

## Supporting Information

### Nanosized Anatase TiO<sub>2</sub> Single Crystals for Enhanced Photocatalytic Activity

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#### Experimental Section

##### Sample synthesis of nanosized anatase TiO<sub>2</sub> with preferential {001} facets.

Hydrofluoric acid (HF) (50 wt%, very corrosive!) was used to obtain 0.2 M HF solution. A certain amount of titanium sulfate (Ti(SO<sub>4</sub>)<sub>2</sub>) precursor was then dissolved in 0.2 M HF solution to a concentration of 100 mM. In a typical synthesis route, 40 mL of Ti(SO<sub>4</sub>)<sub>2</sub> aqueous solution was transferred to a Teflon-lined autoclave, and treated at 180 °C for 22 h. After reaction, the products were collected by centrifugation method and washed with de-ionized water 3 times to remove dissoluble ionic impurities. Then the samples were dried at 80 °C in air for 12 h.

**Micron sized anatase TiO<sub>2</sub> sheets with preferential {001} facets.** A certain of titanium sulfate (Ti(SO<sub>4</sub>)<sub>2</sub>) precursor was then dissolved in 0.2 M HF solution to a concentration of 10 mM. In a typical synthesis route, 40 mL of Ti(SO<sub>4</sub>)<sub>2</sub> aqueous solution was transferred to a Teflon-lined autoclave, and treated at 180 °C for 22 h. After reaction, the products were collected by centrifugation method and washed with de-ionized water 3 times to remove dissoluble ionic impurities. Then the samples were dried at 80 °C in air for 12 h.

**Surface fluorine removal from as-prepared anatase TiO<sub>2</sub>.** The powder samples of as-prepared nanosized/micron sized anatase TiO<sub>2</sub> with preferential {001} facets were heated at 600 °C in static air atmosphere in a furnace for 2 h. Then, the samples were naturally cooled to room temperature.

**Co-catalyst loading.** Pt species loading was conducted by an impregnation method from an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O. A sample of TiO<sub>2</sub> was added into aqueous solution containing a desirable amount of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (1 mg·mL<sup>-1</sup> Pt) in an evaporating dish at 60 °C. The suspension was evaporated under constant stirring with a glass rod, and the resulting powder was collected and heated in air at 180 °C.

**Characterization.** X-ray diffraction (XRD) patterns of the samples were recorded on Rigaku diffractometer using Cu irradiation. Their morphology and crystalline structure were determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) performed on JEOL (6300) and Tecnai F30, respectively. The Brunauer-Emmett-Teller (BET) surface area was determined by nitrogen adsorption-desorption isotherm measurements at 77 K (ASAP 2010). Raman spectra were collected with LabRam HR 800. Chemical compositions and valence band spectra of TiO<sub>2</sub> were analyzed using X-ray photoelectron spectroscopy (Thermo Escalab 250, a monochromatic Al K<sub>α</sub> X-ray source). All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon. The optical absorbance spectra of the samples were recorded in a UV-visible spectrophotometer (JACSCO-550).

**Photoactivity Tests.** 5 mg of photocatalyst was suspended in 80 mL aqueous solution containing 0.01 M NaOH and 3 mM terephthalic acid. Before exposure to light

irradiation, the suspension was stirred in dark for 30 min. Then 5 mL of the solution was taken out after 25 min, and centrifuged for fluorescence spectrum measurements. During the photoreactions, no oxygen was bubbled into suspension. A fluorescence spectrophotometer (Hitachi, F-4500) was used to measure the fluorescence signal of the 2-hydroxy terephthalic acid generated. The excitation light employed in recording fluorescence spectra was 320 nm. The light source was a 300 W Xe lamp (Beijing Trusttech Co. Ltd, PLS-SXE-300UV), whose emission spectrum is given in Fig. S11.

**Water-splitting Tests.** Water splitting reactions were carried out in a top-irradiation vessel connected to a glass closed gas circulation system. 100 mg of the photocatalyst powder was dispersed in 300 ml aqueous solution containing 10% methanol in volume. The reaction temperature was maintained at between 4 °C and 9 °C. The light source was a 300 W Xe lamp. The amount of H<sub>2</sub> evolved was determined using a gas chromatography (Agilent Technologies: 6890N). The detailed schematic of water splitting measurement equipment can be found in the reference [S1].

