Development of low-cost and earth-abundant metal catalysts, as alternative to noble metals, is a promising approach for direct hydrogen production from solar light with integrated photoelectrochemical devices. Herein, a mild electrochemical method is used to directly synthesize two earth-abundant catalysts, namely, CoP and CoSe, on planar-junction p–nn+–Si solar cells. It is observed that the CoP–Si photocathodes achieve the best performance with ≈12 h of stability, a photocurrent density of up to 38 mA cm⁻² at 0 V versus the reversible hydrogen electrode (RHE), and an onset potential of 488 mV versus RHE, and one of the most efficient solar-driven hydrogen generation from earth-abundant systems to date. Overall solar water splitting is also demonstrated in a tandem device configuration with a top TiO₂ nanorod arrays photoanode achieving more than 5 h continuous hydrogen production. These results demonstrate the feasibility of using low-cost earth-abundant materials and the established Si solar cells technology for direct water splitting powered from sunlight.

1. Introduction

Hydrogen production via solar water splitting is considered as a promising route for tackling the raising demand for renewable and environmentally friendly fuels.¹ The direct low-temperature conversion of solar energy into clean hydrogen has become focus of increasing interest in recent years.² Three main paths are pursued for the low-temperature production of solar hydrogen via water splitting: photocatalytic, photoelectrochemical (PEC), and photovoltaic (PV)-electrolysis systems.³ Despite the benefits of each systems, the production of H₂ via these technologies is not competitive in terms of costs to replace current fossil fuels with H₂.⁴⁻⁵

For PEC water splitting, photoelectrodes play a key role to drive the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).⁶⁻⁷ To achieve overall water splitting without external bias, it requires the semiconductor photoelectrodes to have a suitably large bandgap to overcome the energy potential and also for the conduction and valence band positions of the photodeelectrodes to straddle the HER and OER potentials.¹ Few photoelectrodes can satisfy these requirements and achieve self-powered solar water splitting with good solar-to-hydrogen (STH) efficiency and stability.²

A tandem photoelectrode configuration can decouple these requirements on a photoanode and photocathode alleviating the strict requirements for a single semiconductor-based photoelectrode. However, there are only relatively few tandem systems, mainly metal oxide-based photoelectrodes, that have achieved good overall solar water splitting performance.⁸ As an alternative path, solar cells have been integrated into PEC systems as light absorbers to provide photovoltage to drive the solar water splitting reactions.⁹

Compared with traditional metal oxide-based photoelectrodes,⁷ such as WO₃, BiVO₄, and hematite, solar cell-based photoelectrodes have a relatively wide light absorption, good power conversion efficiency (PCE), and a well-developed fabrication technology.⁸ Among them, silicon solar cells have demonstrated an attractive performance with stabilities in excess of 25 years and high solar-to-electricity efficiencies.⁹ Importantly, their price has dropped by 80% since 2008, currently reaching energy costs of less than $1 per watt peak.¹⁰ Therefore, implementation of Si solar cells as integrated photoelectrodes for PEC solar hydrogen production is attractive.

To improve the PEC performance of Si-based photoelectrodes, various strategies have been adopted, including passivation,¹¹ engineering work function of catalysts,¹² and the construction of effective protection layers.¹³ The long-term stability has been greatly improved to more than 100 h after the introduction of either an amorphous TiO₂ or anatase TiO₂ layer on n or p type of Si photoelectrodes as a protection layer.¹⁴⁻¹⁵ Meanwhile,
the successful construction of a metal–insulator–semiconductor structure results in an inferred photovoltage of \( \approx 550 \text{ mV} \) on the Si photoelectrodes,\(^{[16,17]} \) greatly improving the onset potential.\(^{[18]} \)

