Supporting Information

Synthesis of nano-sized anatase TiO$_2$ with reactive \{001\} facets using lamellar protonated titanate as precursor

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**Experimental section**

1. Preparation of lamellar protonated titanate (LPT) precursor

   In a typical preparation procedure, 9 mL of tetrabutyl titanate (TBT) was dissolved in 66 mL of absolute ethanol, and then the solution was added dropwise into 90 mL of deionized water under magnetic stirring at room temperature. After complete addition, the white suspension was mechanically agitated at 70 °C for about 2 h to obtain a condensed suspension. 300 mL of 1 M NaOH was then added into the above suspension, and the mixture was further stirred for 12 h in airproof conditions. After centrifugation, deionized water and isopropanol were used in turn to thoroughly wash the precipitate. Thus the wet LPT precursor is obtained for future use.

2. Synthesis of LPT-TiO₂ with exposed {001} facets

   LPT precursor, 6 mL of isopropanol and 0.5 mL of hydrofluoric (HF) acid solution (40 wt%) were mixed in a dried Teflon autoclave, and then the vessel was sealed and heated at 180 °C for 12 h. The molar ratio of F to Ti in the reaction system was calculated to be 1:1. After the solvothermal treatment, the reaction system was cooled to room temperature and washed by deionized water and absolute ethanol for several times. The samples were collected by vacuum drying at 60 °C for 24 h and milling into ultrafine powders, which were labeled as LPT-TiO₂. To investigate the effect of HF concentration on the morphology, crystal structure and photocatalytic activity of the samples, the molar ratio of F to Ti was varied at 0:1, 1:1 and 2:1 by varying the volume of HF solution. For LPT-TiO₂ (F:Ti=0:1), 0.5 mL of deionized water was added in the reaction system instead of HF solution.

   **Caution:** HF is extremely corrosive and poisonous, and it should be handled in a fume hood!

3. Synthesis of TBT-TiO₂ and Std-TiO₂ with exposed {001} facets for references

   For references, another two samples were obtained using TBT instead of LPT as precursor. TBT-TiO₂ with {001} facets was prepared by solvothermal treatment similar to that of LPT-TiO₂, except that stoichiometric TBT was directly added into a dried Teflon autoclave and reacted with HF and isopropanol. Std-TiO₂ with {001} facets was fabricated according to the literature [3], which also directly used TBT as precursor. Typically, 5 mL of TBT and 1.0 mL of HF solution (40 wt%) were mixed in a dried Teflon autoclave. The reaction system was then kept at 180 °C for 24 h. After the hydrothermal treatment, the precipitate was separated by centrifugation, washed with absolute ethanol and deionized water, and dried by vacuum.
4. Characterizations

Powder X-ray diffraction (XRD) patterns were obtained over the diffraction angle (2θ) 5°–80° on an XRD-6000 X-ray diffractometer with Cu Kα radiation as X-ray source (Shimadzu, Japan). Transmission electron microscopy (TEM) images were performed on an FEI Tecnai G2 T20 S-Twin microscope with an accelerating voltage of 200 kV (FEI, USA). The surface areas of samples were measured by using the Brunauer-Emmett-Teller (BET) method on an ASAP 2020M instrument in liquid nitrogen (Micromeritics, USA). X-ray photoelectron spectroscopy (XPS) measurement was carried out on a PHI5700 ESCA system (Physical Electronics) with an Mg Kα X-ray source. The binding energy (BE) shifts were corrected using the C1s level at 284.8 eV as an internal standard to compensate for the surface-charging effect during data analysis. Surface elemental stoichiometry was determined by the ratios of peak areas corrected with empirical sensitivity factors. Fourier-transform infrared (FT-IR) spectrum was recorded on a Nicolet Avatar 360 FT-IR Spectrometric Analyzer in the range of 400–4000 cm⁻¹ with KBr pellet. UV-visible diffuse reflectance spectrum (UV-vis DRS) was measured on a TU 1901 UV–vis spectrophotometer (Puxi, Inc. Beijing) equipped with an integrating sphere attachment over a range of 230-900 nm. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA851e at a heating rate of 5 °C min⁻¹ from room temperature to 600 °C under air atmosphere.

