Electronic Supplementary Information

Cobalt and nickel selenide nanowalls anchored on graphene as bifunctional electrocatalysts for overall water splitting

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S1. Graphene/Ni mesh substrate preparation

Graphene/Ni mesh acted as the basic substrate for electrodeposition. It was prepared through a typical atmospheric pressure chemical vapor deposition (APCVD) method that utilized Ni mesh (purity: 99.99%, aperture: 100 μm, wire diameter: 70 μm, Alfa Aesar) as the template. The process was carried out at a tube furnace (Lindberg/Blue M). Prior to CVD, the Ni mesh underwent ultrasonic cleaning in dilute hydrochloric (HCl) acid, ethanol and deionized (DI) water successively. First, the Ni mesh was put in a quartz tube in an argon (Ar) flow (400 mL/min, 30 min) to exhaust gases. Then, the temperature was heated to 1000 ºC in 90 min with Ar/H_2 (300/50 mL/min) flow protection. With the temperature maintained, CH_4 was introduced with an $Ar/H_2/CH_4$ (250/10/30 mL/min) flow for 20 min, acting as the carbon source. After this reaction stage, CH_4 and H_2 were switched off, meanwhile the furnace was turned off, and finally the sample was pulled out quickly to cool down.

S2. Electrochemical measurements

A three-electrode configuration using saturated calomel electrode (SCE) as the reference electrode, Pt foil as the counter electrode, and transition metal based nanowalls based samples as the working electrode was adopted for electrochemical HER and OER tests in a high-purity N_2 saturated 1 M KOH electrolyte. Polarization curves were recorded by a CHI 660B electrochemical workstation (Shanghai CH Instrument Co.) at a scan rate of 5 mV/s. All potentials measured were calibrated to a RHE by adding a value of 1.069 V, using the following equation: E (RHE) = E (SCE) + 0.2412 V + 0.0591PH. The EIS tests were performed at open circuit potentials with a frequency range of 0.1 to 2×10^5 Hz with an amplitude of 5 mV. The long-term durability test was performed using chronoamperometric measurement.

S3. Electrochemical active surface area (ECSA) determination[S1]

Electrochemical capacitance was measured by performing cyclic voltammetry (CV) scans in a potential range where no apparent Faradic process was observed at different scan rates of 40, 80, 160, 240, 320, 400 mV/s. The capacitive currents were collected at 0.23, 0.32, 0.31 and 0.31 V for $Co(OH)_2$, $Ni(OH)_2$, CoSe and NiSe, respectively (**Figure S13a,b** and **Figure 4d,e**), then these values were plotted as a function of scan rates in **Figure 4f**. Finally, the specific capacitances were obtained by linear fitting and listed in **Figure S13c**. Assume that the specific capacitance for a flat surface was about 40 μF/cm^2 for 1 cm^2 of real surface area, then the ECSA was calculated as: ECSA = specific capacitance (mF/cm^2) / 40μF/cm^2 per cm^2.

S4. Characterizations

Raman spectroscope (LabRAM HR Evolution, 532 nm), X-ray photoelectron spectroscopy (XPS, PHI Quantera SXMTM, Scanning X-ray MicroprobeTM), scanning electron microscope (SEM, Merlin, InlensDuo, 15 kV), transmission electron microscopy (TEM, JEM-2010, 120-200 kV), X-ray diffraction (XRD, D/max2550HB+/PC). A Newport 69907 solar simulator was used to measure the photovoltaic properties of the solar cell under AM 1.5 (100 mW/cm^2). Keithley 2601A SourceMeter is used to keep track of I-V data.

S5. Supporting figures: Figure S1~S17.

