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

\[ j = j_{\text{light}} - j_{\text{dark}} \]  

(Eq. S1)

where \( j \) is the net photocurrent, \( j_{\text{light}} \) and \( j_{\text{dark}} \) 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 \( (j_{\text{sc}} \times V_{\text{OC}}) \), determined by short circuit current \( (j_{\text{sc}}) \) and open circuit potential \( (V_{\text{OC}}) \).

In the PEC system, the FF in Scheme S1 is usually defined as:\textsuperscript{1,2}

\[ FF = \frac{j_{\text{max}} (E_{\text{redox}} - E_{\text{max}})}{j_{\text{redox}} (E_{\text{redox}} - E_{\text{onset}})} \]  

(Eq. S2)

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

![Scheme S1. The definition of fill factor (FF) for PEC research.](image-url)
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. $R_s$ is the serial resistance generated by the electrode contact and electrolyte. $C_{sc}$ is the space charge layer capacitance. $R_{ss}$ is the resistance for charge capture by surface states. $R_{ct}$ 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$_2$O$_3$ and NiFeP electrode. The much smaller Tafel slope and overpotential of NiFeP suggests profoundly better reaction kinetic than Fe$_2$O$_3$.

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.

<table>
<thead>
<tr>
<th></th>
<th>Short circuit current $J_{SC}$ / mA</th>
<th>Open circuit voltage $V_{OC}$ / V</th>
<th>Fill factor FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curve I</td>
<td>3.5</td>
<td>1.0</td>
<td>0.85</td>
</tr>
<tr>
<td>Curve II</td>
<td>3.0</td>
<td>0.8</td>
<td>0.37</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>Overpotential $\eta(1 \text{ mA})$ / mV</th>
<th>Tafel slope / mV dec$^{-1}$</th>
<th>Exchange current $(j_0)$ / mA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curve i</td>
<td>400</td>
<td>59</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>Curve ii</td>
<td>534</td>
<td>166</td>
<td>$3 \times 10^{-4}$</td>
</tr>
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</table>

Table S2. The measured $j_{SC}$, $V_{OC}$, FF and PCE of the two perovskite solar cells.

<table>
<thead>
<tr>
<th></th>
<th>$j_{SC}$ / mA</th>
<th>$V_{OC}$ / V</th>
<th>FF</th>
<th>PCE / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>psc-1</td>
<td>3.6</td>
<td>1</td>
<td>0.675</td>
<td>14.6</td>
</tr>
<tr>
<td>psc-2</td>
<td>2.5</td>
<td>1.04</td>
<td>0.654</td>
<td>10.3</td>
</tr>
</tbody>
</table>

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:

