Supplementary Materials

Photogenerated-Carrier Separation along Edge Dislocation of WO$_3$ Single Crystal Nanoflower Photoanode

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Fig. S1. Vertical growth WO$_3$ nanosheet on polished Ti substrate. (A) low resolution; (B) high resolution.

Fig. S2. The UV/Vis diffuse reflectance spectra of WO$_3$-E8-2h.
Fig. S3. The XPS spectra of the WO$_3$-E8-2h. (A) the total XPS survey spectrum; (B) the W4f core level XPS spectrum; (C) the O2p core level XPS spectrum; (D) the Ti2p core level XPS spectrum.
Fig. S4. (A) Top SEM image of WO$_3$-E8-2h, insert is the high-resolution SEM of it; (B) Cross-section SEM image of WO$_3$-E8-2h; (C) Selected area of the SEM image on the top of WO$_3$-E8-2h; (D) distribution of the O and W elements in the selected area. (E) Top SEM image of WO$_3$-E8-12h, insert is the high-resolution SEM of it.

Fig. S5. XRD results of WO$_3$-E8 with different annealing time (2, 4, 8, 12 hours) at 500 $^\circ$C.
Fig. S6. (A) PEC Water splitting for O$_2$ and H$_2$ evolution properties of WO$_3$-E8-2h and WO$_3$-E8-12h (bias potential 1.5 V vs Ag/AgCl); (B) Spectral energy distribution curve of the Xe light used in this study.

The Faradic efficiency can be described as follows:

$$\text{Faradic efficiency} = \frac{m \cdot n \cdot F}{i \cdot t} \times 100\% \quad (1)$$

In which Equ., the $m$ is the mole value for O$_2$ at a time. $n$ is the electrons exchange number for one O$_2$ molecular production. $F$ is the faraday constant. $i$ is the photocurrent density. $t$ is the reaction time.

Because of the photocurrent density of WO$_3$-E8-2h photoanode just can keep at near 2.1 mA cm$^{-2}$ in the initial one hour, so we calculated the Faradic efficiency in this term. Combination the information in Fig. 5C and Fig. S6A, the Faradic efficiency =

$$\frac{18.4 \times 10^{-6} \times 4 \times 96487}{2.1 \times 10^{-3} \times 3600} \times 100\% \approx 93.93\%$$

So, in the initial one hour, the WO$_3$-E8-2h photoanode shows higher than 90% Faradic efficiency. The losing Faradic efficiency may contributed to the photoanode corrosion.

**Tab. S1.** Comparison of the photoelectrochemical performance of the typical WO$_3$ photoelectrodes reported in literature and in the present study.

<table>
<thead>
<tr>
<th>WO$_3$ with different structure</th>
<th>Light intensity (mW cm$^{-2}$)</th>
<th>Bias potential (V)</th>
<th>Electrolyte</th>
<th>Photoinduced current density (mA cm$^{-2}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_3$ Flakes</td>
<td>100 (AM 1.5)</td>
<td>1.0 (vs Ag/AgCl)</td>
<td>Na$_2$SO$_4$ (0.1 M)</td>
<td>1.4</td>
<td>[1]</td>
</tr>
<tr>
<td>Molecular iron modified WO$_3$</td>
<td>100 (AM 1.5)</td>
<td>1.0 (vs Ag/AgCl)</td>
<td>Na$_2$SO$_4$ (0.1 M)</td>
<td>1.1</td>
<td>[2]</td>
</tr>
<tr>
<td>WO$_3$ planar film</td>
<td>100 (AM 1.5)</td>
<td>1.0 (vs Ag/AgCl)</td>
<td>Na$_2$SO$_4$ (0.5 M)</td>
<td>1.0</td>
<td>[3]</td>
</tr>
</tbody>
</table>
Tab. S1 shows the photoelectrochemical performance of WO₃ with different morphologies prepared in recent years and compared them with this work. According to the reports from the literatures, the best photoelectrochemical performance was obtained by WO₃ with flake wall like structure in Na₂SO₄ solution under the illumination of AM 1.5 (100 mW·cm⁻²) and at the bias potential of 1 V (vs Ag/AgCl), and the photoinduced current density of WO₃ with this structure could reach 1.4 mA·cm⁻². In the present work, for the nanoflower-structured WO₃ thin-film photoelectrode with 8 h of hydrothermal reaction, a photoinduced current density of 1.8 mA·cm⁻² was obtained under the same test condition as in the compared references, which is significantly enhanced compared with that in the previous reports.

<table>
<thead>
<tr>
<th>WO₃ morphology</th>
<th>Preparation</th>
<th>Bias Potential</th>
<th>Electrolyte</th>
<th>Current Density</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar film</td>
<td>100 (AM 1.5)</td>
<td>1.0 V (vs Ag/AgCl)</td>
<td>Na₂SO₄ (0.5 M)</td>
<td>0.5</td>
<td>[4]</td>
</tr>
<tr>
<td>Nanorod array</td>
<td>100 (AM 1.5)</td>
<td>1.0 V (vs Ag/AgCl)</td>
<td>Na₂SO₄ (0.5 M)</td>
<td>0.25</td>
<td>[5]</td>
</tr>
<tr>
<td>Nanoflower</td>
<td>100 (AM 1.5)</td>
<td>1.0 V (vs Ag/AgCl)</td>
<td>Na₂SO₄ (0.1 M)</td>
<td>1.8</td>
<td>Present study</td>
</tr>
</tbody>
</table>

Fig. S7. Time-resolved photoluminescence (TR-PL) spectrum of WO₃ photoanodes with different annealing times (2 h to 12 h) at the emission wavelength of 440 nm.
Fig. S8. TEM images of WO$_3$-E8-2h thin film. (A) low and (B-D) high resolution; Selected area electron diffraction (SAED) pattern for this sample is inserted in (B); and the corresponding IFFT images insert in (C) and (D).

Reference