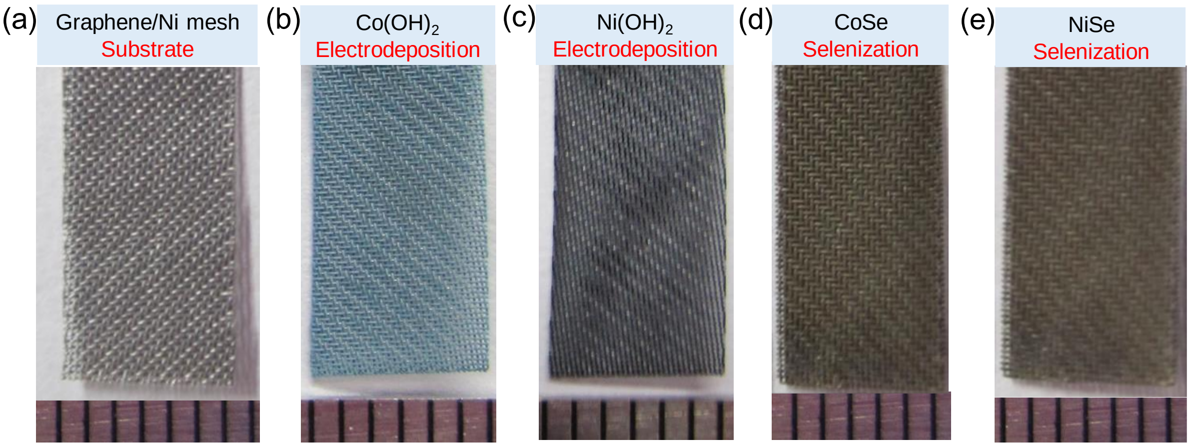


Figure S1. Photographs of (a) pristine graphene/Ni mesh, after electrodeposition: (b) Co(OH)$_2$, (c) Ni(OH)$_2$, and after selenization: (d) CoSe, (e) NiSe.

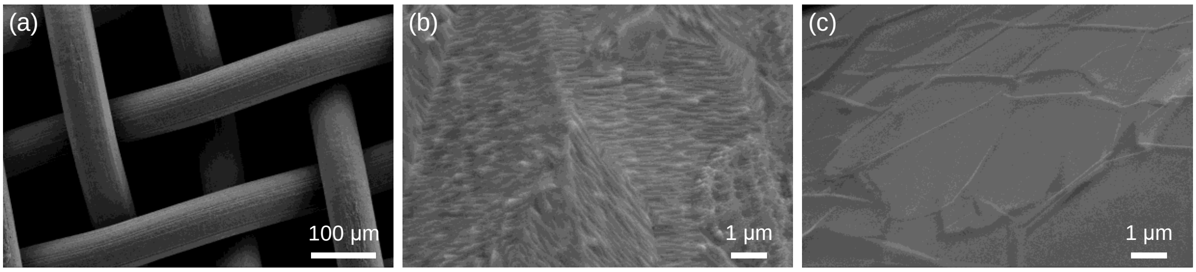


Figure S2. SEM characterizations of (a, b) Ni mesh, (c) graphene/Ni mesh.

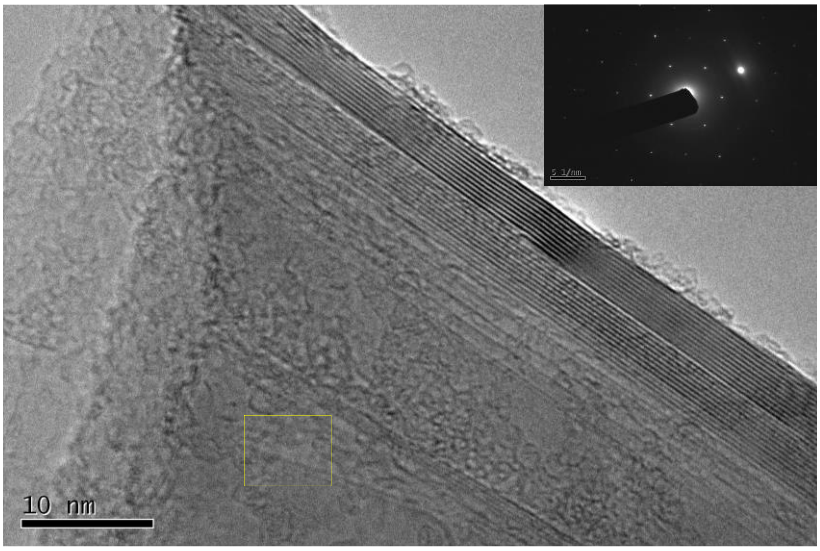


Figure S3. TEM characterization of graphene. The inset is the SAED pattern of the area marked with the yellow square.

