Seebeck-voltage-triggered self-biased photoelectrochemical water splitting using HfO$_x$/SiO$_x$ bi-layer protected Si photocathodes

Jin-Young Jung$^1$, Dae Woong Kim$^1$, Dong-Hyung Kim$^1$, Tae Joo Park$^1$, Ralf B. Wehrspohn$^{2,3}$ & Jung-Ho Lee$^1$

The use of a photoelectrochemical device is an efficient method of converting solar energy into hydrogen fuel via water splitting reactions. One of the best photoelectrode materials is Si, which absorbs a broad wavelength range of incident light and produces a high photocurrent level (~44 mA·cm$^{-2}$). However, the maximum photovoltage that can be generated in single-junction Si devices (~0.75 V) is much lower than the voltage required for a water splitting reaction (>1.6 V). In addition, the Si surface is electrochemically oxidized or reduced when it comes into direct contact with the aqueous electrolyte. Here, we propose the hybridization of the photoelectrochemical device with a thermoelectric device, where the Seebeck voltage generated by the thermal energy triggers the self-biased water splitting reaction without compromising the photocurrent level at 42 mA cm$^{-2}$. In this hybrid device p-Si, where the surface is protected by HfO$_x$/SiO$_x$ bilayers, is used as a photocathode. The HfO$_x$ exhibits high corrosion resistance and protection ability, thereby ensuring stability. On applying the Seebeck voltage, the tunneling barrier of HfO$_x$ is placed at a negligible energy level in the electron transfer from Si to the electrolyte, showing charge transfer kinetics independent of the HfO$_x$ thickness. These findings serve as a proof-of-concept of the stable and high-efficiency production of hydrogen fuel by the photoelectrochemical-thermoelectric hybrid devices.

Solar water-splitting systems that directly convert solar energy into storable and transportable hydrogen fuel are a promising approach to sustainably providing cost-effective renewable energy$^{1–3}$. In order to realize self-biased solar water splitting, intensive efforts have been made in the past decades to exploit designed prototype systems including photovoltaic-electrolysis combination cells$^{6–9}$, tandem photoelectrochemical (PEC) cells using the dual-semiconductor light absorber$^{10–14}$, and colloid-based “Z-scheme” photocatalytic cells$^{15–25}$. These systems are normally better suited to generating an output voltage higher than the sum of thermodynamic potential (1.23 V) and kinetic overpotential (>0.3 V), which is required for a practical water-splitting reaction. However, it compromises the photocurrent level because a tradeoff relationship exists between the photovoltage and photocurrent in systems that operate based on the photovoltaic effect. This fundamental obstacle has limited the solar-to-hydrogen efficiency.

As a new approach to overcoming the aforementioned limitation, recently, the hybridization of the PEC cell with other energy-harvesting devices such as thermoelectric (TE) and piezoelectric generators—which generate an output voltage through the conversion of thermal and mechanical energy resources, respectively—has been proposed$^{26–28}$. In particular, the PEC-TE hybrid device is expected to be a commercially viable approach because it can be operated with absorbed solar energy in the form of photons (using the PEC component) and phonons (using the TE component)$^{26,29}$. The PEC-TE hybrid system—in which the PEC device is electrically connected with the TE device in series—could provide an additional output Seebeck voltage ($V_{TE}$) as a result of a thermal gradient in the TE in order to overcome the potential barrier required for the water-splitting reaction. In this...
hybrid system, the overall current is determined by the high photocurrent level of the PEC cell (i.e., the TE is only used as a voltage booster). This feature of the PEC-TE hybrid system can decouple the tradeoff relation between the voltage and current, thus maximizing the H2 power generation ($P_{\text{H}_2}$).

Various light-absorbing semiconductors including narrow bandgap (Si, InP, and GaAs) and wide bandgap (TiO$_2$, Cu$_2$O, Fe$_2$O, and BiVO$_4$) materials have been used as photoelectrodes of PEC cell. In the PEC-TE hybrid systems, because the output Seebeck voltage of the TE can further applied to drive the water splitting reaction, the narrow bandgap semiconductors with a higher photocurrent relative to the wide bandgap semiconductors are effective in maximizing the H2 power generation. Thus, Si with comparatively narrow bandgap (1.1 eV) is capable of generating a high photocurrent of ~44 mA·cm$^{-2}$ via harnessing a large portion of the solar spectrum and is a suitable material as a light-absorbing semiconductor photoelectrode. However, the poor corrosion-resistance of Si is an inherent drawback in terms of the long-term stable operation of the PEC reaction. One suitable strategy for offsetting this drawback is to use a high-atomic-density insulating material as a protective layer that would enable the complete blocking of the electrolyte permeation. In general, a high-atomic-density insulator of significant thickness provides excellent protection ability but results in an increase in the transfer resistance of the light-induced charge carriers owing to the tunneling barrier of the insulator. Therefore, for Si PEC devices, it is of paramount importance to design a protection layer that guarantees both long-term stability and facile charge-transfer kinetics.

