# **Supplementary Information**

# Over 12% efficiency solar-powered green hydrogen production from seawater

Xuanjie Wang<sup>1,2</sup>, Jintong Gao<sup>3</sup>, Yipu Wang<sup>3</sup>, Yayuan Liu<sup>4,\*</sup>, Xinyue Liu<sup>1,5,\*</sup>, Lenan Zhang<sup>1,3,\*</sup>

<sup>1</sup>Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

<sup>2</sup>Department of Mechanical Engineering and Mechanics, Lehigh University, Bethlehem, PA 18015, USA

<sup>3</sup>Sibley School of Mechanical and Aerospace Engineering, Cornell University, NY 14853, USA

<sup>4</sup>Department of Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, MD 21218, USA

<sup>5</sup>Department of Chemical Engineering and Materials Science, Michigan State University, MI 48824, USA

\*Corresponding authors: <u>yayuanliu@jhu.edu</u> (Y. Liu), <u>xyliu@msu.edu</u> (X. Liu), and <u>lzhang@cornell.edu</u> (L. Zhang)

### **Design and Fabrication of the HSD-WE Prototype**

The detailed design of the HSD-WE prototype involves two major parts: (1) the photovoltaic (PV) panel and (2) the electrolyzer. The projected area of the HSD-WE device was  $10 \times 10$  cm<sup>2</sup>, while the PV panel provided a total solar-absorbing area of  $7 \times 7$  cm<sup>2</sup> (Fig. S1a). The PV panel included four series-connected cells (custom-designed from Mars Rock Science Technology) optimized to meet the power demand of the electrolyzer. The series connection was achieved by soldering thin metallic ribbons onto the busbar of each solar cell before the encapsulating step. Behind the PV panel, a piece of wick material  $(28 \times 7 \text{ cm}^2, \text{ from Bounty})$  was adhered to the back of PV panel using a small amount of glue at the corner (Fig. S1a). The wick at the wet state serves as an interfacial thermal evaporator to cool the PV panel and distill seawater. Note that the black color of interfacial thermal evaporator was used in the salt rejection experiments only for a better visualization of salt crystals. The electrolyzer (custom-designed from Sinero Technology) includes a polycarbonate spacer, bipolar plates (BPs), gas diffusion layers (GDLs), proton exchange membrane (PEM), gasket, heat sink, and end plate. Specifically, a polycarbonate spacer, with an inner aperture area of  $5 \times 5$  cm<sup>2</sup>, maintained a 1.5 cm air gap between the interfacial thermal evaporator and the anode side's bipolar plate (BP) (Fig. S1b). Two ports were drilled from the side wall on the spacer, one for placing the thermocouple inside, the other for oxygen and extra water vapor venting. The BP of the anode side was constructed using a 10 cm width L-shape stainless steel plate (13 cm long parallel to the PEM, 15 cm long perpendicular to it) with parallel slots (25 slots, each with 5 cm in length and 1 mm in width) on the side facing the evaporator (Fig. S1b). The proton exchange membrane (PEM) was coated with electrocatalyst (Ir/Pt) and sandwiched by two titanium gas diffusion layers (GDLs), with both GDLs and PEM measuring 5  $\times$  5 cm<sup>2</sup>. The BP of the cathode side was made by a stainless-steel plate with the same dimensions as the anode side except for the 15 cm heat sink. The polycarbonate end plate  $(10 \times 10 \text{ cm}^2)$  had two vent ports for hydrogen collection. The soft silicone gaskets were applied in between every two stiff components to seal the device appropriately. For assembly of the HSD-WE device, eight sets of bolts and screws were used to first tighten the electrolyzer and then the PV was added to the front avoiding excess force applied directly on the PV. We note that the pure titanium could be prone to oxidation at high anodic potentials, which might increase the electrolyzer voltage. To further improve the performance of PEM electrolyzer, we will investigate the gold-coated titanium GDL as an alternative in future work [1].



