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Supporting Information

Rutile TiO_2 Single Crystals Delivering Enhanced Photocatalytic Oxygen Evolution Performance

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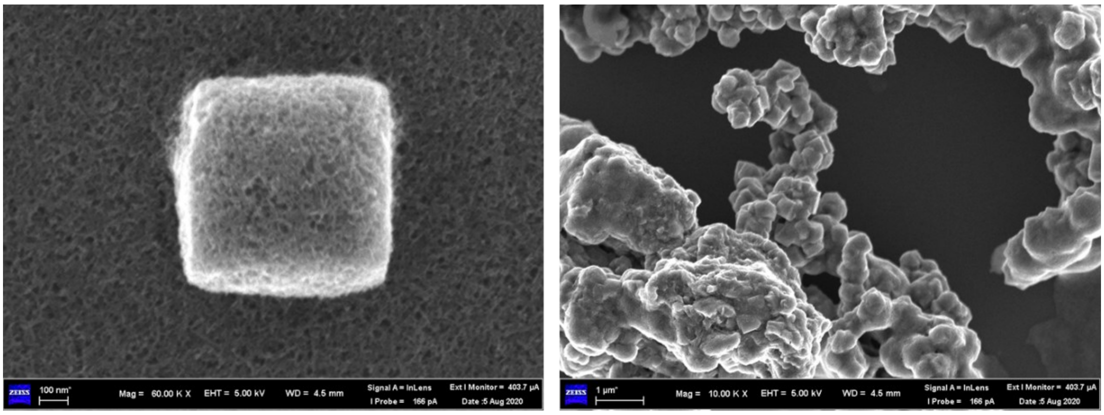


Fig. S1. SEM images of irregular rutile TiO_2 crystals obtained with 5 mL 0.60 M NaF solution. Reaction conditions: 1.0 M glycolic acid (GA) aqueous solution, 180 °C, 12 h.

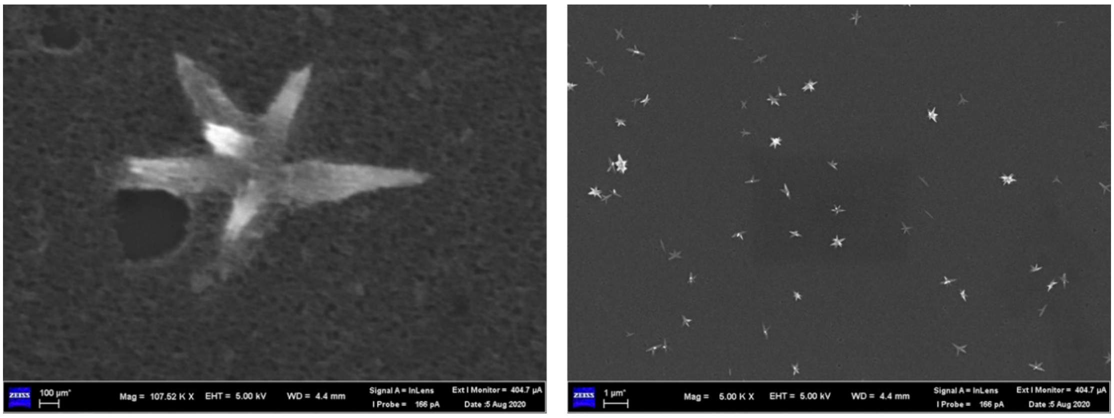


Fig. S2. SEM images of rutile TiO_2 crystals synthesized at 180 °C for 12 h. Reaction conditions: 1.0 M glycolic acid (GA) aqueous solution.