In this study, we present a PEC-TE hybrid system with a HfO$_x$/SiO$_x$ bilayer protected Si photocathode to ensure its long-term stability without the deterioration of the charge-transfer kinetics. The PEC-TE hybrid device based on an antireflective Si nanostructure photocathode enables the self-biased PEC water-splitting reaction at a high photocurrent level of ~42 mA·cm$^{-2}$, which has a maximum H2 power generation of 55 mW·cm$^{-2}$. The HfO$_x$, which has strong corrosion resistance in an acidic electrolyte and a relatively higher atomic density (9.97 g·cm$^{-3}$) than other dielectric materials such as SiO$_2$ (2.65), Al$_2$O$_3$ (3.95), and TiO$_2$ (4.23), physically prevents the permeation of the electrolyte into the Si surface, thereby ensuring the charge transfer kinetics.

Results

H-terminated and SiO$_x$-grown p-Si (100) wafers were prepared through the treatment of diluted hydrofluoric acid and hot-water-oxidation, respectively, and these wafers were deposited with an amorphous HfO$_x$ thin film using the atomic layer deposition (ALD) process. The chemical composition of HfO$_x$ was confirmed using energy-dispersive X-ray spectroscopy (EDXS) mapping and X-ray photoelectron spectroscopy (XPS) spectra (See Supplementary Figs 1 and 2). Figure 1a,b show the high-resolution transmission electron microscope (HRTEM) images for the ALD HfO$_x$ thin film deposited on the H-terminated and SiO$_x$-grown Si wafers. The HfO$_x$ deposited on the H-terminated Si was observed to have a 3-nm-thick HfSiO$_x$ interfacial layer, which is caused by a diffusion of the Si atoms during the ALD (see Fig. 1a). In contrast, the interfacial layer was not found in the SiO$_x$-grown Si. Figure 1b shows the TEM image for the atomically thin SiO$_x$ interlayer inserted between the HfO$_x$ and Si without the formation of a HfSiO$_x$ layer. This difference is likely due to the bond strength of Si–O ($\approx$190 kcal·mol$^{-1}$) being higher than that of Si–H ($\approx$80 kcal·mol$^{-1}$). The stronger Si–O binding formed by SiO$_x$ growth prevents the Si diffusion on the Si surface, thereby creating the HfO$_x$/SiO$_x$ bilayer without formation of HfSiO$_x$. The chemical quality of the interface between HfO$_x$ and Si is clearly confirmed by the angle-resolved X-ray photoelectron spectroscopy (ARXPS) results. For the Si2p XPS spectra at the low incident angle that represents the interface information, the H-terminated Si wafer has one dominant state of Si$^{3+}$ originating from the HfSiO$_x$ interfacial layer (Fig. 1c), whereas the SiO$_x$-grown Si wafer has various sub-oxide states of Si$^{3+}$, Si$^{2+}$, Si$^{3+}$, and Si$^{4+}$ (corresponding to Si$_2$O, Si$_3$O, Si$_4$O$_2$, and Si$_5$O$_3$, respectively; see Fig. 1d).