However, the use of noble metal-based catalysts, such as Pt, Ir, and RuO\(_2\), hampers their commercial application for clean hydrogen production.\(^{[5,12,15,17]} \) Very recently, various low-cost earth-abundant catalysts have been developed and implemented onto Si photoelectrodes for replacing noble metal-based catalysts to reduce its cost for solar hydrogen production.\(^{[19]} \) For example, Ni,\(^{[20,21]} \) Ni–Mo,\(^{[21–23]} \) CoSe\(_2\),\(^{[24]} \) CoP,\(^{[25–27]} \) FeP,\(^{[28]} \) CoPS,\(^{[29]} \) Ni\(_{12}\)P\(_5\),\(^{[30]} \) MoS\(_2\),\(^{[31]} \) and others\(^{[32,33]} \) have been reported as efficient HER catalysts to facilitate hydrogen evolution. However, most of these catalysts are fabricated through either high-temperature chemical vapor deposition (CVD)\(^{[26–29,31,33]} \) or multistep wet-chemical synthesis methods,\(^{[24,30,34]} \) requiring an additional step for the modification of Si photoelectrodes. As an alternative, electrochemical deposition is a milder route, which allows the direct preparation of the catalysts on Si photoelectrode surfaces at room temperature avoiding detrimental high-temperature treatment that may damage the solar cell materials and performance. Based on the abovementioned considerations, CoP and CoSe are chosen as two typical low-cost catalysts to integrate with Si solar cells as photocathodes and further investigate their HER performances.

Here, two earth-abundant catalysts of CoP and CoSe were PEC deposited on p’nn’+Si solar cells to fabricate efficient photocathodes for solar water splitting. The CoP–Si photocathode demonstrated a significantly better PEC performance than the CoSe ones, achieving 38 mA cm\(^{-2}\) at 0 V versus the reversible hydrogen electrode (RHE) for more than 12 h and an onset potential as high as 488 mV, one of the most efficient Si-based photocathodes with earth-abundant catalysts for H\(_2\) production (Table S1, Supporting Information).\(^{[20–26,29–32,33,35]} \) A self-powered tandem device for overall water splitting is demonstrated by the integration of a top TiO\(_2\) nanorod array photoanode with continuous H\(_2\) production for 5 h. These results demonstrate the potential of Si-based solar cell technology and low-cost earth-abundant materials for direct hydrogen production from sunlight.

2. Results and Discussion

To achieve self-powered solar water splitting for solar hydrogen production, a tandem device was constructed, as shown in Figure 1a. A TiO\(_2\) nanorod array grown on a fluorine-doped tin oxide (FTO) substrate was used as the top photoanode, and a Si solar cell with earth-abundant catalysts was used as the bottom photocathode. When the tandem device is illuminated by simulated sunlight, the top TiO\(_2\) photoanode will absorb the ultraviolet portion of sunlight, and the rest will pass through and shine on the bottom Si photocathode. In this tandem configuration, sunlight can be fully utilized to generate enough photovoltage to drive overall water splitting, in which the OER will occur on the TiO\(_2\) nanorod arrays photoanode and the Si photocathode will be responsible for the HER.

The surface morphologies and chemical compositions of the CoP and CoSe catalyst layers were investigated by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). Figure 1b and Figure S1a, Supporting Information,

**Figure 1.** Schematic illustration of the tandem device for overall solar water splitting, along with morphological characterizations. a) Illustration of the tandem device consisting of a top TiO\(_2\) nanorod arrays photoanode and a bottom CoP–Si photocathode for overall water splitting. SEM images of representative b) CoP catalyst and c) CoSe catalyst layers on the photocathode.
show the SEM images of the deposited CoP catalyst layer, revealing a relatively compact film with a distribution of mainly spherical particles with micrometer size. The CoSe catalyst layer (Figure 1c and Figure S1b, Supporting Information) displayed a denser morphology consisting of closely aggregated particles with a size distribution between 100 nm and 1 μm. The morphologies of these catalyst layers can provide a highly accessible surface area for HER. The typical elemental peaks of Co, P, and Se were found in the EDS spectra of these catalyst layers (Figure S1c,d, Supporting Information), further confirming a successful preparation of the CoP and CoSe catalysts. The Co 2p XPS spectra of CoP catalysts show a peak at 778.5 eV (Figure S2a, Supporting Information), and the P 2p core levels reveal the presence of phosphide (129.1 and 130.1 eV) and phosphate (131.8 and 132.6 eV) (Figure S2d, Supporting Information), suggesting that the synthesized CoP catalysts are composed with CoP and phosphate phases.[36,37,38] Peak fitting analysis for the Co 2p (Figure S2c, Supporting Information) and Se 3d (Figure S2d, Supporting Information) of the as-deposited CoSe catalysts indicates the presence of CoSe phase (778.8 eV for Co 2p3/2 and 54.6 eV for Se 3d).[37,38] Due to the peak overlapping between the Co 3p and the Se 3d, the peaks of Co 2p and Se 3p are used to calculate the stoichiometry and the atomic ratio between Co and Se (1:1.3:1), which is far away from the most common stoichiometry (CoSe2), the atomic ratio between Co and Se is 1:2.[24,17,39] For cobalt selenide under Se-rich conditions. The crystallinity of CoSe catalysts was also investigated by XRD (Figure S3, Supporting Information), and there is no obvious difference between the underlying substrate with and without CoSe catalysts, indicating that the synthesized CoSe catalysts are amorphous.

