Tunable photocatalytic selectivity of TiO_2 films consisted of flower-like microspheres with exposed {001} facets

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Experimental

Synthesis of titania samples. All chemicals used in this study were analytical grade and were used without further purification. Deionized water was used in all experiments. Before hydrothermal treatment, Ti foils (99% purity) of 25 x 25 x 0.25 mm were respectively degreased by sonicating in acetone and distilled water for 5 min each, and then dried in air. The films of flower-like TiO₂ microspheres were directly synthesized using Ti foils in a dilute HF-H₂O mixed solution by a simple one-pot hydrothermal method. In a typical synthesis, the cleaned Ti foil was put into a 60 mL of 0.02 M HF aqueous solution in a 100 mL Teflon-lined autoclave, and then kept at 180 °C for 1 h. After the hydrothermal treatment, the as-prepared thin films were rinsed with distilled water, and dried in an oven at 80 °C. Control experiments, as above, but with other reaction times varying from 0 to 10 h were also performed.

Surface modification. For the NaOH-washing treatment, the as-prepared TiO_2 films were immersed in 50 mL of 5 M NaOH aqueous solution for about 30 min. Next, the resulting films were washed 3-4 times with distilled water to reach pH = 7. For the NaF or HNO₃ treatment, the NaOH-treated TiO₂ films were immersed in 50 mL of 2 M NaF or 2 M HNO₃ aqueous solution for about 30 min, and rinsed with distilled water to reach pH = 7.

Characterization. XRD patterns were obtained on a D/Max-RB X-ray diffractometer (Rigaku, Japan) using Cu K α radiation at a scan rate of 0.05° 2 θ s⁻¹. SEM was performed using a Hitachi-4800S microscope (Hitachi, Japan). TEM analysis was conducted using a JEM-2100F electron microscope (JEOL, Japan). XPS measurements were done on a VG ESCALAB 210 electron

spectrometer using Mg K α radiation. XPS data were calibrated using the binding energy of C1s (285.00 eV) as the internal standard.

Photocatalytic testing. The selective photocatalytic decomposition of mixed methyl orange (MO) and methyl violet (MV) dyes was conducted in an aqueous solution containing the TiO₂ film under xenon lamp irradiation at ambient temperature. Experimental details were as follows: $2.5 \times 2.5 \text{ cm}^2 \text{ TiO}_2$ sample was placed in a 10 mL mixed MO ($2 \times 10^{-5} \text{ mol L}^{-1}$) and MV ($1 \times 10^{-5} \text{ mol L}^{-1}$) aqueous solution in a 60 ml beaker. The mixed aqueous solution of the aforementioned dyes with the photocatalyst added was allowed to reach an adsorption-desorption equilibrium before xenon lamp irradiation. A 300 W xenon lamp positioned 10 cm away from the cell was used as a light source to trigger the photocatalytic reaction. The average light intensity striking on the surface of the reaction solution was about 20 mW/cm². The concentration of MO and MV was monitored by a UV-2550 UV-visible spectrophotometer (Shimadzu, Japan).



Fig. S1. A) Slab model of anatase TiO_2 single crystal. B) Equilibrium model of anatase TiO_2 single crystal.

C) Percentage of {001} facets was calculated as follows [1-3]:

$$S_{001} = 2a^{2}$$

$$S_{101} = 8(\frac{1}{2}EG \times b - \frac{1}{2}EF \times a)$$

$$S_{001}\% = \frac{S_{001}}{S_{001} + S_{101}}$$

$$= \frac{2a^{2}}{2a^{2} + 8(\frac{1}{2}EG \times b - \frac{1}{2}EF \times a)}$$

$$= \frac{a^{2}}{a^{2} + 4(\frac{1}{2} \times \frac{\frac{1}{2}b}{\cos\theta} \times b - \frac{1}{2}\frac{\frac{1}{2}a}{\cos\theta} \times a)}$$

$$= \frac{a^{2}}{a^{2} + \frac{b^{2} - a^{2}}{\cos\theta}} = \frac{1}{1 + \frac{\frac{b^{2}}{a^{2}} - 1}{\cos\theta}}$$

$$= \frac{\cos\theta}{\cos\theta + \frac{b^{2}}{a^{2}} - 1}$$

$$= \frac{\cos\theta}{\cos\theta + (\frac{a}{b})^{-2} - 1}$$

$$= \frac{\cos 8.3^{\circ}}{\cos 8.3^{\circ} + (\frac{350}{475})^{-2} - 1} = 30.4\%$$

Here θ is the theoretical value for the angle between the [001] and [101] facets of anatase. As indicated in the slab model, two independent parameters *b* and *a* denote lengths of the side of the bipyramid and the side of the square {001} 'truncation' facets, respectively. The ratio of highly reactive {001} facets to total surface area can thus be described by the value of S_{001}/S or a/b (where $0 \le a/b \le 1$). a/b is the degree of truncation).

References

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Fig. S2 High-resolution XPS spectra of F 1s of the as-prepared fluorinated TiO_2 films (a); TiO_2 films modified by NaOH washing (b); NaOH-treated TiO_2 films modified by NaF washing (c); NaOH-treated TiO_2 films modified by HNO₃ washing (d).



Fig. S3 XRD patterns of the Ti substrate and TiO_2 films prepared at 180 °C for 15, 30, 60, 180 and 600 min.



Fig. S4 SEM images of the Ti substrate and TiO_2 films prepared at 180 °C for 5, 10, 15, 30, 60, 180 and 600 min.



Fig. S5 SEM images of the Ti substrate and TiO₂ films prepared at 120 °C for 60 min.



Fig. S6 SEM images of the NaOH-treated TiO₂ film prepared at 180 °C for 1 h.



Fig. S7 Schematic illustration of the selective adsorption of charged contaminants on the surface of TiO_2 . A and B represent negatively and positively charged contaminants, respectively.



Fig. S8 A comparison of photocatalytic activity and selectivity of the TiO_2 films prepared at 180 $^{\circ}C$ for (A) 1 h (T1), (B) 3 h (T3) and (C) 10 h (T10) towards photodecomposition of MO and MB before (T1-F, T3-F, T10-F) and after NaOH washing (T1-OH, T3-OH, T10-OH). The photocatalytic activity and selectivity is defined by the apparent rate constant (*k*) and the ratio (*r*) of *k*, respectively.