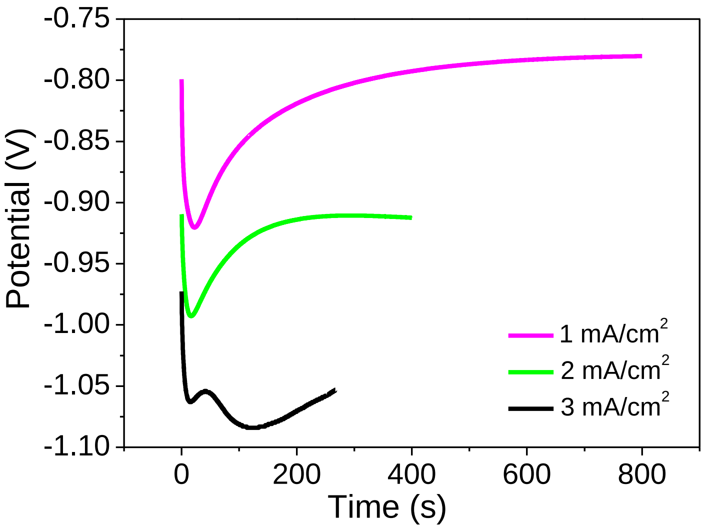


Figure S4. Electrodeposition curves of $Co(OH)_2$ at different current density.

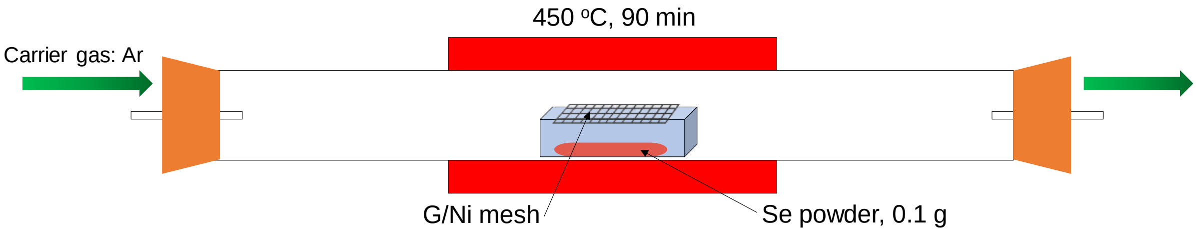


Figure S5. Schematic diagram of the selenization process.

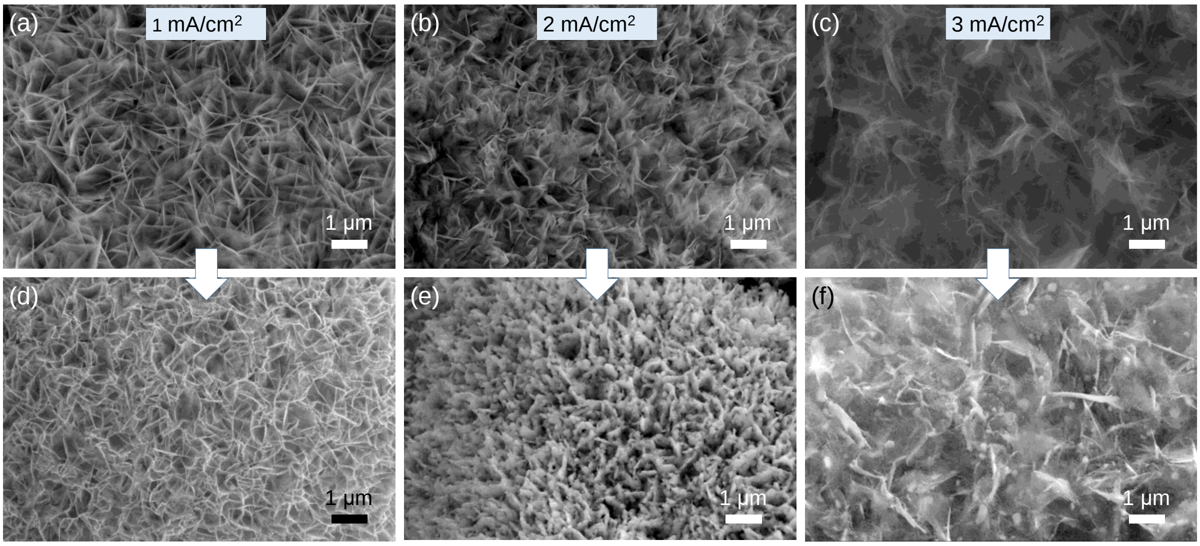


Figure S6. SEM characterizations of (a, b, c) $Co(OH)_2$ (electrodeposited at different current densities) and (d, e, f) corresponding CoSe nanowalls.

