

Electronic Supplementary Information

Formation mechanism of rectangular-ambulatory-plane TiO₂ plates: an insight into the role of hydrofluoric acid†

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1. EXPERIMENTAL

1.1 Preparation of etched TiO₂

In a typical synthesis, 0.04 M titanium tetrafluoride aqueous solution was prepared by dissolving 1.24 g of titanium tetrafluoride in 250 mL of deionized water which contains 0.2 mL of hydrochloric acid (37%). Then 0.83 mL of hydrofluoric acid (40%) was added to 50 mL of 0.04 M titanium tetrafluoride aqueous solution under stirring. The mixture was sealed in a Teflon-lined double-walled digestion vessel and heated in a microwave oven (XH-800S, Beijing Xianghu Co., Ltd.) with the power and temperature set at 1000 W and 210 °C, respectively. The whole hydrothermal process includes the heating-up stage and the holding stage. The heating-up procedure was shown in Table S1 (ESI†) and the whole hydrothermal process was simulated in Fig. S1 (ESI†) according to the realistic process (Fig. S2, ESI†). During the holding stage, the reaction was kept at 210 °C for 10, 30, 60, 90, 120 and 150 min, respectively. (The total reaction time was 70, 90, 120, 150, 180, and 210 min, respectively.) Moreover, to get a better understanding of the growth mechanism of the etched {001} facets of anatase TiO₂ crystals, we also collected the products during the heating-up stage with the heating-up time of 42.5, 45, 47.5 and 50 min, respectively. After the hydrothermal process, the vessel was naturally cooled down to room temperature. The products were collected by centrifugation, and washed with deionized water and ethanol, and then dried in a vacuum oven at 80 °C for 4 h. The obtained products were calcined at 600 °C in air for 2 h to remove surface fluorine.

1.2 Characterization

X-ray diffraction patterns were obtained from a Bruker D2 Pharser using Cu/K α radiation ($\lambda = 1.5418 \text{ \AA}$). Scanning electron microscopy (SEM) images were obtained by FEI Quanta 250

equipment. N₂ adsorption-desorption isotherms were conducted on a Quantachrome at liquid N₂ temperature. The specific area was determined from the linear portion of the BET plot. Ultraviolet-visible (UV-vis) diffuse reflectance spectroscopies (DRS) were recorded by a V-670 spectrophotometer equipped with an integrating sphere. The reflectances were re-calculated to the absorption using the Kubelka-Munk equation, $F(r) = (1 - r)^2/2r$, where r is the diffuse reflectance. Here, a relative value of r was measured using a BaSO₄ white standard as a reference. Photoluminescence (PL) spectra were measured on a FLS980 spectrometer at room temperature using a 385 nm excitation wavelength.

1.3 Photocatalytic measurements

The photocatalytic water splitting reaction was carried out in a top-irradiation quartz cell connected to a closed glass gas circulation system (CEL-SPH2N, Beijing). In a typical photocatalytic reaction, 10 mg of sample was dispersed in a 20 mL aqueous solution containing 20% methanol. 3 wt% Pt was photodeposited on the photocatalysts using H₂PtCl₆ dissolved in the reactant solution. The suspension was thoroughly evacuated and then irradiated by a 300 W Xe lamp (PLS-SXE300). The temperature of the reaction solution was maintained at 6 °C by a flow of cooling water during the photocatalytic reaction. The gases evolved were analyzed with an on-line TCD gas chromatograph (GC-9720, nitrogen carrier).

1.4 Photoelectrochemical measurements

The photocurrent, electrochemical impedance spectroscopy (EIS) were carried out an electrochemical analyzer (CHI 660E) in a standard three-electrode quartz cell. The working electrode was prepared as follows: 5 mg of sample was suspended in 0.5 mL of deionized water with 0.05 mL of 5 wt% Nafion D-520 dispersion, and then the mixture was dispersed by

ultrasonication and spread onto an FTO glass. After being dried naturally, the FTO glass was heated at 120 °C for 1 h to evaporate the solvent. The prepared thin film acted as working electrode, using a platinum plate as counter electrode and saturation calomel electrode (SCE) as reference electrode. 0.1 M Na₂SO₄ aqueous solution was used as the electrolyte. A 300 W Xe lamp with a 420 nm filter was used as light source for photocurrent measurement.