Figure S4, Supporting Information, shows a schematic cross section of a p-n+Si-type Si solar cell and its PV performance before evaluation of the PEC performance. An excellent short-circuit current density ($J_{sc}$) of 41.3 mA cm$^{-2}$, an open-circuit voltage ($V_{oc}$) of 0.67 V, a fill factor (FF) of 75.9%, and a PCE of 21.0% were observed. The electrochemical performance of CoP and CoSe catalysts was investigated for HER in alkaline electrolyte, as shown in Figure S5, Supporting Information. Compared with bare Ni foam, both CoP and CoSe catalysts demonstrate good HER activities, in which CoP reaches 10 mA cm$^{-2}$ at the overpotential of 57 mV and the CoSe catalysts at 62 mV (Figure S5a, Supporting Information). The CoP catalysts demonstrate much better HER activity than that of CoSe ones especially at large current density. To evaluate their stability, both catalysts conducted continuous cyclic voltammetry. As shown in Figure S5b, Supporting Information, CoSe catalysts experience a much quicker degradation within 20 cycles. In contrast, CoP has only slight degradation during 500 cycles. The good stability of CoP catalysts is also reflected from 50 h of chronopotentiometric measurement under a current density of 30 mA cm$^{-2}$ (Figure S5c, Supporting Information). The different HER activity and stability demonstrated on the CoSe and CoP catalysts might be correlated with their intrinsic chemical bonds.[24,37,39] It has been recently reported that the active phase of the CoP catalysts is cobalt hydroxides that is obtained by transformation of cobalt phosphide/cobalt phosphate into cobalt hydroxides during HER.[38,40]

Figure 2a shows linear sweep voltammograms of the Si photocathodes with and without the catalyst layers. The activity of the CoP–Si photocathode was excellent, with a current density of 37.7 mA cm$^{-2}$ at 0 V versus RHE, an onset potential of 488 mV versus RHE to reach 1 mA cm$^{-2}$, and a potential of 373 mV versus RHE to reach 10 mA cm$^{-2}$ (Figure S7a, Supporting Information). This is significantly better than the Si photocathodes modified with the CoSe catalysts (22.8 mA cm$^{-2}$ at 0 V vs RHE and an onset potential of 355 mV), which is consistent with their electrocatalytic activity of catalysts shown in Figure S5a,b, Supporting Information. Neutral or acid electrolyte should be much helpful for the HER process and stability of electrode due to the reactivity of Si in alkaline electrolyte. This was mitigated by the metal layer of Cr/Ag used here to avoid the direct contact between the Si solar cells and the alkaline electrolyte.

The performance of these CoP–Si photocathodes is also one of the best reported for Si-photocathode-based PEC for solar-driven hydrogen generation with earth-abundant catalysts (Table S1, Supporting Information).[20–26,29–32,33,35] For comparison, the bare and noble metal Pt-modified Si photoelectrodes were also evaluated. The morphology and EDS characterization results of the bare and Pt catalyst are reported in Figure S6, Supporting Information. As shown in Figure 2a and Figure S7a, Supporting Information, the linear sweep...
voltammograms of the Pt–Si photocathode reveal a current density of 37.5 mA cm\(^{-2}\) at 0 V versus RHE and an onset potential of 616 mV, showing a better but comparable catalytic performance to the earth-abundant CoP and CoSe ones. The bare Si photocathodes, instead, only produced a current density of 3.5 mA cm\(^{-2}\) at 0 V versus RHE with an onset potential of 83 mV (Figure 2a). This comparison reveals that the catalysts are necessary to facilitate HER, and the PEC performance is largely dependent on the intrinsic electrocatalytic activity of HER catalyst. The solar energy conversion efficiencies of the CoP–Si and Pt–Si photocathodes were 5.99% and 7.60% (Figure S7b, Supporting Information), respectively. However, these solar energy conversion efficiencies are well below the 21.0% achieved by the Si solar cell (Figure S4b, Supporting Information), mainly because of lower photovoltage and FF,\(^{[41]}\) indicating the need for further improvement of the charge transport and electrocatalytic activity.