**Fig. S1** Detailed design of the HSD-WE Prototype. The photograph of (a) the Silicon PV panel (passivated emitter and rear contact solar cells) with interfacial thermal evaporator (capillary wick) at the back and (b) the electrolyzer with polycarbonate spacer, BPs, GDLs, PEM, gasket, heat sink and end plate.

Table S1 Summary of equipment and material information

Equipment/Material	Series number	Brand	
Solar simulator	92192	Newport Oriel Inc.	
Potentiostat	<b>VSP-300</b>	BioLogic	
Refractometer	HI 96801	Hanna Instruments	
Sourcemeter	2425	Keithley Instrument	
Balance	SJX6201N/E	Ohaus	
Camera	B07TYWPM67	Logitech	
Pyranometer	LP-02	Hukseflux	
Seawater		Carolina Biological Supply Company	

Table S2 Details of PEM and GDL used in the HSD-WE device

Components	Specifications	Manufacturer	
	Nafion 115 membrane		
PEM	Pt: 1 mg/cm <sup>2</sup> (cathode)	SUZHOU SINERO TECHNOLOGY CO., LTD	
	Ir: 2 mg/cm <sup>2</sup> (anode)		
GDL	Pure Ti felt		
	Thickness: 250 μm		
	Porosity: 0.5 – 0.6		
	Fiber diameter: $30 - 60 \ \mu m$		

### **Experimental Setups and Temperature Measurements for PV Cooling**

To investigate the effect of interfacial thermal evaporator on PV cooling, we measured the PV temperature profiles with different PV cooling setups. Two identical PV panels were prepared and placed in ambient conditions with uniform solar illumination provided from above by a solar simulator (92192, Newport Oriel Inc.). In the baseline setup, the backside of the PV was exposed directly to ambient air (Fig. S2a). In the cooling setup, an interfacial thermal evaporator was attached to the backside of the PV panel (Fig. S2c). This evaporator was continuously supplied with seawater, where two reservoirs were placed at different heights to create the unidirectional flow. The T-type thermocouples (Omega) were positioned on these two PV panels ( $T_1$ ,  $T_3$ ), in the ambient air ( $T_2$ ), and within the water reservoir ( $T_4$ ) to monitor temperature during solar illumination. At the steady state, the PV panel with the interfacial thermal evaporator reached a temperature of 40.9 °C, compared to 55.5 °C in the baseline setup, demonstrating a significant cooling effect (Fig. S2b and S2d).



**Fig. S2** Schematic of the PV cooling measurement setups and temperature profiles (a, b) with baseline air cooling and (c, d) with the interfacial thermal evaporator cooling.

## Experimental Setups for Characterizing Salt Rejection with the Unidirectional Flow

The salt rejection measurement setup consists of the PV panel with an interfacial thermal evaporator attached to the backside. In the baseline configuration, the inlet of the capillary wick was submerged in a reservoir containing saline solution. For the unidirectional flow setup, the inlet and outlet of the capillary wick were connected with two separate reservoirs: one containing saline and the other collecting the brine discharge. A camera (StreamCam, Logitech) was positioned at the backside of the setup to monitor the salt accumulation during solar evaporation for both cases. To initiate the siphon effect, the saline reservoir was elevated 6 cm above the brine reservoir (h = 6 cm). This hydraulic head between the two reservoirs generated unidirectional flow, carrying the accumulated salt out of the evaporator. We conducted seawater distillation and measured the salinity at the evaporator outlet, using real seawater (3.5 wt% salinity, Carolina biological supply company) with a complex composition. The salinity was measured with a digital refractometer (HI 96801, Hanna Instruments).



**Fig. S3** Schematic of the salt rejection measurement setups consisting of the PV panel and an interfacial thermal evaporator with (a) conventional wick and (b) unidirectional flow.