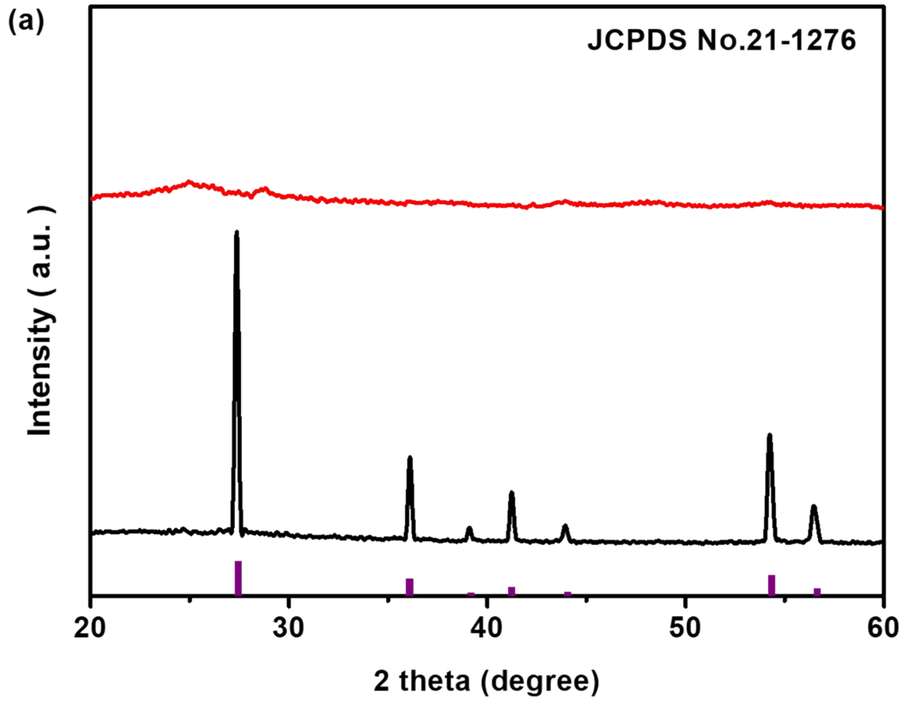


Fig. S3. XRD patterns of as-prepared TiO_2 particles synthesized with different halogen addition (red, 1 mL 0.06 M NaCl; black, 1 mL 0.06 M NaF (R1)). Reaction conditions: 1.0 M glycolic acid (GA) aqueous solution, 180 °C, 12 h.