In addition to the initial PEC performance, the stability of the photoelectrode is an important parameter to evaluate potential application in solar water splitting. Figure 2b shows that the CoP-modified Si photoelectrode achieves a good stability, maintaining a current density of 37 mA cm\(^{-2}\) for 12 h of continuous operation at 0 V versus RHE. In contrast, the current density of the bare Si photoelectrode has an obvious increase in the first 10 min and then gradually decreases in the rest time, and the CoSe one gradually decreased from initial 23.1 to 18.9 mA cm\(^{-2}\) after 2 h of continuous operation at 0 V versus RHE. The initial activation observed on bare Si photoelectrode might be ascribed to the photo-reduction of the natural Ag\(_2\)O oxidation layer into metallic Ag surface, which reduces the resistance and facilitates the electron transfer from the photocathode to the electrolyte for hydrogen evolution. The gradual degradation of CoSe–Si photocathode might derive from the poor stability of CoSe catalysts, as indicated from 20 continuous cyclic voltammetric cycles of CoSe on Ni foam (Figure S5b, Supporting Information). The Pt-modified electrode also shows a good stability within 2 h of continuous operation (Figure 2b, inset).

Although \(\approx 500\) mV of photovoltage can be generated on the CoP–Si photocathode, this is still significantly below the required bias (1.6–1.7 V) to drive overall solar water splitting. To provide additional bias, TiO\(_2\) was chosen as a top photoanode and combined with a bottom CoP–Si photocathode as a tandem device to achieve overall solar water splitting without external bias input (Figure 1a). Representative top and cross-sectional SEM images of the TiO\(_2\) nanorod arrays on the FTO substrates are shown in Figure S8a,b, Supporting Information. The XRD patterns of the TiO\(_2\) photoanodes are shown in Figure S8c, Supporting Information, indicating a rutile phase of TiO\(_2\) nanorod arrays (JCPDS No. 88-1175).\(^{[42]}\) The PEC performance of the TiO\(_2\) nanorod arrays photoanode is shown in Figure S9a, Supporting Information.

**Figure 3.** Overall solar water splitting performance of the earth-abundant tandem device consisting of a top TiO\(_2\) nanorod arrays photoanode and a bottom CoP–Si photocathode under simulated 1 sun irradiation. a) Linear sweep voltammograms of the TiO\(_2\) nanorod arrays photoanode (black) and CoP–Si photocathode (blue) showing intersections of the curves under a three-electrode configuration; the inset shows the enlarged part. b) Linear sweep voltammograms of the tandem device under a two-photoelectrode configuration. c) Current density versus time curve of the tandem device under a two-photoelectrode configuration for overall water splitting without external bias under simulated AM 1.5G 100 mW cm\(^{-2}\) illumination.
Information, with a current density of 0.82 mA cm\(^{-2}\) at 1.23 V versus RHE and an onset potential of 0.22 V. Due to the light absorption at the top TiO\(_2\) nanorod arrays and the underlying FTO glass, the current density of the bottom CoP–Si photocathode was reduced to 19.6 mA cm\(^{-2}\) at 0 V versus RHE under the simulated sunlight (Figure S9b, Supporting Information).

The linear sweep voltammograms of the top TiO\(_2\) nanorod arrays–FTO photoanode and the bottom CoP–Si photocathode are shown in Figure 3a. The intersection of their linear sweep voltammograms predicts an operating photocurrent density of 0.39 mA cm\(^{-2}\) (inset) for overall solar water splitting without additional external bias input. This is validated by measurement of the tandem device in a two-electrode configuration shown in Figure 3b. A current density of 0.43 mA cm\(^{-2}\) was obtained at a bias of 0 V, consistent with the measurement of the individual photodiodes (Figure 3a). Figure 3c shows 5 h of continuous operation with the tandem device, and the current density gradually stabilizes after more than 1 h. If we assume 100% of Faradaic efficiency for hydrogen production, the STH efficiency is \(\approx 0.48\%\). Some small fluctuation in photocurrents is ascribed to bubble formation on the photoelectrode surfaces.

