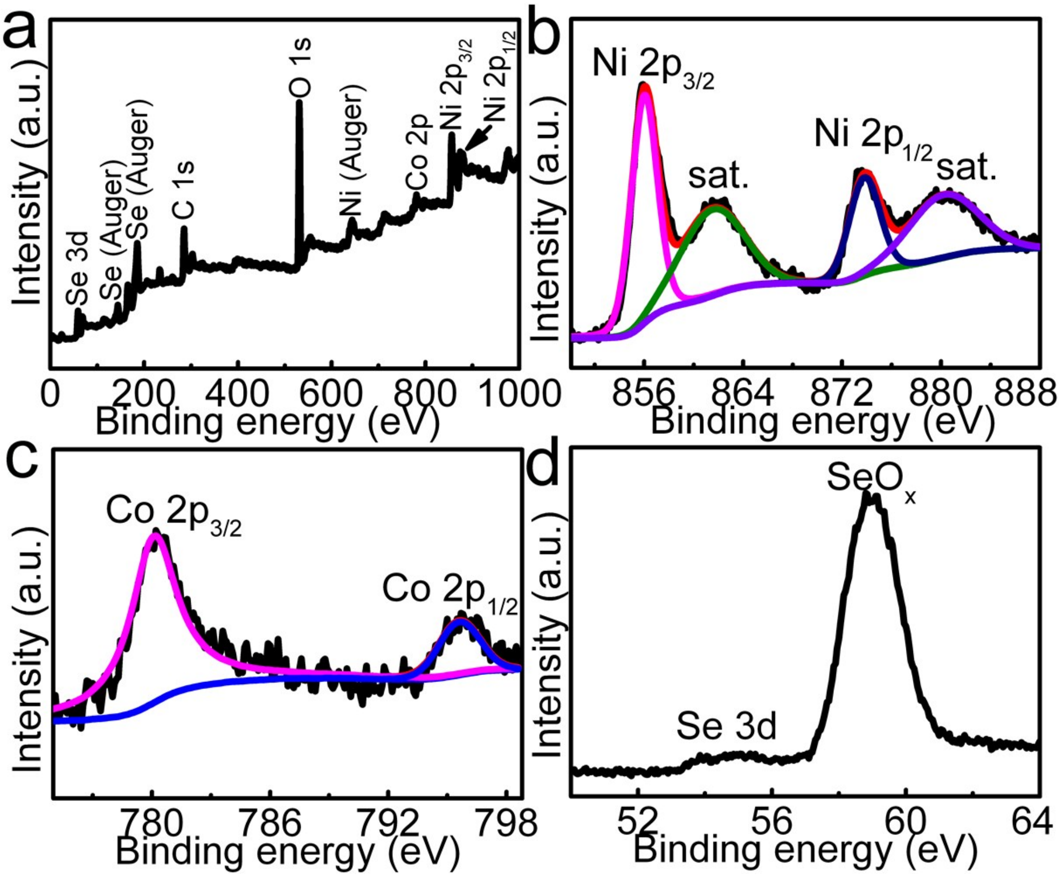

Fig. S2 (A) XPS survey spectrum of the $Co_{0.13}Ni_{0.87}Se_2$/Ti. High-resolution XPS spectra in the (B) Ni 2p, (C) Co 2p and (D) Se 3d regions for $Co_{0.13}Ni_{0.87}Se_2$/Ti.

