

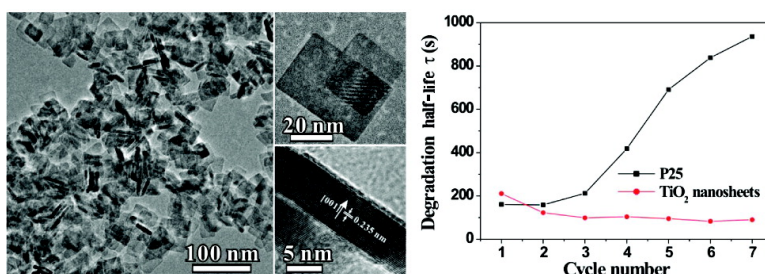
Communication

Synthesis of Titania Nanosheets with a High Percentage of Exposed (001) Facets and Related Photocatalytic Properties

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Synthesis of Titania Nanosheets with a High Percentage of Exposed (001) Facets and Related Photocatalytic Properties

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Over the past decades, surface chemists have made great achievements in the study of chemical properties of definite crystal planes by employing bulk single crystals.¹ However, it is difficult to directly apply single crystals in many technical fields, such as real catalysis. It is therefore necessary to set up a bridge between the surface chemistry of bulk single crystals and the real technical fields. The surface-controlled growth of micro- and nanocrystallites could be such a bridge.² TiO₂, as a wide-band-gap semiconducting material, is expected to play an important role in helping to ease the environmental and energy crisis through effective utilization of solar energy derived from photocatalysis, photovoltaics, and water photocatalysis.³ Surface scientists have demonstrated that the order of the average surface energies of anatase TiO₂ is 0.90 J/m² for {001} > 0.53 J/m² for {100} > 0.44 J/m² for {101}.⁴ Although it can be expected that the higher-surface-energy (001) surface has much higher chemical activities, almost all of anatase TiO₂ nanostructures reported to date have had low-energy (101) surfaces (few have had {100} facets).⁵ Important progress was made very recently by Lu and co-workers,⁶ who reported the synthesis of micron-sized anatase TiO₂ crystallites with highly energetic (001) facets exposed. However, the percentage of exposed (001) facets was only 47%, and the crystallite size was relatively large. In this communication, we report a facile hydrothermal route for synthesizing sheet-like anatase TiO₂ with the highly reactive (001) facets exposed that takes advantage of a specific stabilization effect of fluorine ions on the (001) facets. Excitingly, the percentage of highly reactive (001) facets in such TiO₂ nanosheets is very high (up to 89%). In addition, the as-prepared TiO₂ nanosheets exhibit excellent activity in the photocatalytic degradation of organic contaminants.

Sheet-like anatase TiO₂ was synthesized via a simple hydrothermal route using tetrabutyl titanate, Ti(OBu)₄, as a source and 47% hydrofluoric acid solution as the solvent (see the Supporting Information for experimental details). **Caution!** Hydrofluoric acid is extremely corrosive and a contact poison, and it should be handled with extreme care. Figure 1A showed a typical X-ray diffraction (XRD) pattern (PANalytical X-Pert) of TiO₂ nanosheets synthesized at 180 °C. The diffraction peaks could be indexed to anatase-phase TiO₂ (JCPDS No. 21-1272), indicating that the as-synthesized product was pure anatase TiO₂. Transmission electron microscopy (TEM) analysis (JEM-2100) showed that the product consisted of well-defined sheet-shaped structures having a rectangular outline, side length of ~40 nm, and thickness of ~6 nm (Figure 1B). A high-magnification TEM image and its corresponding selected-area electron diffraction (SAED) pattern (indexed as the [001] zone axis diffraction) indicated that the top and bottom facets of the nanosheets were the (001) planes, as shown in Figure 1C. The high-resolution TEM image (Figure 1D) directly showed that the lattice spacing parallel to the top and bottom facets was ~0.235 nm, corresponding to the (001) planes of anatase TiO₂. On the basis of the above structural information, the percentage of

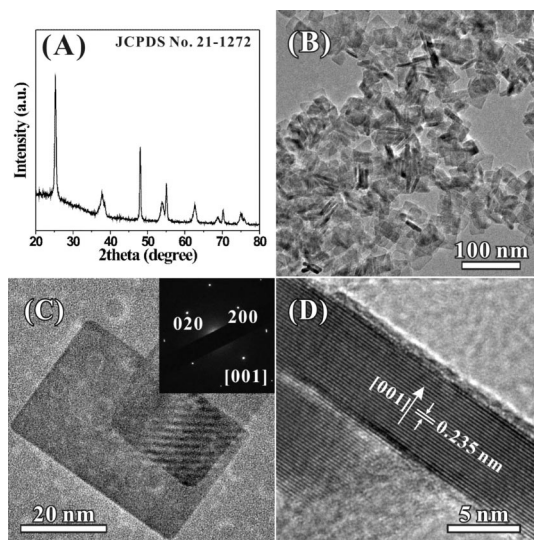


Figure 1. (A) Typical XRD pattern and (B) low-magnification TEM image of TiO₂ nanosheets synthesized at 180 °C using 5 mL of Ti(OBu)₄ and 0.6 mL of HF. (C) High-magnification TEM image of an individual TiO₂ nanosheet; the inset shows the corresponding SAED pattern. (D) High-resolution TEM image from the vertical nanosheets.

highly reactive (001) facets in the TiO₂ nanosheets shown in Figure 1 was estimated to be ~77%.

First-principles calculations indicate that fluorine ions can markedly reduce the surface energy of the (001) surface to a level lower than that of {101} surfaces.⁶ As a result, the fluorine ions may play a key role in the formation of the exposed (001) surface, and a series of experiments was carried out by introducing different amounts of fluorine ions. When the volume of hydrofluoric acid was increased from 0.6 to 0.8 mL, the TiO₂ nanosheets became larger (~50 nm) (Figure 2A,B). The percentage of (001) facets in the sheets is surprisingly as high as ~80%. On the contrary, decreasing the volume of hydrofluoric acid resulted in a decrease in the size of the nanosheets (see Table S1 in the Supporting Information). Furthermore, the reaction temperature was also found to play a key role in controlling the thickness and size of the TiO₂ nanosheets. When the reaction temperature was raised, the TiO₂ nanosheets became larger and slightly thicker (Figure 2C,D). The optimum reaction conditions to give the maximum percentage of (001) facets were 200 °C, 5 mL of Ti(OBu)₄, and 0.8 mL of hydrofluoric acid. The average size of the as-prepared nanosheets reached 130 nm with a thickness of ~8 nm, and the average percentage of the (001) facets was as high as 89% (Figure 2D). All of the structural information [i.e., size, thickness, and percentage of (001) facets] for TiO₂ nanosheets synthesized under different reaction conditions are listed in Table S1 in the Supporting Information for comparison.

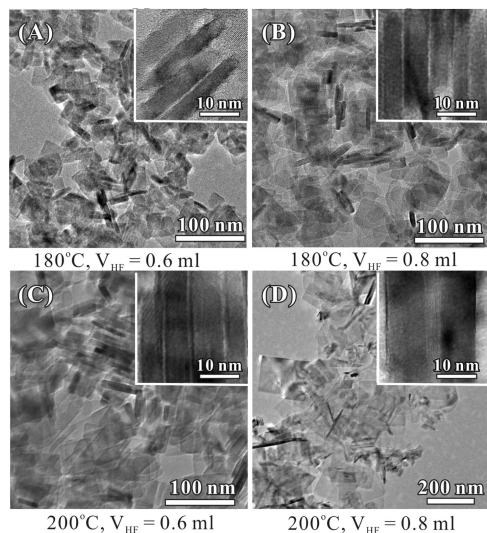


Figure 2. TEM images of TiO₂ nanosheets synthesized at (A) 180 °C, 5 mL of Ti(OBu)₄, and 0.6 mL of hydrofluoric acid; (B) 180 °C, 5 mL of Ti(OBu)₄, and 0.8 mL of hydrofluoric acid; (C) 200 °C, 5 mL of Ti(OBu)₄, and 0.6 mL of hydrofluoric acid; and (D) 200 °C, 5 mL of Ti(OBu)₄, and 0.8 mL of hydrofluoric acid. The insets show corresponding transmission electron microscopy images of vertical TiO₂ nanosheets that show the thickness of the nanosheets.

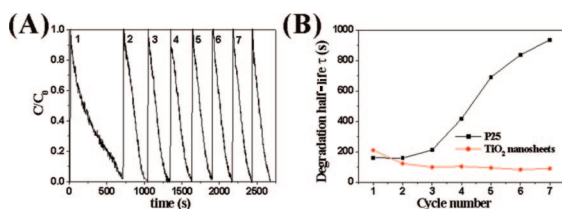


Figure 3. (A) Cycling degradation curve for TiO₂ nanosheets [89% (001) facets] synthesized under the optimum reaction conditions, using 1 mmol/L MO as a probe. (B) Degradation half-life of MO for as-synthesized TiO₂ nanosheets and commercial P25 as a function of cycle number. The vertical axis here shows the degradation half-life of MO, i.e., the time required for half of the MO molecules to degrade.