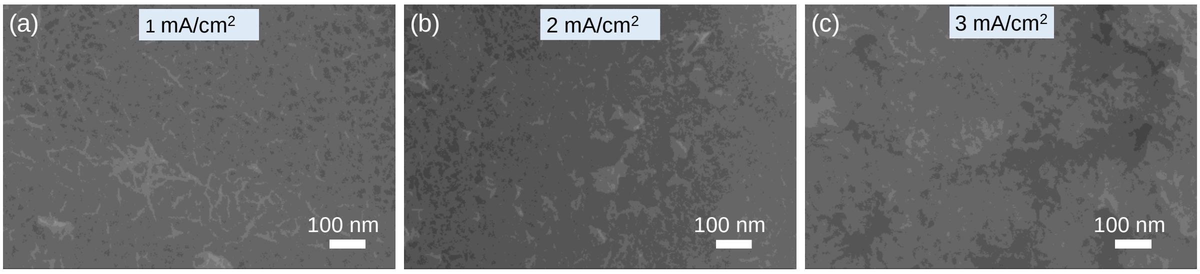


Figure S7. SEM characterizations of (a, b, c) $Ni(OH)_2$ (electrodeposited at different current densities)

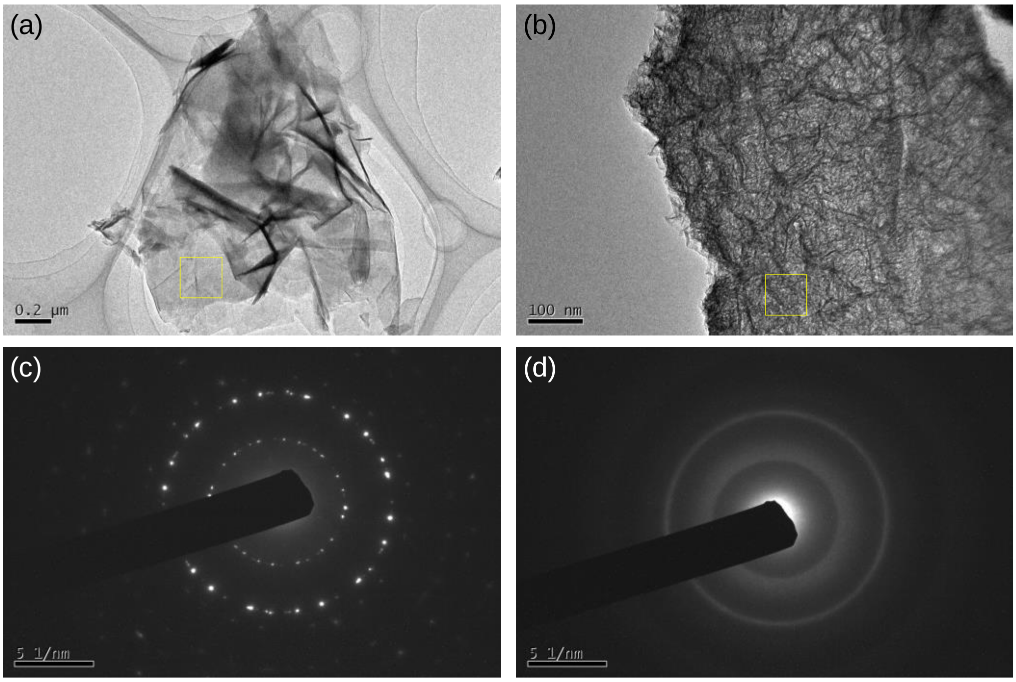


Figure S8. TEM characterizations of (a) $Co(OH)_2$, (b) $Ni(OH)_2$. (c, d) SAED patterns of the areas marked with yellow squares in (a) and (b), respectively.