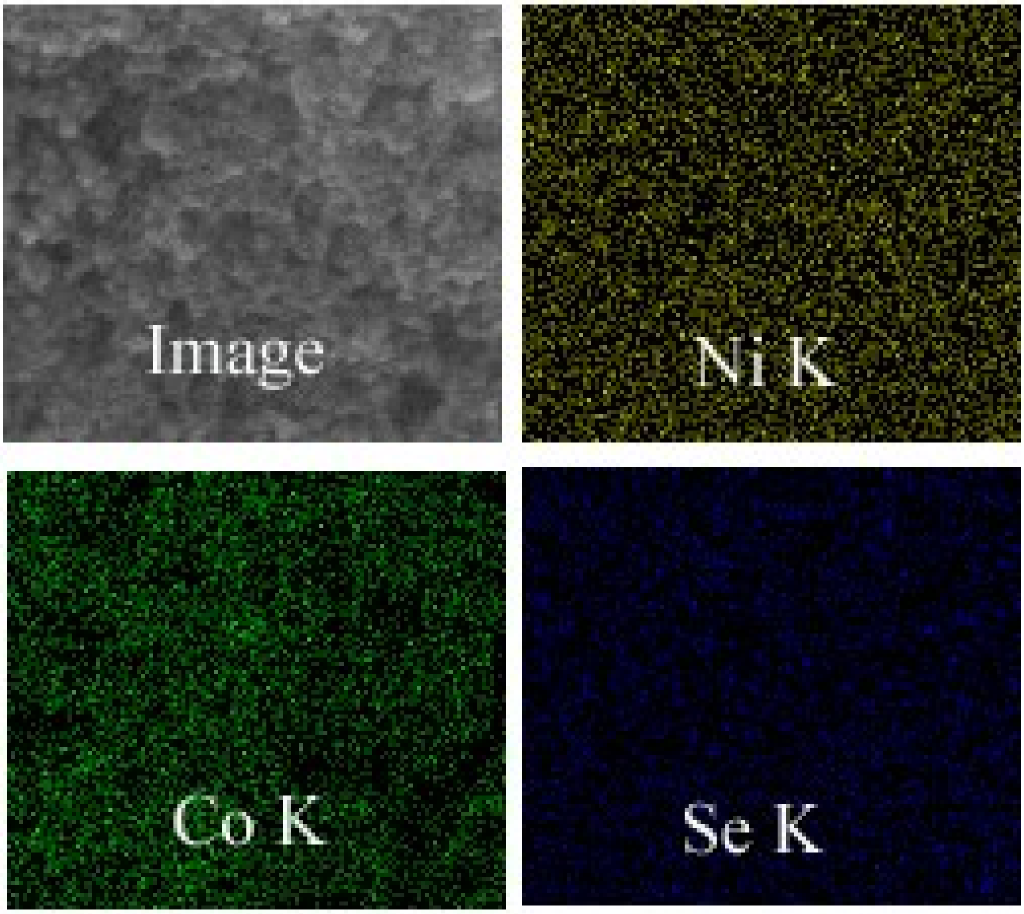

Fig. S3 Elemental mapping of Ni, Co and Se for $Co_{0.13}Ni_{0.87}Se_2$/Ti.

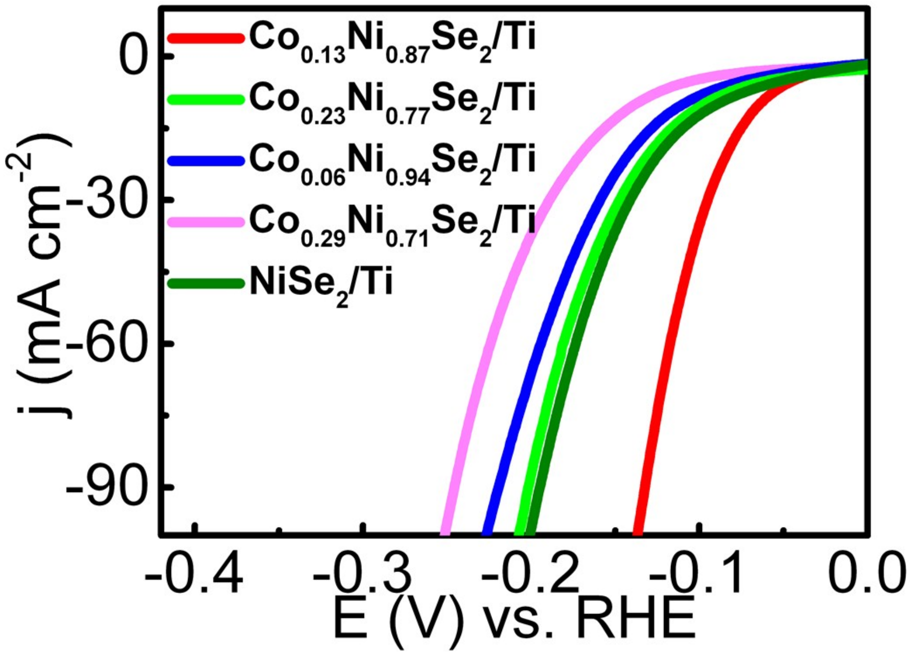

Fig. S4 Polarization curves for a series of $Co_xNi_{1-x}Se_2$/Ti and $NiSe_2$/Ti at a scan rate of 5 mV s^{-1} in 1.0 M KOH.

