

Supporting Information

A New Insight into Regulating High Energy Facets of Rutile TiO₂

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1. Experimental Section

1.1 Synthesis

The rutile TiO₂ single crystals with tunable ratio of (111) and (110) facets were prepared through a facile hydrothermal method. In a typical synthesis, 3.5 M hydrochloric acid (HCl) solution was prepared first, then the reaction solution containing 0.015 M titanium tetrachloride (TiCl₄) was made by dissolving TiCl₄ directly into the HCl solutions under strong stirring in the ice water bath. After that, 60 mL reaction solution was transferred to a teflon-lined autoclave added with 0.015 M sodium fluoride (NaF). The subsequent hydrothermal reaction was carried out at 220 °C for 12 h in an oven. After the reaction, the autoclave was naturally cooled down to room temperature. The products were simply collected by centrifugal separation and washed with deionized water for 4-5 times. Ultimately, the resultant material was dried in a vacuum oven at 80 °C for 24 h. The surface F species were easily removed by heating treatment in air ambience at 600 °C for 2 h. According to the Ti/F molar ratio of reaction precursors to the additive (Scheme 1), these as-prepared products were denoted as R-(1:0), R-(1:0.5), R-(1:1), R-(1:2), R-(1:2.5) and R-(1:3), respectively.

1.2 Photocatalytic test

The photocatalytic activity was measured directly by a fluorescent method, which can examine the concentration of active hydroxyl radicals (\bullet OH) generated by the reaction of photogenerated holes with water or hydroxyl groups under light irradiation. In the reaction, the terephthalic acid (C₈H₆O₄, TA) was used as a fluorescent probe to detect the resultant \bullet OH, since \bullet OH reacts with TA and generates luminescent TAOH ((C₈H₆O₄)OH). In a typical procedure, certain amount of catalyst (28 mg) was added into 280 mL aqueous solution containing 0.01 M NaOH and 3.0 mM terephthalic acid. After being stirred in dark for 1 h, the suspension was irradiated under UV-vis light with a constant rate of air bubbling into the reaction solution. In the reaction process, 6.0 mL of solution was taken out every 30 min and

centrifugated to separate the catalyst. The upper clear liquid was tested through a Hitachi F-4500 FL spectrophotometer. The excitation wavelength used in the fluorescence test is 320 nm. A 500 W Xe lamp was applied in the reaction as the light source with a wide range of wavelengths from 220 to 770 nm.

1.3 Characterization

The structure of the as-prepared rutile TiO₂ single crystals were investigated by X-ray spectroscopy (XRD, Bruker D8 Advanced Diffractometer with Cu Ka radiation (40 kV, 40 mA)) and performed in an angle range of 10–80°. The surface morphology of the as-prepared specimens were characterized by field emission scanning electron microscopy (FESEM, LEO 1530 VP) at an acceleration voltage of 15 kV. The selected area electron diffraction (SAED) patterns and high resolution transmission electron microscopy (HRTEM) images were all taken in a JEOL JEM-2100HR at 200 kV. The chemical composition of the samples were analyzed by X-ray photoelectron spectrum (XPS, Kratos AXis Ultra DLD equipped with Al Ka X-ray (hν=1486.6 eV) at 15 kV and 150 W) and all the XPS spectra were calibrated by the C 1s signal to the binding energy of 284.6 eV.

