

Supporting Information

A simple preparation of nitrogen doped titanium dioxide nanocrystals with exposed (001) facets with high visible light activity

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Preparation of samples. In a typical synthesis, 500 mg TiN (Hefei Kaier Nano Company (China)) was added to a 30 ml of 2 M NaBF₄ and hydrochloric acid aqueous solution. The mixture was stirred for 30 min and then transferred into a 100 ml Teflon-lined stainless steel autoclave. The autoclave was sealed and put into a preheated oven to perform hydrothermal decomposition treatment at 140 °C for 24 h. After hydrothermal processing, the gray fluffy powder was collected and washed with copious amounts of distilled water and absolute alcohol three times, respectively, then dried in air at 80 °C overnight, and the obtained sample with gray color was denoted as NT-001. In addition, 500 mg of P25 TiO₂ powder (Degussa) was annealed under NH₃ flow at 550 °C for 3 h as a reference sample,^{S1} and was denoted as N-P25. The anatase N-doped TiO₂ powders were prepared as the reference.^{S2} In a typical synthesis, 50 mL of 15% titanium trichloride (48.6 mmol) was slowly dropped into 50 mL of Na₂S solution (51.2 mmol). The pH of this solution was adjusted to 8.5 by NH₃ solution. Then the mixture was continuously stirred for 4 h. The precipitate was filtered and washed with double distilled water until the filtrate was free from chloride and sulfide ions, then dried in air at 80 °C overnight. The oxide was calcined at 500°C for 4 h in air.

Characterization of samples. The crystal structure of samples was characterized by powder X-ray diffraction (XRD) (D/max-III A, Japan) using Cu K α radiation. The morphology was observed with a field-emission scanning electron microscope (FESEM) (LEO1530VP, LEO Company) and a transmission electron microscope (TEM, JEOL, JEM2010). The UV-Vis absorption spectra were measured in a Hitachi UV-3010 spectrophotometer equipped with an integrating sphere assembly and using the diffuse reflection method and BaSO₄ as a reference to measure all the samples. The

Brunauer-Emmett-Teller (BET) surface area (S_{BET}) was determined by nitrogen adsorption-desorption isotherm at 77 K in a Micromeritics ASAP 2010 system. The samples were degassed in vacuum at 473 K until a pressure lower than 10^{-6} Torr before the actual measurements. The X-ray photoelectron spectroscopy (XPS) was performed with Krato Axis Ultra DLD spectrometer (Al Ka X-ray, $h\nu=1486.6$ eV). The binding energy (BE) was calibrated with the reference to C 1s peak at 284.6 eV.

Photocatalytic activity test. The photocatalytic reaction was conducted in a 200 mL cylindrical glass vessel fixed in an XPA-II photochemical reactor (Nanjing Xujiang Machine-electronic Plant). A 500W Xe lamp was used as the simulated solar light source (UV-Visible light), and a house-made filter was mounted on the lamp to eliminate infrared irradiation. The visible-light was obtained by using a cut-off filter made up of 2M sodium nitrite solution, which can absorb the light with wavelength under 400 nm.^{S3} Methylene blue dye (MB) of 20 mg/L was used as contamination. In order to obtain an optimally dispersed system and reach complete adsorption/desorption equilibration, 50 mg photocatalyst powder dispersed in 200 mL reaction solutions by ultrasonicing for 15 min and then the suspension was magnetically stirred in dark for 1 h. During the photocatalytic reaction, air was blown into the reaction medium at a flow rate of 200 mL/min. At regular intervals, 8 mL of the suspension was filtered and then centrifuged. The concentration of the remaining MB was measured by its absorbance (A) at 664 nm with a Hitachi UV-3010 spectrophotometer. The degradation ratio of MB could be calculated by $(A_0-A)/A_0 \times 100\%$.