2. The calculation of apparent quantum efficiency

The apparent quantum efficiency (AQE) was analyzed at different wavelength (365 and 380 nm, ± 10 nm) under the 300 W Xenon lamp irradiation. The other experimental conditions are similar to the photocatalytic hydrogen evolution measurement as described before. The light intensity was obtained with an optical power meter (CEL-NP2000, CEAULIGHT, Beijing). For example, if 365 nm is used, the average light intensity is 2.9 mW/cm². The irradiation area was 28.3 cm² (3 cm radius). The number of incident photons (*N*) is 2.67×10²⁰ calculated by equation (1). The amount of H₂ molecules generated for 3 h are ~8.6 μmol. The AQE was then calculated in equation (2).

$$N = \frac{E\lambda}{hc} = \frac{2.9 \times 28.3 \times 10^{-3} \times 3 \times 3600 \times 365 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^8} = 1.63 \times 10^{21} \quad (1)$$

$$\begin{aligned} AQE &= \frac{\text{the number of reacted electrons}}{\text{the number of incident photons}} \times 100\% \\ &= \frac{2 \times \text{the number of evolved H}_2 \text{ molecules}}{N} \times 100\% \quad (2) \\ &= \frac{2 \times 6.02 \times 10^{23} \times 8.6 \times 10^{-6}}{1.63 \times 10^{21}} \times 100\% = 0.64\% \end{aligned}$$

2. TABLES

Table S1. Heating up procedure of the hydrothermal process

Step	Target temperature/°C	Heating up time/min	Total time/min	Pressure/Mpa	Power/W
1	80	10	10	5	1000
2	140	10	20	5	1000
3	160	10	30	5	1000
4	180	10	40	5	1000
5	210	20	60	5	1000

Table S2. Structural parameters of photocatalysts

sample	BET surface area/m ² ·g ⁻¹	Pore volume/cm ³ ·g ⁻¹	Pore Diameter/nm
TiO ₂ -90 min	5.569	0.058	1.996
TiO ₂ -120 min	5.763	0.049	1.625
TiO ₂ -150 min	4.751	0.051	1.459
TiO ₂ -180 min	4.133	0.035	1.996
TiO ₂ -210 min	3.036	0.035	2.248

3. FIGURES

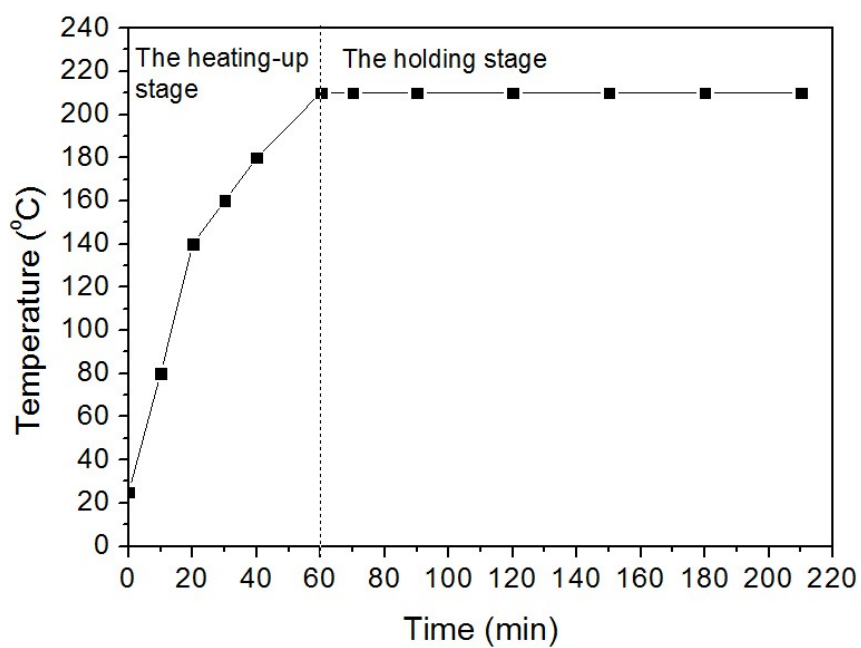


Fig. S1 Simulated hydrothermal process based on the realistic process.