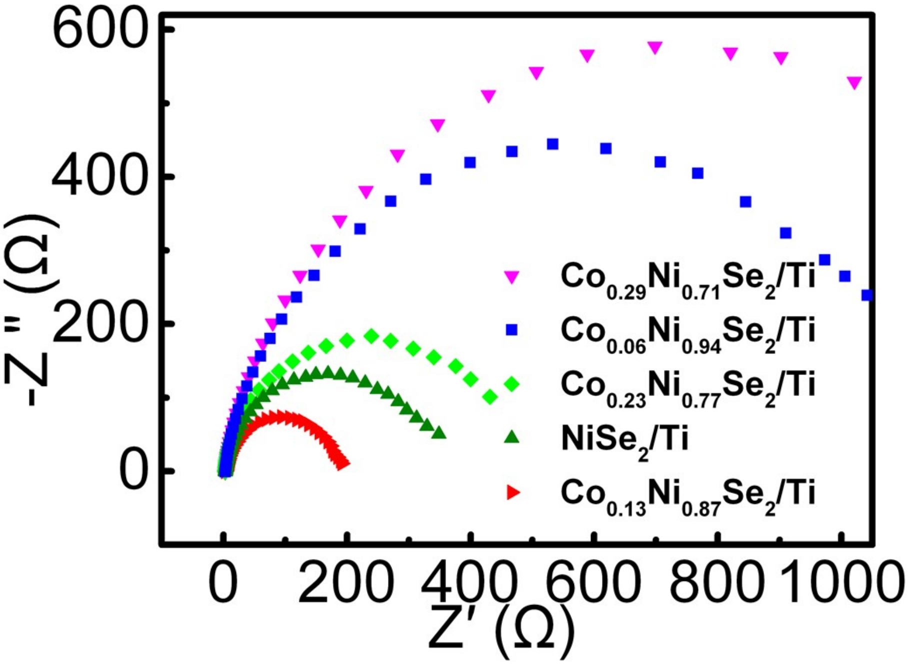

Fig. S5 Nyquist plots of $Co_{0.13}Ni_{0.87}Se_2$/Ti, $NiSe_2$/Ti, $Co_{0.23}Ni_{0.77}Se_2$/Ti, $Co_{0.06}Ni_{0.94}Se_2$/Ti and $Co_{0.29}Ni_{0.71}Se_2$/Ti recorded in 1.0 M KOH.