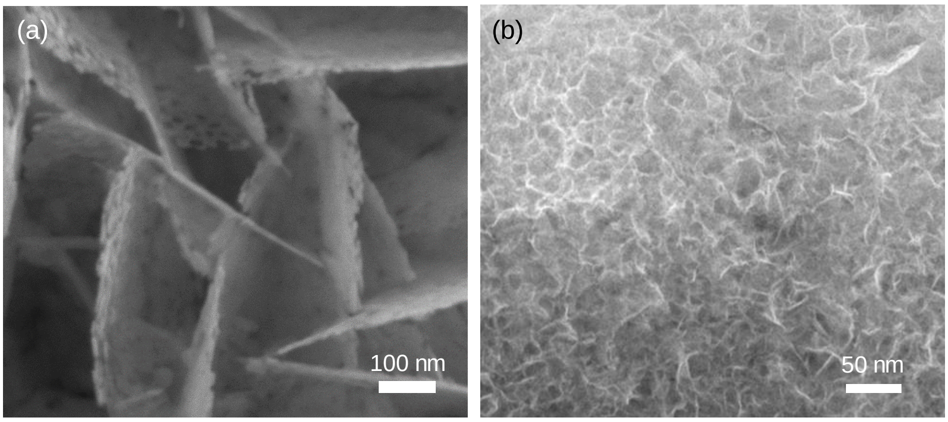


Figure S9. High resolution SEM images of (a) CoSe and (b) NiSe.

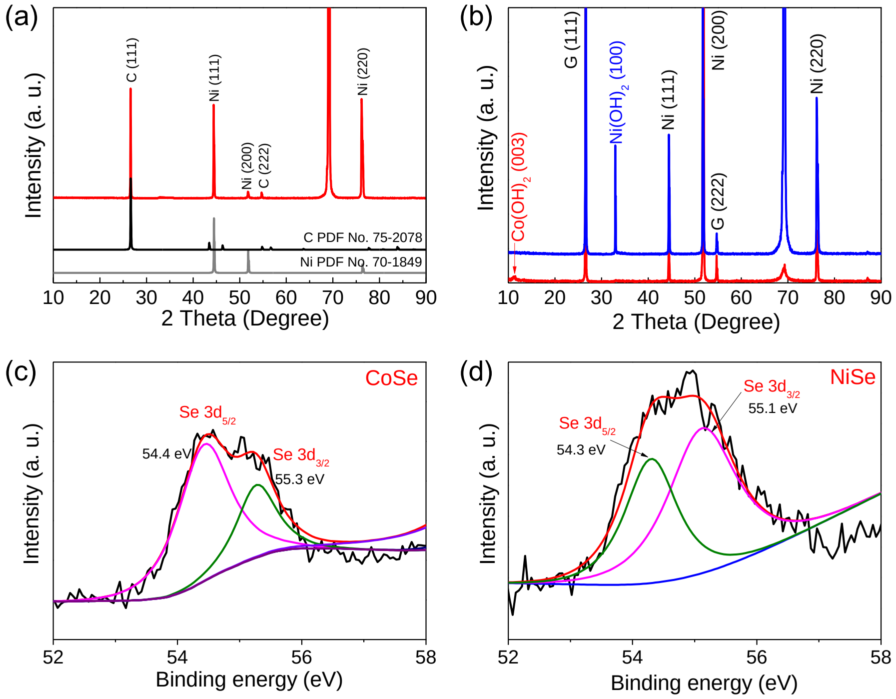


Figure S10. XRD profiles of (a) Ni mesh and G/Ni mesh substrate, (b) $Co(OH)_2$ and $Ni(OH)_2$. High resolution XPS spectra of CoSe (c) Se 3d and NiSe (d) Se 3d.