### **Characterizing Heating Effect on PEM Electrolyzer Performance**

To understand the effect of operating temperature on the performance of PEM electrolyzer, we heated the feed water using a hot plate and measured the temperature with a T-type thermocouple positioned close to the anode side (Fig. S4). Deionized (DI) water was used in this experiment. A micropump (Cole-Parmer 07522-20) was used to maintain water circulation through the electrolyzer. Once thermal equilibrium was reached, the polarization curves were measured potentiostatically using a sourcemeter (Keithley Instrument 2425) with a feed water temperature of 23 °C, 40 °C, and 60 °C (Fig. S5). Linear sweep voltammetry was performed at a sweep rate of 15 mV/s, with data points recorded at two-second intervals.



**Fig. S4** Schematic of the heating effect measurement setup consisting of a PEM electrolyzer and a hot plate for temperature control.



**Fig. S5** Current density-based polarization curve of the PEM electrolyzer at representative temperatures. Grey dashed line: the PEM electrolyzer performance at 1.65 V, where an increase of the current density from 0.0119 A/cm<sup>2</sup> to 0.0198 A/cm<sup>2</sup> was shown by elevating the operating temperature from 23 °C to 60 °C.

### **Condensation Heating Effect on Electrolysis Performance**

To investigate the effect of condensation heating on electrolysis performance, we conducted a controlled experiment by comparing the HSD-WE device with a control group device (Fig. S6). The control group device is featured by decoupling the PV panel and interfacial thermal evaporator from the PEM electrolyzer, which eliminates vapor condensation on the PEM electrolyzer. One-sun illumination was applied to both the HSD-WE device and the control group device. To make a fair comparison, we maintained temperatures of PV panels in both devices the same, ensuring the same solar-to-electricity conversion efficiency. We performed two-hour tests on both devices and measured the resulting hydrogen production rates.

Figure S7a shows the temperature responses of the HSD-WE device and the control group device during a two-hour operation. At the steady state, PV panels of both devices exhibited similar temperatures ( $T_1$ ) around 47 – 48 °C, indicating a similar solar-to-electricity conversion efficiency. Owing to condensation heating, however, the temperature of the PEM electrolyzer in the HSD-WE device ( $T_2 \approx 35.5$  °C) was much higher than that of the PEM electrolyzer in the control group device ( $T_2 \approx 19$  °C). Figure S7b shows the resulting hydrogen collection of the HSD-WE device and the control group device during the two-hour operation, where hydrogen production rates were extracted through linear fitting. Hydrogen production rate of the Control group device was 165.0 ml/h (Fig. S7c). In contrast, hydrogen production rate of the HSD-WE device reached 180.5 ml/h, indicating a 9.4% increase (Fig. S7c). Figure S8 further shows the time-lapse images of hydrogen collections during the two-hour operation, where 361 ml and 330 ml green hydrogen were produced by the HSD-WE device and the control group device and the control group device.



**Fig. S6** Schematic of controlled experiment to quantify the impact of condensation heating on hydrogen production. (a) HSD-WE device. (b) Control group device by decoupling the PEM electrolyzer from the PV panel and interfacial thermal evaporator. Both devices were operated under one-sun illumination and the same ambient conditions.



**Fig. S7** Performance comparison between the HSD-WE device and the control group device. (a) Temperature responses of PV panels (blue curves) and PEM electrolyzers (red curves) for both devices. The solid line and dashed line represent the HSD-WE device and the control group device, respectively. (b) Hydrogen collections of both devices as a function of time. (c) Average hydrogen production rates of both devices during the two-hour operation.



Fig. S8 Time-lapse images of continuous green hydrogen production from (a) the HSD-WE device and (b) the control group device.