Linear sweep voltammetry (LSV) responses for the Si photocathodes protected with HfO$_x$, SiO$_x$, and HfO$_x$/SiO$_x$ were obtained in 0.5-M H$_2$SO$_4$ to compare the charge transfer kinetics for the PEC water-splitting reaction (Fig. 2a). Two electrode systems consisting of a Si photocathode and Pt anode were used to determine the potential requirement for the self-biased water-splitting reaction. With a thermodynamic potential barrier of 1.23 eV, additional kinetic overpotential is required for the water-splitting reaction. Owing to the sluggish kinetics of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), the application of a minimum potential of ~2.8 V vs. Pt is required for realizing a high photocurrent level of 30 mA·cm$^{-2}$. The deposition of a 5-nm-thick HfO$_x$ results in an additional overpotential of 1.1 V at 30 mA·cm$^{-2}$ owing to the tunneling barrier of HfO$_x$, and the increase in the thickness to ~9 nm further increases the overpotential by 1.2 V (indicated by blue curves in Fig. 2a). Interestingly, on inserting a thin SiO$_x$ interlayer between the HfO$_x$ and Si (creating a HfO$_x$/SiO$_x$ bilayer), the additional overpotential is completely reduced regardless of the HfO$_x$ thickness (indicated by the pink curves in Fig. 2a). The same behavior was observed in the dark LSV characteristics for the degenerated doped n-type (n$^-$)Si wafer, which is only attributed to the charge transfer kinetics (Supplementary Fig. 3). This result indicates that the insertion of SiO$_x$ makes the charge transport independent of the tunneling barrier of the HfO$_x$, which is also verified by the electrochemical impedance spectra (Supplementary Fig. 4).

The negligible tunneling barrier can be explained by the effective engineering of an energy band after the insertion of SiO$_x$, under the application of a voltage for driving the PEC water-splitting reaction. When applying potential to the electrolyte/insulator/semiconductor configuration, the electric field can be built up across the insulator, thereby inducing a potential drop at the insulator layers. When the potential is applied across the HfO$_x$/SiO$_x$ bilayer, the potential drop can be expressed as $V_{\text{TE}} = \frac{Q_{\text{HfO}_x}}{C_{\text{SiO}_x}}$. The negligible tunneling barrier of HfO$_x$ to be located at a level lower than the conduction band of Si. Therefore, $V_{\text{TE}}$ is not only applicable on applying $V_{\text{TE}}$, the electrical tunneling barrier of HfO$_x$ becomes irrelevant to the charge transport because the potential drop caused by the application of $V_{\text{TE}}$ mainly occurs in the SiO$_x$ layer, which induces the tunneling barrier of HfO$_x$ to be located at a level lower than the conduction band of Si. Therefore, $V_{\text{TE}}$ is not only applicable for driving a water-splitting reaction but also for reducing the kinetic overpotential required for charge transfer.
where $E$ and $t$ are the electric field and thickness, respectively. $E_{SiO}$ and $E_{HfO}$ are related as

$$E_{HfO} = \left( \frac{\varepsilon_{SiO}}{\varepsilon_{HfO}} \right) E_{SiO}$$

The electric field is dominantly applied in the SiO$_x$ layer rather than in HfO$_x$ owing to a dielectric constant of SiO$_x$ (3.9) being much lower than that of HfO$_x$ (11)\(^{47}\). This allows a predominant potential drop across the SiO$_x$ layer. The potential drop across the SiO$_x$ layer under the application of potential results in a lying conduction band of HfO$_x$ that is relatively lower than that of Si, as described in Fig. 2b, which shows the band diagram of the HfO$_x$/SiO$_x$ bilayer. As a result, a tunneling barrier of SiO$_x$ only affects the transport of the charged carrier in the HfO$_x$/SiO$_x$ bilayer, and consequently, the effective tunneling distance becomes equal to the thickness of the SiO$_x$ monolayer. In contrast, the potential drop for the HfO$_x$ monolayer occurred entirely in the HfO$_x$ monolayer, thus creating a triangular barrier as described in Fig. 2c\(^{48}\). Because of the triangular barrier, the tunneling resistance is differentiated with the current density. In the case of a low current level ($<\sim$10 mA·cm$^{-2}$), the charge carriers are mostly transferred through the upper region of the triangular barrier in order to minimize the tunneling distance and resistance. Consequently, in the low-current level, the overpotential induced by the tunneling resistance is independent of the thickness. However, in the case of a high photocurrent region ($>\sim$10 mA·cm$^{-2}$), charge carriers transfer through all the regions of the barrier and suffer from a large tunneling distance and resistance. Therefore, the overpotential in the high-current level is greatly increased with the thickness.