The as-synthesized TiO₂ nanosheets surrounded by (001) facets are expected to exhibit high photocatalytic efficiency. In our experiments, methyl orange (MO) was used as a probe molecule to investigate the photocatalytic performance. Furthermore, commercially available Degussa P25 TiO₂ (average particle size of 25 nm) was used as a reference for comparison (Figure S1 in the Supporting Information). It was found that the as-prepared TiO₂ nanosheets exhibited a gradually accelerating degradation rate (Figure 3A,B) and that the degradation efficiency was higher than that of P25 TiO₂ after the first degradation cycle. Furthermore, TiO₂ nanosheets with a higher percentage of (001) facets exhibited more effective photocatalytic performance (Figure S2 in the Supporting Information), demonstrating the high catalytic activity of the (001) facets.

Interestingly, the degradation rate for the as-prepared nanosheets was relatively small during the first cycle. The abnormal performance of the TiO₂ nanosheets in the first cycle could be due to the presence of superficial inorganic species and organic adsorbates on the TiO₂ nanosheets at the beginning. After the first cycle, the inorganic species were desorbed from the surface and the organic adsorbates degraded, resulting in the accelerating degradation rate

in the following degradation cycles. This hypothesis was also certified by directly cleaning the TiO₂ nanosheets with 0.1 M NaOH, during which the adsorbed fluorine ions on the surface of TiO₂ are easily replaced by hydroxyl groups.⁷ The degradation efficiency of the TiO₂ nanosheets after cleaning with alkaline solution was found to be remarkably improved, as shown in Figure S3 in the Supporting Information. As for the P25, conversely, the degradation rates gradually decreased after three degradation cycles, possibly because of adsorption of incompletely photodecomposed products on the surface of the P25.

In conclusion, rectangular TiO₂ nanosheets with highly reactive (001) facets as the top and bottom surfaces have been successfully synthesized by a simple hydrothermal route with the assistance of hydrofluoric acid solution. The percentage of (001) facets in the sheets was 89% with the optimal adjustment of the amount of hydrofluoric acid and reaction temperature. Such TiO₂ nanosheets show excellent photocatalytic efficiency, far exceeding that of commercially available Degussa P25, due to exposure of the high percentage of (001) facets. The present study motivates us to further explore the hydrothermal synthetic method for the preparation of other metallic oxides with a high percentage of reactive facets, which have promising applications as gas sensors, photocatalysts, solar cells, and photonic and optoelectronic devices.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grants 20725310, 20721001, 20673085, and 20801045) and the National Basic Research Program of China (Grants 2007CB815303 and 2009CB939804).

Supporting Information Available: Experimental details, structural information for TiO₂ nanosheets synthesized under different reaction conditions, cycling degradation curves for commercial P25 and TiO₂ nanosheets with different percentages of (001) facets, and degradation curves of TiO₂ nanosheets with and without the 0.1 M NaOH washing treatment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Supporting Information

Synthesis of Titania Nanosheets with a Large Percentage of Exposed (001) Facets and Related Photocatalytic Properties

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1. Experimental Section

Materials

The synthesis of anatase TiO₂ nanosheets was carried out using commercially available reagents. Tetrabutyl titanate (Ti(OBu)₄, 98%) and hydrofluoric acid (47%) were purchased from Sinopharm Chemical Reagent Co., Ltd., Degussa P25 from Shanghai Haiyi Co., Ltd. and all were used as received without further purification.

Caution: Hydrofluoric acid is extremely corrosive and a contact poison, and it should be handled with extreme care! Hydrofluoric acid solution is stored in Teflon containers in use.

Synthesis of TiO₂ nanosheets. In a typical experimental procedure, 5 mL of Ti(OBu)₄ and 0.6 mL of hydrofluoric acid solution were mixed in a dried Teflon autoclave with a capacity of 20 mL, and then kept at 180 °C for 24 h. After being cooled to room temperature, the white powder was separated by high-speed centrifugation and washed with ethanol and distilled water for several times. A series of TiO₂ nanosheets with different thicknesses and lengths were synthesized by varying the volume of hydrofluoric acid and reaction temperature. The detailed

reaction conditions were listed in Table S1.