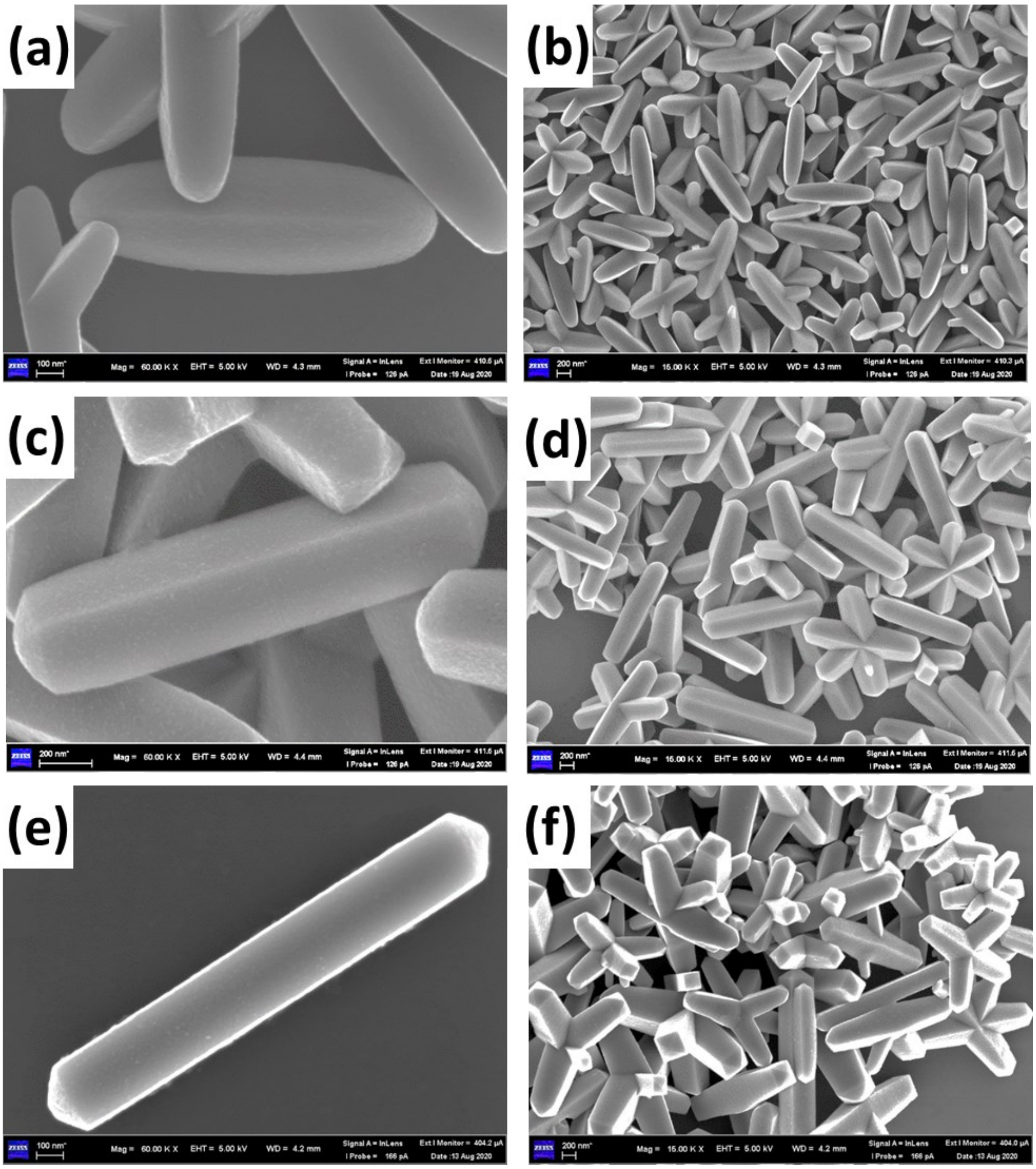


Fig. S4. SEM images of rutile TiO_2 crystals synthesized at 180 °C for different hydrothermal treatment time (a-b, 4h; c-d, 8h; e-f, 36h). Reaction conditions: 1.0 M glycolic acid (GA) aqueous solution, 1 mL 0.06 M NaF aqueous solution (R1).