2 supplementary figures

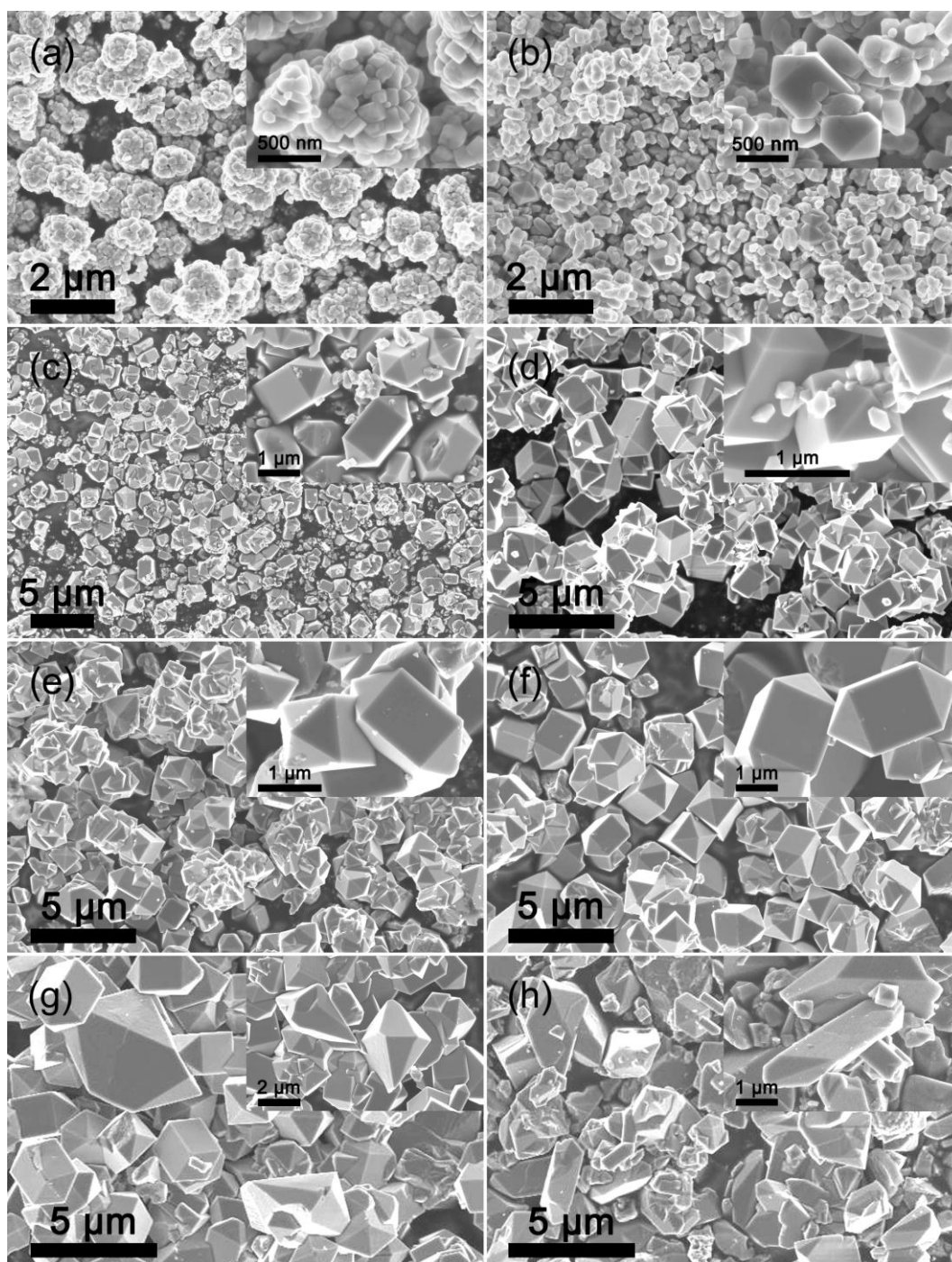


Figure S1. FESEM images of TiO_2 synthesized at 220 °C for 12 h with 0.015 M NaF in different concentrations of HCl solution: (a) 0.5 M, (b) 1.0 M, (c) 2.0 M, (d) 2.5 M, (e) 3.0 M, (f) 3.5 M, (g) 4.0 M and (h) 5.0 M. The insets of (a), (b), (c), (d), (e), (f), (g) and (h) are the corresponding high resolution FESEM images.

