Supporting Information

Hydrogen from Sunlight and Water: A Side-by-Side Comparison between Photoelectrochemical and Solar Thermochemical Water-Splitting

Wen-Hui Cheng,[1,2†] Alberto de la Calle,[3†] Harry A. Atwater,[2] Ellen B. Stechel,[4*] Chengxiang Xiang[2*]

*To whom correspondence should be addressed: Ellen.Stechel@asu.edu, cxx@caltech.edu

† Wen-Hui Cheng and Alberto de la Calle contributed equally to this work.

The PDF file includes:

Figure S1-S4

Table S1

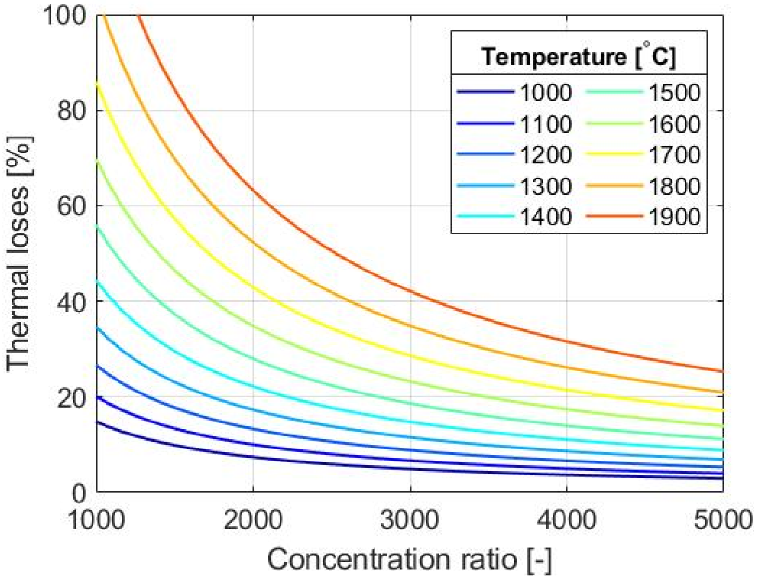
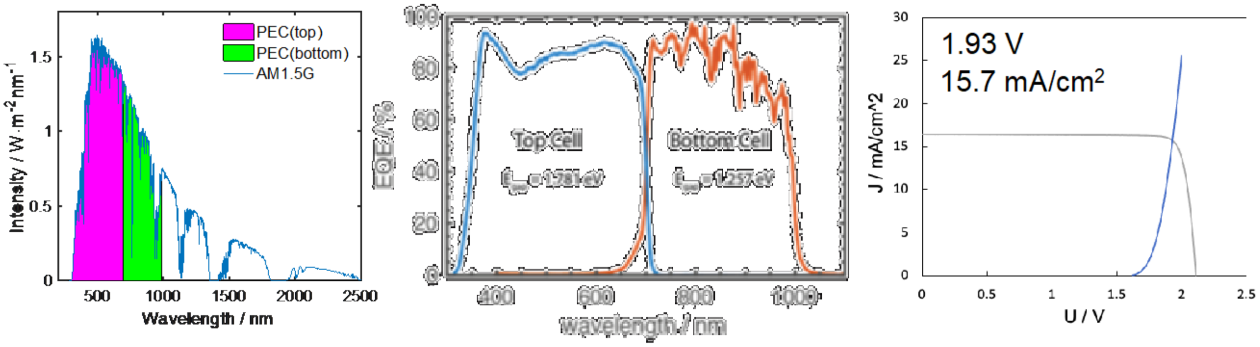


Figure S1 Correlation of the re-radiation and convection losses to the concentration ratio at different temperature.