### ***Computational Methods and Reliability***

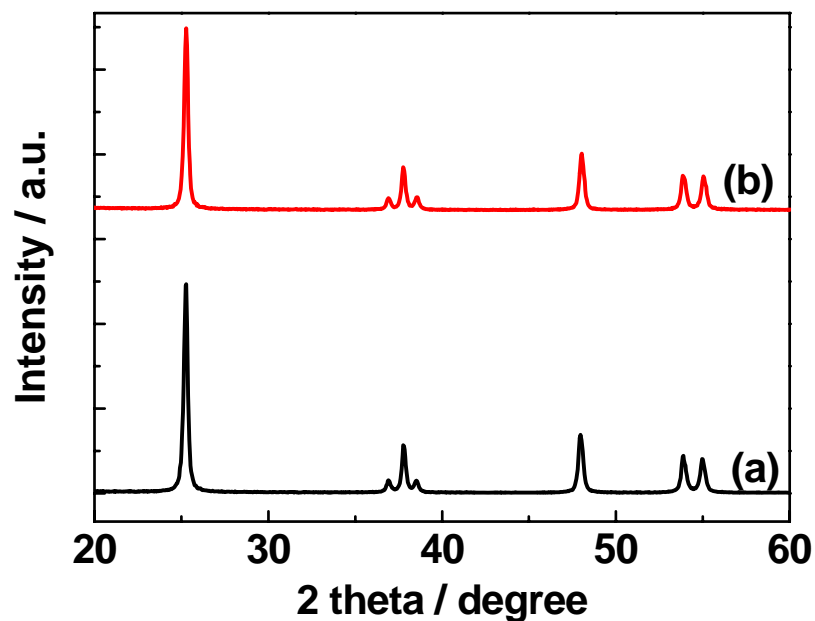
**Computational parameters.** Spin-polarized Density functional theory (DFT) calculations have been carried out using the DMol3 code [S2, S3]. The generalized gradient approximation (GGA) with the functional of Perdew–Burke–Ernzerhof functional (PBE) [S4] was utilized for all geometric optimization and single-point energy calculations. Effective core potentials with double-numeric quality basis and all electron potentials with double-numeric polarized basis have been employed for the description of core electrons during the optimization and the energy calculation, respectively. During our calculations, the convergence criteria for structure optimizations were set to (1) energy tolerance of  $1.0 \times 10^{-6}$  Ha per atom, (2) maximum force tolerance of  $1.0 \times 10^{-4}$  Ha/Å and (3) maximum displacement tolerance of  $1.0 \times 10^{-3}$  Å. The parameters for self-consistent field iterations for optimizations (*energy calculations*) are set as: (1) energy tolerance of  $5.0 \times 10^{-6}$  Ha ( $1.0 \times 10^{-6}$  Ha) and (2) Monkhorst-Pack **k**-point sampling: 3×3 (5×5). Larger sets of k points were tested, making sure that there is no significant change in the calculated energies when a larger number of k points were used.

**Structural models.** In our calculation (001) surface is modeled by 2×2 slabs with 12 atomic layers, with a vacuum of 15 Å between neighboring slabs. During the geometric optimization, no atom is fixed, except that lattice parameters *a*, *c* and *u* were fixed to experimental values. Details about the calculation of surface energies can be found in our previous publication Ref. 4.