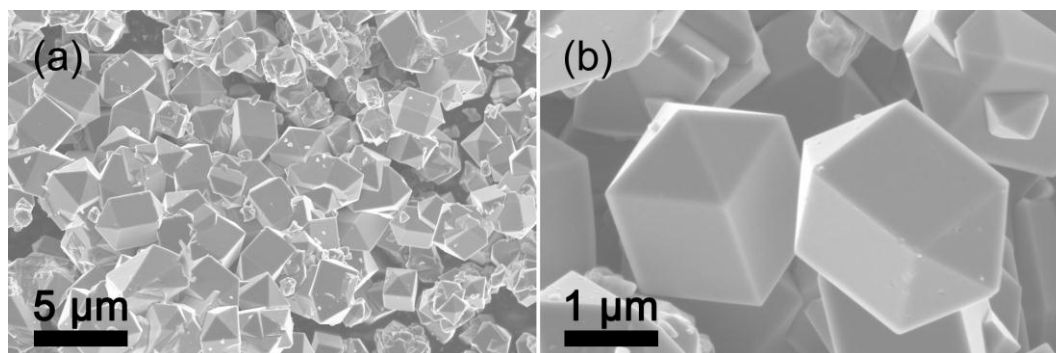


Figure S2. (a) Low FESEM images of R-(1:1) after heat treatment at 600 °C in air ambience for 2 h; (b) the corresponding high resolution FESEM images.

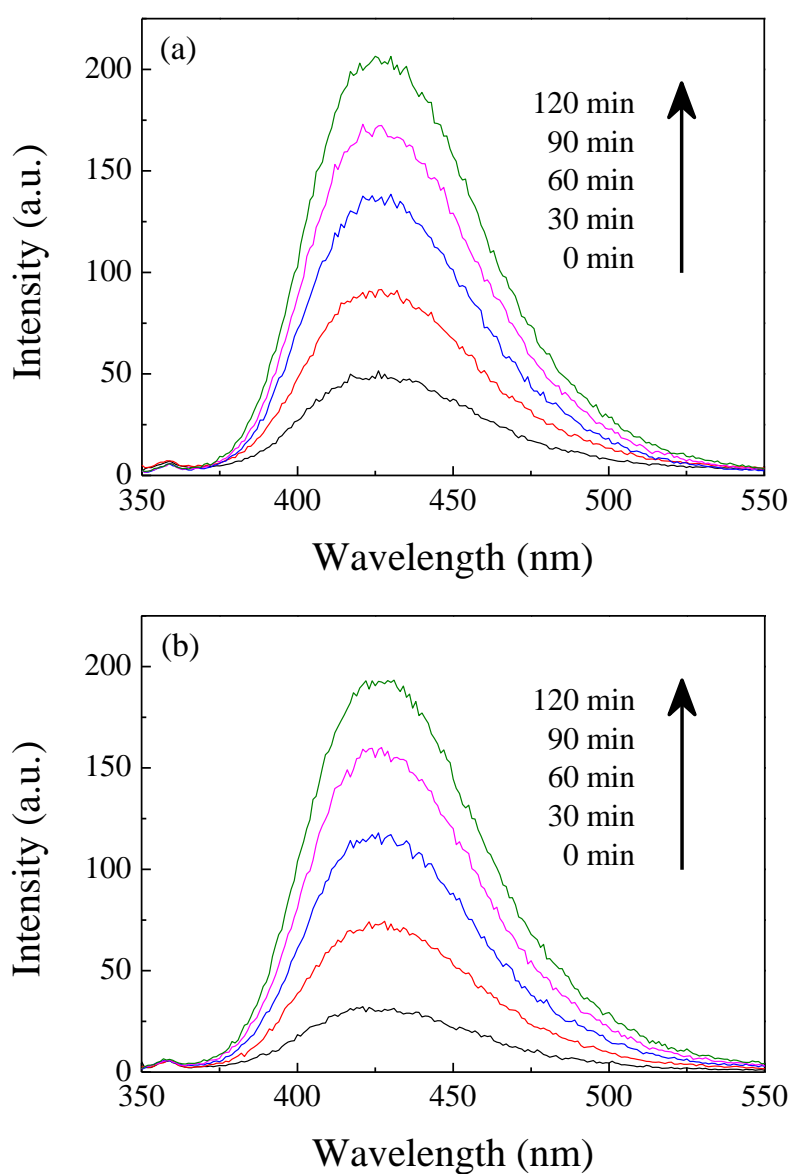


Figure S3. Fluorescence spectra of UV light irradiation of R-(1:0.5) (a) and R-(1:1) (b) samples in 3 mM terephthalic acid and 0.01 M NaOH solution at different irradiation times.