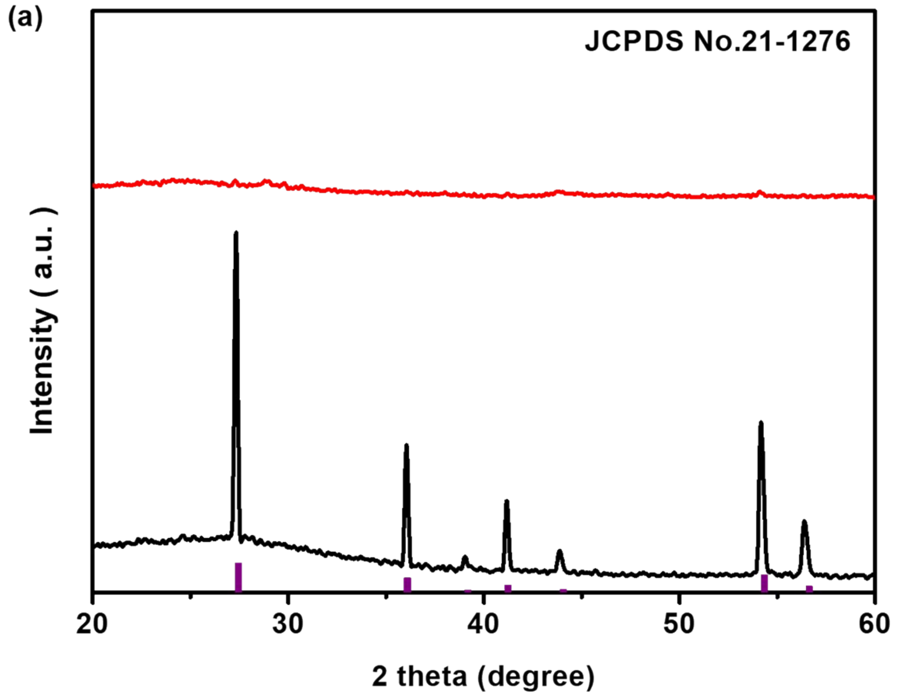


Fig. S5. XRD patterns of as-prepared TiO_2 particles synthesized at different hydrothermal temperature (red, 140 °C; black, 180 °C). Reaction conditions: 1.0 M glycolic acid (GA) aqueous solution, 3 mL 0.06 M NaF aqueous solution (R3), 12 h.

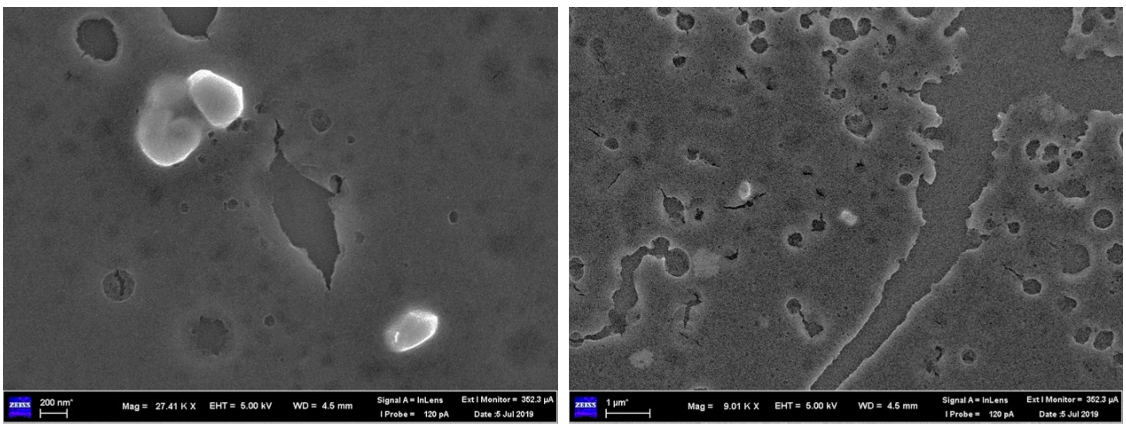


Fig. S6. SEM images of as-prepared TiO_2 particles synthesized at 140 °C. Reaction conditions: 1.0 M glycolic acid (GA) aqueous solution, 3 mL 0.06 NaF aqueous solution (R3), 12 h.