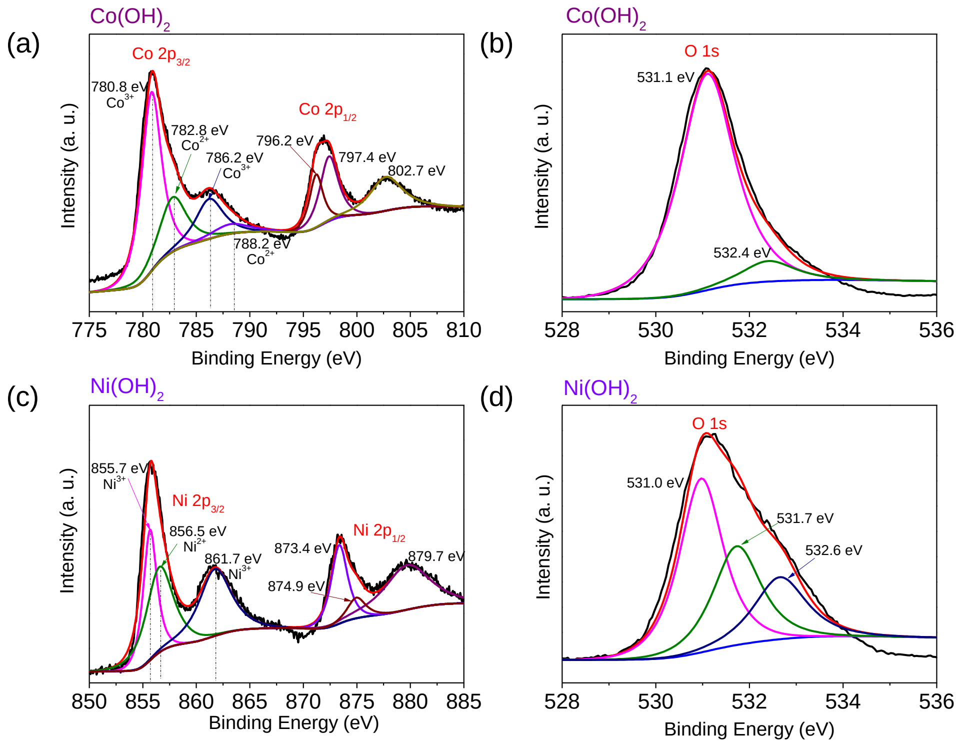


Figure S11. High resolution XPS spectra of $Co(OH)_2$: (a) Co 2p, (b) O 1s, and $Ni(OH)_2$: (c) Ni 2p, (d) O 1s.

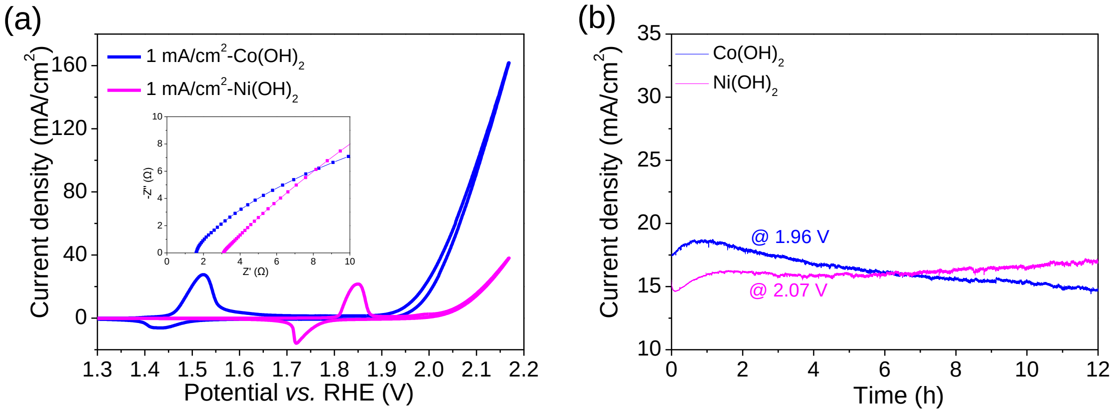


Figure S12. (a) OER tests of Co(OH)$_2$ and Ni(OH)$_2$ in 1 M KOH. Inset shows the corresponding EIS tests. (b) Chronoamperometric tests of (a). The applied voltages are 1.96 and 2.07 V, respectively.

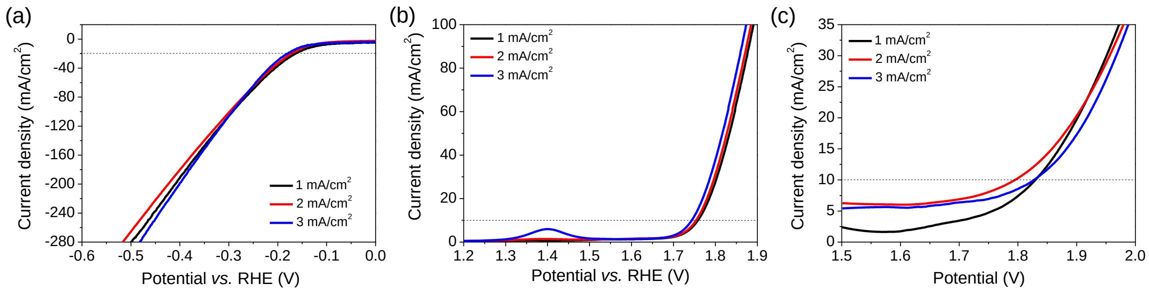


Figure S13. (a) OER, (b) HER tests of CoSe at 1, 2 and 3 mA/cm^2 refer to the electrodeposition current density when Co(OH)$_2$ nanowall is formed; (c) Two electrode tests of CoSe (+) and CoSe (-). The electrolyte is 1 M KOH.