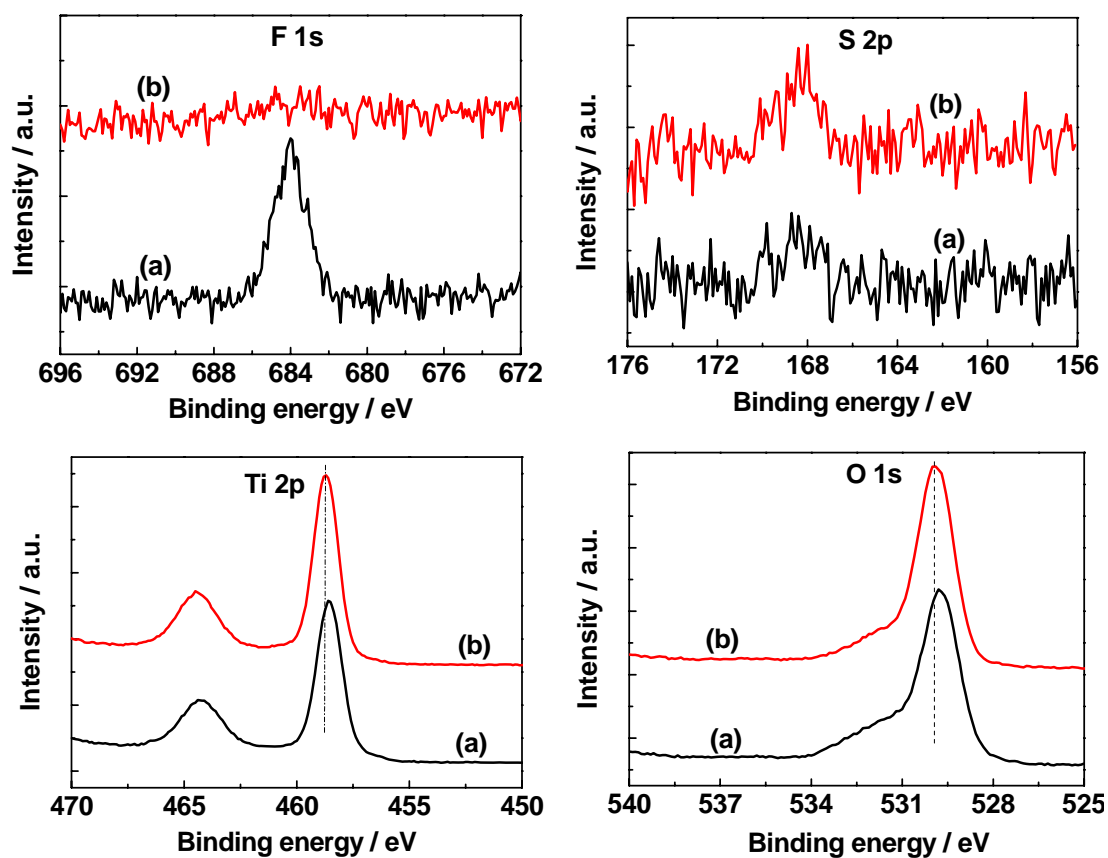
**Reliability test.** With using the above parameters, the cohesive energy per TiO<sub>2</sub> for bulk anatase TiO<sub>2</sub> is 21.599 eV, which is highly consistent with the literature (like 21.60 eV in Ref. 4 and 21.54 eV in [S5]). In addition, for clean (001) and (101) surfaces, the calculated surface energies are 0.96 J/m<sup>2</sup> and 0.41 J/m<sup>2</sup>, which are also highly consistent with Ref. 4 and Ref. [S4]. The size of slab models is also tested. For clean (001) surfaces, calculated surface energies for 1×1, 2×2 and 4×4 slabs are 0.98 J/m<sup>2</sup>, 0.96 J/m<sup>2</sup> and 0.90 J/m<sup>2</sup>, suggesting that 2×2 slab used in this work is good enough for our analysis.

## References

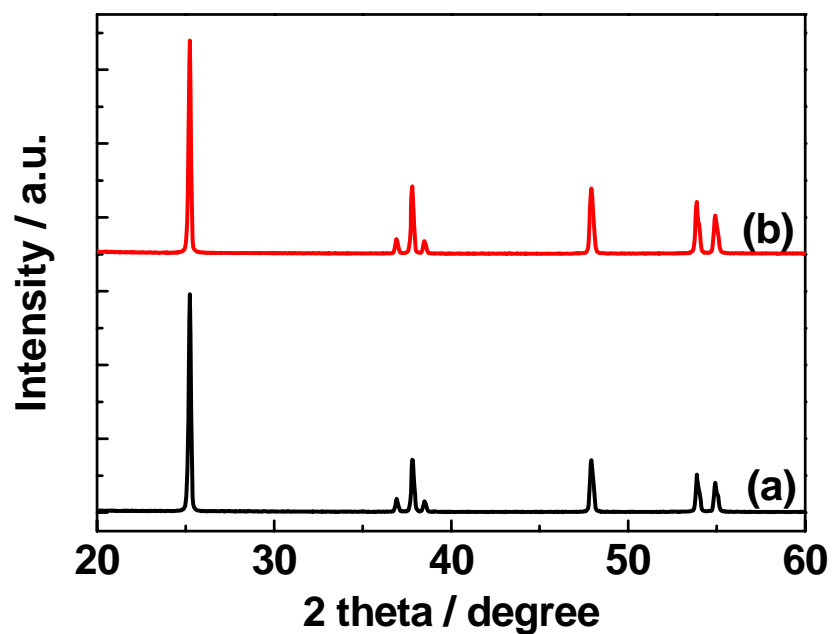
- [S1] X. W. Wang,; G. Liu, Z. G. Chen, F. Li, L. Z. Wang, G. Q. Lu, H. M. Cheng, *Chem. Commun.* **2009**, 3452.
- [S2] B. Delley, *J. Chem. Phys.* **1990**, 92, 508.
- [S3] B. Delley, *J. Chem. Phys.* **2000**, 113, 7756.
- [S4] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. B.* **1996**, 77, 3865.
- [S5] M. Lazzeri, M., A. Vittadini, A. Selloni. *Phys. Rev. B* **2001**, 63, 155409