It is also worth noting that the formation of the HfSiO$_x$ interfacial layer in the HfO$_x$ monolayer induces a hysteresis phenomenon owing to a negative charge trapping/detrapping mechanism at the interfacial layer\(^{49}\); the LSV curve is shifted into the anodic direction during the 10 cycles of the LSV scan (see Supplementary Fig. 5). This suggests that the HfSiO$_x$ interfacial layer with a high defect density acts as a recombination site for the charge carrier and also causes an increase in the charge transfer resistance. By contrast, the HfO$_x$/SiO$_x$ bilayer prevented the formation of HfSiO$_x$ interfacial layer and the hysteresis. To observe the effect of the SiO$_x$ interlayer on the PEC performance of the bilayer protected Si photocathodes, the LSV responses were characterized for the samples with

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**Figure 1.** Formation of a-HfO$_x$/SiO$_x$ bilayer protected p-Si photocathode. TEM images and XPS spectra for the a-HfO$_x$ deposited on (a,c) H-terminated and (b,d) SiO$_x$-grown Si wafers.
the wet-chemically-grown SiOₓ interlayer with oxidation times of 10 min (thin-SiOₓ) and 30 min (thick-SiOₓ) and with a thermally grown 1.8-nm-thick SiO₂ interlayer (Supplementary Fig. 6). A wet-chemically-grown thin-SiOₓ shows the lowest overpotential as compared to the thicker one and the thermally grown SiO₂ interlayer.

The engineering of the HfOₓ barrier height under the application of a voltage gives a further advantage in the PEC-TE hybrid system based on the HfOₓ/SiOₓ bilayer protected Si photocathode. As demonstrated in previous works, a hybrid system in which a PEC device is electrically combined in series with a TE device could promote a self-biased solar water-splitting reaction. The Seebeck voltage generated in the TE device owing to the thermal gradient (ΔT) causes the Fermi level of the counter electrodes to be lower than the oxygen evolution level, as depicted in Fig. 3a. This can effectively offset the potential required for driving the self-biased water-splitting reaction while the overall current is determined by the photocurrent of the PEC cell (i.e., the TE is only used as a voltage source). This was proven by the LSV responses with the driven Vₜₑ; the LSV curve for the bare Si photocathode (with DHF treatments) was shifted in the anodic direction in proportion to the applied Vₜₑ (see

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**Figure 2.** Comparison of PEC performances for p-Si photocathode protected with a-HfOₓ monolayer and a-HfOₓ/SiOₓ bilayer. (a) LSV curves of HfOₓ monolayer and HfOₓ/SiOₓ bilayer protected Si photocathodes. Energy band diagrams of (b) HfOₓ monolayer and (c) HfOₓ/SiOₓ bilayer protected Si photocathodes under application of voltage for the water-splitting reactions.

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**Figure 3.** PEC-TE hybrid devices (a) Energy band diagram of PEC-TE hybrid device for Seebeck-voltage-driven PEC water-splitting reaction. (b) LSV curves of the HfOₓ/SiOₓ bilayer protected Si photocathode under application of Seebeck voltage as a function of temperature difference (ΔT). (c) Plots indicating ΔT-dependent reduced potential for PEC water-splitting reaction; Si photocathodes protected by various insulator layers. (d) Photocurrent and Pₘₐₓ for PEC-TE device using planar Si and nanostructured Si (nano-Si) at ΔT of 62 K and 70 K. The grey line indicates the Pₘₐₓ for the photovoltaic-electrolysis (PV-EC) device.
Supplementary Fig. 7). Interestingly, in the case of the HfOx/SiOx bilayer protected Si photocathode, an anodic shift degree is larger than the applied VTE, and the overpotential is further reduced by 350 mV at a 70 °C temperature gradient (see Fig. 3b). To clearly differentiate the shifts, the anodic shift degrees of the LSV curve (reducing overpotential) at a photocurrent of 30 mA·cm⁻² were plotted as a function of ΔT along with the VTE (Fig. 3c). It should be noted that the slope of the linear plot for VTE is the Seebeck coefficient and is represented by the relation $V_{TE} = S \Delta T$. It is apparent that the slope for the HfOx/SiOx bilayer protected Si photocathode (41 mV·K⁻¹) is much greater than that for $V_{TE}$ (35 mV·K⁻¹). For the purpose of comparison, we also characterized the slope for the Si photocathodes grown with monolayers of HfOx and SiOx (see Supplementary Fig. 8 for the LSV curves). The SiOx has a slope (36 mV·K⁻¹) that is analogous with that of $V_{TE}$. In contrast, the slope for the HfOx is much greater than that for $V_{TE}$ but smaller than that for the HfOx/SiOx bilayer. These results are obtained owing to a different tunneling barrier height and potential drop under the applied VTE (see Supplementary Fig. 9 for the band diagrams).

