Electronic Supplementary Information of

Energy Loss Analysis in Photoelectrochemical Water Splitting: A Case Study of Hematite Photoanode

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Net photocurrent

The net photocurrent used in Figure 1 is calculated by Eq. S1

$$j = j_{light} - j_{dark} \qquad \text{(Eq. S1)}$$

where j is the net photocurrent, j_{light} and j_{dark} is the current recorded under light or dark at the same scan rate.

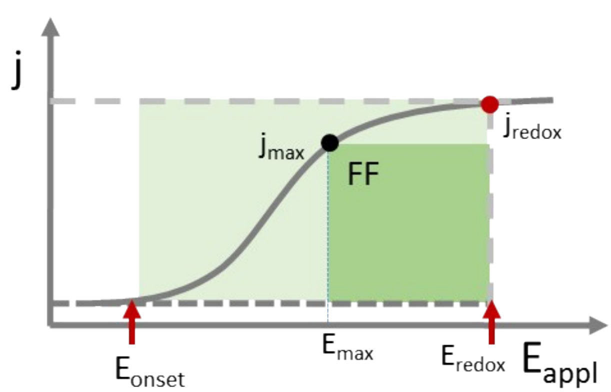
Fill factor

The item of fill factor (FF) is normally used in solar cell which is defined as the ratio of maximum output power over the theoretical power (j_{sc}*V_{OC} , determined by short circuit current (j_{sc}) and open circuit potential (V_{OC}))

In the PEC system , the FF in Scheme S1 is usually defined as:[1,2]

$$FF = \frac{j_{\max}(E_{redox} - E_{\max})}{j_{redox}({}_{redox} - E_{onset})} \qquad \text{(Eq. S2)}$$

Here (j_{max}, E_{max}) is the point where there is the highest solar conversion efficiency, E_{redox} represents the redox potential of the reactant, which is 1.23 V vs RHE for water splitting. And j_{redox} is the photocurrent at the potential of E_{redox}.



Scheme S1. The definition of fill factor (FF) for PEC research.

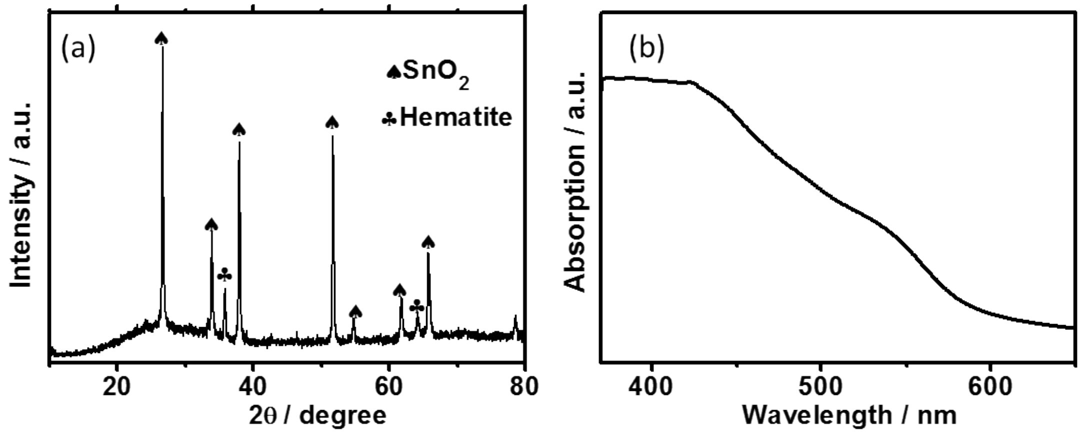


Figure S1 (a) The XRD pattern and (b) absorption spectrum of hematite photoelectrode.