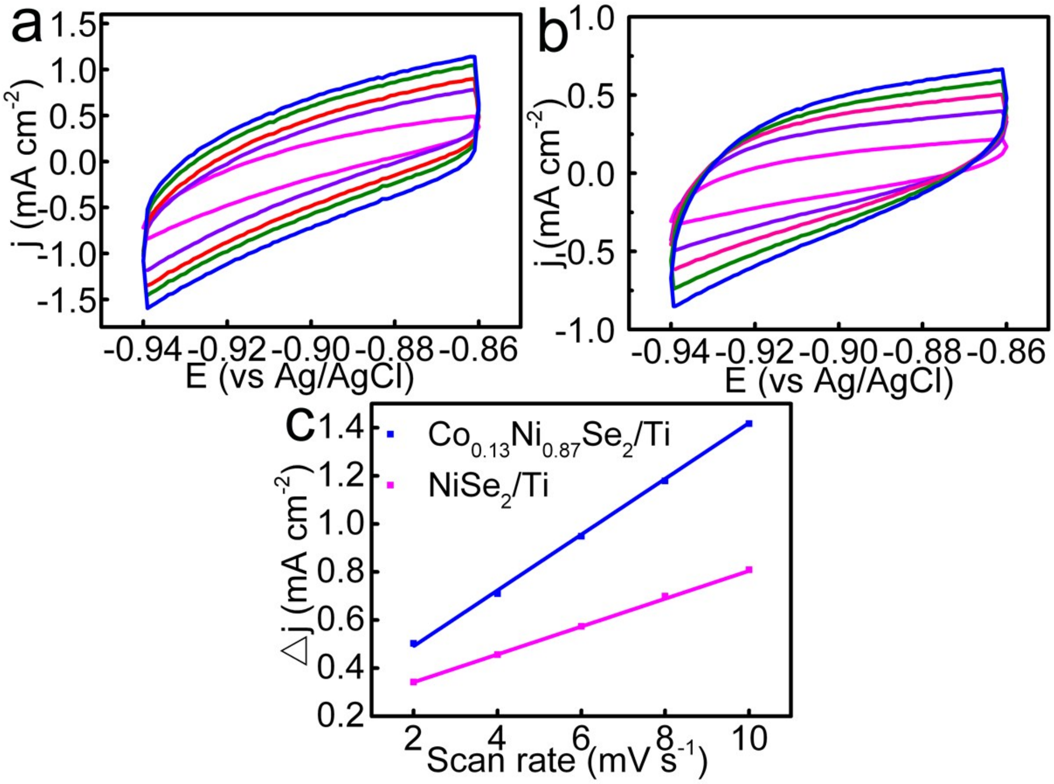

Fig. S6 CVs for (A) $Co_{0.13}Ni_{0.87}Se_2$/Ti and (B) $NiSe_2$/Ti. (C) The capacitive currents at -0.9 V vs. Ag/AgCl as a function of scan rate for $Co_{0.13}Ni_{0.87}Se_2$/Ti and $NiSe_2$/Ti ($\Delta j = j_a - j_c$).

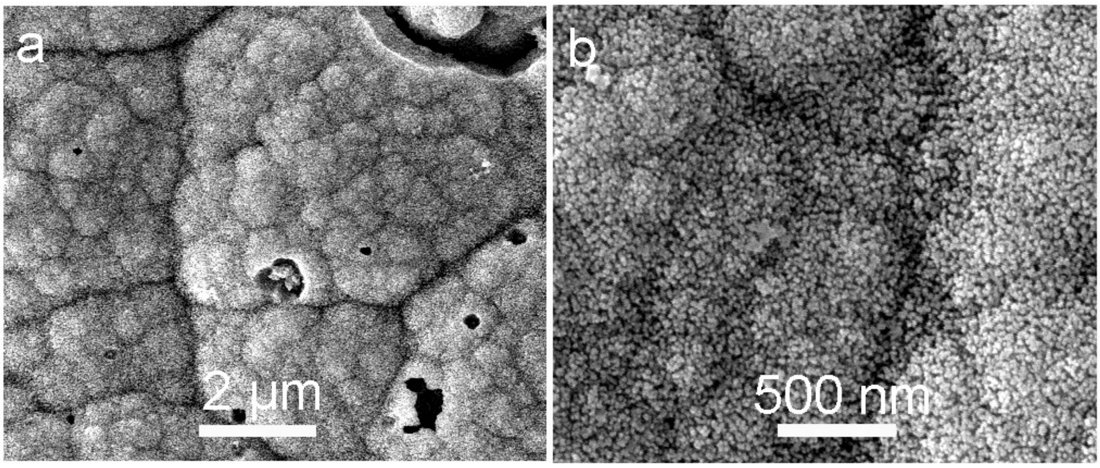

Fig. S7 SEM images of $Co_{0.13}Ni_{0.87}Se_2$/Ti after HER electrolysis.

