

Electronic Supplementary Information for

p-Si/NiCoSe_x Core/Shell Nanopillar Array Photocathode for

Enhanced Photoelectrochemical Hydrogen Production

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Contents

I. Experimental details.....	S3
II. Structural characterization.....	S8
III. Electrochemical and photoelectrochemical characterization.....	S8
IV. The line scan profile, TEM/EDS spectra and XRD pattern of p-Si/NiCoSe _x NP.....	S11
V. SEM image and EDS spectrum of NiCoSe _x / graphite electrode.....	S12
VI. Stability measurement of NiCoSe _x / graphite electrode.....	S12
VII. The electrochemical measurements of different catalysts electrodeposited on graphite disk substrate.....	S13
VIII. Calibration process of illumination intensity.....	S14
IX. The light spectrum of irradiation.....	S15
X. SEM images of NiCoSe _x electrodeposited on Si NP array with various time.....	S16
XI. Polarization curves of p-Si/NiCoSe _x NP photocathodes deposited with different time.....	S17
XII. SEM images of planar silicon and NiCoSe _x electrodeposited on planar silicon	S17
XIII. Polarization curve of p-Si/Pt NP photocathode.....	S18
XIV. SEM image of p-Si/Pt NP photocathode.....	S18
XV. SEM images of different catalysts electrodeposited on p-Si NP array	S19
XVI. Photoelectrochemical measurements of p-Si NP array with different catalysts.....	S19
XVII. Photograph of Faradaic efficiency measurement device	S20
XVIII. Faradaic efficiency of generated H ₂ and O ₂	S20
Table S1. Comparison of PEC-HER performance of silicon based photocathodes.....	S22
References.....	S23

I. Experimental details

1. Materials and chemicals

Cobalt chloride hexahydrate, nickel chloride hexahydrate, selenium dioxide, potassium chloride, ethanol, hydrochloric acid, nitric acid, sulfuric acid, acetone, cesium chloride, deionized water was used to prepare all solutions. All chemical compounds were in analytical grade and used as received without further purification. A customized quartz electrolytic cell was employed for photo-assisted deposition and photoelectrochemical characterizations. Ultra-high purity nitrogen (99.999%) and gas mixture (10% H₂ and 90% N₂) were supplied by Hangzhou Jingong Co. Ltd.

2. Preparation of graphite disk supports for NiCoSe_x deposition

The graphite rods are cut into thin disks with a diameter of 6 mm and a thickness of ~0.4 mm. Such graphite disks have a geometric area of 0.2826 cm². They are sonicated subsequently in deionized water for 20 min, and then were dried in an oven at 105 °C for 10 min before use. The prepared graphite disks were used as the working electrode for NiCoSe_x photo-assisted electrodeposition.

3. Fabrication of silicon nanopillars and photocathodes

Si wafers with resistivity of 3 Ω • cm (p-type, B-doped, (100) orientation, 525 μm thickness, 2 inches in diameter) were purchased from Resemi Semiconductor Co Ltd. The Si nanopillar array was prepared by Cesium Chloride (CsCl) lithography, with a ratio of reaction gas C₄F₈:SF₆: He=8:4:1, excitation power of 200 W, bias power of 10 W and chamber pressure of 3.5 Pa for 4 min.

The as prepared silicon nanopillar arrays (defined as Si NP array, 200 nm in average diameter and 1 μm in height) were cut into pieces for photocathodes fabrication and catalysts growth. Electrodes for catalysts electrodeposition and photoelectrochemical measurements were fabricated by following procedures. Briefly,

the back side of the Si substrate was first scratched with a diamond scribe. Instantly, a Cu wire was embedding in a Ga/In mixture to form an ohmic contact. Silver paint was then used to immobilize the Cu wire and the Ga/In liquid. After drying, the Cu wire was passed into a glass tube (diameter 2 mm), and the Si electrode and Cu wire were encased in Hysol 9460 epoxy. All photocathodes were etched in aqueous buffered HF solution for 30 s to remove the native silicon oxide on the surface prior to use.

4. Preparation of NiCoSe_x films on graphite disks (GD)

The deposition of NiCoSe_x films on graphite disks was conducted in a standard three-electrode, single-compartment configuration. The working electrode was a graphite sheet fixed on the bottom of an electrode bar by conductive carbon adhesives. A platinum plate of high purity with a large-area (1 cm * 1 cm) and saturated calomel electrode (SCE, saturated KCl) were used as counter electrode and reference electrode, respectively. A deposition electrolyte contained 10 mM CoCl₂•6H₂O, 10 mM NiCl₂•6H₂O, 10 mM SeO₂ and 50 mM potassium chloride solution. The electrolyte was bubbled with ultra-high purity N₂ (99.999%) under stirring for 30 min prior to deposition to achieve an oxygen-free solution. The amorphous NiCoSe_x films were obtained by chronoamperometry at -0.7 V vs. SCE (saturated KCl). The deposition mechanism was discussed in the following section of “Photo-assisted electrodeposition of NiCoSe_x films on Si NP array”. After deposition, the electrode surface was carefully rinsed with large amounts of ultrapure water and alcohol. The freshly prepared NiCoSe_x/graphite samples were dried in a vacuum oven at 30 °C for 12 hours.

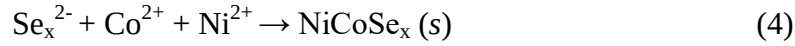
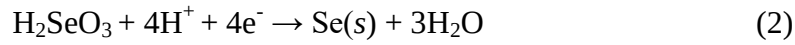
5. Photo-assisted electrodeposition of NiCoSe_x films on Si NP array photocathodes

A standard three-electrode, single-compartment quartz electrolytic cell was used

in photo-assisted electrochemical deposition experiment. The electrolyte was also bubbled with ultra-high purity N_2 (99.999%) under stirring for 20 min prior to deposition to achieve an oxygen-free solution. The working electrode was the home-made Si NP array photocathode as described above. Such photocathodes have a geometric area about 0.15 to 0.25 cm^2 . The counter electrode was a platinum electrode of high purity with a large area (1 cm * 1 cm). The reference electrode was a commercially available saturated calomel electrode (SCE, saturated KCl, CH Instruments).

Electrolyte solution was prepared by adding 10 mmol cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), 10 mmol nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) and 10 mmol selenium dioxide (SeO_2) to 1 L potassium chloride (50 mmol) solution. The photo-assisted electrodeposition was conducted by diluting the electrolyte to different multiple, and optimized desaturation multiple 7 (diluting the stock solution by a factor of 7 with 6 parts ultrapure water) was determined to prepare the $NiCoSe_x$ film. The $NiCoSe_x$ film was obtained by chronoamperometry at -0.7 V (vs. SCE) under simulated 100 mW/cm^2 illumination with an AM 1.5 G filter.

The deposition mechanism can be explained below: The photo-assisted deposition of $NiCoSe_x$ onto semiconductor surface employs the photo-generated electrons within the p-Si conduction band as reducing agent. Firstly, SeO_2 can be hydrolyzed to H_2SeO_3 ; when imposing negative voltage and light on p-Si photocathode, the Se^{4+} of H_2SeO_3 will be reduced to Se_x^{2-} . Simultaneously, the Co^{2+} and Ni^{2+} in the electrolyte will move to the cathode under the action of electric force. On the surface of Si photocathode, the reduced Se_x^{2-} will bond with Co^{2+} and Ni^{2+} to form amorphous $NiCoSe_x$ films. We tentatively proposed that the deposition process was achieved through the following steps (equations (1)-(4)):



The thickness of NiCoSe_x deposited on the Si nanopillar arrays was controlled by regulating the deposition time. The catalyst loading can be approximatively calculated, take the optimum sample with 90 s deposition time for example (the sample SEM was showed in Fig. 2c and the photoelectrochemical performance was shown in Fig. 4), the detailed calculation process as below (equations (5)-(7)):

$$Q = I \times t \quad (5)$$

$$N = Q/q \quad (6)$$

$$n = N/N_A \quad (7)$$

Q is the total deposition charge density, and the Q of the optimum sample (a deposition time of 90 s) is 41.65 mC/cm² (obtained from the current-time plot of chronoamperometry deposition); N is the number of electrons; q is the charge of a single electron, q=1.6 × 10⁻¹⁹ C; n is the molecular weight of NiCoSe_x; N_A is the Avogadro constant, N_A=6.022×10²³. For the optimum sample (90 s for NiCoSe_x deposition), the loading amount of NiCoSe_x (with an approximate chemical formula of NiCoSe_{4.5}) deposited on the Si NP was calculated to be ~ 0.2 mg/cm².

After deposition for 10-300 s, the electrode surface was carefully rinsed with large amounts of ultrapure water in order to remove any residues of bath chemicals. The freshly prepared p-Si/NiCoSe_x NP array photocathodes was also dried and stored in a vacuum oven in 30 °C for 12 hours. The amorphous films of binary metal selenides (NiSe_x and CoSe_x), Pt nanoparticles coated on p-Si NP were also prepared for PEC performance comparison. In specific, the binary metal selenides was obtained by

chronoamperometry at -0.7 V (vs. SCE) under simulated 100 mW/cm² with an AM 1.5 G filter. The electrolyte solution for NiSe_x deposition was prepared by adding 20 mmol cobalt chloride hexahydrate (NiCl₂•6H₂O), and 10 mmol selenium dioxide (SeO₂) to 1 L potassium chloride (50 mmol) solution. The desaturation multiple 7 (diluting the stock solution by a factor of 7 with 6 parts ultrapure water) was determined to prepare the NiSe_x samples. The electrolyte solution for CoSe_x deposition was the same as NiSe_x when the NiCl₂•6H₂O be replaced with CoCl₂•6H₂O. The preparation of p-Si/Pt was also conducted by photo-assistant electrodeposition at -0.7 V (vs. SCE) with different deposition time. The electrolyte solution was 1.0 mmol H₂PtCl₆.

6. Electrodeposition of NiCoSe_x films on indium doped tin oxide for optical transparency test

The samples of NiCoSe_x grown on indium doped tin oxide (ITO) glass for absorbance spectra measurements were prepared with different deposition time (0, 30, 90, and 180 s). The deposition conditions of NiCoSe_x/ITO samples were same with the preparation of p-Si/NiCoSe_x NP photocathodes. More specifically, the working electrode was the ITO glass (2 cm * 5 cm). The area of ITO glass immersed in the electrolyte was controlled to 4 cm² (2 cm * 2 cm). The counter electrode was a platinum electrode (1 cm * 1 cm). The reference electrode was a commercially available saturated calomel electrode (SCE, saturated KCl, CH Instruments). The photo-assisted electrodeposition was conducted in optimum electrolyte solution (See I. 5 for preparation details). The as-prepared electrodes were also carefully rinsed with ultrapure water and dried in a vacuum oven at 30 °C for 12 hours.