### **Theoretical Model and System-level Optimization**

To understand the efficiency limit and optimal configuration of the HSD-WE device, we applied the equivalent circuit method (ECM) to model the electrical behaviors of the PV panel and the PEM electrolyzer [2,3]. For the PV panel, the ECM considered the generated photocurrent, recombination current, and ohmic losses. When *n* solar cells are connected in series, the output current density  $j_{PV}$  can be expressed as,

$$nj_{\rm PV} = j_{\rm L} - j_{\rm PV,0} \exp\left[\frac{q(V_{\rm PV}/n + nj_{\rm PV}R_{\rm s})}{n_{\rm f}kT_{\rm PV}}\right] - \frac{(V_{\rm PV}/n + nj_{\rm PV}R_{\rm s})}{R_{\rm sh}}$$
(S1)

where  $j_{\rm L}$  is light generated current density,  $j_{\rm PV,0}$  is the dark saturation current density, q is electron charge,  $V_{\rm PV}$  is voltage,  $n_{\rm f}$  is ideality factor, k is Boltzmann constant,  $T_{\rm PV}$  is PV temperature,  $R_{\rm s}$  is series resistance and  $R_{\rm sh}$  is shunt resistance. The current can be expressed as  $I_{\rm PV} = j_{\rm PV}A_{\rm PV}$ , where  $A_{\rm PV}$  is the area of PV panel.

The solar-to-electricity conversion efficiency of the PV panel can be expressed as,

$$\eta_{\rm PV}(\%) = \left[\frac{V_{\rm MPP}I_{\rm MPP}}{\text{Total solar irradiation \times area}}\right]$$
(S2)

where  $V_{MPP}$  and  $I_{MPP}$  are the voltage and current at the maximum power point (MPP) of the PV panel, respectively.

We modeled the PEM electrolyzer by considering the thermodynamic voltage, activation overvoltage, and ohmic losses [4]. The total voltage applied to the PEM electrolyzer  $V_{\text{EC}}$  can hence be expressed as,

$$V_{\rm EC} = \mu_{\rm th} + \tau_0 \log\left(\frac{j_{\rm EC}}{j_{\rm EC,0}}\right) + j_{\rm EC}R_{\rm ohm} \tag{S3}$$

where  $\mu_{\text{th}}$  is thermodynamic voltage (1.23 V),  $\tau_0$  is Tafel slope,  $j_{\text{EC},0}$  is exchange current density, and  $R_{\text{ohm}}$  is total ohmic resistance of the PEM electrolyzer. The current can be expressed as  $I_{\text{EC}} = j_{\text{EC}}A_{\text{EC}}$ , where  $A_{\text{EC}}$  represents the reaction area of electrolyzer.

Figure S9a shows that the PV model (Eq. S1) can fit with the experimental measurements very well when n = 4,  $j_{\rm L} = 38.2 \text{ mA/cm}^2$  and  $R_{\rm sh} = 700 \,\Omega \cdot \text{cm}^2$ . To investigate the coupling between the PEM electrolyzer and PV panels with different efficiencies, we varied the generated photocurrent density from 31.8 to 43.2 mA/cm<sup>2</sup> while fixing the shunt resistance. As a result, the corresponding PV panel efficiency increased from 15% to 20% (Fig. S9b). To determine the optimal number of solar cells for the HSD-WE device, we further altered the number of solar cells in series (n = 2 - 7) in our model and calculated the intersection points of the PEM electrolyzer polarization curve and the PV panel current-voltage (I-V) curves (Fig. S9c). Our modeling shows that the configuration with four solar cells in the series circuit connection yields the highest current at the

intersection point between PV and electrolyzer, indicating the optimal solar-to-hydrogen (STH) efficiency.

Our electrolyzer model shows an excellent agreement with experimental measurements when  $\tau_0 = 0.27$  V/dec, and  $R_{ohm} = 14 \ \Omega \cdot cm^2$  (Fig. S9d). To investigate the effect of electrocatalysts on the STH efficiency of the HSD-WE device, we varied the Tafel slope while remaining the ohmic resistance the constant, in which way we could model the change of activation overvoltage due to different electrocatalysts. Figure S9e shows representative PEM electrolyzer polarization curve by varying the Tafel slope from 0.1 V/dec to 0.4 V/dec. For the convenience of comparison, we chose the overvoltage values at 500 mA (20 mA/cm<sup>2</sup>) as a performance indicator of the PEM electrolyzer. The STH efficiency under each overvoltage value (or Tafel slope) was calculated from the intersection points of the PEM electrolyzer polarization curves in the form of current density.