Integration over the AM1.5G spectrum we obtained a power of 1000 W m^{-2}. The lower bandgap of the light absorber (1.26 eV) constrains the power to 729 W m^{-2}. The bandgap photon loss is calculated to be 27.1%. ($\frac{1000-729}{1000}=27.1\%$) Applying the additional EQE spectrum the power dropped to 655 W m^{-2}, and the reflection loss is calculated to be 7.4%. ($\frac{729-655}{1000}=7.4\%$) Multiplying the current and voltage at the operation point (J=15.7 mA cm^{-2}, U=1.93 V) we obtained the power of 303 W m^{-2}. The thermalization and recombination lass at operation point is calculated to be 35.2%. ($\frac{655-303}{1000}=35.2\%$) Since the power actually preserved in the chemical bond is limited by the thermodynamic potential of the water splitting reaction (1.23 V), the resulting hydrogen generation power is 193 W m^{-2}. The electrocatalysis loss is then calculated to be 11.0%. ($\frac{303-193}{1000}=11.0\%$) The annual average case for all the loss analysis is then based on the actual annual GHI irradiance data in Daggett (CA) with average power of 244 W m^{-2}. While the percentage of bandgap photon loss (27.1%) and reflection loss (7.4%) are constant regardless the illumination condition, the remaining power after each steps are 178 W m^{-2} and 160 W m^{-2}. The J-U characteristic is then simulated according to the irradiance to obtain the power at operation point. The average power is 72 W m^{-2}. The thermalization and recombination loss under average irradiance is calculated to be 36.1%. ($\frac{160-72}{244} = 36.1\%$) Finally, the average hydrogen generation power of 47 W m^{-2} is realized, corresponding to electrocatalysis loss of 10.2%. ($\frac{72-47}{244} = 10.2\%$)



Power (W/m^2)	Loss (%)	
1000	0	
729	27.1	bandgap photon loss
655	7.4	reflection loss
303	35.2	thermalization and recombination lass at operation point
193	11	electrocatalysis loss

Figure S2 Information for the calculation of power loss.