5. Photocatalytic tests

Photocatalytic properties of the samples were compared by measuring the degradation rate of 2,4-dichlorophenol (2,4-DCP) under UV light irradiation. In the experiment, 10 mg of photocatalyst and 40 µL of 2,4-DCP aqueous solution (0.2 wt%) were mixed in 10 mL of 0.005 M hydrochloric acid. A high-pressure 100 W mercury (Hg) lamp was used as the UV-light source. Before irradiation, the suspensions were stirred for about 40 min in the darkness for the establishment of adsorption-desorption equilibrium. During the photocatalytic test, the suspension was sampled and analyzed by testing the residual concentration of 2,4-DCP every 20 min. The residual concentration was evaluated by recording the change of absorbance at 284 nm in the UV-vis absorption spectra.
Figures

Fig. S1 Nitrogen adsorption/desorption isotherms and corresponding pore size distributions (insets) of (a) LPT-TiO₂, (b) TBT-TiO₂ and (c) Std-TiO₂.
Fig. S2 TEM image (a) and XRD pattern (b) of lamellar protonated titanate (LPT). The standard diffraction pattern of one type of titanate (H$_2$Ti$_5$O$_{11}$·3H$_2$O) is also reported in (b) (JCPDS 44-0130).
Fig. S3 FT-IR spectrum of as-prepared LPT.
Fig. S4 TGA curve of as-prepared LPT.
Fig. S5 UV-vis DRS spectrum of as-synthesized LPT.
Fig. S6 TEM images of (a) sample obtained with the molar ratio of F:Ti at 0:1 and (b) LPT-TiO$_2$ (F:Ti = 2:1).
Fig. S7 XRD patterns of (a) sample obtained with the molar ratio of F:Ti at 0:1 and (b) LPT-TiO$_2$ (F:Ti = 2:1).
**Fig. S8** Nitrogen adsorption/desorption isotherm and corresponding pore size distribution (inset) of LPT-TiO$_2$ (F:Ti = 2:1).
Fig. S9 The effect of molar ratio of F to Ti on the photocatalytic properties of as-synthesized LPT-TiO$_2$ for decomposing 2,4-DCP under UV light irradiation.
Table S1  Structure information of as-synthesized anatase TiO₂ with exposed {001} facets

<table>
<thead>
<tr>
<th>Samples</th>
<th>Length /nm</th>
<th>Thickness /nm</th>
<th>Exposed {001}</th>
<th>Exposed {101}</th>
<th>S_{BET} /m² g⁻¹</th>
<th>S_{001} /m² g⁻¹</th>
<th>S_{101} /m² g⁻¹</th>
<th>Fluorine content d</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPT-TiO₂</td>
<td>11.3</td>
<td>8.5</td>
<td>26.1%</td>
<td>73.9%</td>
<td>155</td>
<td>40</td>
<td>115</td>
<td>4.70%</td>
</tr>
<tr>
<td>TBT-TiO₂</td>
<td>33.5</td>
<td>5.9</td>
<td>73.9%</td>
<td>26.1%</td>
<td>78</td>
<td>58</td>
<td>20</td>
<td>5.63%</td>
</tr>
<tr>
<td>Std-TiO₂</td>
<td>76.2</td>
<td>5.0</td>
<td>88.4%</td>
<td>11.6%</td>
<td>58</td>
<td>51</td>
<td>7</td>
<td>5.29%</td>
</tr>
<tr>
<td>LPT-TiO₂ (2:1) a</td>
<td>24.4</td>
<td>6.4</td>
<td>65.7%</td>
<td>34.3%</td>
<td>77</td>
<td>51</td>
<td>26</td>
<td>6.49%</td>
</tr>
</tbody>
</table>

a LPT-TiO₂(2:1) means LPT-TiO₂ synthesized with the molar ratio of F to Ti at 2:1. b, c S_{001} and S_{101} represent the specific surface areas of exposed {001} and {101} facets in anatase TiO₂, respectively. d The fluorine content is the content of surface-terminated fluorine on the surface of high-energy TiO₂ samples calculated from XPS results.