II. Structural characterization

Scanning electron microscopy (SEM) was performed on a SIRON-100(FEI America) field emission scanning electron microscopy. The samples were pretreated by spraying gold for 60 s. The transmission electron microscopy (TEM) and the energy dispersive spectroscopy (EDS) spectra were gained by field emission transmission electron microscope (Tecnai G2 F20 S-TWIN) coupled with energy-dispersive X-ray spectrometer at an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) were obtained on Escalab 250Xi (Thermo Fisher Scientific) X-ray photoelectron spectrometer with an Mg K α X-ray resource. Calibration of binding energy was carried out by setting binding energy of C1s peak to 284.6 eV. UV-Vis spectra were recorded on a UV-3150 UV-Vis spectrophotometer and were collected over the range of 400-1200 nm. The crystal structures of samples were characterized using a X'Pert PRO X-ray diffractometer (XRD) (PNAlytical Netherlands) using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). Employing a sampling width of 0.033° in the 2θ range of $10-90^\circ$.

III. Electrochemical and Photoelectrochemical Characterization

Electrochemical measurements were performed in a three-electrode electrochemical cell using a Bio-Logic VSP potentiostat. All measurements were performed in 100 mL of 0.5 M H₂SO₄(aq) electrolyte and constantly purged with H₂ gas to maintain a constant Nernst potential for H⁺/H₂ redox couple. Using a graphite rod as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. To allow potentials to be referenced against the reversible hydrogen electrode (RHE), the SCE was calibrated against the reversible hydrogen potential using platinum wire as both the working and counter electrodes. Cyclic voltammograms was measured from +0.25 V to -0.45 V vs. RHE at a scan rate of 3

mV/s. Electrochemical impedance spectroscopy (EIS) was performed in potentiostatic mode at -0.5 V (vs. SCE) from 200 kHz to 50 mHz.

The photoelectrochemical characterizations of photocathodes were also measured in a three-electrode configuration using a Bio-Logic VSP potentiostat. The prepared p-Si/NiCoSe_x NP served as the working electrode, a graphite rod as a counter electrode, and SCE as reference electrode. The simulated 1.0 Sun illumination was supported by 500 W Xe short arc lamp solar simulator (Aulight, Beijing, CEL-S500) with an AM 1.5 G filter. The light intensity was calibrated to 100 mW/cm² with an AM 1.5 G filter by an irradiatometer (Aulight, Beijing, CEL-VIS 400). The “1 sun” calibration was carried out by the irradiatometer inside the cell. We calibrated the solar simulator with the Oriel PV Reference Cell (Newport Model 91150V). All measurements were performed in 100 mL of 0.5 M H₂SO₄ (aq) electrolyte and constantly purged with H₂. The potentials were also referenced against the reversible hydrogen electrode (RHE). Electrochemical impedance spectroscopy (EIS) was performed when the working electrode was biased at a constant potential of -0.1 (vs. SCE) in 100 mW/cm² (AM 1.5 G filter), while sweeping the frequency from 200 kHz to 50 mHz.

The capacitance measurement on the electrode/electrolyte was employed to determine the flat band potential (E_{fb}) and carrier density (N_A), which can be obtained in a Mott-Schottky (M-S) plot with $1/C^2$ vs. potential at a fixed frequency of 100 kHz in dark. The capacitance-potential measurements on p-Si/NiCoSe_x NP and bare Si NP photocathodes were presented as M-S plot following the equation below:

$$1/C^2 = 2(E_a - E_{fb} - \kappa T/q) / (q N_A \epsilon_0 \epsilon_s A^2)$$

Where C is the space charge capacity, E_a is the applied potential, κ is the Boltzmann constant, E_{fb} is the flat band potential and can be determined by extrapolation to a

capacitance of zero, T is the absolute temperature, q is the electron charge, N_A is the carrier density, which can be calculated from the slope, ϵ_s is the dielectric constant of materials (11.8), ϵ_0 is the electric permittivity of a vacuum, and the A is the area of electrode.

The Faradaic efficiency of the photoelectrochemical cell was determined by measured the amount of generated H_2 and O_2 using a gas chromatography (GC, 9790II, Hangzhou Gatai Scientific Instruments). A chronoamperometry test was conducted on the p-Si/NiCoSe_x NP photocathode at 0 V (vs. RHE) under simulated 1.0 sun irradiation. A syringe was used to transfer 150 μ L gas from the sealed polytetrafluoroethylene cell to the GC instrument every 30 minutes. The Faradaic efficiency was then calculated by comparing the theoretical amount with the GC-detected amount of generated H_2 and O_2 . The spectra were measured by a thermal conductivity detector (TCD), at a column temperature of 60 $^{\circ}C$, injection temperature of 80 $^{\circ}C$, and thermal conductivity cell of 100 $^{\circ}C$.