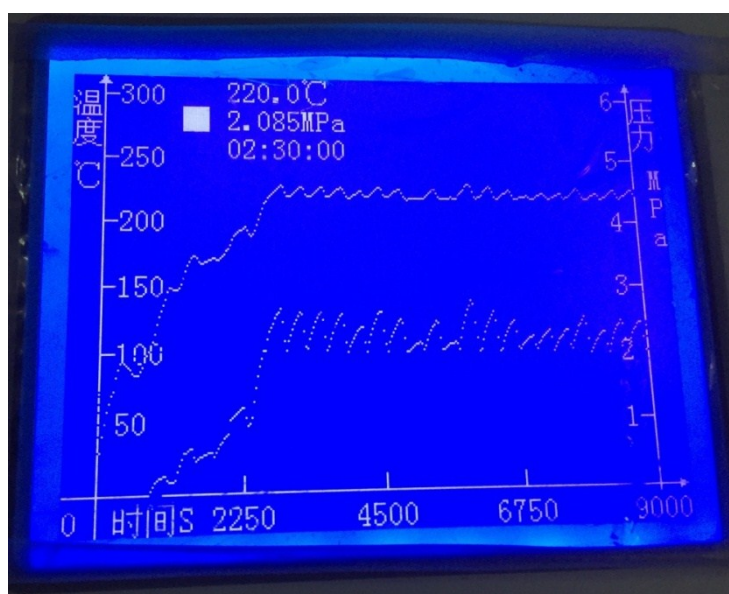


Fig. S2 The realistic process of the hydrothermal reaction.

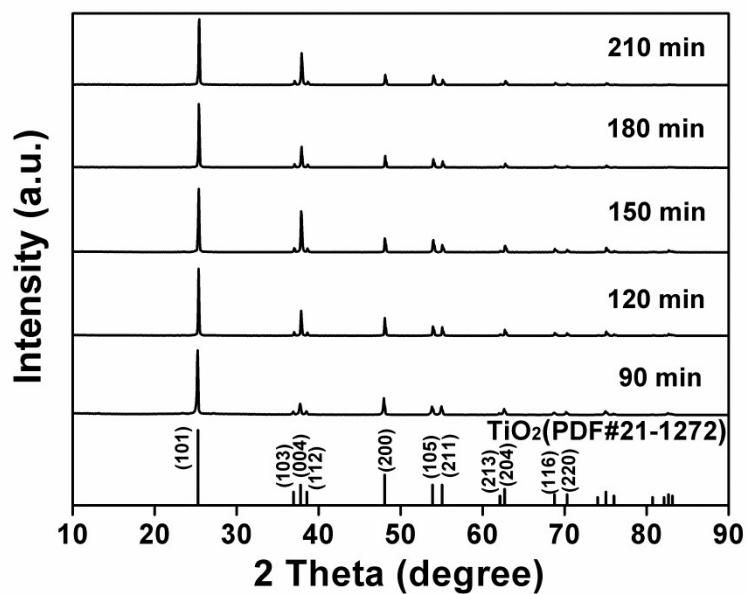


Fig. S3 XRD patterns of anatase TiO₂ single crystals with the preparation time of 90, 120, 150, 180 and 210 min.

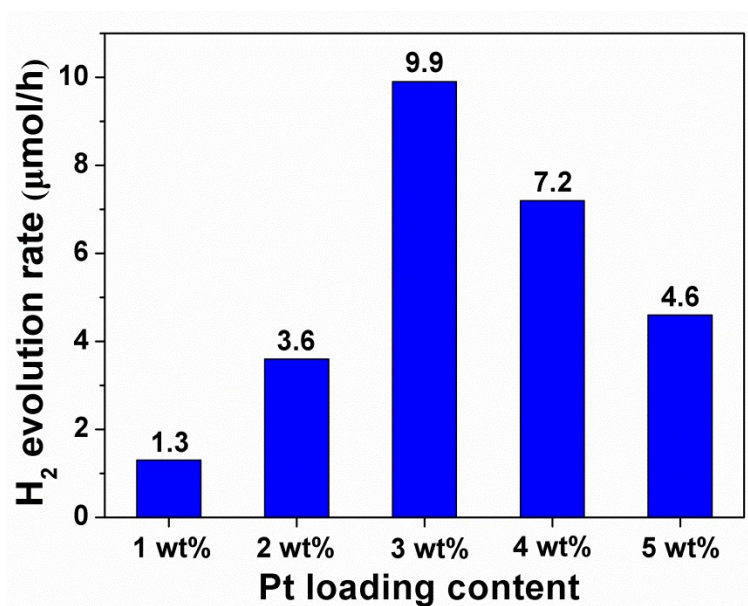


Fig. S4 The average photocatalytic H₂ production rates over 10 mg of anatase TiO₂ with the preparation time of 150 min loaded with different content of Pt under full-spectrum light irradiation.