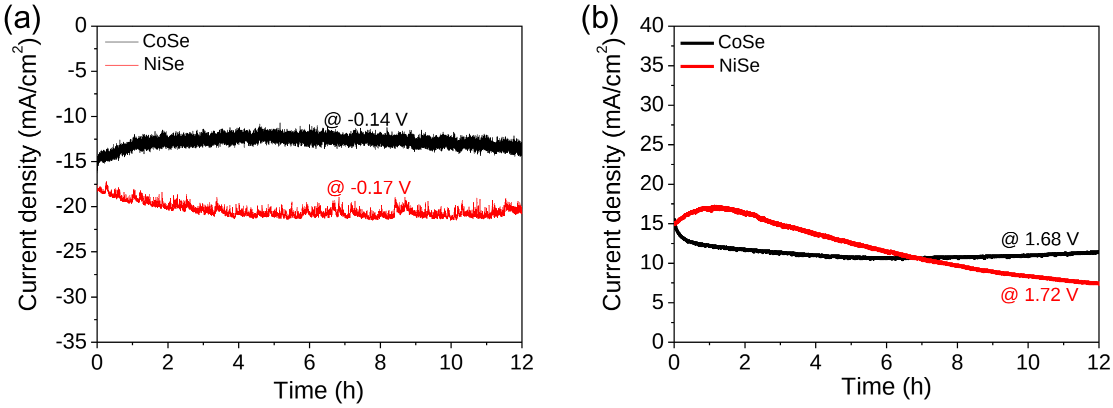
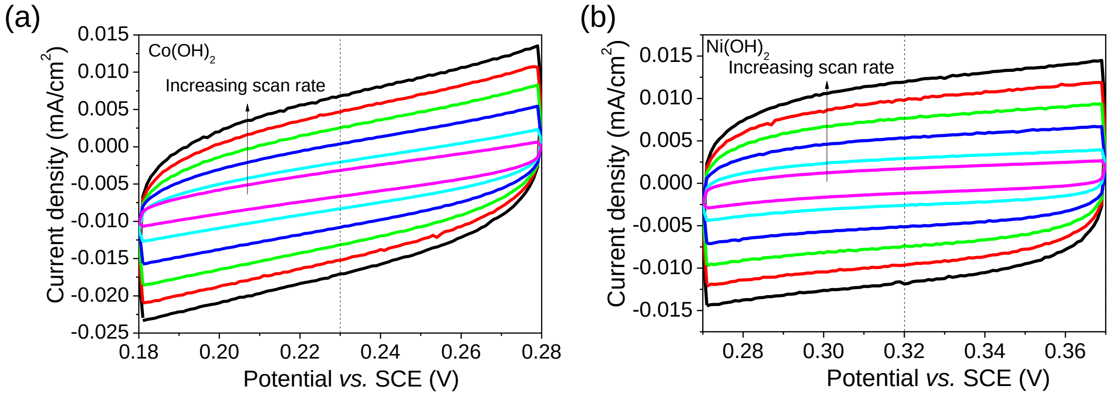


Figure S14. (a) HER, (b) OER Chronoamperometric tests of CoSe and NiSe in 1 M KOH at different applied voltages.



(c)

	$Co(OH)_2$	$Ni(OH)_2$	CoSe	NiSe
Specific Capacitance (mF/cm^2)	0.0278	0.0284	6.88	6.17
ECSA (cm^2)	0.70	0.71	172	154

Figure S15. CV in potential range where no Faradaic processes are present for (a) $Co(OH)_2$ and (b) $Ni(OH)_2$. The capacitive currents are collected at 0.23 V and 0.32V for $Co(OH)_2$ and $Ni(OH)_2$, respectively. (c) Determination of the ECSA for each sample. The electrolyte is 1 M KOH.