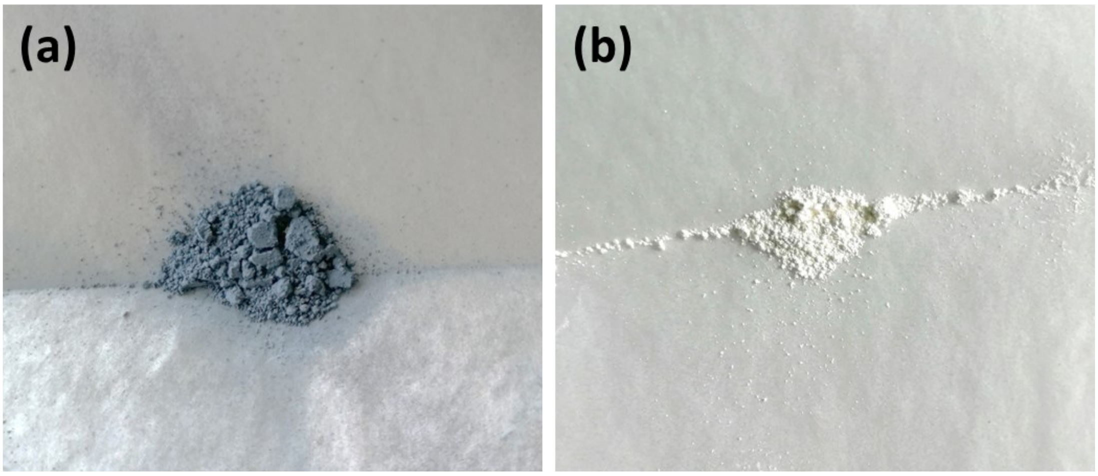


Fig. S7. Digital photographs of as-prepared rutile TiO_2 single crystals (R3) before and after thermal treatment.

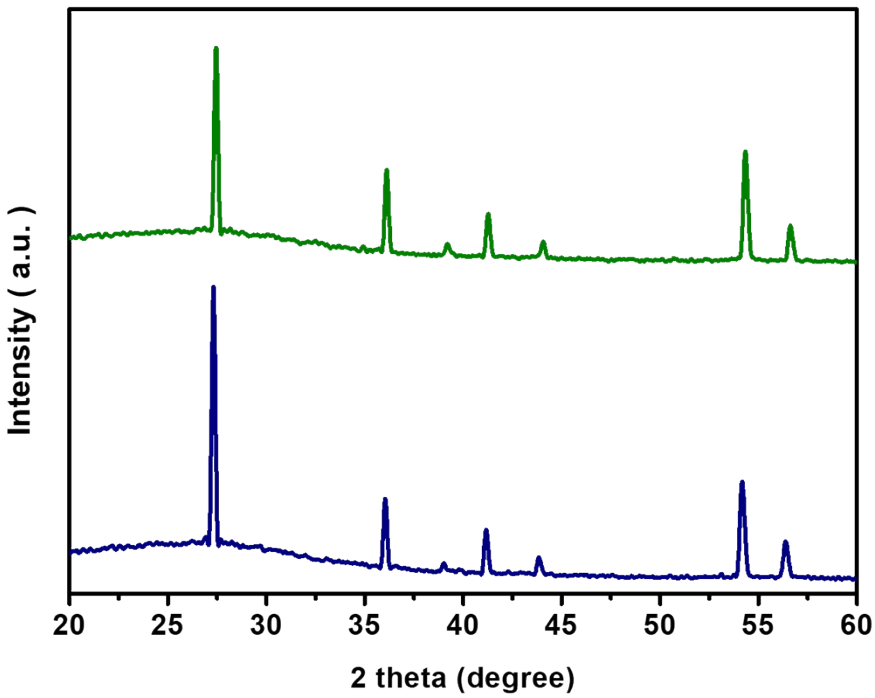


Fig. S8. XRD patterns of R1 sample before (blue) and after (green) 600 °C thermal treatment.

