Supporting Information

An In-situ Photoelectroreduced Approach to Fabricate Bi/BiOCl Heterostructure Photocathode: Understanding the Role of Bi Metal for Solar Water Splitting

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**Fig. S1.** SEM images of TiO$_2$ nanorods (a), and BiOCl with different cycle times prepared by the CBD method on FTO substrate for BiOCl/25 (b), BiOCl/50 (c), BiOCl/75 (d) and BiOCl/100 (e). The EDS profile recorded from Bi/BiOCl/75 nanosheets (f).
Fig. S2. SEM images of Bi/BiOCl/25(a), Bi/BiOCl/50(b), Bi/BiOCl/75(c) and Bi/BiOCl/100 (d).
**Fig. S3.** SEM images of Bi/BiOCl/75/0.5h (a), Bi/BiOCl/75/1h (b), Bi/BiOCl/75/2h (c) and Bi/BiOCl/75/8h.
Fig. S4. The cross-sectional SEM images of BiOCl/75 nanosheets (a) and Bi/BiOCl/75 photocathode (b).
Fig. S5. UV-vis diffuse reflectance spectra (DRS) (a) and Kubelka-Munk function plot (b) of synthesized BiOCl/75 and Bi/BiOCl/75. The color change of the samples on the surface can be clearly seen in the inset.
Fig. S6. The EPR spectra (a) and XPS spectra (b)
Fig. S7. Topography (a) and SCM-Data (b) of SRAM sample. The SRAM sample was obtained from Bruker Company (CA, USA).
Fig. S8. Mott-Schottky plots of bare BiOCl.
Fig. S9. Transient photocurrent responded with intermittent light
Fig. S10. Cross experiment analysis of Bi/BiOCl photocathode based on the conditions of CBD circle times and photoelectroreduced time.
Equivalent circuit

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sc}$ (Ω)</th>
<th>$R_{ce}$ (Ω)</th>
</tr>
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<tbody>
<tr>
<td>TiO$_2$-Pt</td>
<td>193.7</td>
<td>$2.762 \times 10^3$</td>
<td>$1.318 \times 10^3$</td>
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<tr>
<td>TiO$_2$-BiOCl/75</td>
<td>205.7</td>
<td>$1.873 \times 10^3$</td>
<td>$1.219 \times 10^3$</td>
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<tr>
<td>TiO$_2$-Bi/BiOCl/75/2h</td>
<td>165.5</td>
<td>$7.17 \times 10^3$</td>
<td>$0.561 \times 10^3$</td>
</tr>
</tbody>
</table>

*Table S1. Equivalent circuit-fitting results*
Fig. S11. Overlaid current density-potential behaviors for TiO$_2$ and Bi/BiOCl.
Fig. S12 Chematic diagram of equipment for PEC hydrogen production.
The stability of Bi/BiOCl/75/2h was measured in the TiO$_2$–Bi/BiOCl/75/2h water splitting photocell (0 V vs Ag/AgCl).