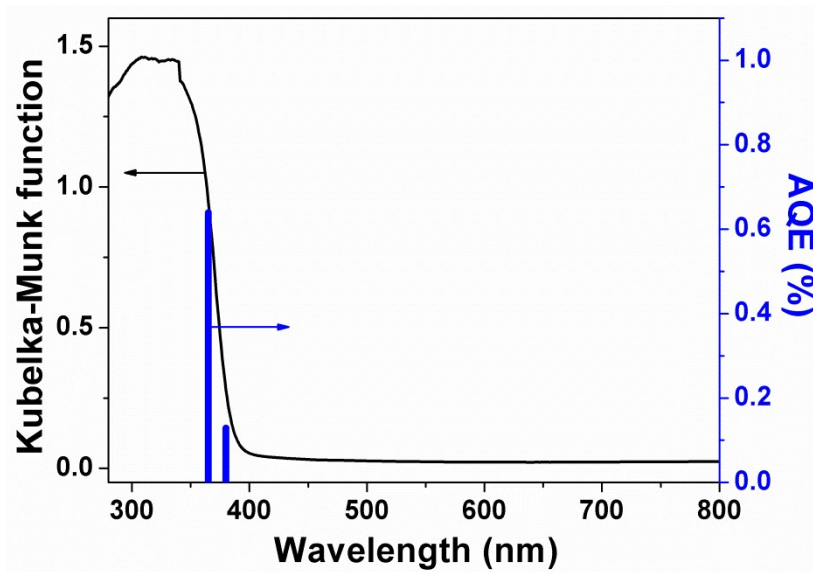


Fig. S5 Kubelka-Munk function and AQE of TiO₂ sample prepared for 150 min.

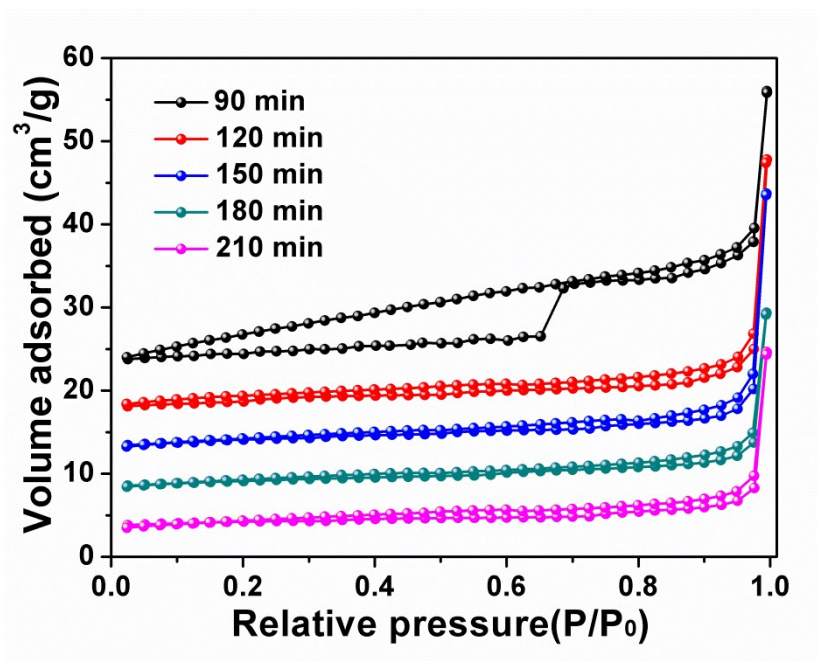


Fig. S6 N₂ adsorption-desorption isotherms of anatase TiO₂ single crystals with the preparation time of 90, 120, 150, 180 and 210 min.