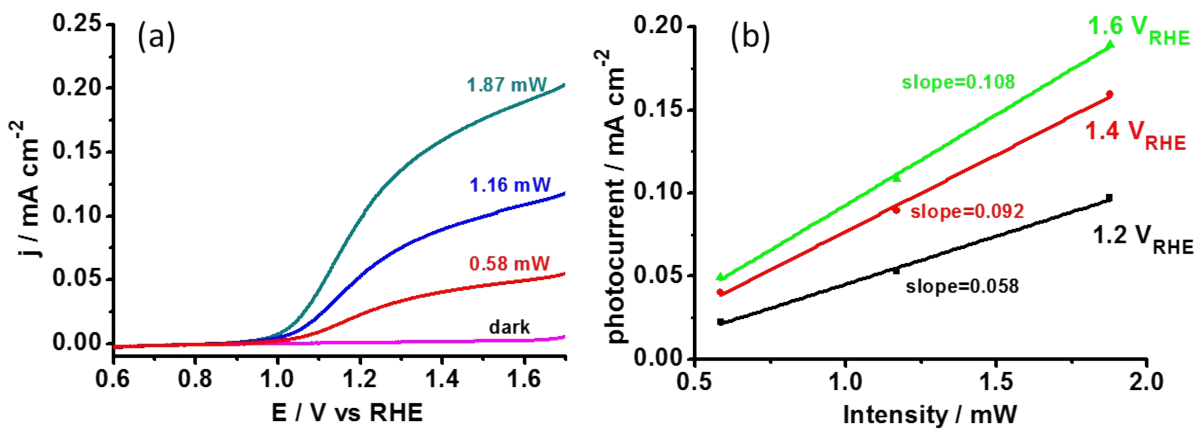


Figure S2. (a) The photocurrent-potential curves recorded under different intensity of monolight with a wavelength of 460 nm. (b) The photocurrent-light intensity curves under different bias.

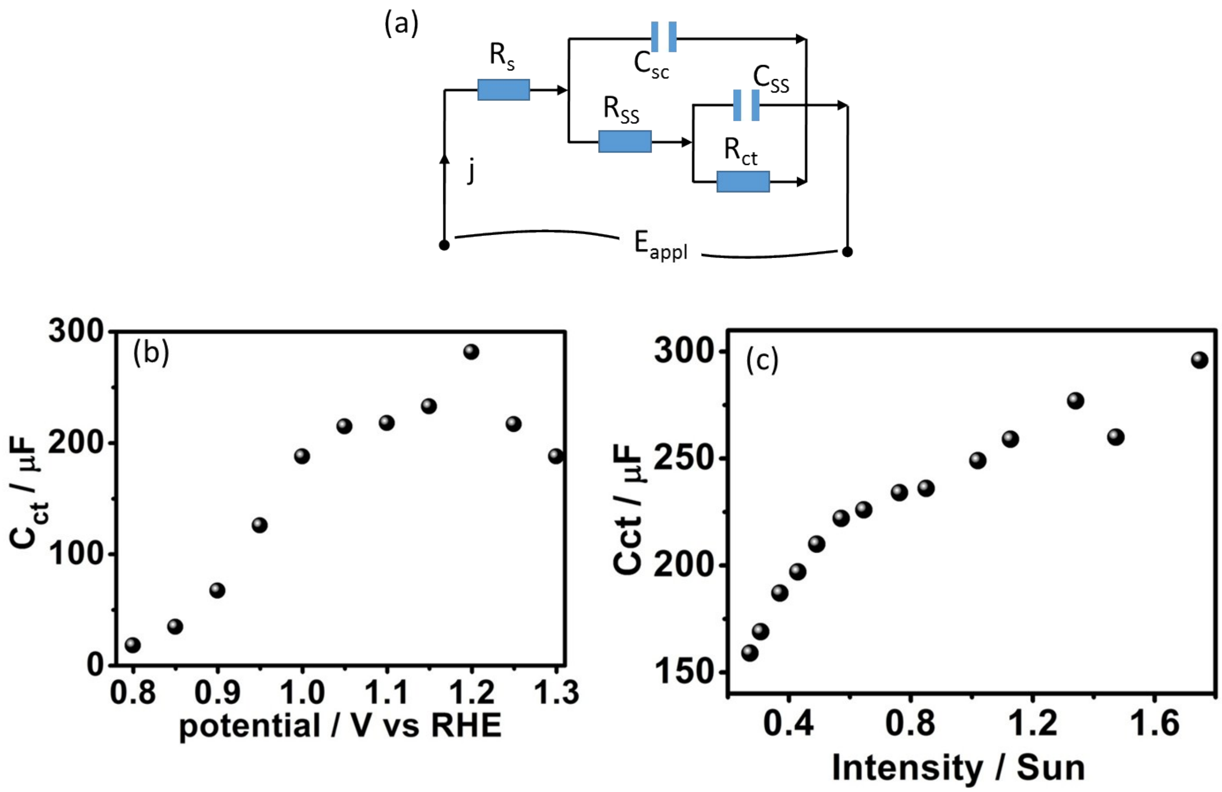


Figure S3. (a) The equivalent circuit of the photoelectrochemical process on hematite photoanode. $\mathbf{R_s}$ is the serial resistance generated by the electrode contact and electrolyte. $\mathbf{C_{sc}}$ is the space charge layer capacitance. $\mathbf{R_{ss}}$ is the resistance for charge capture by surface states. $\mathbf{R_{ct}}$ is the charge transfer resistance for water oxidation reaction. (b) The change of charge transfer resistance with the applied potential. The light intensity is 1 Sun. (c) The change of charge transfer resistance with the light intensity. The applied bias is 1.2 V_{RHE}.