Characterization of TiO₂ nanosheets. The composition and phase of the as-prepared products were measured by the powder X-ray diffraction (XRD) pattern using a Panalytical X-pert diffractometer with Cu K α radiation. The morphology and structure of as-prepared products were observed by high-resolution transmission electron microscopy (HRTEM, JEM-2100) with an acceleration voltage of 200 kV. All TEM samples were created by depositing a drop of diluted suspensions in ethanol on a carbon film coated copper grid.

Photocatalysis of TiO₂ nanosheets. Before measuring photocatalytic properties, both the TiO₂ nanosheets and P25 were washed with 0.1 M NaOH and distilled water for several times. The photodegradation of methyl orange (50 μ L, 1 mmol/L) was carried out in a quartz cell (1.0 cm \times 1.0 cm \times 4.5 cm) (using a small magneton for stirring) in the presence of TiO₂ photocatalysts (3 mL, 0.06 g/L) under the irradiation of UV light (300 W Hg lamp, 365 nm). The photodegradation efficiency was monitored at 465 nm by real time detection on a Halogen Light Source HL-2000 (Ocean Optics, Inc.).

2. Experimental Results

Table S1. Structural information of as-synthesized TiO₂ nanosheets synthesized at different reaction conditions.

Reaction conditions	Average Thickness (nm)	Average Length (nm)	Percentage of (001)
5 mL of Ti(OBu) ₄ + 0.4 mL of hydrofluoric acid, 180°C, 24h	7	30	68%
5 mL of Ti(OBu) ₄ + 0.6 mL of hydrofluoric acid, 180°C, 24h	6	40	77%
5 mL of Ti(OBu) ₄ + 0.8 mL of hydrofluoric acid, 80°C, 24h	6	50	80%
5 mL of Ti(OBu) ₄ + 0.4 mL of hydrofluoric acid, 200 °C, 24h	8	52	76%
5 mL of Ti(OBu) ₄ + 0.6 mL of hydrofluoric acid, 200 °C, 24h	7	60	81%
5 mL of Ti(OBu) ₄ + 0.8 mL of hydrofluoric acid, 200 °C, 24h	8	130	89%

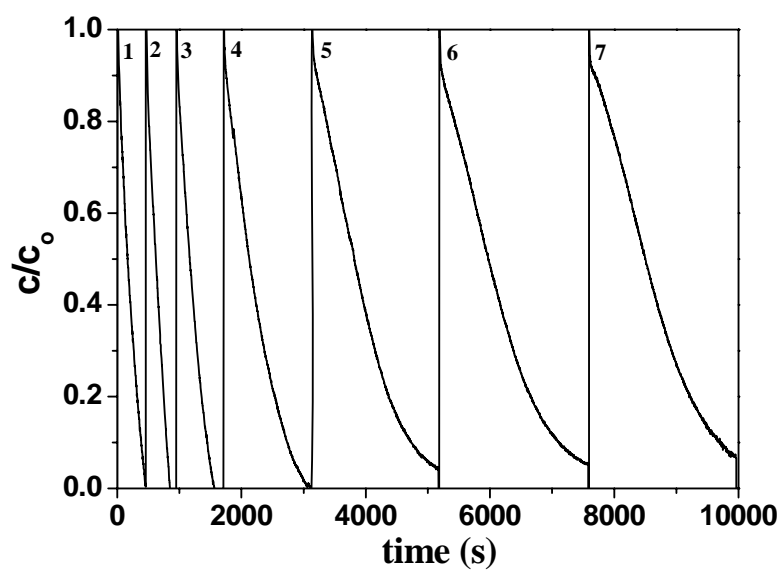


Figure S1. Cycling degradation curve of Degussa P25.

As shown in the figure, it took the P25 at least 10000 s to finish a seven-cycling degradation process. Additionally, the degradation rate become more and more slow after circulating degradation for three times, which could be due to the adsorption of incomplete photo-decomposed products on the surface of the P25.