IV. The line scan profile, TEM/EDS spectra, and XRD pattern of p-Si/NiCoSe_x NP

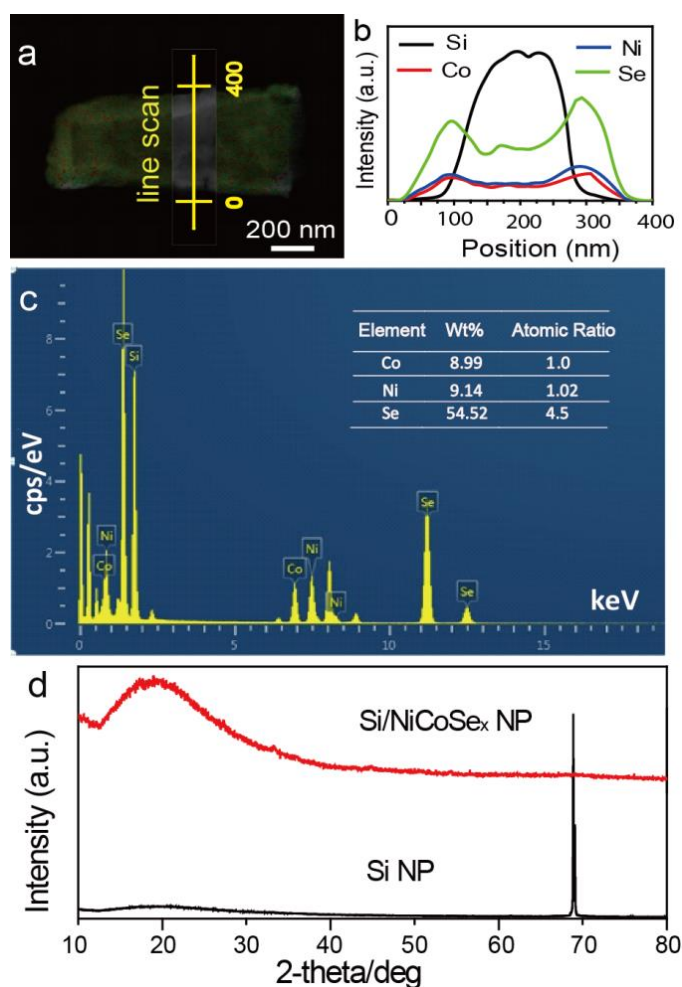


Fig. S1 (a) The EDS multi-layer image of the p-Si/NiCoSe_x NP. (b) Line scan result of one single p-Si/NiCoSe_x NP corresponding to (a). (c) EDS spectra of p-Si/NiCoSe_x NP showing the presence of Ni, Co, Se and Si element. (d) The XRD pattern of NiCoSe_x deposited on p-Si NP array. The peak at 68.9 °(black line) was corresponded to the monocrystalline silicon (PDF 27-1402). The wide peak between 12-25 °(red line) showed the existence of amorphous NiCoSe_x.

V. SEM image and EDS spectrum of NiCoSe_x / graphite electrode

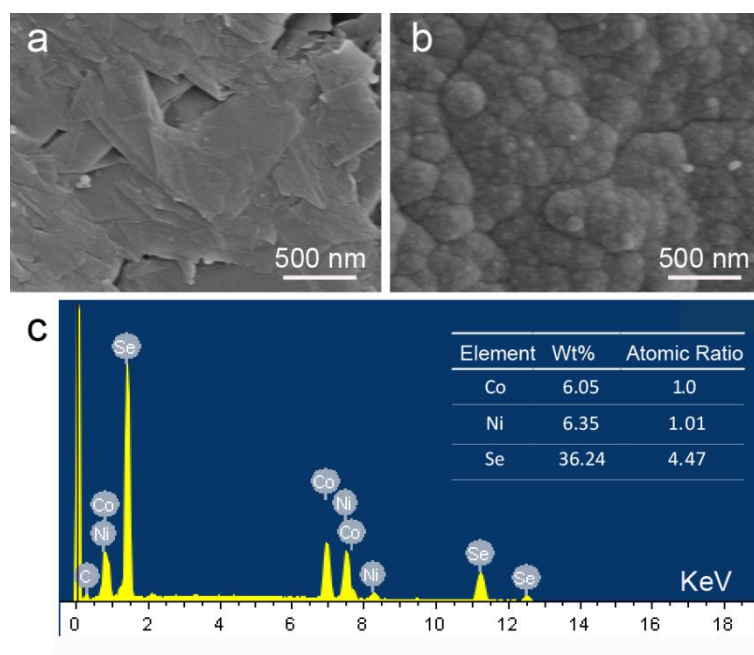


Fig. S2 (a) SEM image of blank graphite disk substrate. (b) SEM image of NiCoSe_x deposited on a graphite disk substrate. The NiCoSe_x film was obtained by chronoamperometry at -0.7 V (vs. SCE) for 30 min. (c) EDS spectra of NiCoSe_x /graphite. The element of cobalt, nickel, and selenium were detected with a molar ratio close to 1:1:4.5, yielding an approximate formula of NiCoSe_{4.5}.

VI. Stability measurement of NiCoSe_x / graphite electrode

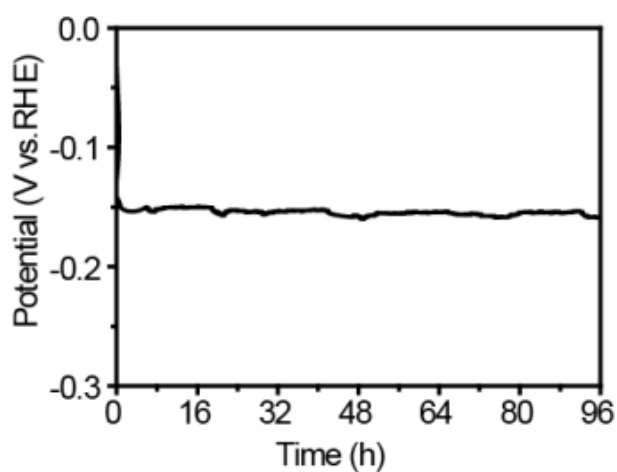


Fig. S3 Long-term stability measurement of a NiCoSe_x/graphite electrode.