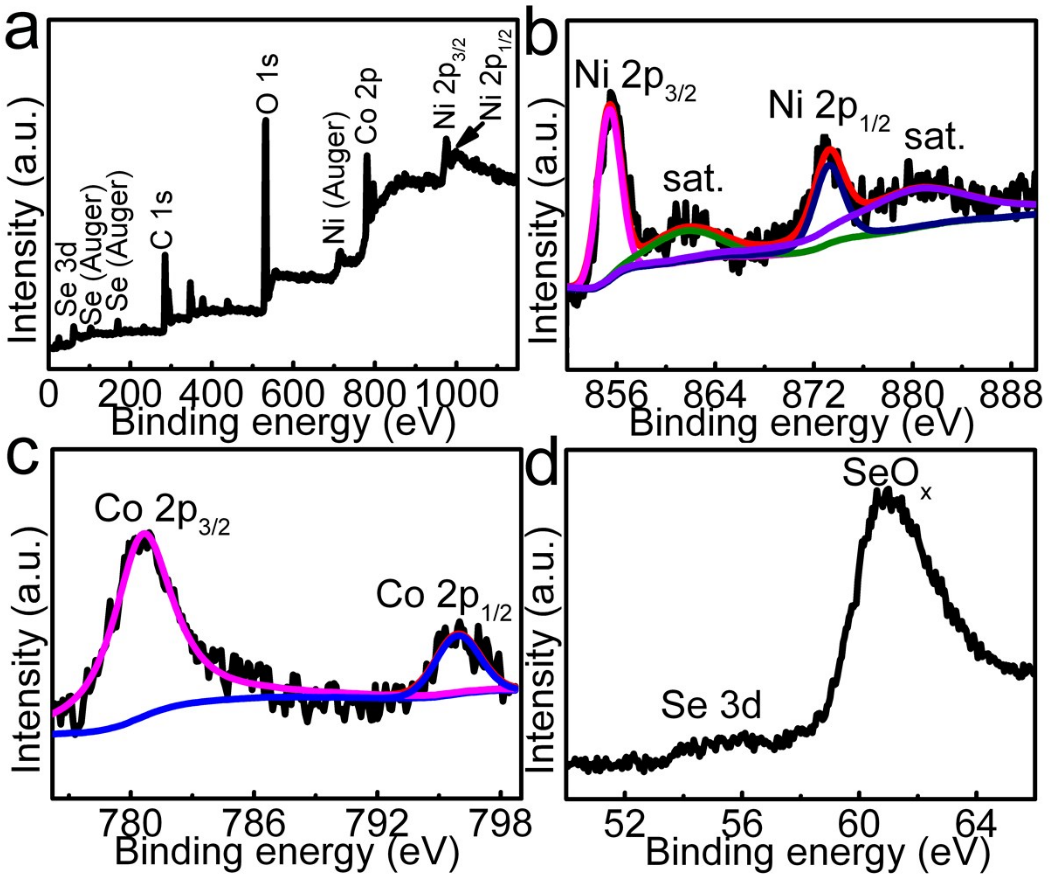

Fig. S8 (A) XPS survey spectrum for $Co_{0.13}Ni_{0.87}Se_2$/Ti after HER electrolysis. XPS spectra for the post- HER $Co_{0.13}Ni_{0.87}Se_2$/Ti in the (B) Ni 2p, (C) Co 2p and (D) Se 3d regions.