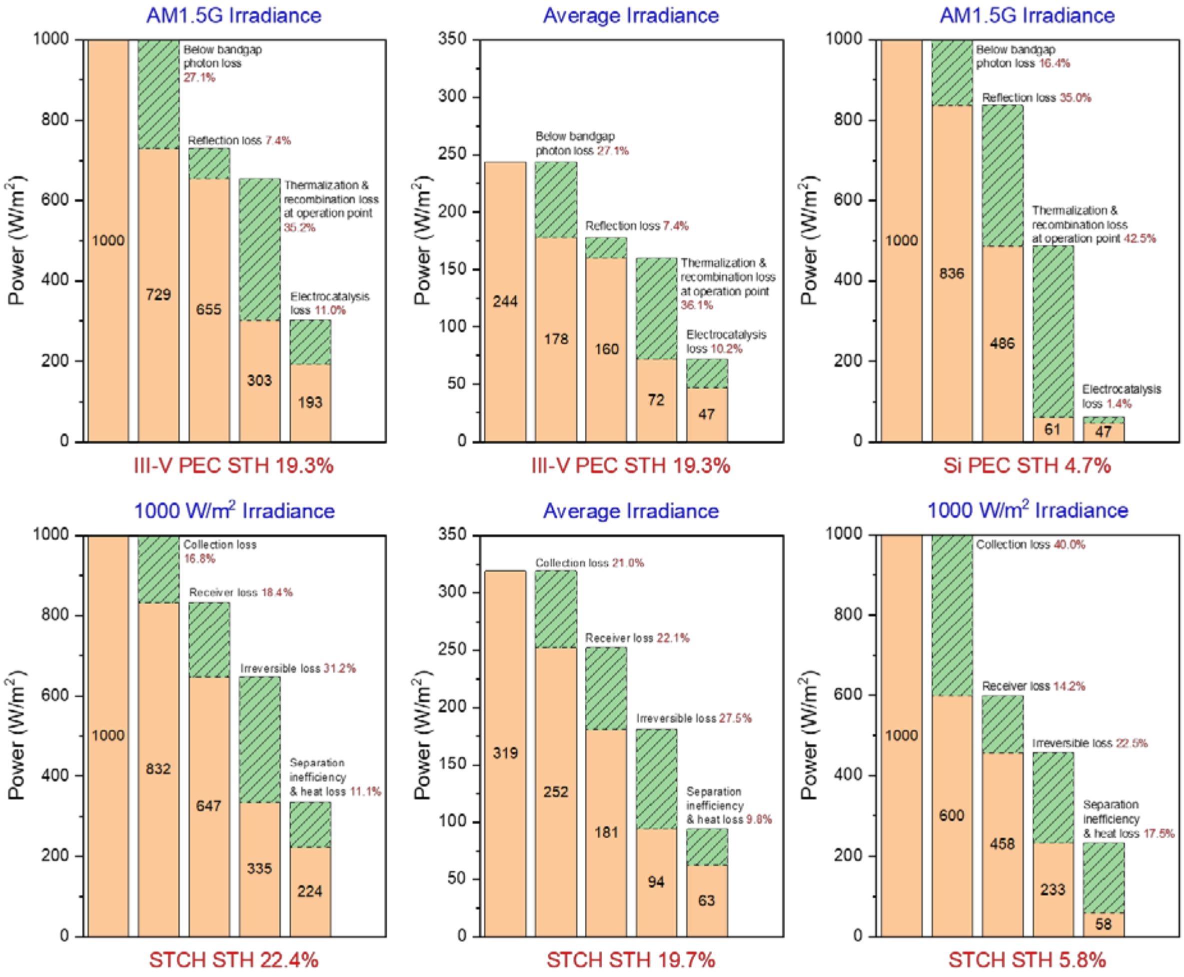


Figure S3 Summary of the PEC and STCH devices presented as 2D chart plot under variance irradiance condition.

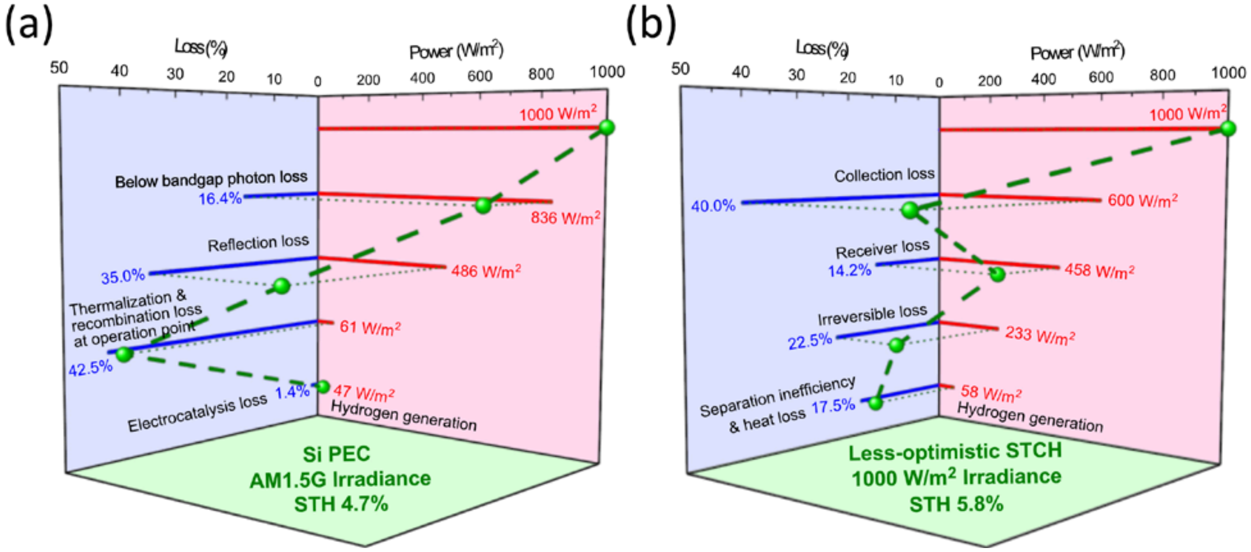


Figure S4 (a) An example of Si PEC with 4.7% STH conversion efficiency and the corresponding power loss analysis under AM1.5G irradiance.[5,30] (b) An example of less optimistic scenario STCH with 5.8% STH conversion efficiency and the corresponding power loss analysis under 1000 W/m^2 irradiance.

Table S1 The potential range of the operating parameters and scenarios selected of the STCH model.

Parameter	Range	Less -optimistic scenario	Best-case scenario
Reduction temperature	1350-1800 °C	1500 °C	1700 °C
Re-oxidation temperature	600-1250 °C	950 °C	950 °C
Inlet pO_2	10-100 Pa	10 Pa	10 Pa
Sweep ratio (λ)	1-10	5	5
Water conversion	≥10%	10%	10%
Gas-gas effectiveness	80-95%	95%	95%
Solid-solid effectiveness	70-85%	70%	85%
Separation efficiency	10-25%	25%	10%
Collection efficiency	≥40%	60%	83.2%
Concentration ratio	≥2500	3000	5000

STCH model equations:

Molar balances

Total extent of non-stoichiometry $\Delta\delta = \delta_R - \delta_{OX}$ S. 1

H_2 molar flow rate: $\dot{n}_{\mathrm{H_2}} = \dot{n}_{\mathrm{MO_x}}\Delta\delta$ S. 2

H_2O molar flow rate: $\dot{n}_{\mathrm{H_2O}} = (1+\xi)\dot{n}_{\mathrm{H_2}}$ S. 3

H_2/H_2O conversion: $\theta_{out} = \frac{\dot{n}_{\mathrm{H_2}}}{\dot{n}_{\mathrm{H_2O}}} = \frac{1}{1+\xi}$ S. 4

Reduction reactor energy balances

Receiver input heat flow $\dot{Q}_{R,in} = \dot{Q}_{ch,R} + \dot{Q}_{th,\mathrm{MO_x}} + \dot{Q}_{th,\mathrm{N_2}}$ S. 5

Reduction endotherm $\dot{Q}_{ch,R} = \dot{n}_{\mathrm{MO_x}}\Delta H_{ch,R}$ S. 6

MO_x heating: $\dot{Q}_{th,\mathrm{MO_x}} = \dot{n}_{\mathrm{MO_x}} C_{p,\mathrm{MO_x}}(T_R - T_{OX})\left(1-\varepsilon_{\mathrm{MO_x}}\right)$ S. 7

N_2 heating: $\dot{Q}_{th,\mathrm{N_2}} = \dot{n}_{\mathrm{N_2}} C_{p,\mathrm{N_2}}\left(T_R - T_{sep,\mathrm{N_2}}\right)\left(1-\varepsilon_{\mathrm{N_2}}\right)$ S. 8

Re-oxidation reactor energy balances

Total secondary proc.: $\dot{Q}_{proc} = \dot{Q}_{th,\mathrm{H_2O},recycle} + \dot{Q}_{th,\mathrm{H_2O},new} + \dot{Q}_{sep,\mathrm{H_2}} + \dot{Q}_{sep,\mathrm{N_2}}$ S. 9

Recycled H_2O heating: $\dot{Q}_{th,\mathrm{H_2O},recycle} = \dot{n}_{\mathrm{H_2O}}\xi\left(h_{\mathrm{H_2O},OX} - h_{\mathrm{H_2O,sep}}\right)\left(1-\varepsilon_{\mathrm{H_2O}}\right)$ S. 10

Replacement H_2O heating: $\dot{Q}_{th,\mathrm{H_2O},new} = \dot{n}_{\mathrm{H_2O}}(1-\xi)\left(h_{\mathrm{H_2O},OX} - h_{\mathrm{H_2O},0}\right)$ S. 11

H_2O/H_2 separation: S. 12

$$\dot{Q}_{sep,\mathrm{H_2}} = -\frac{\dot{n}_{\mathrm{H_2}} R T_{sep,\mathrm{H_2}}}{\eta_{sep,\mathrm{H_2}}}\left[\left(\theta_{out}\ln\theta_{out} + (1-\theta_{out})\ln(1-\theta_{out})\right)\right.$$
$$\left. - \left(\theta_{in}\ln\theta_{in} + (1-\theta_{in})\ln(1-\theta_{in})\right)\right]$$

N_2/O_2 separation: S. 13

$$\dot{Q}_{sep,\mathrm{N_2}} = -\frac{\dot{n}_{\mathrm{N_2}} R T_{sep,\mathrm{N_2}}}{\eta_{sep,\mathrm{N_2}}}\left[\left(x_{\mathrm{O_2},out}\ln x_{O_2,out}\right.\right.$$
$$\left. + \left(1 - x_{\mathrm{O_2},out}\right)\ln\left(1 - x_{\mathrm{O_2},out}\right)\right)$$
$$\left. - \left(x_{\mathrm{O_2},in}\ln x_{\mathrm{O_2},in} + \left(1 - x_{\mathrm{O_2},in}\right)\ln\left(1 - x_{\mathrm{O_2},in}\right)\right)\right]$$

Auxiliar input: $\dot{Q}_{aux} = \max\left(0, \dot{Q}_{proc} - \left(\dot{Q}_{ch,R} + \dot{Q}_{th,\mathrm{MO_x}}\right)\right)$ S. 14

Efficiencies

Collection efficiency $\eta_{coll} = \eta_{ref}\eta_{soil}\eta_{surf}\eta_{inter}$ S. 15