To provide a comparison, a Pt–Si photocathode was also combined with a TiO\(_2\) nanorod arrays–FTO photoanode for the measurement under the same tandem configuration (Figure S10, Supporting Information). A current density of 0.54 mA cm\(^{-2}\) with an STH efficiency of \(\approx 0.66\%\) was obtained if assuming 100% of Faradaic efficiency. This is slightly better but comparable to the earth-abundant TiO\(_2\) and CoP–Si-based tandem device, and also other tandem devices consisting of a Si-based photodiode as either photoanode or photocathode (Table S2, Supporting Information).\(^{[23,43,44]}\) In general, the electrocatalytic water splitting can get an energy conversion efficiency of 70–80% from the solar cells; therefore, it is expected to achieve an STH efficiency of \(\approx 15\%\). However, only STH efficiencies of \(\approx 0.48\%\) and \(\approx 0.66\%\) were obtained on the abovementioned devices. The analyses of Figure 3a and Figure S10b, Supporting Information, indicate that the overall PEC performance of the tandem device is mostly limited by the low current density of TiO\(_2\) photoanode. Therefore, the overall water splitting performance of these Si-based photodiodes can be significantly improved by integration of more efficient photoanodes to replace TiO\(_2\) photoanode\(^{[23,43]}\) such as the formation of p–n junction by deposition of Fini-layered double hydroxide on CoP.\(^{[45]}\)

### 3. Conclusion

We have introduced a facile light-assisted electrochemical method for the deposition of earth-abundant catalysts of CoP and CoSe directly on Si photocathodes. The CoP–Si photocathodes demonstrate a significantly better performance than the CoSe–Si ones, achieving a current density of 38 mA cm\(^{-2}\) at 0 V versus RHE, an onset potential of 488 mV, and a stability of 12 h during HER in 0.5 M NaOH solution. A tandem device consisting of a top TiO\(_2\) nanorod arrays–FTO photoanode and a bottom CoP–Si photocathode was fabricated to demonstrate overall self-powered solar water splitting with continuous operation for 5 h. The performance of this earth-abundant catalyst tandem devices was comparable to that achieved with a noble metal Pt–Si-based photocathode. Improvement of the overall water splitting efficiencies is expected by substitution of the top TiO\(_2\)-based photoanode with more efficient light absorbers. These findings demonstrate the potential of earth-abundant catalysts as an alternative to noble metal catalysts for direct production of hydrogen from sunlight providing directions for the future development of high-efficiency and low-cost PEC tandem devices.

### 4. Experimental Section

Fabrication of Si Solar Cells: N-type 4 in. 250 μm Czochralski (Cz)-grown silicon wafers with a resistivity of \(\approx 1\) Ω cm were used to fabricate several 2 × 2 cm\(^2\) cells, as shown in Figure S4a, Supporting Information. An etching mask was used to form random pyramids only inside the active area of the cells and to preserve narrow ridges along which the metal grid fingers will eventually run. To increase the sensitivity to the rear passivated contact, a low recombination hole conductor was implemented at the front by means of two BB2 filter processes, consisting of a deep and highly doped p\(^{++}\) region under the metal fingers (with a final sheet resistance of \(\approx 60\) Ω sq\(^{-1}\)) and a lighter and moderately doped p\(^{+}\) region (with a final sheet resistance of \(\approx 200\) Ω sq\(^{-1}\)), the latter passivated with Al2O3. The front metal grid was defined by photolithography, metal evaporation (Cr/Pd/Ag), and liftoff, followed by silver electroplating. The metal fingers had a 1% direct metal/semitransparent contact and were about 14 μm wide after plating, shading 1.75% of the active area of the cell. The electron-selective passivating contacts were formed using the optimized conditions. First, an ultrathin SiO\(_x\) layer was grown in hot nitric acid, and then, a 50 nm thick Ag film was deposited on the rear surface by plasma-enhanced chemical vapor deposition (PECVD). Subsequently, the wafers were placed in a quartz furnace and subjected to phosphorus diffusion from POCl\(_3\) at the optimized diffusion temperature of 810 °C.

A dielectric stack consisting of SiO\(_x\)/SiNx/AIO\(_x\) for antireflection and surface passivation was deposited by combination of PECVD and atomic layer deposition (ALD) on the boron-doped textured front surface. The rear metallic electrode was formed by evaporating a uniform 900 nm thick layer of silver onto the electron-selective passivating contacts. Because of its good conductivity and relatively chemical inertness, Ag was chosen as an ohmic contact layer on the photocathode. However, Ag deposited directly on the dielectric layers has poor adhesion and is easily delaminated. Therefore, Cr was added to improve the adhesion of the Ag layer.