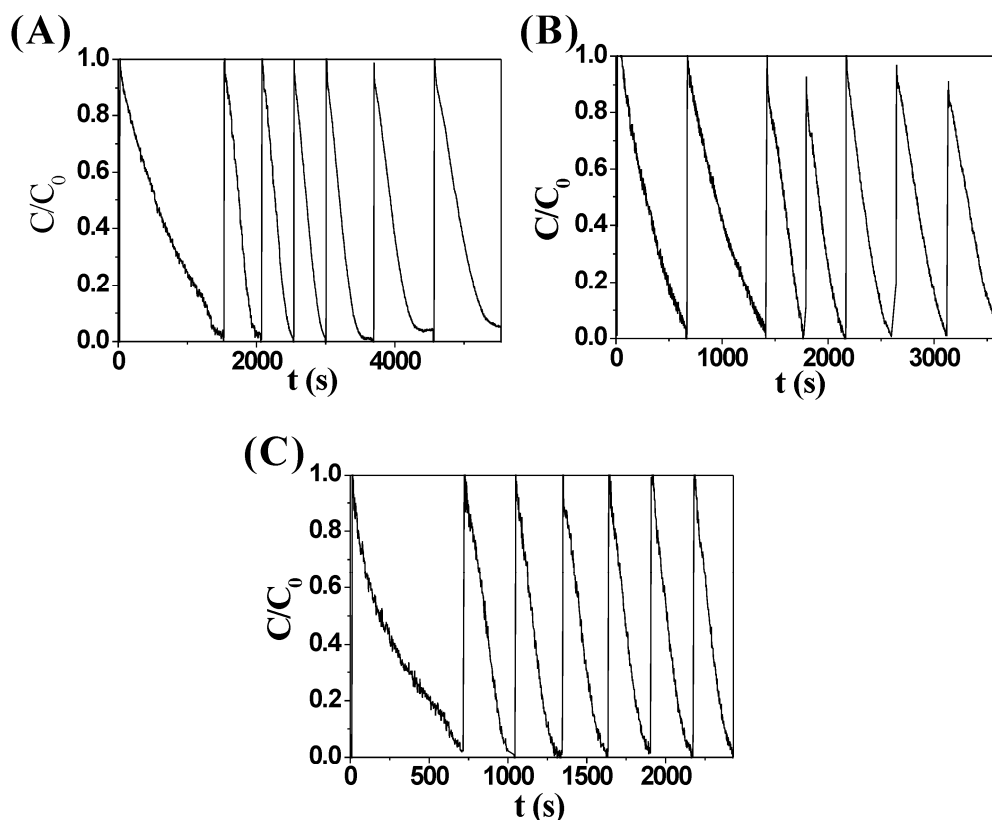


Figure S2. Cycling degradation curve of TiO_2 nanosheets with different percentages of the (001) facets: (A) 68%, (B) 77%, (C) 89%

For TiO_2 nanosheets with 68% exposed (001) facets, it took about 5500 s to circulate photocatalytic measurement seven times (Figure S2-A). And for TiO_2 nanosheets with 77% exposed (001) facets, the time required for a seven-cycling degradation process decreased to 3500 s (Figure S2-B). For TiO_2 nanosheets with 89% exposed (001) facets, the time required was only 2500 s (Figure S2-C). The results indicate that the sample with higher percentage of (001) facets exhibits more effective photocatalytic property, which adequately proved the high photocatalytic activity of the (001) facets of anatase TiO_2 .

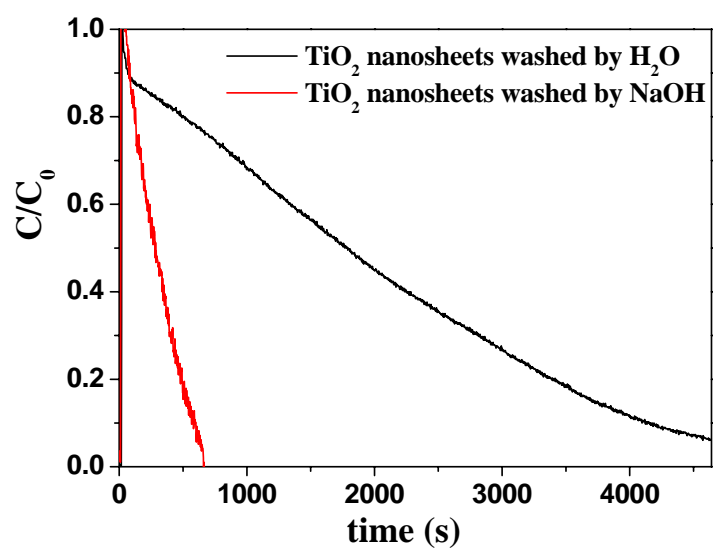


Figure S3. Degradation curves of the TiO₂ nanosheets washed with de-ionized water (the black curve) and 0.1 M NaOH (the red curve).

The photocatalytic efficiency of as-synthesized TiO₂ nanosheets was greatly improved by the washing treatment with 0.1 M NaOH.