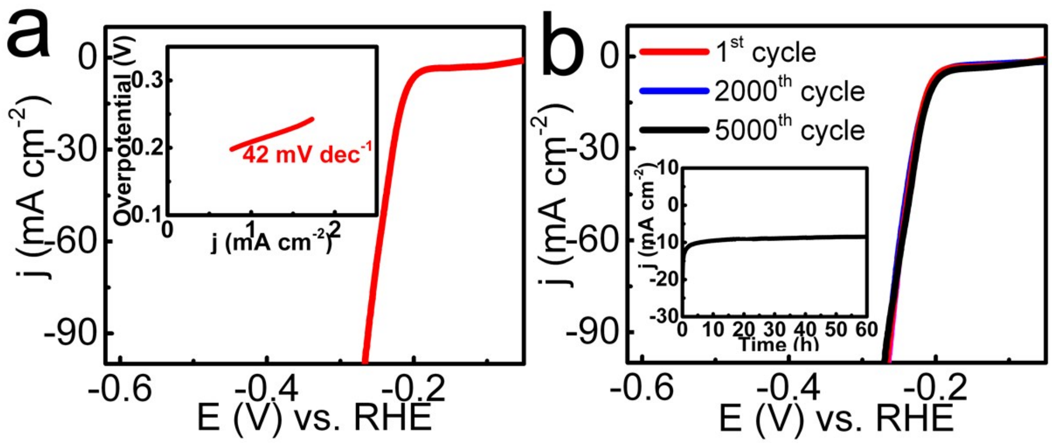

Fig. S9 (A) Polarization curve with a scan rate of 5 mV s^{-1} and Tafel plot (inset) for $Co_{0.13}Ni_{0.87}Se_2$/Ti. (B) Polarization curves for $Co_{0.13}Ni_{0.87}Se_2$/Ti before and after 2000 (5000) CV cycles at a scan rate of 5 mV s^{-1}. Inset: time-dependent current density curve for $Co_{0.13}Ni_{0.87}Se_2$/Ti under static overpotential of 212 mV for 60 h.

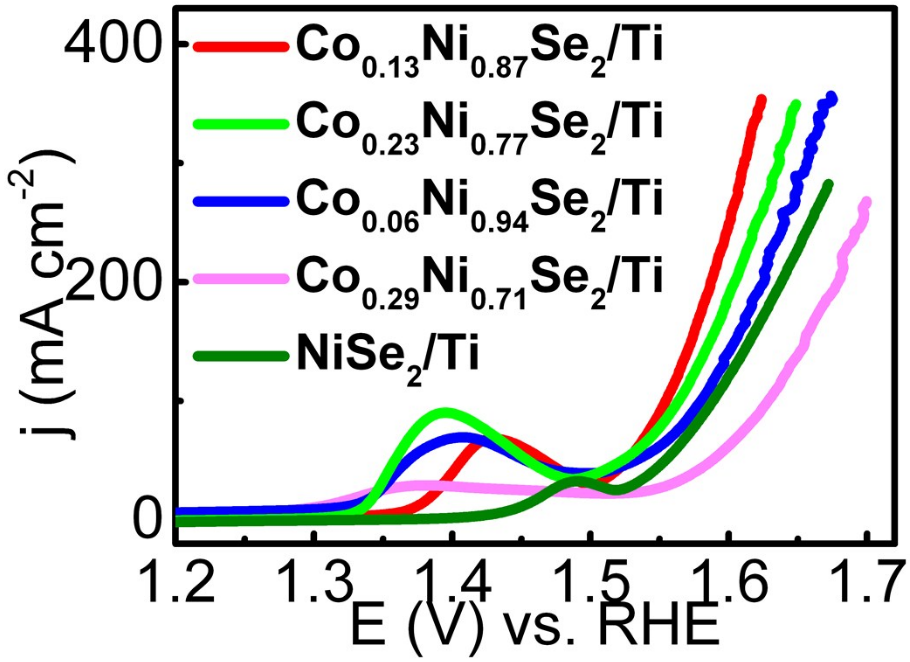

Fig. S10 Polarization curves for a series of $Co_xNi_{1-x}Se_2$/Ti and $NiSe_2$/Ti at a scan rate of 2 mV s^{-1} in 1.0 M KOH.