**Fig. S9** Theoretical optimization of the HSD-WE device. (a) Validation of PV modeling with experimental measurement. (b) Modeled I-V curves of PV panels with different efficiency  $(\eta_{PV})$  from 15% to 20%. (c) Effect of solar cell number (n = 3, 4, 5) with a fixed PEM electrolyzer. (d) Validation of PEM electrolyzer modeling with experimental measurement. (e) Effect of Tafel slope  $(\tau_0 = 0.1, 0.27, 0.4 \text{ V/dec})$  on PEM electrolyzer polarization curves. (f) Effect of electrocatalysts (Tafel slopes) on the HSD-WE device performance with a fixed number of solar cells (n = 4). Three representative Tafel slopes (0.1 V/dec, 0.27 V/dec, 0.4 V/dec) correspond to STH efficiencies of 15.5%, 13.4%, and 11.0%, respectively.



**Fig. S10** Polarization curves in the form of current density. (a) Validation of PV modeling. (b) Modeled I-V curves of PV panels with different efficiency ( $\eta_{PV}$ ). (c) Effect of solar cell number (n = 3, 4, 5) with a fixed PEM electrolyzer. (d) Validation of PEM electrolyzer modeling. (e) Effect of Tafel slope ( $\tau_0 = 0.1, 0.27, 0.4 \text{ V/dec}$ ) on PEM electrolyzer polarization curves. (f) Effect of electrocatalysts (Tafel slopes) on the HSD-WE device performance with a fixed number of solar cells (n = 4). Three representative Tafel slopes (0.1 V/dec, 0.27 V/dec, 0.4 V/dec) correspond to STH efficiencies of 15.5%, 13.4%, and 11.0%, respectively.

### **Dry Hydrogen and Efficiency Calculation**

The hydrogen collected in the gas cylinder is considered as wet hydrogen, comprising both dry hydrogen and minor water vapor. The partial pressure of dry hydrogen is calculated as,

$$P_{\rm H_2} = P_{\rm atm} - P_{\rm H_2O} \tag{S4}$$

where  $P_{\text{atm}}$  is the atmosphere pressure,  $P_{\text{H}_2\text{O}}$  is water vapor saturation pressure, determined based on temperature measurements. We first calculated the partial pressure of dry hydrogen by excluding the partial pressure of water vapor from the total atmospheric pressure. Then, we applied the combined gas law to convert the state of dry hydrogen to the standard temperature and pressure (STP) conditions (273.15 K, 10<sup>5</sup> Pa) and hence obtained the volume of dry hydrogen under the standard condition [5].

The solar-to-hydrogen (STH) efficiency was evaluated using both the Gibbs free energy and the higher heating value (HHV) definitions [6,7]. Gibbs free energy of water electrolysis ( $\Delta G_{H_2} = 237$  kJ/mol (1.23 V) at standard conditions) represents the maximum amount of work achievable from a unit quantity of hydrogen, assuming no entropy generation, and is commonly used in solar-to-fuel metrics within photoelectrochemical processes. Higher heating value of hydrogen (HHV = 39.4 kWh/kg (1.48 V)) is defined as the total heat released during combustion where the initial and final state is 25 °C. This represents the total amount of heat recoverable from combustion of the fuel and is equivalent to the enthalpy under standard conditions. The STH efficiency is calculated based on the following equation,

$$\eta_{\text{STH}}(\%) = \left[\frac{\text{Rate of H}_2 \text{ production} \times \text{Gibbs free energy (or HHV)}}{\text{Total solar irradiation} \times \text{area}}\right]$$
(S5)