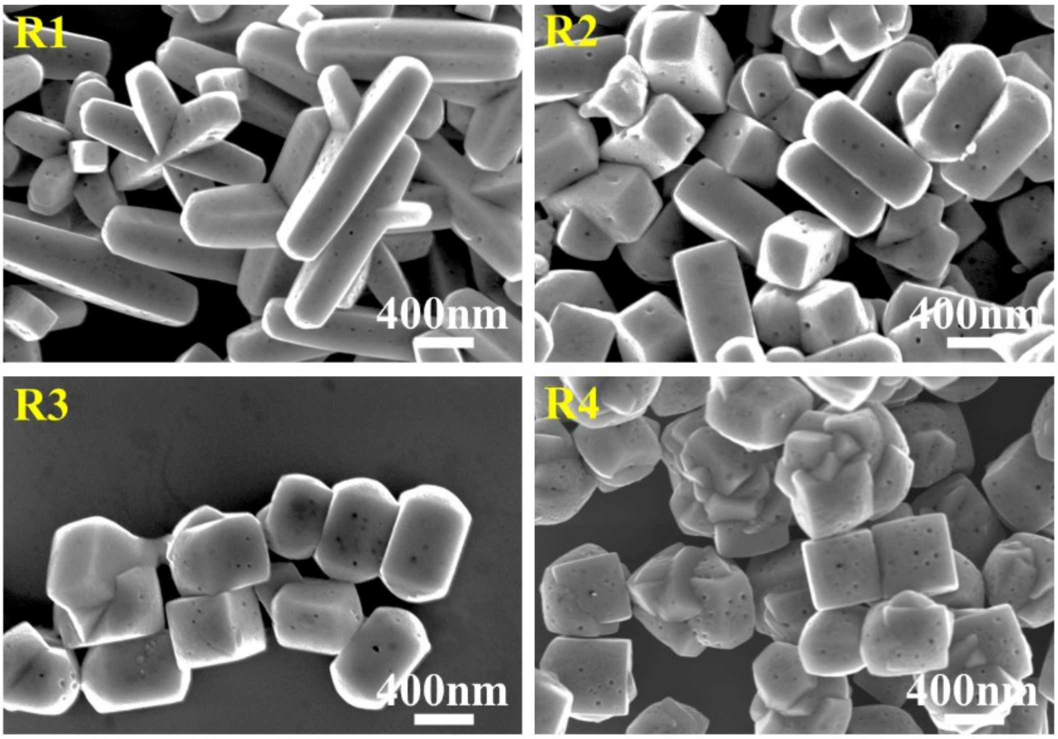


Fig. S9. SEM images of different rutile TiO_2 single crystals after 600 °C thermal treatment.

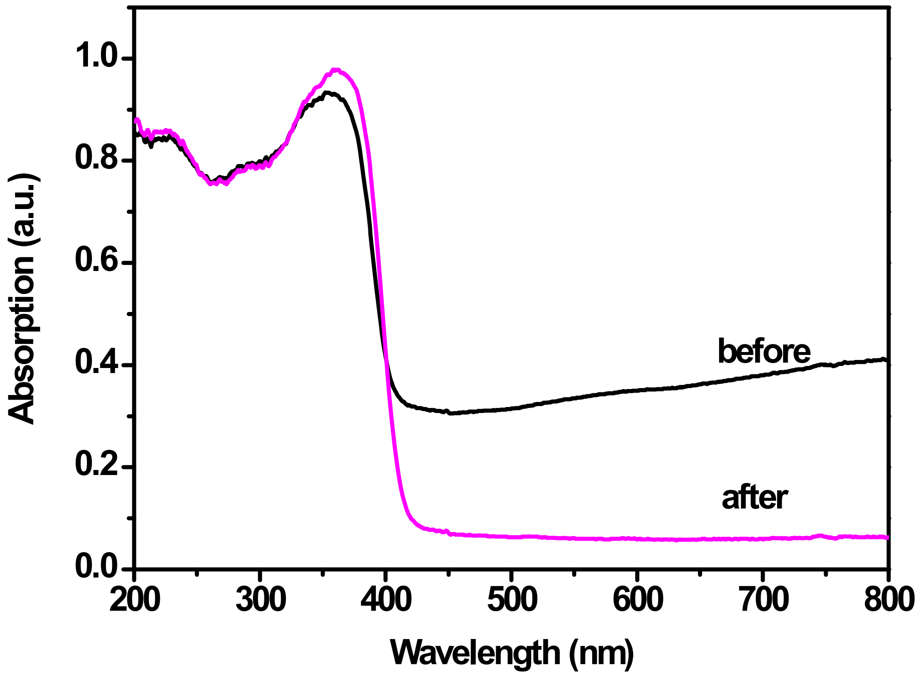


Fig. S10. UV-visible absorption spectra of R1 sample before (black) and after (magenta) 600 °C thermal treatment.