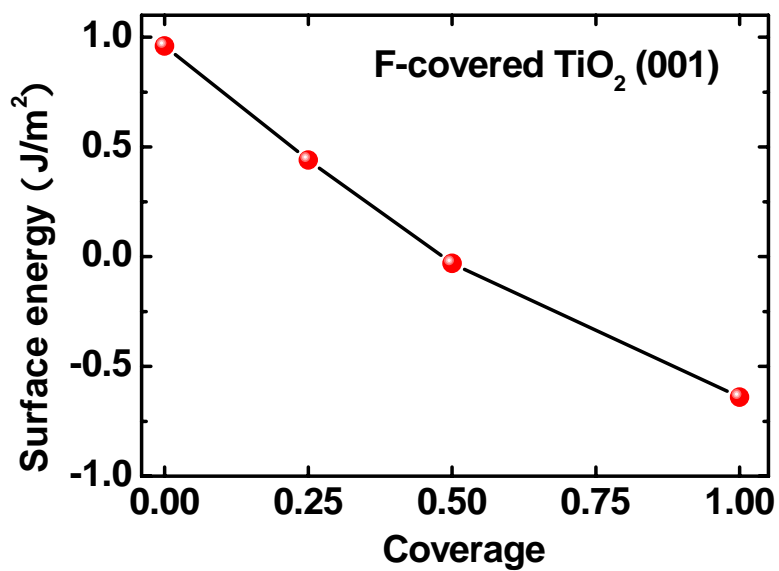
**Fig. S1** XRD patterns of (a) as-prepared nanosized anatase TiO<sub>2</sub> with preferential {001} facets and (b) calcined nanosized anatase TiO<sub>2</sub> with preferential {001} facets.



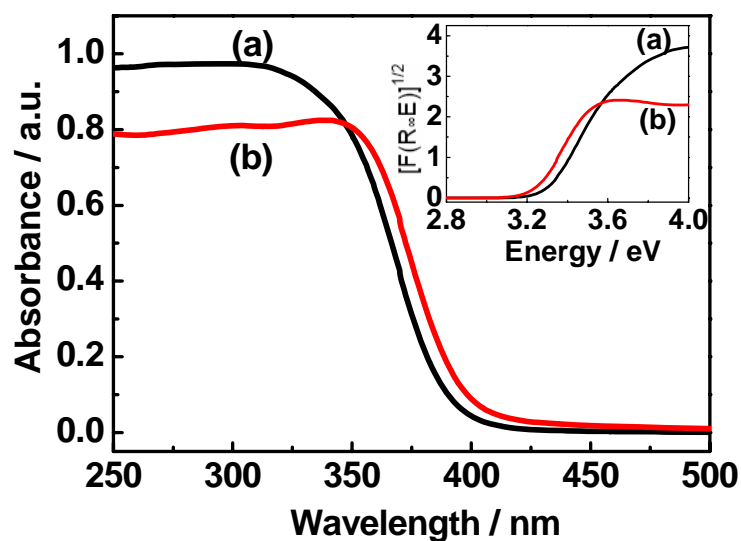
**Fig. S2** High resolution XPS spectra of F 1s, S 2p, Ti 2p and O 1s in (a) as-prepared and (b) calcined nanosized anatase TiO<sub>2</sub> with preferential {001} facets.



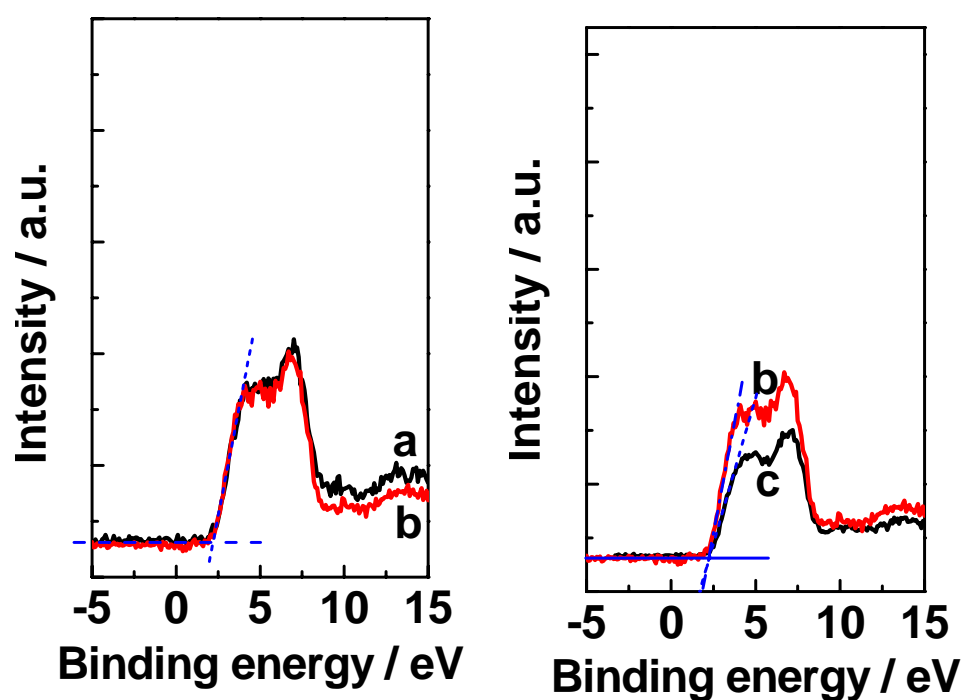
**Fig. S3** XRD patterns of (a) as-prepared and (b) calcined micron sized anatase TiO<sub>2</sub> sheets with preferential {001} facets.