VII. The electrochemical measurements of different catalysts electrodeposited on graphite disk substrate

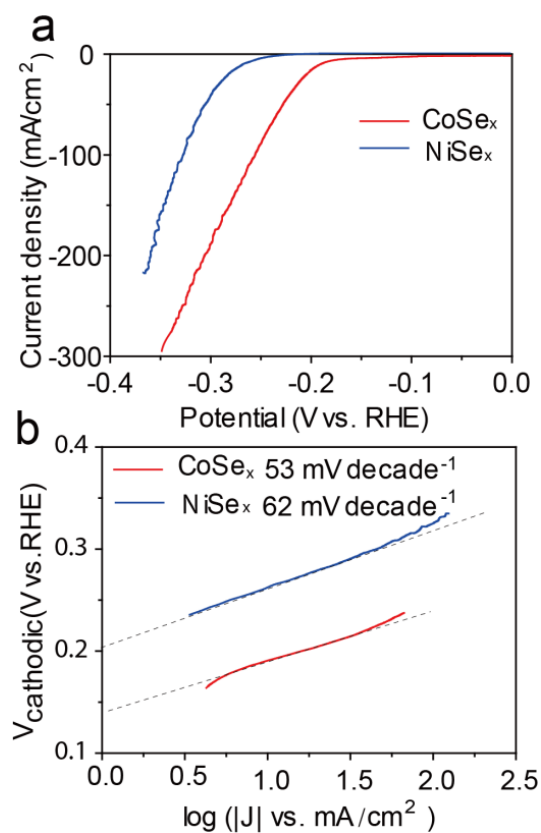


Fig. S4 (a) Polarization curves of CoSe_x and NiSe_x, The amorphous films of binary metal selenides were prepared by deposition for 30 min. (b) Tafel plots derived from data of (a).

VIII. Calibration process of illumination intensity

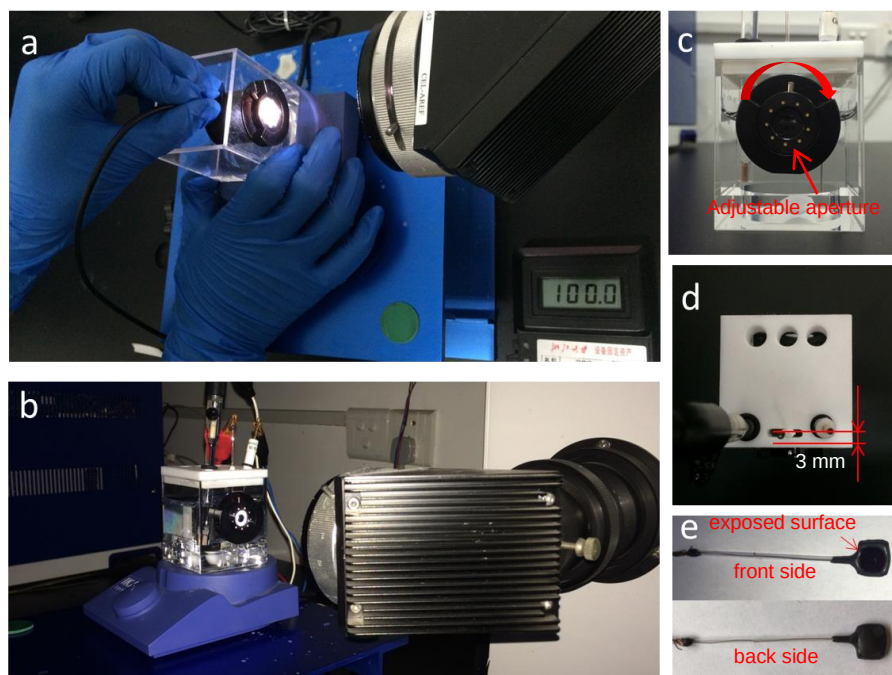


Fig. S5 (a) Calibration process of illumination intensity for PEC-HER measurements and the design of the quartz cell for PEC measurements. The light intensity from a solar simulator (Aulight, Beijing, CEL-S500) with an AM 1.5 G filter was calibrated to 100 mW/cm^2 by an irradiatometer (Aulight, Beijing, CEL-VIS 400). (b) The picture of the setup for PEC measurements. (c) The photograph of the quartz electrolytic cell with an adjustable aperture. (d) The top-down view of the quartz electrolytic cell, the thickness of water in between the electrode and the inner wall of the cell was controlled to about 3 mm (the thickness of the cell wall was about 2 mm). (e) The photograph of a p-Si NP photocathode. The p-Si substrate and Cu wire were encased in Hysol 9460 epoxy with a nearly around surface exposed.

IX. The light spectrum of irradiation

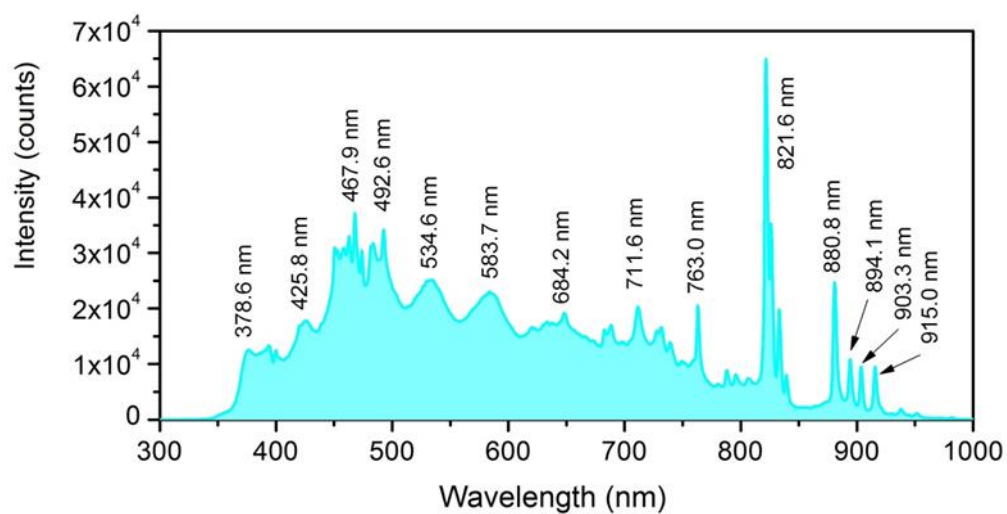


Fig. S6 Spectral distribution of the simulated solar illumination that was supplied by a 500 W Xe short arc lamp solar simulator (Aulight, Beijing, CEL-S500) with an AM 1.5 G filter.

