Supporting Information

Rutile TiO$_2$ Single Crystals Delivering Enhanced Photocatalytic Oxygen Evolution Performance

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**Fig. S1.** SEM images of irregular rutile TiO$_2$ crystals obtained with 5 mL 0.60 M NaF solution. Reaction conditions: 1.0 M glycolic acid (GA) aqueous solution, 180 °C, 12 h.

**Fig. S2.** SEM images of rutile TiO$_2$ crystals synthesized at 180 °C for 12 h. Reaction conditions: 1.0 M glycolic acid (GA) aqueous solution.
Fig. S3. XRD patterns of as-prepared TiO$_2$ particles synthesized with different halogen addition (red, 1 mL 0.06 M NaCl; black, 1 mL 0.06 M NaF (R1)). Reaction conditions: 1.0 M glycolic acid (GA) aqueous solution, 180 °C, 12 h.
**Fig. S4.** SEM images of rutile TiO$_2$ crystals synthesized at 180 °C for different hydrothermal treatment time (a-b, 4h; c-d, 8h; e-f, 36h). Reaction conditions: 1.0 M glycolic acid (GA) aqueous solution, 1 mL 0.06 M NaF aqueous solution (R1).
Fig. S5. XRD patterns of as-prepared TiO$_2$ particles synthesized at different hydrothermal temperature (red, 140 °C; black, 180 °C). Reaction conditions: 1.0 M glycolic acid (GA) aqueous solution, 3 mL 0.06 M NaF aqueous solution (R3), 12 h.

Fig. S6. SEM images of as-prepared TiO$_2$ particles synthesized at 140 °C. Reaction conditions: 1.0 M glycolic acid (GA) aqueous solution, 3 mL 0.06 NaF aqueous solution (R3), 12 h.
Fig. S7. Digital photographs of as-prepared rutile TiO$_2$ single crystals (R3) before and after thermal treatment.

Fig. S8. XRD patterns of R1 sample before (blue) and after (green) 600 °C thermal treatment.
Fig. S9. SEM images of different rutile TiO$_2$ single crystals after 600 °C thermal treatment.

Fig. S10. UV-visible absorption spectra of R1 sample before (black) and after (magenta) 600 °C thermal treatment.
Fig. S11. SEM images of rutile TiO$_2$ single crystals (R3) after the photocatalytic O$_2$ production tests.
<table>
<thead>
<tr>
<th>Samples</th>
<th>$L_{\text{ave}}$</th>
<th>$W_{\text{ave}}$</th>
<th>$r_{\text{asp}}$</th>
<th>Percentage of (111) ##</th>
<th>Percentage of (110) ##</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>1275±152 nm</td>
<td>295±30 nm</td>
<td>4.32</td>
<td>16</td>
<td>84</td>
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<tr>
<td>R2</td>
<td>838±86 nm</td>
<td>379±44 nm</td>
<td>2.21</td>
<td>32</td>
<td>68</td>
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<tr>
<td>R3</td>
<td>564±62 nm</td>
<td>421±46 nm</td>
<td>1.34</td>
<td>57</td>
<td>43</td>
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<tr>
<td>R4</td>
<td>588±57 nm</td>
<td>521±51 nm</td>
<td>1.13</td>
<td>69</td>
<td>31</td>
</tr>
</tbody>
</table>

# Available average lengths ($L_{\text{ave}} \pm \sigma$, $\sigma$ is the standard deviations of $L_{\text{ave}}$) and average widths ($W_{\text{ave}} \pm \sigma$, $\sigma$ is the standard deviations of $W_{\text{ave}}$) are estimated by SEM observation on more than 100 particles, respectively. And the aspect ratio ($r_{\text{asp}}$) is defined as $r_{\text{asp}} = L_{\text{ave}}/W_{\text{ave}}$.

## Detailed determination of the percentage of different facets.

The crystals exhibit a regular prism-shaped morphology with four lateral (110) facets and two pyramidal ends of (111) facets. Based on the crystallographic symmetries and predicted equilibrium shape of rutile, the (110) facets of crystals are parallel to the [001] direction and at an angle of around 130° relative to triangle surface (111) facets. The estimated percentages of exposed (110) and (111) facets on the rutile TiO$_2$ single crystals are calculated via the surface area of each facet.$^{1,2}$
Assuming the average width of prism-shaped crystals is $d$, and assuming the aspect ratio of prism-shaped crystals is $r$, then the surface area and estimated percentage of each facet are given by:

\[
S_{(111)} = \left[0.5 d / \cos (40^\circ)\right] \cdot d \cdot 0.5 = 0.326 \cdot d^2 \\
S_{(110)} = \left[r \cdot d - 2 \cdot 0.5d \cdot \tan (40^\circ)\right] \cdot d = (r - 0.839) \cdot d^2 \\
S_{\text{total}} = \sum S_i = 8 S_{(111)} + 4 S_{(110)} = 2.61 \cdot d^2 + 4 \cdot (r - 0.839) \cdot d^2 \\
(111) \text{ facet } % = 2.61 / [2.61 + 4 \cdot (r - 0.839)] \\
(110) \text{ facet } % = 4 \cdot (r - 0.839) / [2.61 + 4 \cdot (r - 0.839)]
\]

If we assume the aspect ratio of prism-shaped crystals to be 1, then

(111) facet % = 80%
(110) facet % = 20%

If we assume the aspect ratio of prism-shaped crystals to be 100, then

(111) facet % = 1%
(110) facet % = 99%

**Table S2.** Specific surface area of as-synthesized TiO$_2$ single crystals determined by N$_2$ adsorption-desorption isotherm measurements.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before calcining</td>
</tr>
<tr>
<td>R1</td>
<td>3.4</td>
</tr>
<tr>
<td>R2</td>
<td>4.2</td>
</tr>
<tr>
<td>R3</td>
<td>3.5</td>
</tr>
<tr>
<td>R4</td>
<td>5.5</td>
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**References**