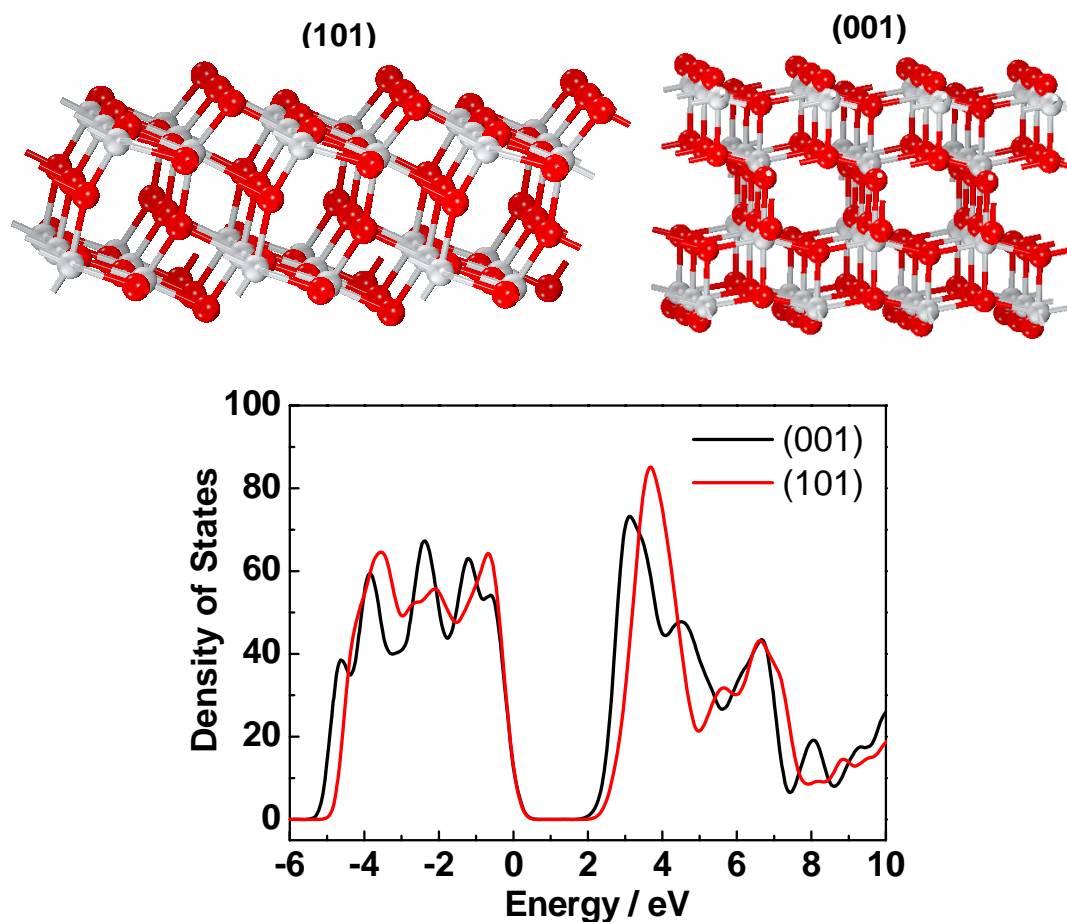
**Fig. S4** Surface energy of (001) terminated with different amount of F.



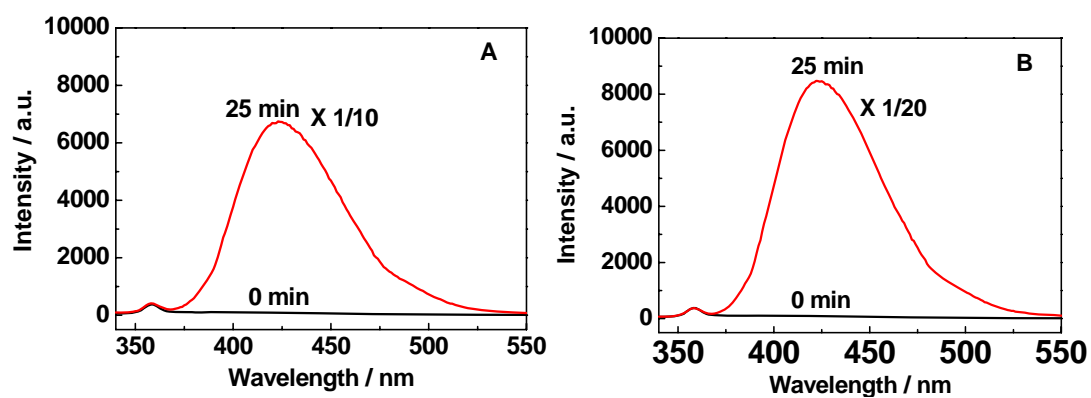
**Fig. S5** UV-visible absorption spectra of calcined nanosized (a) and micron sized (b) anatase  $\text{TiO}_2$  with preferential  $\{001\}$  facets, and the inset is their corresponding plots of transformed Kubelka-Munk function versus the energy of light.