X. SEM images of NiCoSe_x electrodeposited on Si NP array with various time

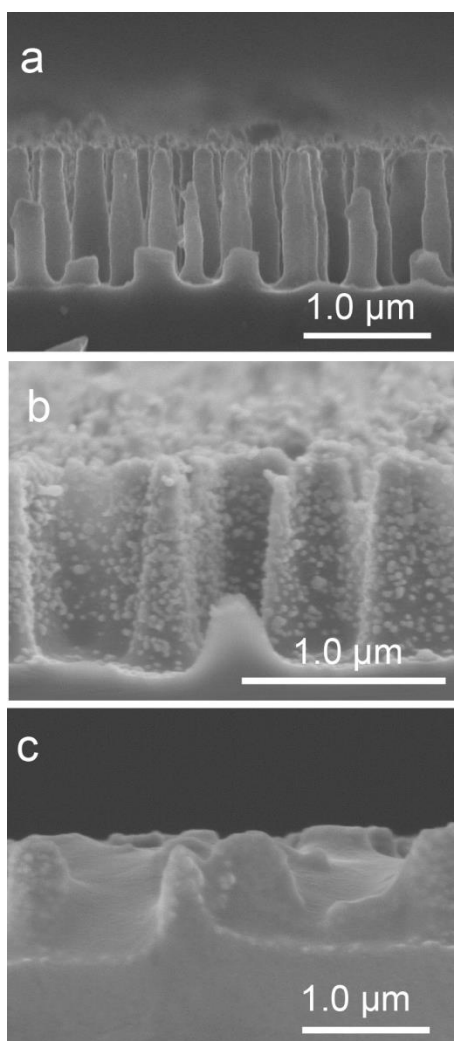


Fig. S7 SEM images of cross-sectional views of amorphous NiCoSe_x catalyst electrodeposited on Si NP with various deposition time. The deposition time was 20 s (a), 40 s (b), and 300 s (c), respectively.

XI. Polarization curves of p-Si/NiCoSe_x NP photocathodes deposited with different time

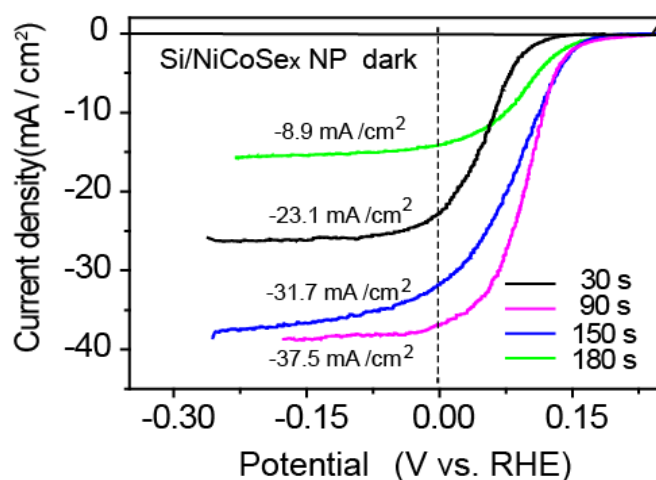


Fig. S8 Polarization curves of p-Si/NiCoSe_x NP array photocathodes deposited with different time.

XII. SEM images of planar silicon and NiCoSe_x electrodeposited on planar silicon

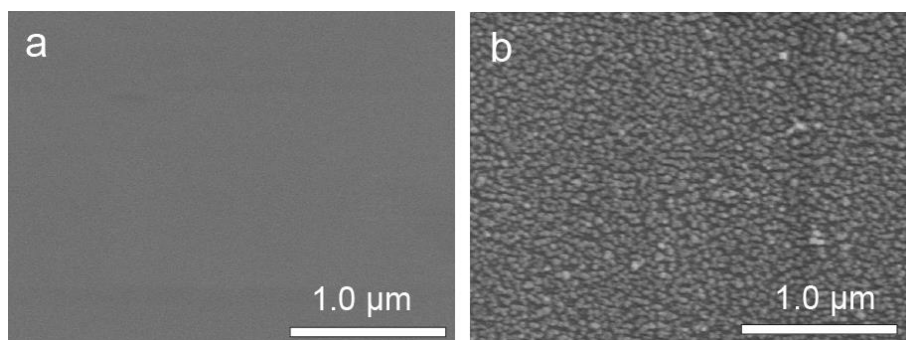


Fig. S9 SEM images of (a) planar silicon and (b) NiCoSe_x electrodeposited on planar silicon. The amorphous NiCoSe_x film was obtained by chronoamperometry at -0.7 V (vs. SCE) for 90 s and the light density was 100 mW/cm² (with AM 1.5 G filter).