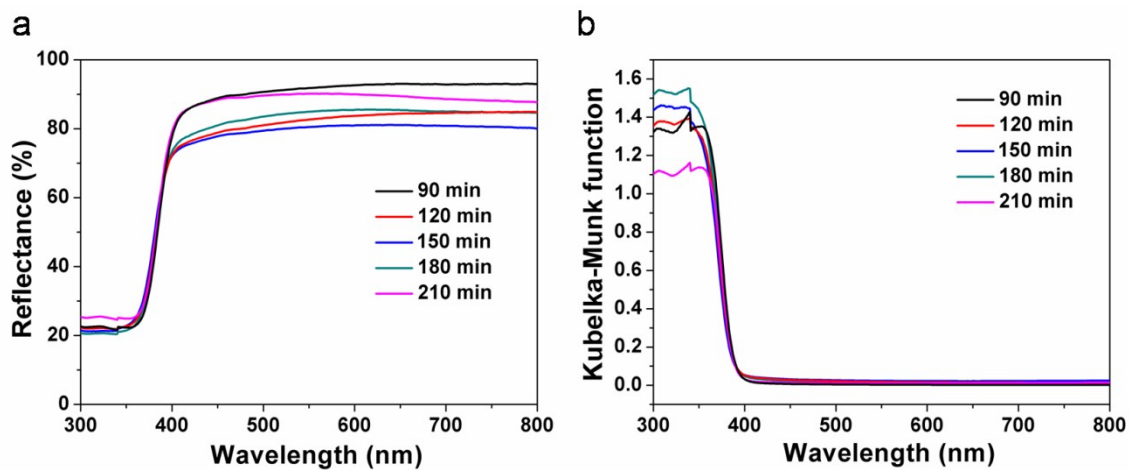


Fig. S7 UV-vis DRS (a) and Kubelka-Munk function (b) of anatase TiO₂ samples with the preparation time of 90, 120, 150, 180 and 210 min.

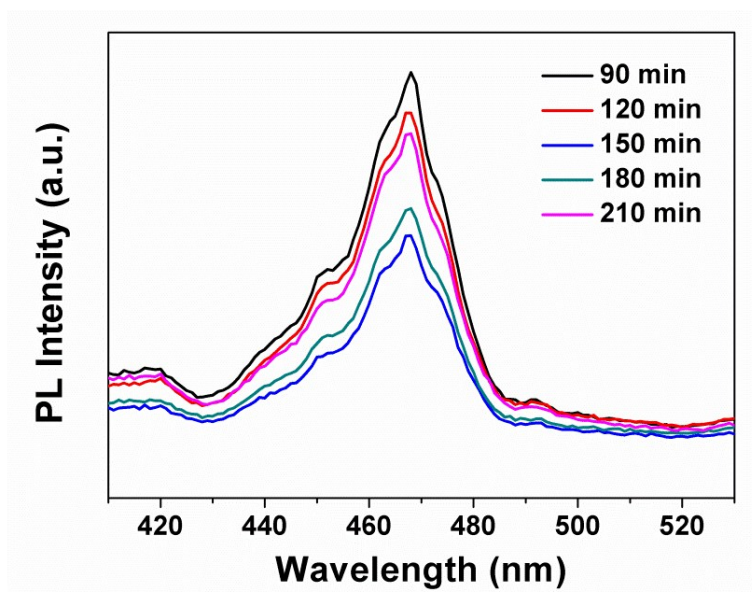


Fig. S8 PL spectra of anatase TiO₂ samples with the preparation time of 90, 120, 150, 180 and 210 min.

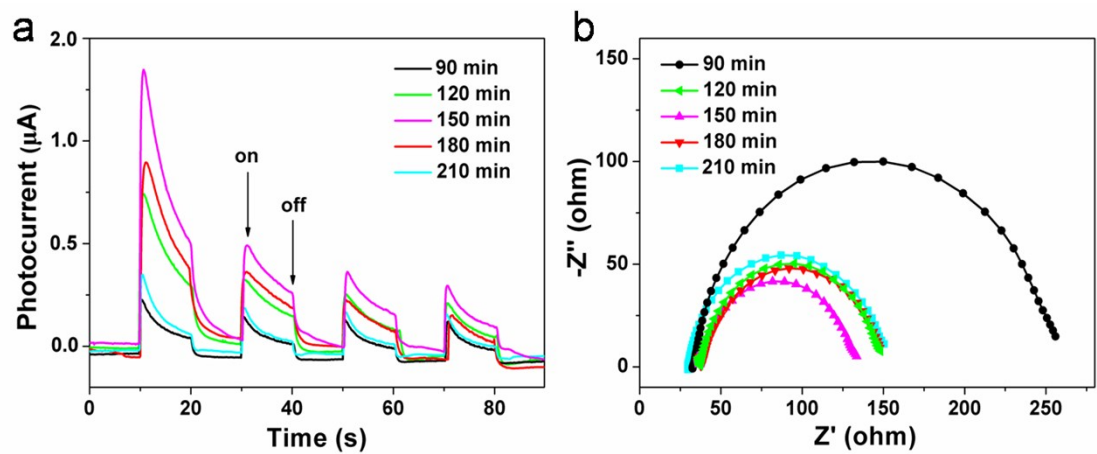


Fig. S9 Photocurrent response (a) and EIS (b) results for anatase TiO₂ with the preparation time of 90, 120, 150, 180 and 210 min.