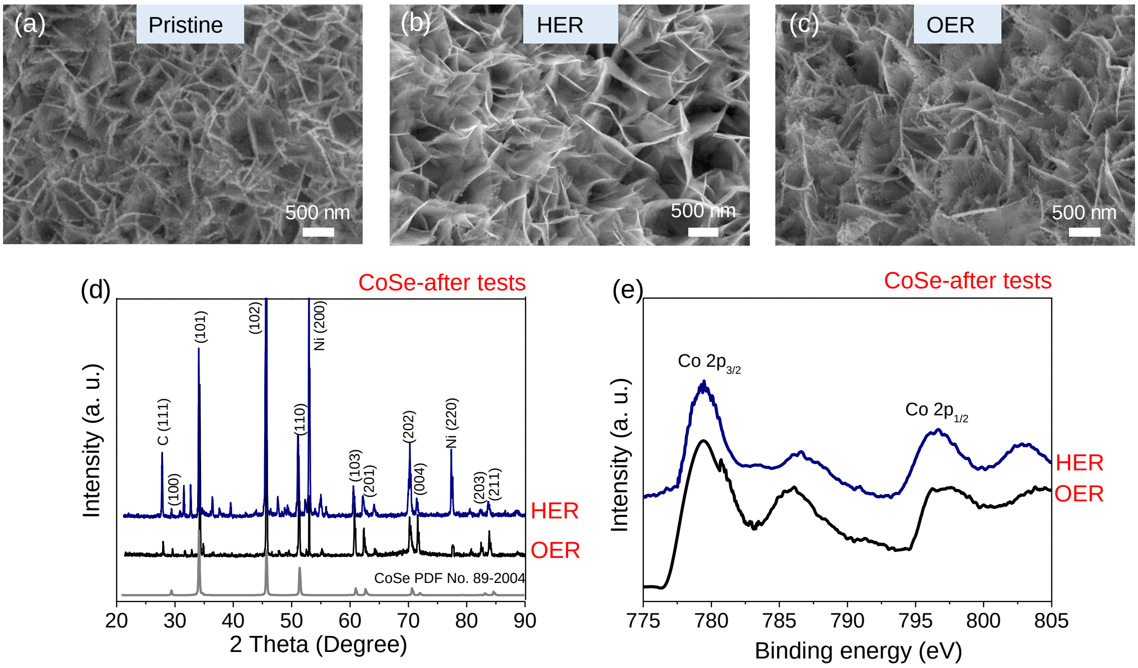


Figure S16. SEM characterizations of (a) pristine CoSe nanowall, after (b) HER (c) OER cycle tests in 1 M KOH. (d) XRD profiles and (e) High resolution XPS spectra (Co 2p) of CoSe after HER (dark blue line) and OER (black line) tests.

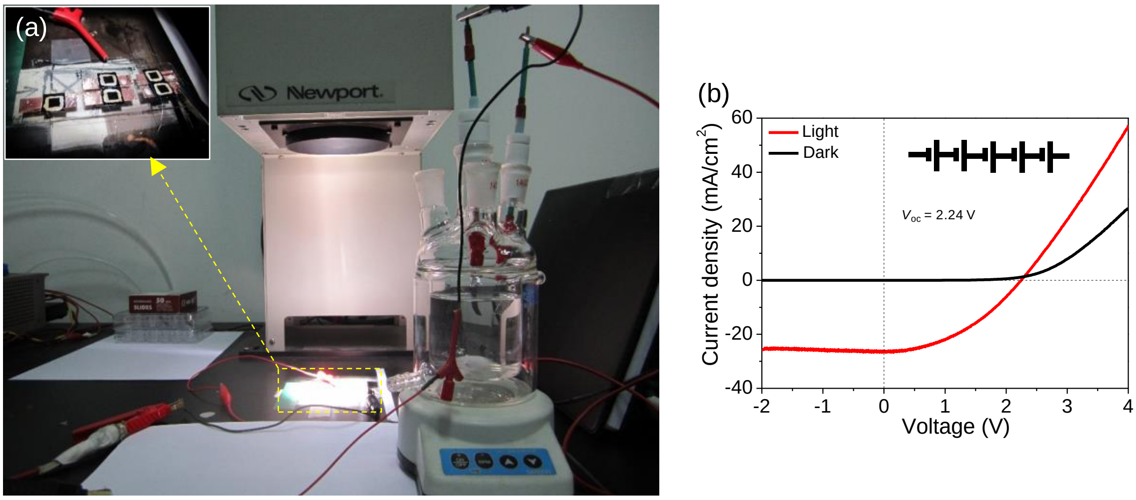


Figure S17. (a) Photographs of the tandem solar water splitting cell under AM 1.5 illumination. (b) Performance of the five-in series hybrid heterojunction and photoelectrochemical solar cell.

Reference

[S1] J. Kibsgaard, Thomas F. Jaramillo, Angew. Chem. Int. Ed., 2014, 53, 14433-14437.