XIII. Polarization curve of p-Si/Pt NP photocathode

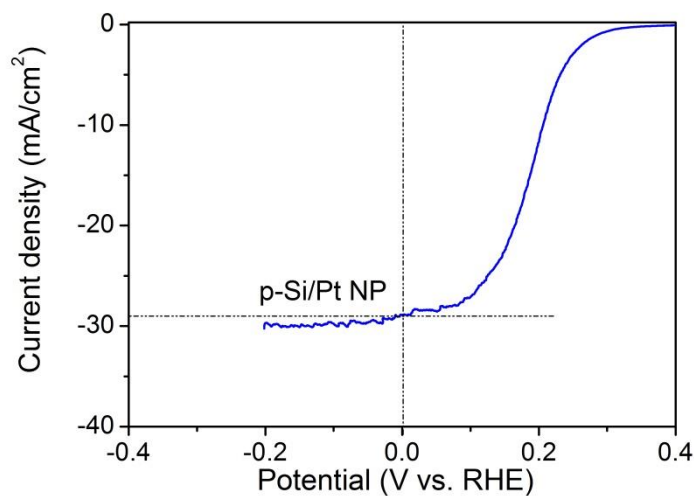


Fig. S10 A typical J-V curve of p-Si/Pt NP photocathode under 100 mW/cm² with an AM 1.5 G filter in 0.5 M H₂SO₄. The Pt coating was deposited on the p-Si NP photocathode by the photo-assisted electrodeposition method with a deposition time of 60 s.

XIV. SEM image of p-Si/Pt NP photocathode

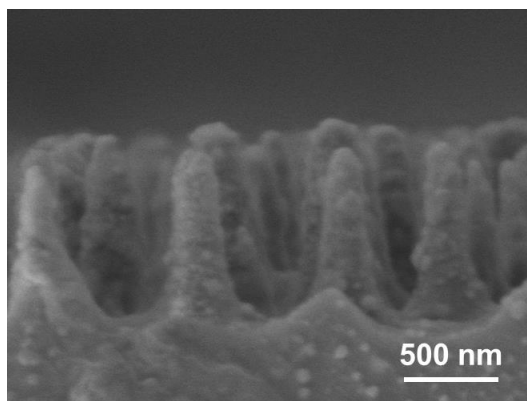


Fig. S11 SEM image of cross-sectional view of Pt electrodeposited on p-Si NP with deposition time of 60 s.

XV. SEM images of different catalysts electrodeposited on Si NP array

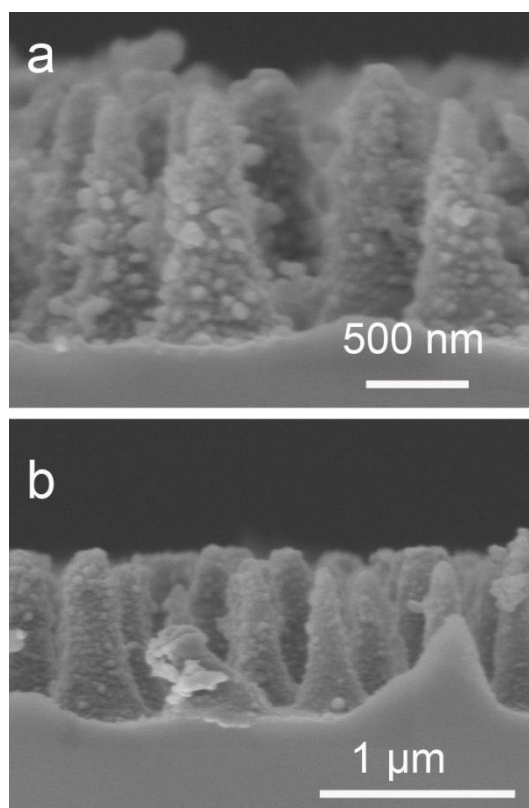


Fig. S12 SEM images of (a) NiSe_x and (b) CoSe_x films electrodeposited on Si NP array with the same deposition time of 90 s.

XVI. Photoelectrochemical measurements of Si NP array deposited with different catalysts

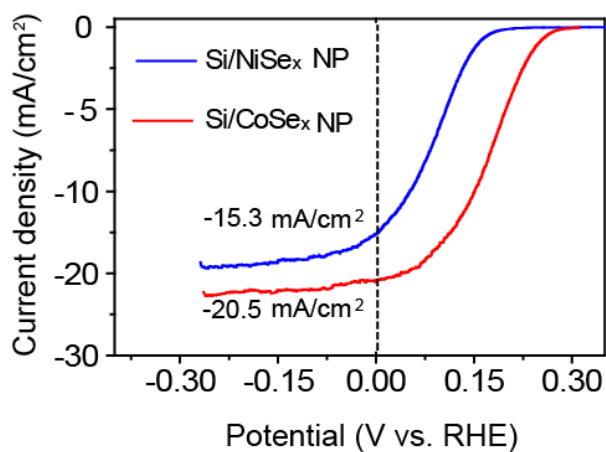


Fig. S13 Polarization curves of Si/CoSe_x NP, Si/NiSe_x NP photocathodes measured under simulated 100 mW/cm² irradiation (under AM 1.5 G filter). The CoSe_x and NiSe_x film was obtained by chronoamperometry at -0.7 V (vs. SCE) for 90 s.