As a result of applying $V_{TE}$, a saturated photocurrent of 34 mA·cm⁻² was obtained at a zero potential (i.e., external bias-free). In the PEC-TE hybrid device, an improvement in the photocurrent level is directly correlated with the solar-to-hydrogen conversion efficiency. Thus, we used antireflective Si nanostructures on Si photocathode, which completely absorbed the incident light⁵⁰,⁵¹ and greatly improved external quantum efficiency (EQE) for the light-induced charge carrier, maximizing the photocurrent of 42 mA·cm⁻² (see Fig. 3d and Supplementary Figs 10 and 11). While the PEC-TE hybrid system with planar Si provided the maximum H₂ power generation ($P_{Max}$) of 42 mW·cm⁻², the antireflective Si nanostructure photocathode achieved a $P_{Max}$ of 55 mW·cm⁻², which is four times greater than that of a photovoltaic-electrolysis combination ($P_{Max}$ of ~12 mW·cm⁻² indicated by the grey line in Fig. 3d).

The long-term stabilities of the HfOx/SiOx bilayer protected Si photocathode were performed using chronopotentiometry at 10 mA cm⁻² and using chronopotentiometry at an applied potential of −3 V. Due to the HfOx thin film which has an (electro)chemical stability in the acidic electrolyte and transparency for all wavelength region of the incident light, the Si photocathode exhibited a stable water-splitting reaction for over 200 h at high photocurrent level of 33 mA/cm² (Fig. 4a). The stability achieved at high photocurrent by HfOx thin film is the best result compared to other metal oxide thin films (see Supplementary Table 1). TiO₂ thin films chemically stable in the acidic and alkaline electrolytes have been widely used as a protection layer and have demonstrated long-term stability over 960 hr⁵². However, it has been recently reported ultraviolet (UV) light absorbed in TiO₂ causes the electrochemical reduction of TiO₂⁵³. Because of this issue, the TiO₂ protected Si photocathode operates reliably only when there is no UV irradiation, resulting in low photocurrent. Under the stable operation, the H₂ evolution was characterized by measuring a volume of the H₂ gas collected under a simulated AM 1.5 G 1-Sun illumination while operating under a certain photocurrent level of 32 mA·cm⁻² for 50 min (Supplementary Fig. 12). The measured H₂ volumes were corresponded well with the theoretically calculated values at a 100% Faraday efficiency based on the total charge passed. After the PEC operation for 200 h, interestingly, the potential was finally shifted in the anodic direction by 200 mV, which was identified by the
anodic shift of the LSV curve (see Fig. 4b). This was found to be the result of the crystallization of the as-deposited a-HfOx, during the PEC water-splitting reaction as observed in the TEM images and X-ray diffraction (XRD) results (Supplementary Fig. 13) of the HfOx layer before and after the 200 h stability test (see Fig. 4c,d). Because of the bulk defect state in the a-HfOx, that trapped the charge carrier, a substantial resistance was induced for the charge transfer across the a-HfOx, as depicted in Fig. 4e. In contrast, the crystallized HfOx significantly reduced the bulk defect density in the a-HfOx in order to improve the charge transfer kinetics. The crystallization during the solar water splitting reaction at the room temperature condition is an intriguing phenomenon, as it is known to crystallize a-HfOx in the monoclinic phase at temperature of 500 °C. This can be attributed to an electroforming phenomenon wherein the transition metal oxide can be reformed under the electrical field. This has been observed in transition-metal-oxide-based solid-state electronic devices. This finding presents a new method of improving the insulator quality used in PEC devices.

Discussion

We have presented the PEC-TE hybrid device using HfOx/SiOx bilayer protected the Si photocathode in which the HfOx thin film has a strong corrosion-resistance against the acidic electrolyte. The application of the Seebeck voltage generated in the TE device to the PEC device not only drove the self-biased solar water-splitting reaction but also promoted the ease of charge transfer through the HfOx tunneling barrier. On applying the Seebeck voltage to the HfOx/SiOx bilayer/Si photocathode, the conduction band of HfOx reached an energy level lower than the conduction band of Si, thereby allowing the electron transfer to become independent of the HfOx tunneling barrier. Because of the kinetic benefit, the voltage required for the self-biased water-splitting reaction of the Si photocathode is lowered by 0.35 V. As a result, the planar-Si-photocathode-based PEC-TE hybrid realized the self-biased water-splitting reaction with the evolved H2 power of 40 mW cm⁻² at a temperature difference of 70 °C. By adopting antireflective Si nanostructures that improve the photocurrent level to 42 mA·cm⁻², we observed the phase transformation of HfOx from the amorphous structure into a crystalline structure, which reduces the bulk defect density and thus the kinetic overpotential for the charge transfer through the HfOx layer.