The terephthalic acid ($\text{C}_8\text{H}_6\text{O}_4$, TA) can be used to confirm the existence of $\cdot\text{OH}$ by fluorescent method, since $\cdot\text{OH}$ reacts with TA and generates luminescent TAOH.^{S4} 50 mg of

photocatalyst were suspended in 160 mL aqueous solution containing 10 mM NaOH and 3 mM terephthalic acid. Before exposure to light, the suspension was magnetically stirred in the dark for 1 h to ensure the establishment of an adsorption/desorption equilibrium. The photoreaction was carried out as the foregoing photocatalytic reaction under visible light without oxygen bubbled into suspension. After photoreaction of 1h, 8 mL suspensions was collected, filtered and centrifuged to remove the photocatalyst particles. A fluorescence spectrophotometer (SPEX Fluoromax-2) was used to measure the fluorescence signal of the 2-hydroxy terephthalic acid generated. The excitation light used in recording fluorescence spectra was 320 nm.

Photocurrent test. To prepare the working electrodes, 250 mg of the hydrothermal treated NT-001 or N-P25 samples was first dispersed into a mixture of 2.0 ml ethanol and 0.1 ml terpinol and sonicated for 30 min to form a slurry, then the resulting slurry was coated on FTO glass (2.3 mm, 15 Ω /square, Nippon Sheet Glass, Japan) using a screen-printing method. The TiO₂ film thickness is dependent on the repeating times of the screen printing process. The TiO₂ films were sintered at 500 °C for 30 min in air. The photocurrents were measured using a standard three electrodes photoelectrochemical cell in an electrochemical workstation (CV-27, BAS). The as-prepared photocatalysts, platinum-gauze and Ag/AgCl were used as working, counter and reference electrode, respectively. A sodium sulfate solution (1 M) was used as electrolyte. The chopped (\approx 0.25 Hz) light for the photocurrent operation was the filtered light ($\lambda > 400$ nm, 150 mW/cm²) from a PLS-SXE300UV Xe lamp (Changtuo, Beijing).