## **Device Indoor Test Setup and Operation**

The PV panel and PEM electrolyzer in the HSD-WE device were electrically connected with electrical cables (Grainger) by alligator clips. Two ports at the endplate were connected with a graduated cylinder (500 ml, Class A, EISCO) for hydrogen collection. The BP of the anode side was immersed into the water bath at room temperature as heat sink. A camera was positioned to the graduated cylinder to record the hydrogen production rate (Fig. S11). Before the experiment, the solar simulator (92192, Newport) was calibrated with the source meter (2936r, Newport) to ensure a solar illumination of one sun (Fig. S11a). At the starting point, the real seawater was added to the reservoir 1 ( $\approx$  445 ml) and reservoir 2 ( $\approx$  5 ml) to initiate the wetting of the evaporator (Fig. S12). During the experiment, temperature (Fig. S12b and S12f), salinity (Fig. S12c and S12g), and mass change (Fig. S12d and S12h) were recorded for indoor tests using both real seawater with salinity of 3.5 wt% (Fig. S12a) and concentrated seawater with salinity of 10 wt% (Fig. S12e).



**Fig. S11** Indoor test setup for the HSD-WE device. (a) Calibration of the solar simulator (92192, Newport Oriel Inc.) to ensure a solar illumination of one sun with a power meter. (b) HSD-WE device positioned under the mirror, receiving one-sun illumination from the solar simulator during testing.



**Fig. S12** (a, e) Schematic of the indoor test setup for the HSD-WE device, showing thermocouple locations and different feed water salinity. Temperature, salinity and mass change profiles for indoor tests using both (b-d) real seawater with salinity of 3.5 wt% and (f-h) concentrated seawater with salinity of 10 wt%.

#### **Quantifying Different Heating Effects on PEM Electrolyzer**

The Joule heating effect could be another possible mechanism to the increased temperature of the PEM electrolyzer in the HSD-WE device. To quantify different heating mechanisms, we estimated the condensation heating and Joule heating as follows,

$$Q_{\rm con} = m_{\rm v} h_{\rm fg} A_{\rm solar} \tag{S6}$$

$$Q_{\rm Joule} = I_{\rm EC}^{2} R_{\rm ohm} \tag{S7}$$

where  $Q_{\rm con}$  and  $Q_{\rm Joule}$  represent the condensation heat and the Joule heat, respectively,  $m_{\rm v}$  is the vapor flux,  $\approx 1.2 \text{ kg/m}^2/\text{h}$  according to our measurements,  $h_{\rm fg}$  is the latent heat of water vaporization,  $\approx 2400 \text{ kJ/kg}$ , and  $A_{\rm solar}$  is the total solar absorbing area, 0.0049 m<sup>2</sup>.  $I_{\rm EC}$  and  $R_{\rm ohm}$  represent the current and ohmic resistance of the PEM electrolyzer,  $\approx 0.4 \text{ A}$  and  $\approx 0.14 \Omega$ . (Note S.6). The results show that the condensation heating effect ( $\approx 3.92 \text{ W}$ ) is 175 times stronger than the Joule heating effect ( $\approx 0.0224 \text{ W}$ ). Therefore, we believe it is appropriate to attribute the increased temperature of the PEM electrolyzer to condensation heating effect.

### **Purity Test Before and After Distillation**

To validate the purity of the distilled water, we conducted four independent 10-hour distillation tests, with a total duration of 40 hours. After each 10-hour continuous operation, we collected the distilled water and tested its purity using a conductivity meter (Mettler Toledo SD30). The average conductivity over the four independent tests was  $3.646 \pm 1.614 \mu$ S/cm (Fig. S13), where the uncertainty was calculated based on the standard deviation of the four measurements. The purity of distilled water met the American Society of Testing Materials (ASTM) standard of high-purity water (< 5  $\mu$ S/cm) [8], indicating its feasibility for water electrolysis. In addition, we calculated the salinity using the following equation [9,10],

$$S = 0.000523\sigma \tag{S8}$$

where S is the salinity, g/kg,  $\sigma$  is the conductivity,  $\mu$ S/cm.