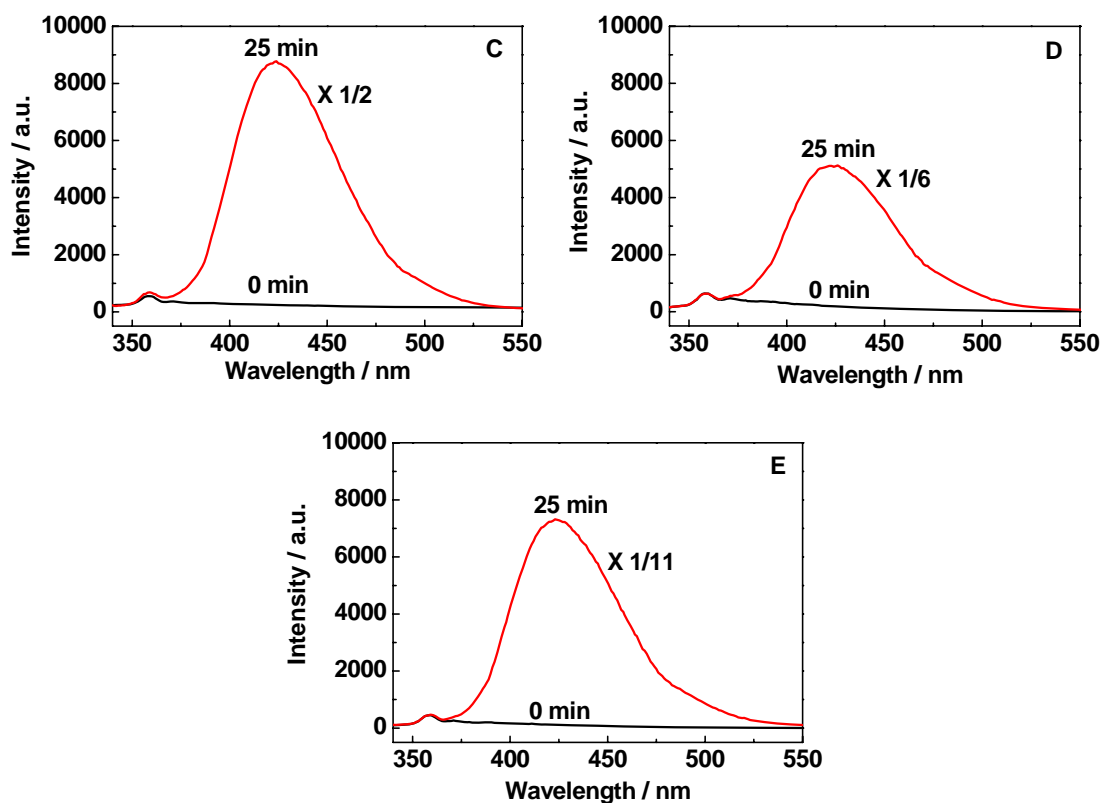
**Fig. S6** XPS valence band spectra of (a) as-prepared and (b) calcined nanosized anatase  $\text{TiO}_2$  with preferential  $\{001\}$  facets, (c) calcined micron sized anatase  $\text{TiO}_2$  with preferential  $\{001\}$  facets.