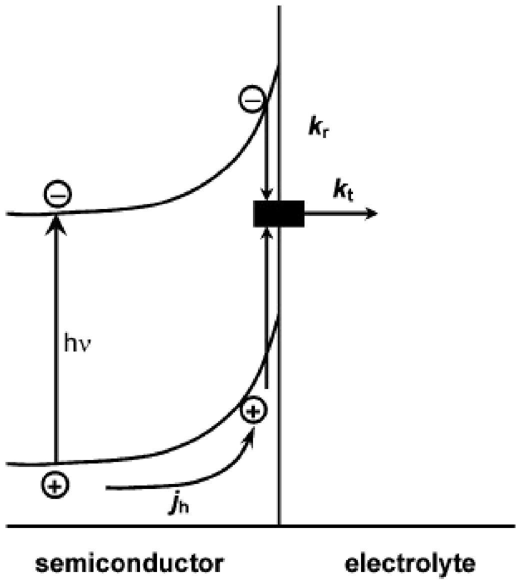


Figure S4. The schematic illustration of the charge transfer process on hematite. k_r and k_t is the rate constant of charge recombination and transfer process induced by the surface states. Adapted from Ref. 3.

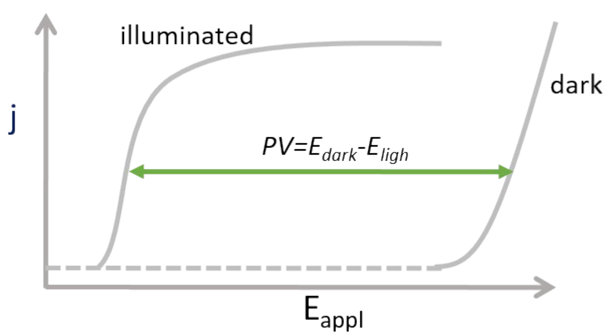


Figure S5. The schematic illustration of photovoltage (PV) generated during a PEC process. It is the voltage difference at the same current between dark and illuminated condition.

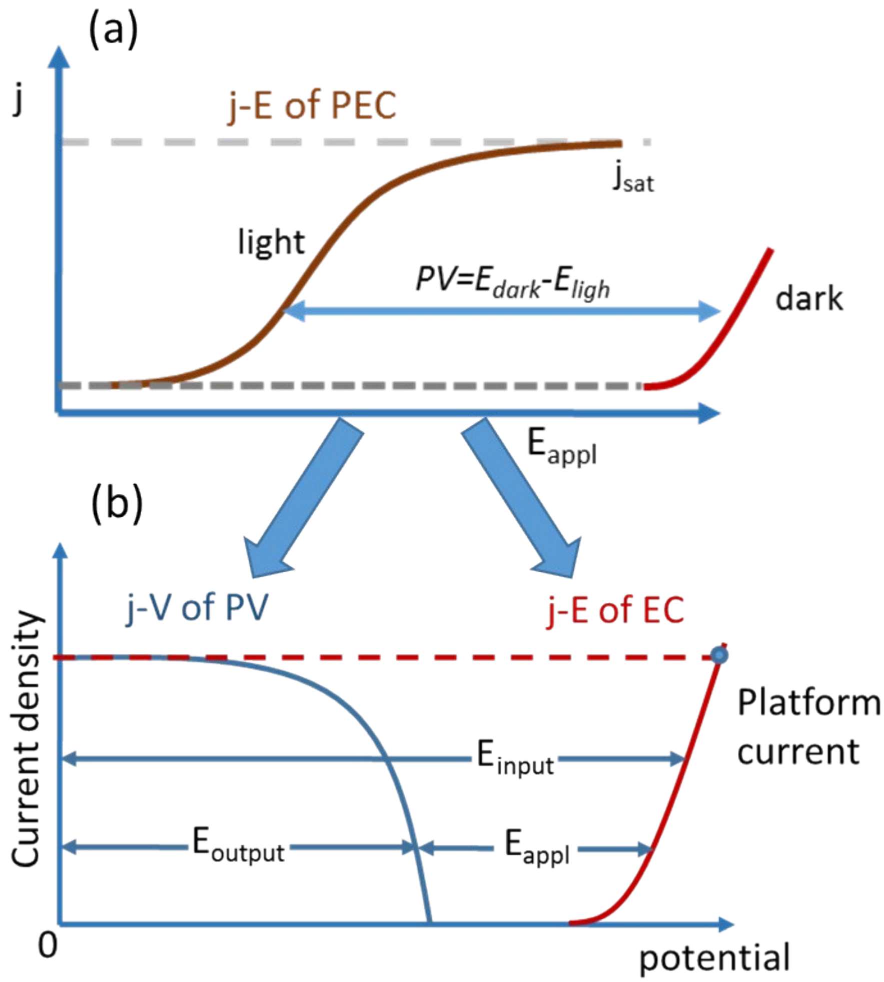


Figure S6. An illustration of how the j-E of PEC (a) can be decoupled into j-V of PV and j-E of EC process (b). The PV in (a) is indeed equal to that in E_{output} of j-V. And the E_{appl} in (b) is the applied bias of j-E in (a).