Fabrication of the Si-Based Photodiodes: A metal wire was soldered to the Ag busbar on the front metal grid side of a Si solar cell. The light harvesting side was sealed with a cover glass slide using acrylic adhesive (AB glue) to protect it from the electrolyte, whereas the back surface was exposed to an area of 0.5 cm\(^2\) for subsequent catalyst modification.

Integrating Catalysts: A three-electrode configuration was used for the deposition of CoP and CoSe catalysts, in which a Ag/AgCl (3 M KCl) electrode was used as the reference electrode, Pt wire as counter electrode, and the fabricated Si photodiodes as working electrodes. For the deposition of CoP catalyst, a typical photoassisted electrodeposition was used. The photocathode was first immersed in the N\(_2\)-saturated electrolyte solution containing 50 mM of CoSO\(_4\), 0.5 M of NaOH, and 0.1 M of NaCl, and then applied five cycles of electrochemical deposition from 0 to –0.5 V versus Ag/AgCl at the scan rate of 10 mV s\(^{-1}\) under the illumination of simulated sunlight (AM 1.5). CoSe catalyst was deposited under simulated sunlight using the electrolyte solution containing 10 mM of CoCl\(_2\), 10 mM of SeO\(_2\), and 50 mM of KCl, and the potentialistic electrodeposition was controlled at –0.3 V versus Ag/AgCl to obtain CoSe catalysts. After rinsing the surface with deionized (DI) water, the photocathode with catalysts is ready for PEC measurements. The deposition of Pt catalyst was very simple, achieved by dropping 5 μL of 1 mM H\(_2\)PtCl\(_6\) ethanolic solution on the Ag surface and formed through a galvanic reaction. After 5 min, the photocathode was rinsed by DI water.

Fabrication of TiO\(_2\) Nanorod Arrays Photoanode: The fabrication of TiO\(_2\) nanorod arrays on FTO glass substrate is shown as follows: 0.5 mL of tita- nium n-butoxide was first mixed with 15 mL of concentrated HCl and
15 mL of DI water, and then transferred into a Teflon-lined stainless-steel autoclave (50 mL volume). A clean FTO substrate with conductive side facing down was submerged in the mixed precursor solution and kept at 150 °C for 6 h in a drying oven, and then cooled down to room temperature. After the sample was thoroughly washed with DI water and air dried, it was calcinated at 500 °C for 2 h under air in a furnace with a ramping rate of 5 °C min⁻¹. Finally, TiO₂ nanorod arrays–FTO is ready for PEC measurement after it was cooled down to room temperature.

**PEC Measurement:** To evaluate the photoelectrode performance, the PEC measurements were conducted in a three-electrode configuration using a CHI 660E potentiostat, 100W Xenon lamp (NewSpec, LCS-100) with an AM 1.5G filter at 1 sun irradiation and a custom-made one-compartment cell with a quartz window. A Pt wire, an Ag/AgCl (3 mM KCl) electrode, and the photoelectrode were used as the counter, reference, and working electrodes, respectively. The electrolyte was an aqueous 0.5 M NaOH solution, and the irradiated area of the working electrodes was measured by ImageJ software. The potentials were converted to the RHE scale according to the Nernst equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.21 + 0.059 \times \text{pH}$. The solar energy conversion efficiency was calculated based on the equation: $\eta = (I_{\text{app}} \times J_{\text{ph}}) / P \times 100\%$, where $I_{\text{app}}$ is the applied potential (vs RHE). $J_{\text{ph}}$ is the photocurrent density (mA cm⁻²), and P is the power of the simulated sunlight (100 mW cm⁻²). For the PEC measurement of the tandem device, TiO₂ nanorod arrays photoanode was immersed in the electrolyte in front of Si photocathode, and the applied potential was 0 V between them in a two-electrode configuration with a potentialstat recording the passing current density.

**Characterizations:** The morphology and EDS of the catalysts and the Si solar cell were investigated using Zeiss Ultra55 (field emission scanning electron microscopy, FESEM) at 3 kV. The crystallinity was characterized by XRD using Bruker system (XRD, D2 Phaser, USA) equipped with Cu Kα radiation of average wavelength 1.54059 Å. XPS was conducted in a Thermofisher Kratos Axis Supra photoelectron spectrometer, with a mono-chromated Al Kα source (1486.7 eV) at pass energy 20 eV.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

earth-abundant catalysts, hydrogen production, photocathode, solar water splitting, tandem configuration

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