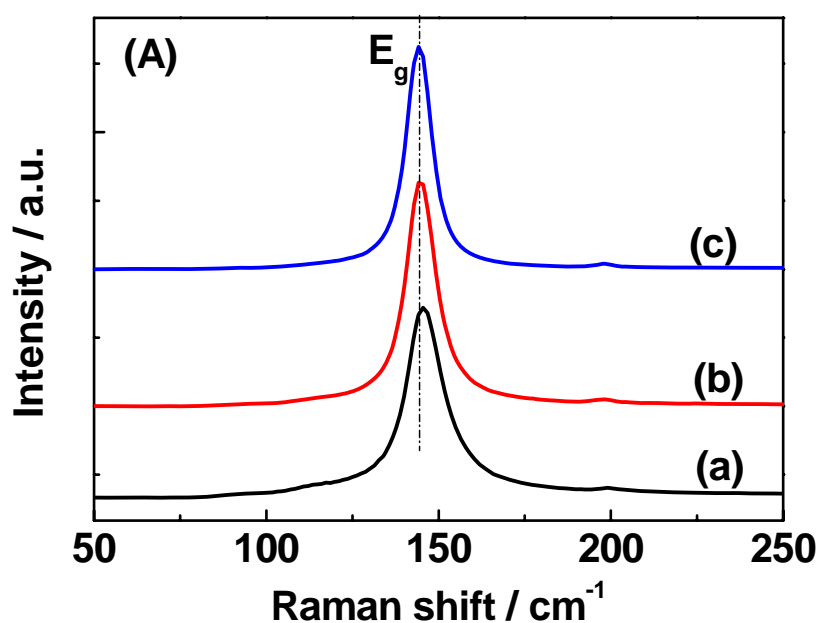
**Fig. S7** Structure modes and calculated density of states for (101) and (001) surface. Oxygen and titanium atoms are indexed by red and grey spheres, respectively.