Method

Preparation of HfOx thin-film protected Si photocathodes. A single-crystalline Si wafer with a resistivity of 1–10 Ω cm and degenerately doped n−type Si (100) wafer with a resistivity of 0.001–0.002 Ω cm were used to characterize the PEC response and charge transfer kinetics, respectively. Prior to the deposition of HfOx, the Si wafer was dipped in dilute hydrofluoric acid to form an H-terminated surface while removing the native oxide. For growing the SiOx thin film on the surface of the Si wafer, the H-terminated Si wafer is oxidized through treatment with hot water at 90°C for 10–30 min. ALD of the HfOx thin film was performed for both the H-terminated and SiOx-grown Si wafers to obtain the HfOx monolayer and HfOx/SiOx bilayer coated Si wafers, respectively. An HfOx thin film was deposited at 280 °C in a 4-inch traveling-wave type ALD reactor (CN-1 Co.) using Tetrakis(a-hydroxyethyl)hafnium (TEMAHf) and H2O precursors with a carrier gas of high purity N2 (99.999%). The TEMAHf, N2, and H2O were sequentially injected for 2.5, 30, and 1.5 s, respectively.

Characterization of HfOx thin films. A HRTEM (JEOL, JEM-2100F, Japan) equipped with an EDXS operated at an accelerating voltage of 200 kV was used to observe the morphology and elemental composition of the HfOx-thin-film-coated Si wafers. The thicknesses of the HfOx and SiOx thin films were measured using spectroscopic ellipsometry (Sopra GES 5E, fitted to a Tauc–Lorentz function using the Cauchy model). The chemical states of the HfOx and SiOx thin films were investigated using ARXPS equipped with a monochromatic Al Kα (1.486 eV) source.

Setup of PEC-TE hybrid devices. The PEC device consists of the Si photocathode and Pt mesh anode for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), respectively. The SiOx thin film was treated with DHF soaking and subsequent scribing using an In–Ga eutectic alloy (Sigma–Aldrich) to fabricate back contacts with a Cu electrode. PEC-TE hybrid systems were used by electrically connecting the PEC device with a TE device in series; the Si photocathode is connected to an anode of the TE device, and a cathode of the TE device is connected to the Pt anode. TE devices with a Seebeck coefficient of 35 mV K⁻¹ and internal resistances of 2.1 Ω, which are commercially available from Kryotherm (Saint-Petersburg, Russia), were employed.

Characterizations of PEC performances. The PEC properties of the Si photocathodes were measured using a potentiostat (Iviumstat, Eindhoven, Netherlands) with a two-electrode configuration (Si photocathode and Pt mesh anode). The PEC responses were characterized using various methods of LSV, chronopotentiometry, and chronoaomperometry in 0.5-M sulfuric acid under a 100-mW cm⁻² illumination (Xenon lamp equipped with AM 1.5 G filter) and calibrated by a Si photodiode standard cell (PV Measurements, Inc.). The LSV responses were measured under dark and illuminated conditions at a scan rate of 50 mV s⁻¹. The stability and H2 evolution measurements were performed using chronopotentiometry and chronoaomperometry. Home-made heating and cooling systems were fabricated to control the temperature and were used for applying a constant temperature difference between the front and back of the TE device. The temperature difference was monitored using K-type thermocouples (Center 306 Data Logger, New Taipei City Taiwan). The quantity of hydrogen evolved at the Si photocathode under illumination and the Seebeck voltage application was measured using the volume displacement method wherein the volume of a water-filled flask changes with the evolution of hydrogen gas. A Pt counter electrode covered with a quartz cylinder and proton exchange membrane was used in order to separately collect hydrogen and oxygen gas. All the PEC-TE hybrid system is shown in Supplementary Fig. 14 as a digital image.
Data Availability
The data supporting the findings of this study are available within the article and its Supplementary Information files. All other relevant source data are available from the corresponding author upon reasonable request.

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Author Contributions
J.-Y.J. and J.-H.L. conceived the idea and designed the experiment and wrote the paper. J.-Y.J., D.W.K. and D.-H.K. performed the experiments. All authors discussed the results.

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