The salinity of the distilled water was  $0.00019 \pm 0.00008$  wt% only (Fig. S13), which was two orders of magnitude lower than the World Health Organization (WHO) standard for drinking water (200 mg/L).



**Fig. S13** Water conductivity and salinity before and after distillation. The black-dashed line shows the ASTM standard for high purity water and WHO standard for drinking water.

# Supplementary Note 11 Cyclic Test

The cyclic test of the HSD-WE device was conducted using seawater under one-sun illumination. Each cycle consisted of two hours of operation and seven cycles were performed in total. We obtained an average hydrogen production rate of  $\approx$  180.0 ml/h for each cycle (Fig. S14). The minimal variations (< 4 ml/h) of hydrogen production rates among these cycles indicate an excellent stability of the HSD-WE device.



**Fig. S14** Hydrogen production rate of the HSD-WE device in seven cycles. The variations of hydrogen production rates among different cycles were within 4 ml/h, indicating a highly stable performance.

## **Comparison of Solar-to-hydrogen Efficiency**

The solar-to-hydrogen (STH) efficiencies of various techniques (photocatalytic water splitting, photoelectrochemical water splitting, and PV electrolysis) are listed in Table S3.

Ref.	Technique	Feed water type	STH efficiency
		reed water type	(%)
This work	Silicon PV electrolysis	Seawater	12.6
[11]			1.1
[12]	Dhotocatalytic		0.4
[13]	Thotocatalytic		0.76
[14]		-	9.2 (38 suns)*
[15]			6
[16]			7.1
[17]			0.34
[18]	Photoelectrochemical		1.046
[19]			3
[20]			4.3
[21]			13 (207 suns)*
[22]			10
[23]		Pure water	3.9
[24]			9.5
[25]	0:1: DV -1**		10.8
[26]	Shicon PV electrolysis		9.8
[27]			12.7
[28]			11.28
[29]			10.48
[30]			12.3
[31]			11.22
[32]	Perovskite PV electrolysis**		12.3
[33]			13.6
[34]			13.5
[35]			5.4
[36]	Organic PV electrolysis**		6
[37]			10
[38]			6.2
[39] [40]	GaAs-based PV electrolysis**		16 10 1
			18.1
[41]			17.6

 Table S3 Comparison of solar-to-hydrogen (STH) efficiency. State-of-the-art studies on photocatalytic water splitting, photoelectrochemical water splitting, and PV electrolysis are included.

\*The STH efficiencies were obtained under concentrated sunlight.

\*\*The solar-to-electricity conversion efficiency of various PV panels are as follows: silicon PV (13.6 - 18.6%), perovskite PV (17.4 - 20.0%), organic PV (6.7 - 11.7%), and GaAs-based PV (23.2 - 33.1%).

## **Device Outdoor Test**

Figure S15 shows results of outdoor test of the HSD-WE device in three different days. The weather conditions, including solar irradiation and ambient temperature, were recorded by a weather station near the test setup (Fig. S15a and S15b). Temperature variations of the HSD-WE device were recorded by thermocouples as described in the main text (Fig. S15b). The hydrogen production rate was determined by the gas collection cylinder, which fluctuated throughout the day due to the varying solar flux (Fig. S15c). The HHV and Gibbs free energy-based STH efficiencies were calculated based on the measured hydrogen production rate with an average over 30-min intervals (Fig. S15d).



**Fig. S15** (a) Solar irradiation, (b) temperature, (c) hydrogen production rate, and (d) STH efficiency profiles for outdoor tests conducted over three days.