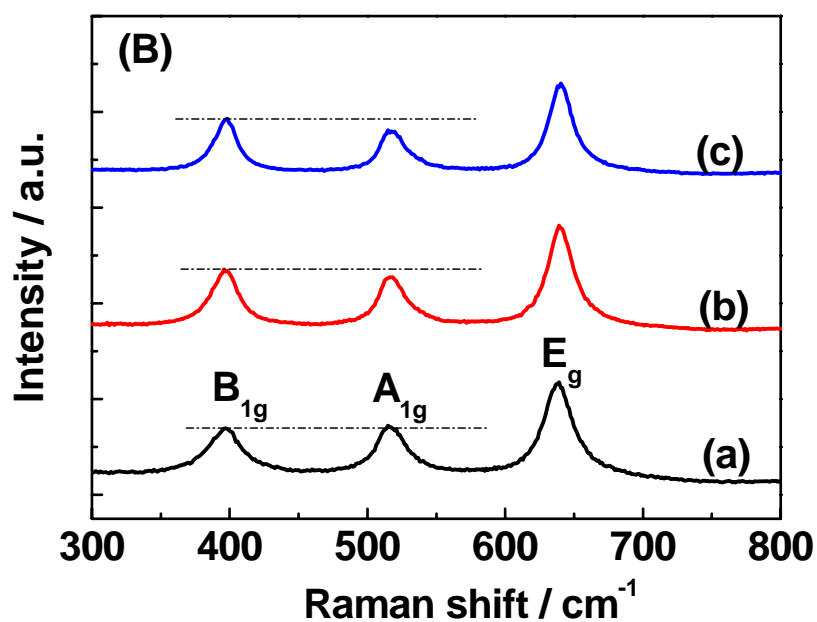




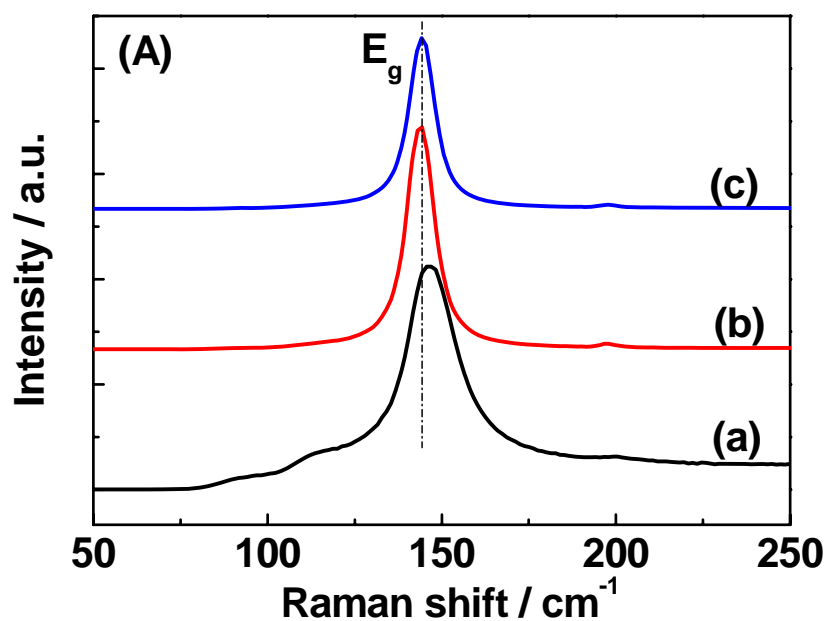


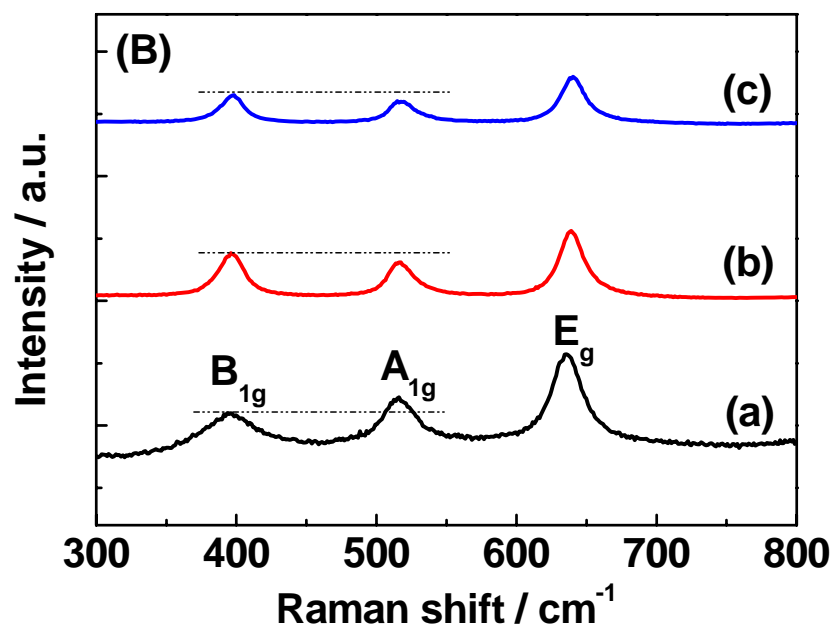
**Fig. S8** Fluorescence spectra of 2-hydroxy terephthalic acid (TAOH) solution generated by anatase TiO<sub>2</sub> with preferential {001} facets: (A) nanosized with surface fluorine termination, (B) nanosized with surface fluorine-free, (C) micron-sized with surface fluorine termination, (D) micron-sized with surface fluorine-free and (E) reference mesoporous TiO<sub>2</sub> in 3 mM terephthalic acid (TA) irradiated by UV-visible light at different irradiation time.



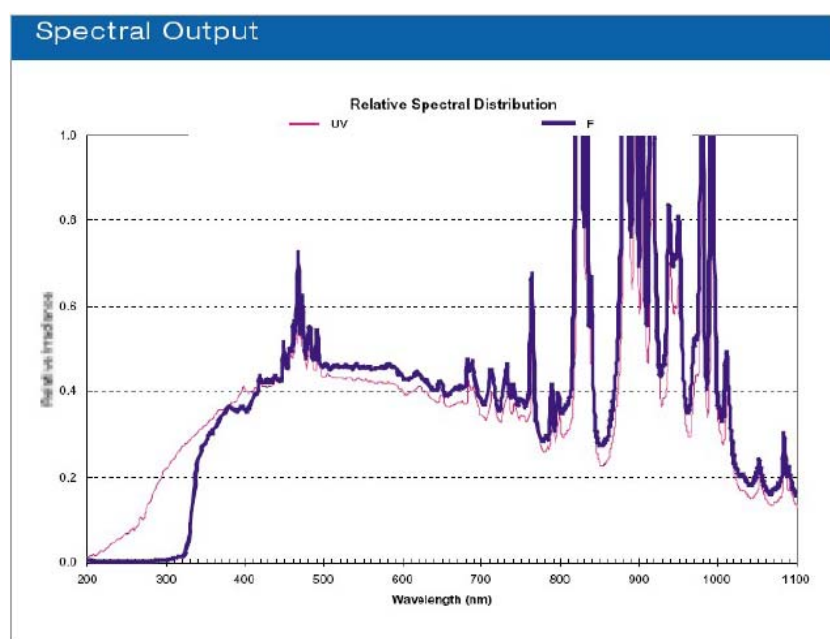


**Fig. S9** Raman spectra between (A) 50~250 cm<sup>-1</sup>, (B) 300~800 cm<sup>-1</sup> of (a) as-prepared, (b) calcined nanosized anatase TiO<sub>2</sub> with preferential {001} facets, and (c) reference anatase TiO<sub>2</sub> without preferential {001} facets (Aldrich, Product No. 232033).





**Fig. S10** Raman spectra between (A) 50~250  $\text{cm}^{-1}$ , (B) 300~800  $\text{cm}^{-1}$  of (a) as-prepared, (b) calcined micron sized anatase  $\text{TiO}_2$  with preferential {001} facets, and (c) reference anatase  $\text{TiO}_2$  without preferential {001} facets (Aldrich, Product No. 232033).



**Fig. S11** The emission spectrum (dark blue one) of the Xe lamp employed in the photoactivity measurement.