XVII. Photograph of Faradic efficiency measurement device

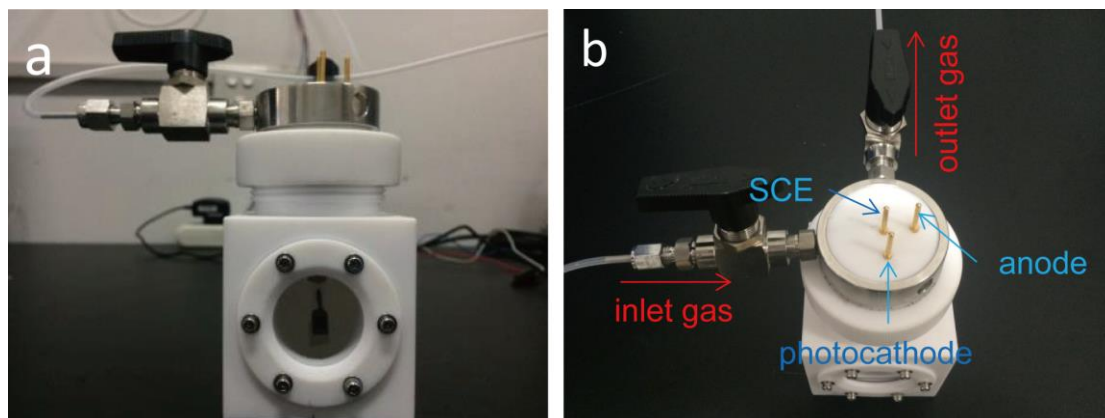


Fig. S14 (a) The front view and (b) the top-down view of the Teflon cell with quartz window for Faradic efficiency measurement.

XVIII. Faradaic efficiency of generated H₂ and O₂

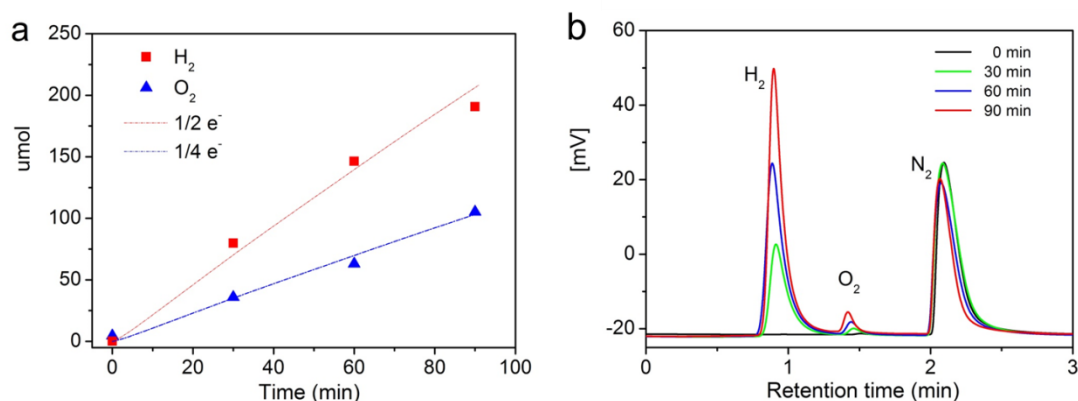


Fig. S15 (a) Evolution of H₂ and O₂ from a p-Si/NiCoSe_x NP photocathode and Pt detected by gas chromatography (GC) to determine the Faradaic efficiency. The measurement was conducted under continuous illumination of 100 mW/cm² (with an AM 1.5 G filter) at 0 V (vs. RHE) in 0.5 M H₂SO₄. Comparing the amount of experimentally detected H₂ and O₂ (squares and up triangles) with the theoretically

amount based on the photocurrent (shown as the red and blue lines), the Faradaic efficiency of the p-Si/NiCoSe_x NP photocathode is close to 100%. (b) The detection signals of H₂ and O₂ by GC during PEC-HER on the p-Si/NiCoSe_x NP photocathode. The peak area increased with reaction time. N₂ served as carrier gas and its peak area remained approximatively constant over time.

Table S1. Comparison of PEC-HER performance of silicon based photocathodes

<i>Substrate</i>	<i>Catalyst</i>	<i>Onset potential (V vs. RHE)</i>	<i>Current density (0 V vs. RHE)</i>	<i>Stability</i>	<i>Reference</i>
p-Si nanopillar array	NiCoSe_x	0.25 V	-37.5 mA/cm²	2 h	Our work
p-Si nanowires	FeP	/	-14 mA/cm ²	5000 s	S1
p-Si porous nanowire	Pt	0.26 V	-16.4mA/cm ²	4 cycles	S2
Planar Silicon	Co-MOS	/	-3.8 mA/cm ²	20 min	S3
Planar p-Si	Pt		-23 mA/cm ²		S4
n ⁺ p-Si nanowire	Ni-Mo	0.5 V	-10.5mA/cm ²	4000 s	S5
n ⁺ p-Si	Pt	0.52 V	-22 mA/cm ²	72 h	S6
Si nanowire	N-doped graphene quantum sheets	0.25 V	-35 mA/cm ²	/	S7
Planar p-Si	1T-MoS ₂	0.2 V	-17.6 mA/cm ²	3 h	S8
p-Si/SnO ₂ /Fe ₂ O ₃ CSS nanowire	/	/	tiny	2.5 h	S9
p-Si nanowire	Pt	0.2 V	-20 mA/cm ²	1.0 h	S10
p-Si nanowire	CoSe ₂	0.2 V	-9 mA/cm ²	50 cycles	S11
n ⁺ -p-p ⁺ -Si micropyramid	CoPS	0.45 V	-35 mA/cm ²	/	S12
Planar p-Si	a-CoMoS _x	0.25 V	-17.5 mA/cm ²	3 h	S13
Planar p-Si	MoS _x Cl _y	0.27 V	-20.6 mA/cm ²	/	S14
n ⁺ -p-Si Micropyramids	MoSe _x Cl _y	0.35 V	-38.8 mA/cm ²	2 h	S15

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