

Supporting Information

A Micrometer-Size TiO₂ Single Crystal Photocatalyst with Remarkable 80 % Level of Reactive Facets

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Experimental Section

In a typical synthesis, 0.02 mol/L titanium tetrafluoride (ACROS) aqueous solution was prepared by dissolving 0.62 g titanium tetrafluoride in 250 mL D.I. water which contains 0.2 mL hydrochloric acid (37 %, MERCK, Germany). Then 1 mL ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([bmin]⁺[BF₄]⁻), purchased from International Laboratory, USA, was added to 30 mL 0.02 mol/L titanium tetrafluoride aqueous solution under stirring. The mixture was sealed in a Teflon-lined double-walled digestion vessel. After treating at 210 °C for 90 min using a microwave digestion system (Ethos TC, Milestone), the vessel was then cooled down to room temperature. The product was collected by centrifugation, washed with deionised water and absolute ethanol, and dried in a vacuum at 80 °C for 4 h.

For comparison, ordinary anatase TiO₂ single-crystals were prepared by adding 5 mL TiCl₄ (ACROS) into a conical flask which contains 40 mL N₂ (l) and 15 mL H₂O. After evaporation of N₂ (l), the clear colourless TiCl₄ solution was used as the stock solution. Then 2 mL stock solution and 2 mL 1-methylimidazolium tetrafluoroborate were added into 48 mL D.I. water under stirring. After treating at a controllable temperature of 210 °C for 90 min using a microwave digestion system (Ethos TC, Milestone), the solution was then cooled down to room temperature. Finally,

the product was collected by centrifugation, washed with deionised water and absolute ethanol, and dried in a vacuum at 80 °C for 4 h.

The photocatalytic activities of the anatase TiO₂ single-crystals were measured by the degradation of 4-chlorophenol in an aqueous solution. The photodegradation experiments were carried out at 25 °C in a 150 ml reactor containing 0.08 g catalyst calcined at 600 °C for 90 min and 60 mL of 10 ppm 4-chlorophenol aqueous solution. A 300 W high-pressure mercury vapor lamp was used as the UV light source, which was mounted at 5 cm around the solution. Vigorous stirring (900 rpm) was employed to ensure the adsorption equilibrium and to eliminate any diffusion effect. The equilibrium 4-chlorophenol concentration was used as the initial concentration of 4-chlorophenol.

The photocatalysis was started by irradiating the reaction mixture with UV light. The reaction time was 2 h. The concentrations of 4-chlorophenol and its degradation products were measured with a HPLC system (Waters Baseline 810) with a Waters 486 tunable UV absorbance detector. A Supelco LC-18-DB column (250 mm×4.6 mm) was applied. The eluent consisted of a 40:60 methanol:water mixture, and the flow rate was 1 mL/min. The aromatic compounds were detected at 220 nm. Millipore discs were used to separate the catalysts before analysis of the solution [W. K. Ho and J. C. Yu, *J. Mol. Catal. A*, 2006, **247**, 268.]. The reproducibility was checked by repeating the runs at least three times and was found to be within acceptable limits (±5 %). The blank experiment shows the 4-chlorophenol degradation was less than 2 %. Conventional anatase TiO₂ single crystals were used as a reference to compare the activities under the same experimental conditions.

X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance diffractometer with high-intensity CuK α 1 irradiation ($\lambda = 1.5406 \text{ \AA}$). Transmission electron microscopy (TEM) observations were carried out on a Tecnai F20 microscope (FEI, 200 kV). The general morphology of the products was characterized by scanning electron microscopy (FEI Quanta 400 FEG microscopes).

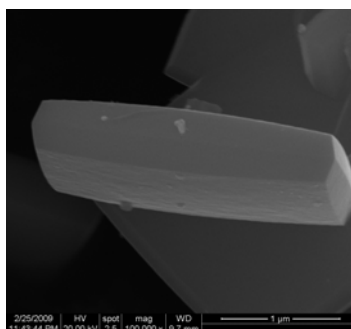


Figure S1. Side-view FESEM images of the anatase single crystals exposed with {001} facets.