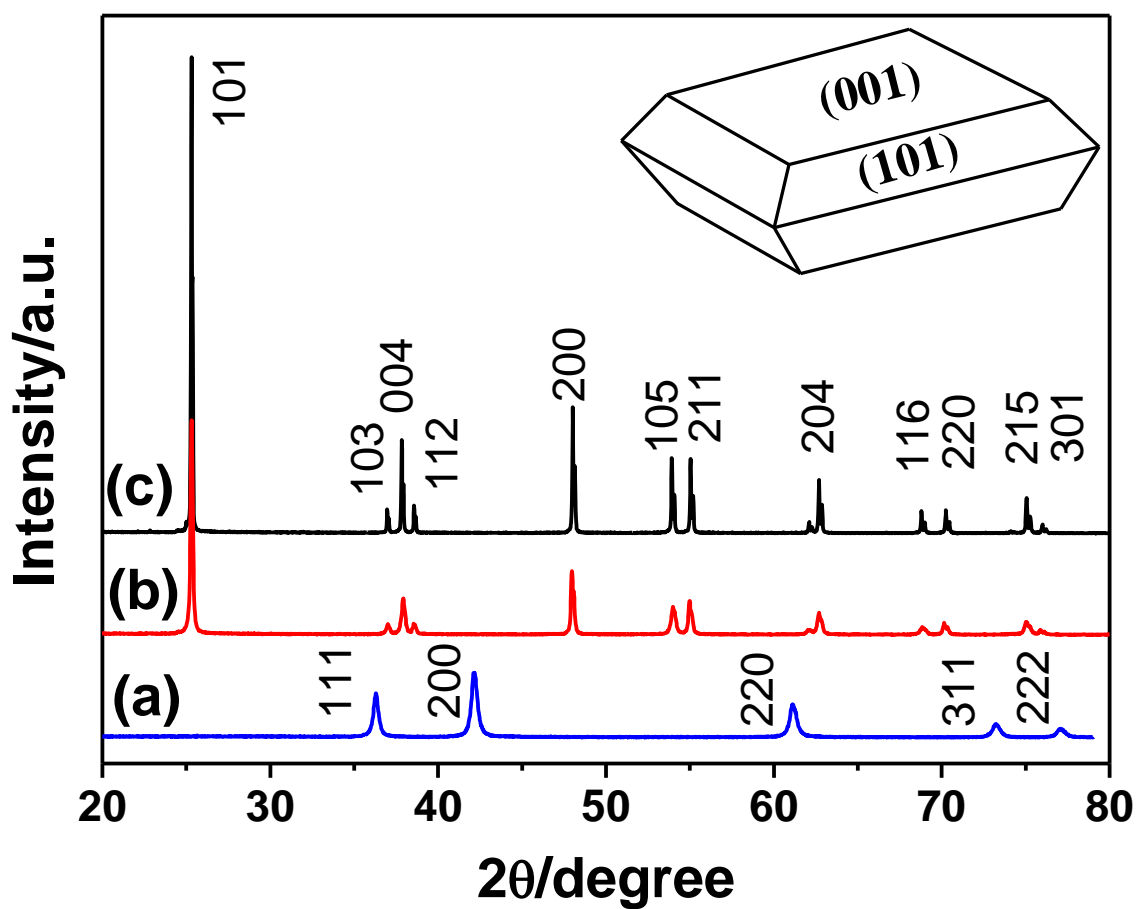


Figure S1. XRD patterns of (a) TiN, (b) raw NT-001 and (d) raw NT-001 after annealing at 500 °C for 2h. The insert is the 2D model of an anatase TiO₂ decahedral nanocrystal with dominant (001) facets.

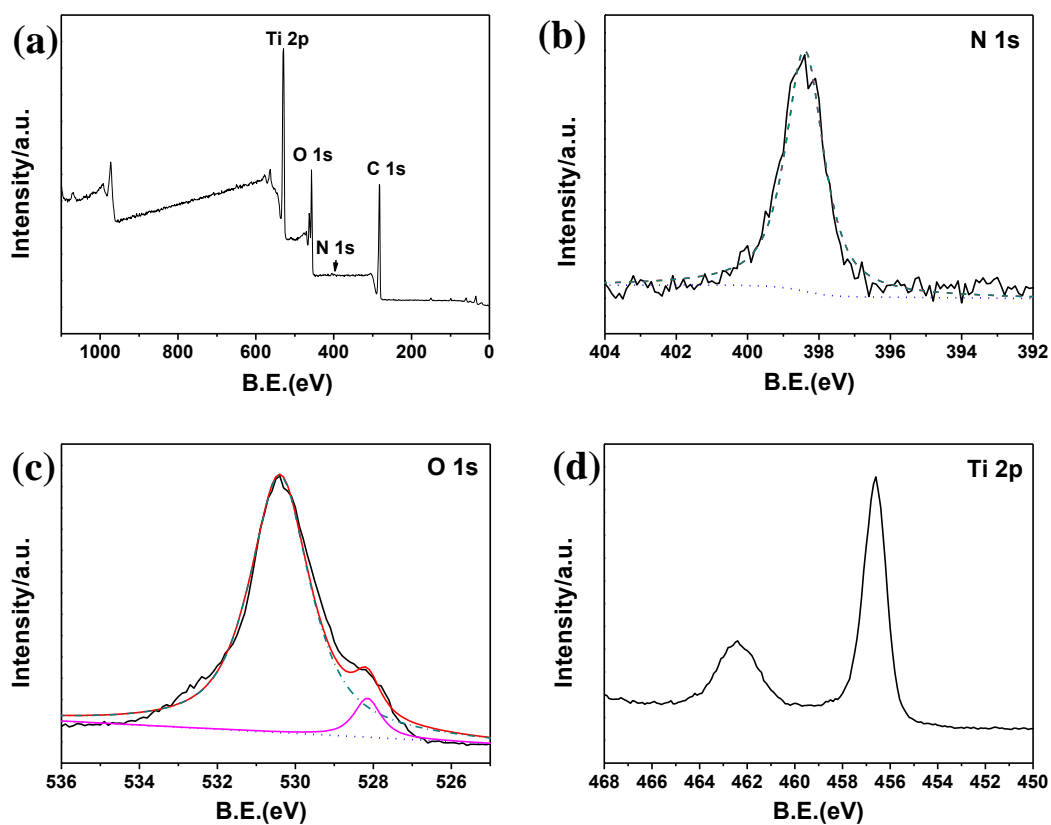


Figure S2 The XPS patterns of the annealed NT-001: (A) survey; (B) N 1s; (C) O 1s; (D) Ti 2p.