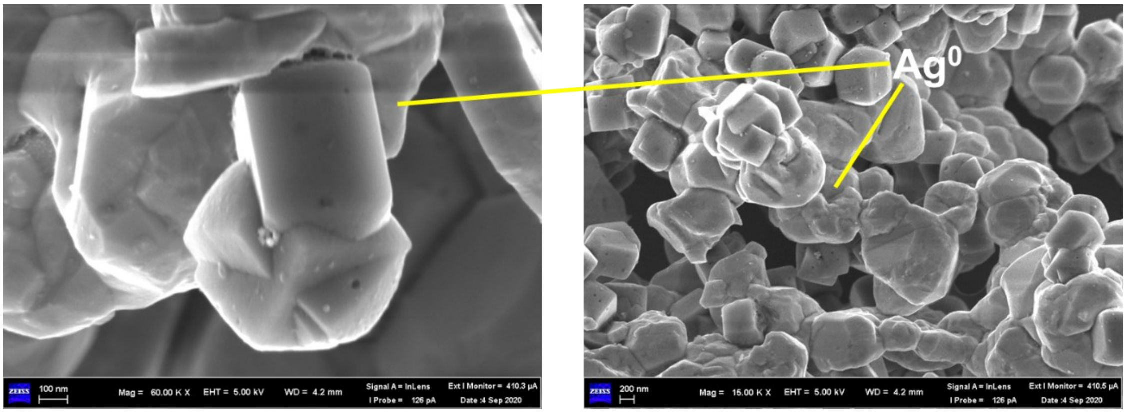


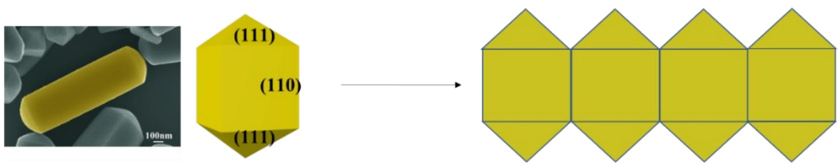
Fig. S11. SEM images of rutile TiO_2 single crystals (R3) after the photocatalytic O_2 production tests.

Table S1. Morphological details of rutile TiO_2 from SEM observation. [#]

Samples	L_{ave}	W_{ave}	r_{asp}	Percentage of (111) [##]	Percentage of (110) [##]
R1	1275±152 nm	295±30 nm	4.32	16	84
R2	838±86 nm	379±44 nm	2.21	32	68
R3	564±62 nm	421±46 nm	1.34	57	43
R4	588±57 nm	521±51 nm	1.13	69	31

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

[##] 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:

$S_{(111)} = [0.5d / \cos(40°)] \cdot d \cdot 0.5 = 0.326 \cdot d^2$

$S_{(110)} = [r \cdot d - 2 \cdot 0.5d \cdot \tan(40°)] \cdot d = (r - 0.839) \cdot d^2$

$S_{\text{total}} = \sum S_{\text{i}} = 8\, S_{(111)} + 4\, S_{(110)} = 2.61 \cdot d^2 + 4 \cdot (r - 0.839) \cdot d^2$

(111) facet % = 2.61 / [2.61 + 4 • (r – 0.839)]

(110) facet % = 4 • (r – 0.839) / [2.61 + 4 • (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.

Samples	S_{BET} (m^2/g)	
	Before calcining	After calcining
R1	3.4	3.8
R2	4.2	2.2
R3	3.5	2.6
R4	5.5	2.1

References

1. Q. J. Xiang, K. L. Lv and J. G. Yu, *Appl. Catal. B-Environ.*, 2010, **96**, 557-564.
2. Q. Zhang, R. Li, Z. Li, A. Li, S. Wang, Z. Liang, S. Liao and C. Li, *J. Catal.*, 2016, **337**, 36-44.