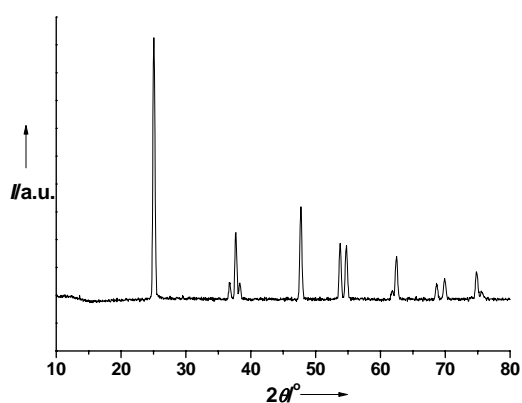


Figure S2. XRD pattern of the anatase single crystal exposed with {001} facets.

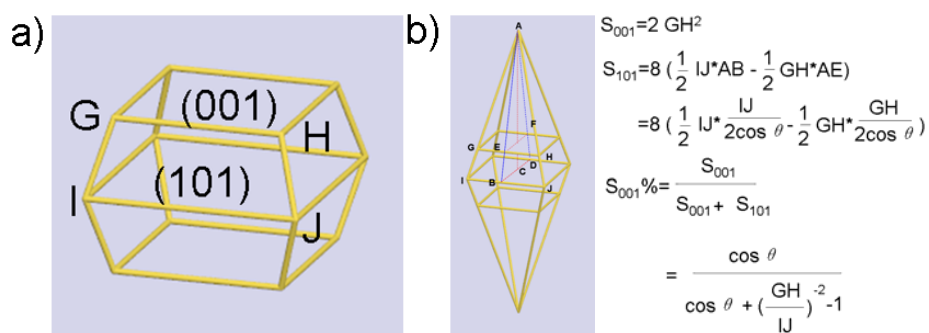


Figure S3. a) Simulated shape of the TiO₂ anatase single crystal samples. b) Equilibrium shape of anatase TiO₂ crystal. c) the calculation process of S₀₀₁% (θ is the theoretical value for the angle between the [001] and [101] facets of anatase, GH/IJ is the degree of truncation).

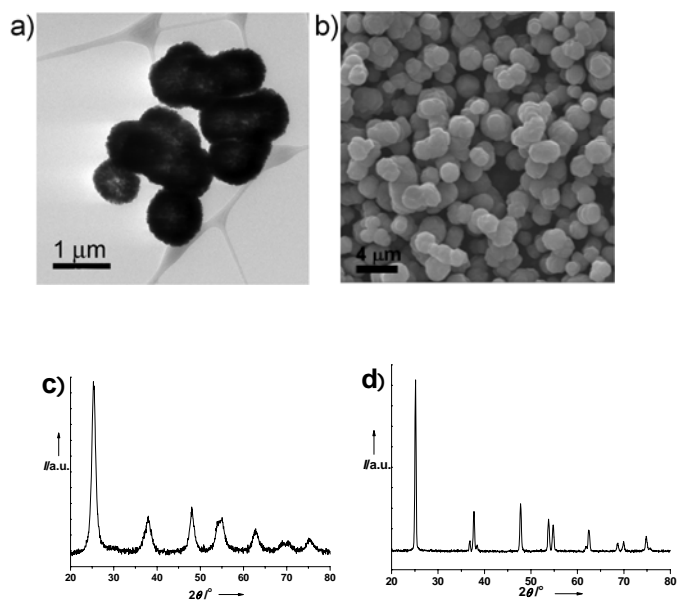


Figure S4. SEM image a) and XRD pattern c) of the anatase hollow spheres prepared without ionic liquid. SEM image b) and XRD pattern d) of the {001} unexposed TiO₂ single crystals.

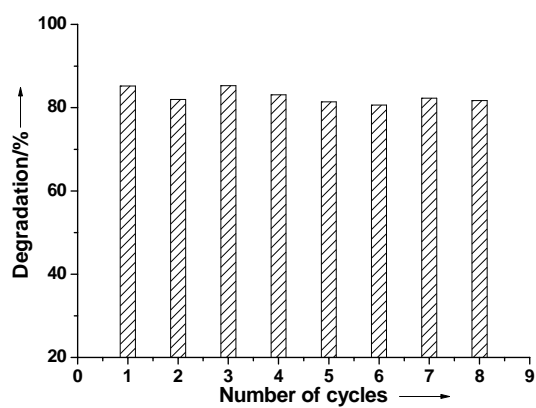


Figure S5. The recycle experiments of anatase TiO₂ single crystal exposed with {001} facets.