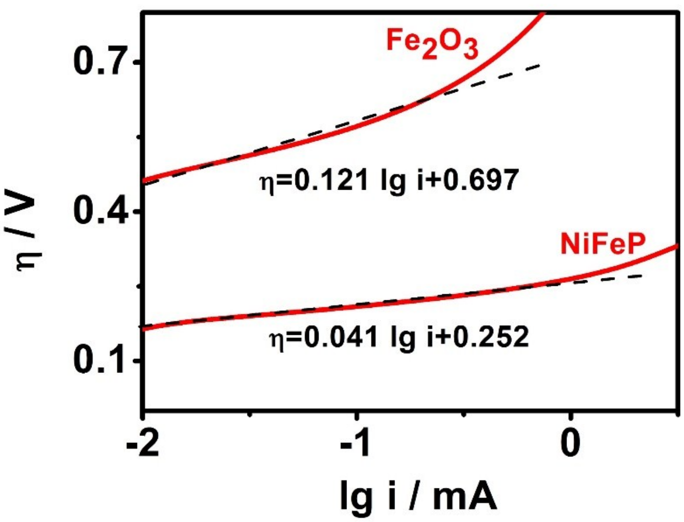


Figure S7. The Tafel plot of Fe_2O_3 and NiFeP electrode. The much smaller Tafel slope and overpotenial of NiFeP suggests profoundly better reaction kinetic than Fe2O3.

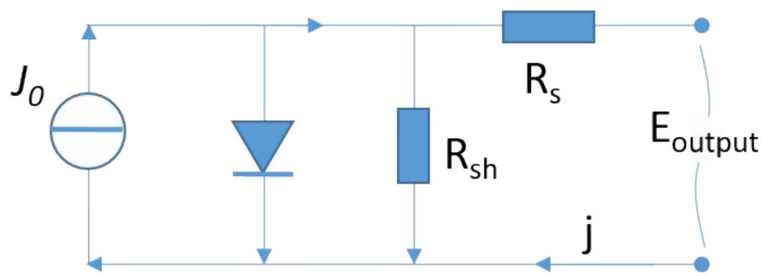


Figure S8. The equivalent circuit of solar cell. J_0 is the ideal current source. R_{sh} and R_s are the shunt resistance and serial resistance, respectively.

Table S1. The parameters for numeric simulation in Figure 4a.

	Short circuit current J_{SC}/ mA	Open circuit voltage V_{OC} / V	Fill factor FF
Curve I	3.5	1.0	0.85
Curve II	3.0	0.8	0.37
	Overpotential η(1 mA) / mV	Tafel slope / mV dec^{-1}	Exchange current (j_0) / mA
Curve i	400	59	10^{-3}
Curve ii	534	166	$3*10^{-4}$

Table S2. The measured j_{sc}, V_{oc}, FF and PCE of the two perovskite solar cells.

	j_{sc} / mA	V_{oc} / V	FF	PCE / %
psc-1	3.6	1	0.675	14.6
psc-2	2.5	1.04	0.654	10.3

The area of the solar cell is 0.165 cm^2. And the light intensity is 100 mW cm^{-2} (AM 1.5 G).

Reference:

(1) Coridan, R. H.; Nielander, A. C.; Francis, S. A.; McDowell, M. T.; Dix, V.; Chatman, S. M.; Lewis, N. S. Methods for comparing the performance of energy-conversion systems for use in solar fuels and solar electricity generation. *Energy Environ. Sci.* **2015**, *8*, 2886-2901.

(2) Kim, T. W.; Choi, K.-S. Nanoporous $BiVO_4$ photoanodes with dual-layer oxygen evolution catalysts for solar water splitting. *Science* **2014**, 1245026.

(3) Wijayantha, K. U.; Saremi-Yarahmadi, S.; Peter, L. M. Kinetics of oxygen evolution at α-Fe_2O_3 photoanodes: a study by photoelectrochemical impedance spectroscopy. *Phys. Chem. Chem.Phys.* **2011**, *13*, 5264-5270.