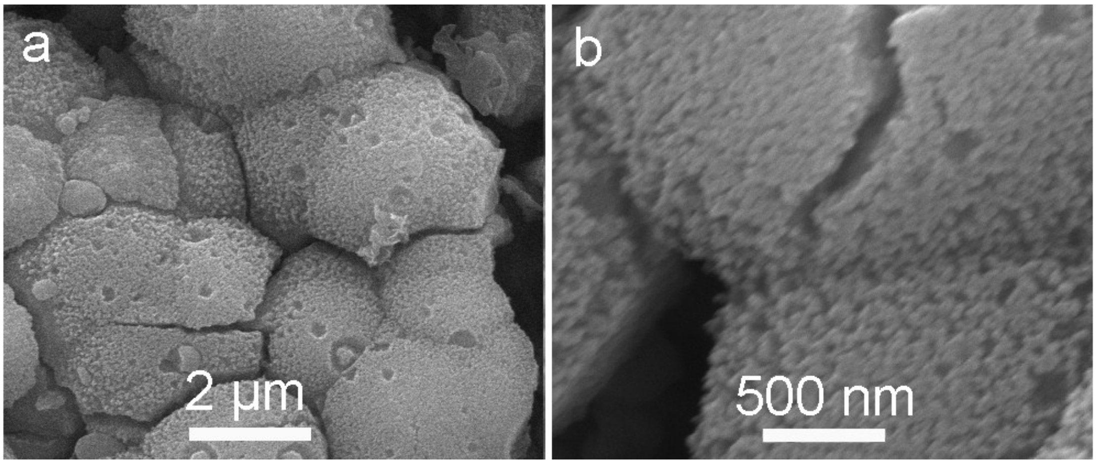

Fig. S11 SEM images of $Co_{0.13}Ni_{0.87}Se_2$/Ti after OER electrolysis.

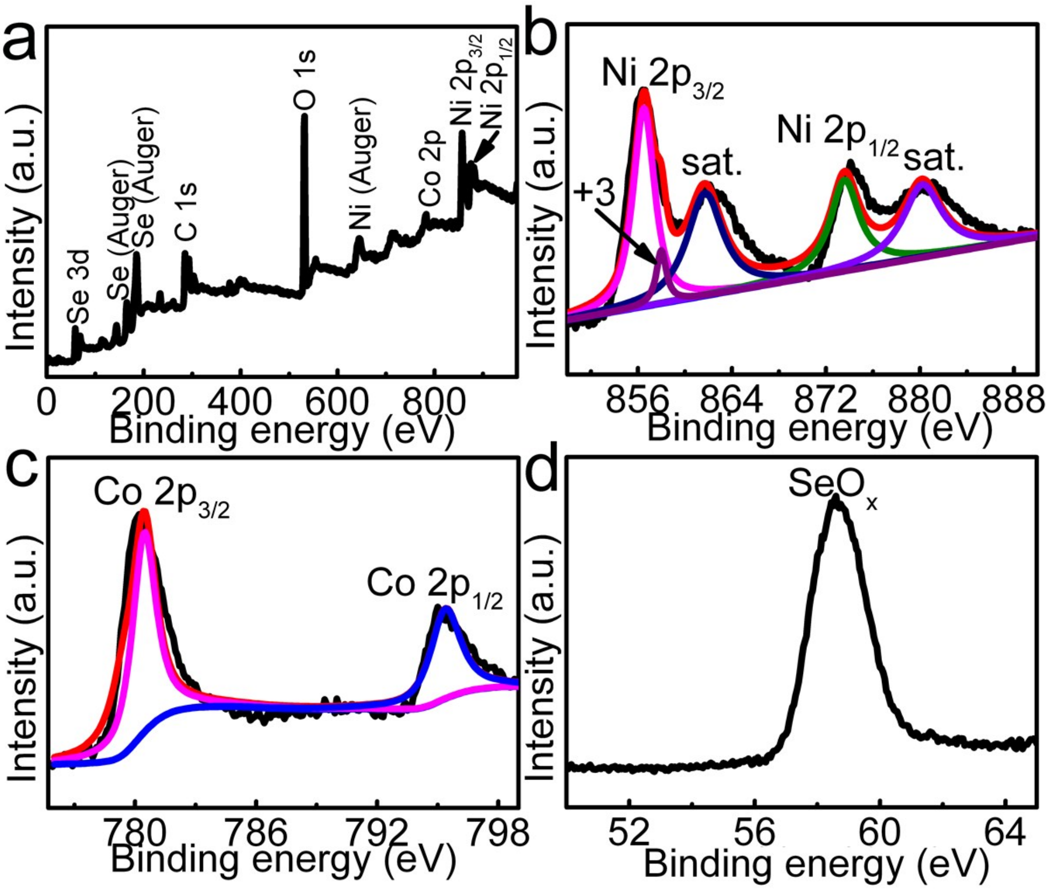

Fig. S12 (A) XPS survey spectrum for $Co_{0.13}Ni_{0.87}Se_2$/Ti after OER electrolysis. XPS spectra for the post-OER $Co_{0.13}Ni_{0.87}Se_2$/Ti in the (B) Ni 2p, (C) Co 2p and (D) Se 3d regions.