Receiver efficiency

$$\eta_{rec} = \tau_{win} - \frac{1}{CG_{DNI}}\sigma\epsilon_{rec}\left({T_R}^4 - {T_0}^4\right) \quad \text{S. 16}$$

Thermochemical efficiency

$$\eta_{th} = \frac{W_{\mathrm{H_2}}}{\dot{Q}_{R,in} + \dot{Q}_{aux}} \quad \text{S. 17}$$

Nomenclature

Symbol	Variable	Units	Symbol	Variable	Units
C	Concentration ratio	-	$T_{sep,\mathrm{H_2}}$	H_2O/H_2 separation temperature	K
$C_{p,\mathrm{MO_x}}$	MO_x specific heat capacity	J·K^{-1}·mol^{-1}	$T_{sep,\mathrm{N_2}}$	N_2/O_2 separation temperature	K
$C_{p,\mathrm{N_2}}$	N_2 specific heat capacity	J·K^{-1}·mol^{-1}	$\Delta\delta$	Total extent of non-stoichiometry	-
G_{DNI}	Direct normal irradiance	J·K^{-1}·mol^{-1}	δ_R	Reduction extent	-
$h_{\mathrm{H_2O},0}$	H_2O specific enthalpy at T_0 and p_{sys}	J·mol^{-1}	δ_{OX}	Re-oxidation extent	-
$h_{\mathrm{H_2O},OX}$	H_2O specific enthalpy at T_{OX} and p_{sys}	J·mol^{-1}	$\varepsilon_{\mathrm{MO_x}}$	Solid-solid heat recovery effectiveness	-
$h_{\mathrm{H_2O},sep}$	H_2O specific enthalpy at $T_{sep,\mathrm{H_2}}$ and p_{sys}	J·mol^{-1}	$\varepsilon_{\mathrm{N_2}}$	Gas-gas heat recovery effectiveness (N_2)	-
$\dot{n}_{\mathrm{H_2}}$	H_2 molar flow	mol·s^{-1}	$\varepsilon_{\mathrm{H_2O}}$	Gas-gas heat recovery effectiveness (H_2O)	-
$\dot{n}_{\mathrm{H_2O}}$	H_2O molar flow	mol·s^{-1}	ϵ_{rec}	Receiver emissivity	-
$\dot{n}_{\mathrm{MO_x}}$	MO_x molar flow	mol·s^{-1}	ξ	H_2O excess per mol of H_2	-
$\dot{Q}_{aux}$	Auxiliar heat flow	W	η_{coll}	Collection efficiency	-
$\dot{Q}_{ch,R}$	Reduction endotherm	W	η_{inter}	Interception	-
$\dot{Q}_{proc}$	Total auxiliary processes heat flow	w	η_{rec}	Receiver efficiency	-
$\dot{Q}_{R,in}$	Inlet receiver heat flow	W	η_{ref}	Reflectivity	-
$\dot{Q}_{th,\mathrm{H_2O},new}$	Replacement H_2O heat flow	W	$\eta_{sep,\mathrm{H_2}}$	H_2O/H_2 separation efficiency	-
$\dot{Q}_{th,\mathrm{H_2O},\mathrm{recycle}}$	Recycled H_2O heat flow	W	$\eta_{sep,\mathrm{N_2}}$	N_2/O_2 separation efficiency	-
$\dot{Q}_{th,\mathrm{MO_x}}$	MO_x heat flow:	W	η_{soil}	Soiling	-
$\dot{Q}_{th,\mathrm{N_2}}$	N_2 heat flow:	W	η_{surf}	Surface reflective ratio	-
$\dot{Q}_{sep,\mathrm{H_2}}$	Heat equivalent H_2O/H_2 separation work	W	η_{th}	Thermochemical efficiency	-
$\dot{Q}_{sep,\mathrm{N_2}}$	Heat equivalent N_2/O_2 separation work	W	θ_{in}	H_2 molar ratio due to water dissociation at T_{OX}	-
T_0	Ambient temperature	K	θ_{out}	H_2 /H_2O outlet conversion	-
T_R	Reduction reactor temperature	K	σ	Stefan-Boltzmann constant	kg s^{-3} K^{-4}
T_{OX}	Re-oxidation reactor temperature	K	τ_{win}	Window transmissivity	-