### Technoeconomic Analysis of Solar-powered Green Hydrogen Production

The penitential economic feasibility of solar-powered seawater electrolysis for green hydrogen production was evaluated and compared to the conventional water electrolysis (WE) using a technoeconomic analysis (TEA). As summarized in Table S4, we used an average daily solar irradiance of 8 kWh/day/m<sup>2</sup> in our calculation. Given a solar receiving area of 49 cm<sup>2</sup> per device, the solar energy input per device is 0.0392 kWh/day. For hydrogen production, we used the STH efficiency demonstrated in this work (12.6%) and converted it to daily hydrogen production based on the daily solar energy input. We calculated the hydrogen production of the conventional WE by considering the HHV-based energy efficiency of a PEM electrolyzer of 77%, which was measured from our experiment. We note that the energy efficiency of conventional WE used in our calculation was comparable with that of state-of-the-art electrolyzers [42,43]. We considered that the conventional WE is operated under the same condition as the HSD-WE device (1.6 V) for a fair comparison. However, distinct from the solar-powered HSD-WE device, the conventional WE can be continuously operated throughout the full day, leading to more daily hydrogen production.

The total device cost includes both operational expenditure (OPEX) and capital expenditure (CAPEX). The OPEX for WE includes the costs of electricity (0.004 USD for 0.018 kWh per device) and clean water (0.003676 USD for 3.676 g per device) required for hydrogen production. Due to the passive operation of the HSD-WE device, both electricity and water costs are zero, leading to a significant reduction of OPEX. The CAPEX of a baseline PEM electrolyzer was derived from the US Department of Energy (DOE) 2020 record, while the CAPEX of the HSD-WE device was estimated by adding the cost of PV panel and capillary wick to the baseline PEM electrolyzer. Details of the data sources and the calculations can be seen in Table S4. The unit price for hydrogen production  $P_{\rm H_2}$  (units: USD/kg), is given by,

$$P_{\rm H_2} = \frac{\rm CAPEX + OPEX}{R_{\rm H_2} \times t}$$
(S9)

where  $R_{\text{H}_2}$  is the daily hydrogen production (unit: kg/day) and t is the device operation time (unit: days).

	WE	HSD-WE	Reference
Solar energy (kWh/day/m <sup>2</sup> )	/	8	pveducation.org
Device solar receiving area (m <sup>2</sup> )	/	0.0049	
Solar energy per device (kWh/day)	/	0.0392	
Energy efficiency (%)	77	/	
Solar-to-hydrogen efficiency (%)	/	12.6	
Hydrogen generated per device (g/day)	0.408	0.148	
Hydrogen power generated per device (W)	0.567	0.206	
Bottle water price (USD/kg)	1		amazon.com
Water consumption (g/day)	3.676	/	
Electricity rate (USD/kWh)	0.01641	/	electricchoice.com
Electricity consumption (kWh/day)	0.018	/	
Total OPEX (USD/day)	0.004	/	
Electrolyzer cost (USD/kW)	1500		hydrogen.energy.gov
CAPEX cost of WE (USD)	0.850		
PV device cost (USD/kWh)	/	260	ourworldindata.org
CAPEX cost of PV (USD)	/	0.054	
Total CAPEX (USD)	0.850	0.904	
Total cost (USD)	0.850+0.004t	0.904	
Total hydrogen generation (kg)	0.000408t	0.000148t	
Hydrogen cost (USD/kg)	(0.850+0.004t)	0.904	
	/0.000408t	/0.000148t	

 Table S4 Detailed calculations of technoeconomic analysis (TEA)

## **Global Map of Solar-powered Green Hydrogen Production**

The long-term average of daily total direct normal irradiation was obtained from Solargis, which provides the solar energy data and analysis software for PV plant investments. The global map of annual green hydrogen production was determined by the product of direct normal incident solar energy and the average STH efficiency (12.6% demonstrated in this work) using the geographic information system software QGIS 3.22.5. Additionally, we converted the unit of hydrogen production (kWh/m<sup>2</sup>/year) to kg/m<sup>2</sup>/year based on the HHV of hydrogen.

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