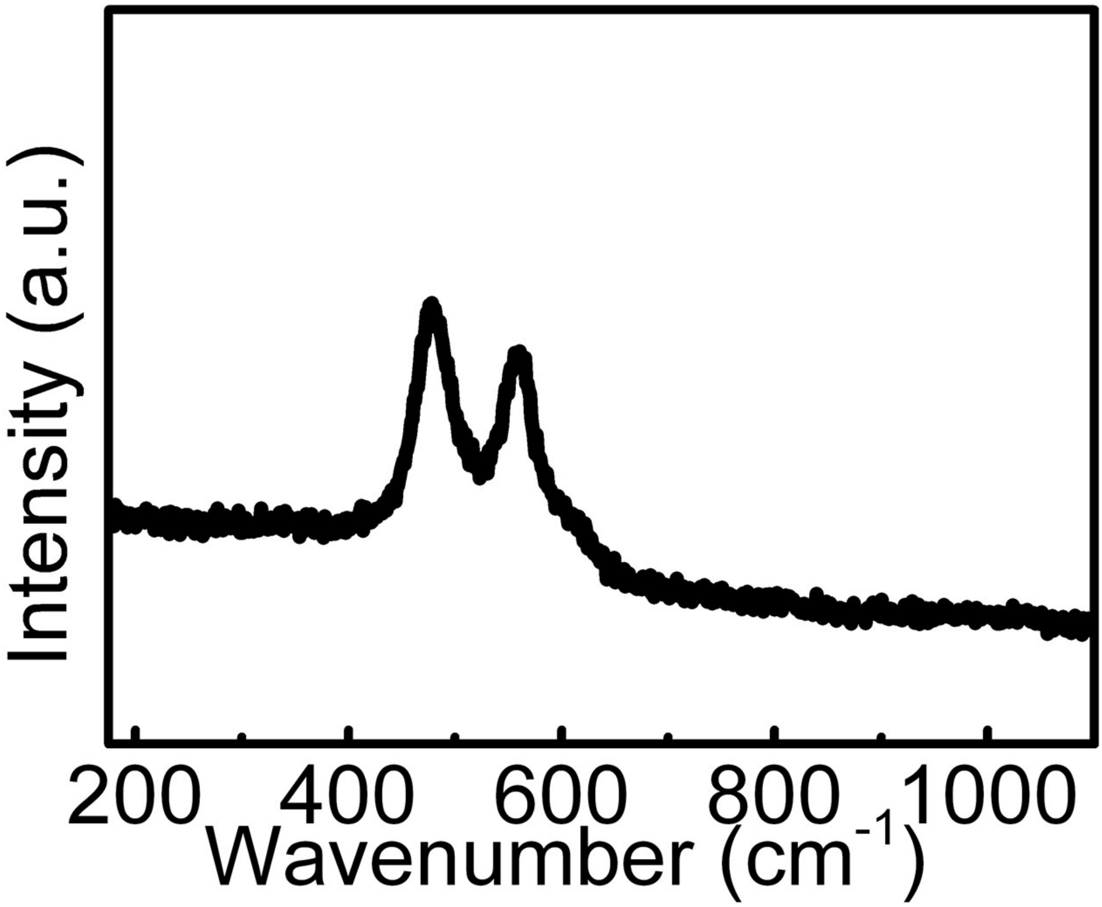

Fig. S13 Raman spectrum for $Co_{0.13}Ni_{0.87}Se_2$/Ti after OER electrolysis in 1.0 M KOH.

Movie S1. This movie shows H_2 and O_2 evolution on $Co_{0.13}Ni_{0.87}Se_2$/Ti electrodes in a two-electrode setup driven by a cell voltage of 1.60 V in 1.0 M KOH.

Reference

1. J. C. Cruz, V. Baglio, S. Siracusano, V. Antonucci, A. S. Aric, R. Ornelas, L. Ortiz-Frade, G. Osorio-Monreal, S. M. Durn-Torres and L. G. Arriaga, *Int. J. Electrochem. Sci.* 2011, **6**, 6607.

2. R. Mohamed, X. Cheng, E. Fabbri, P. Levecque, R. Kotz, O. T. Conrad and J. Schmidt, *J. Electrochem. Soc.* 2015, **162**, 579.