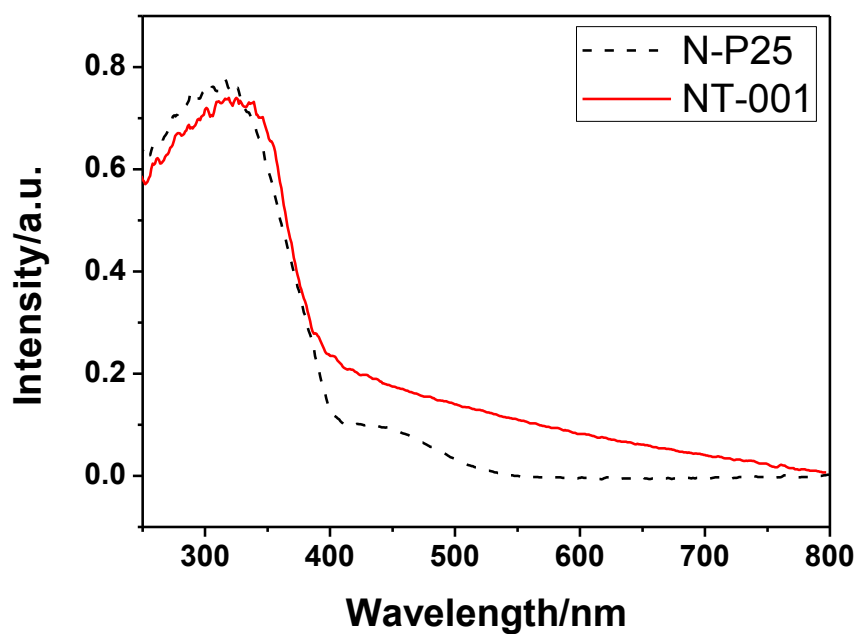


Figure S3 The DRS patterns of as-prepared samples

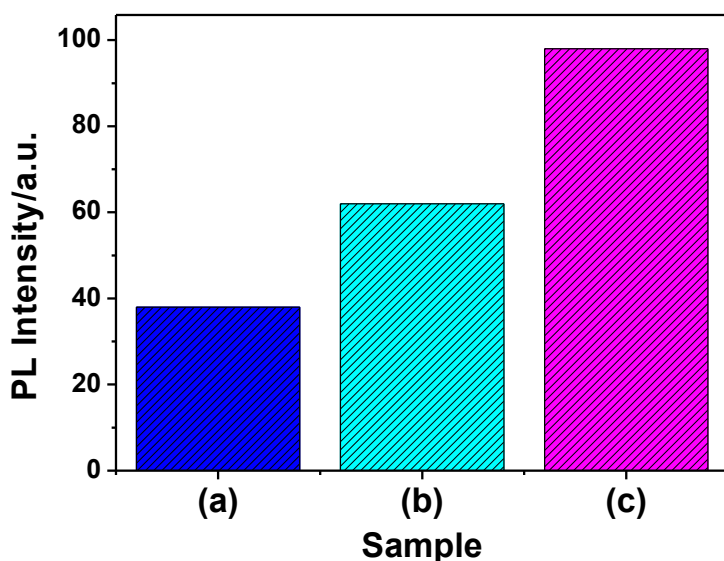


Figure S4 Fluorescence signal intensity of TAOH at 426 nm: (a) N-P25(TiO₂); (b) raw NT-001; (c) NT-001 after annealing at 500 °C for 2h.

The terephthalic acid (C₈H₆O₄, TA) can be used to confirm the existence of •OH by fluorescent method, since TA reacts with •OH and gives highly luminescent TAOH (•OH + TA → TAOH). TA was used as a sensitive probe for the detection of •OH. The intensity of emission band at 426 nm that originates from TAOH indicates the amount of •OH produced by the samples under visible light. As shown in [Figure S4](#), the order of fluorescent intensity is: annealed NT-001 > raw NT-001 > N-P25, which is in good agreement with the degradation ratio under visible light. The TA probe confirms that the photogenerated holes left in the valence band of NT-001 can oxidize hydroxyl to give •OH under visible light.

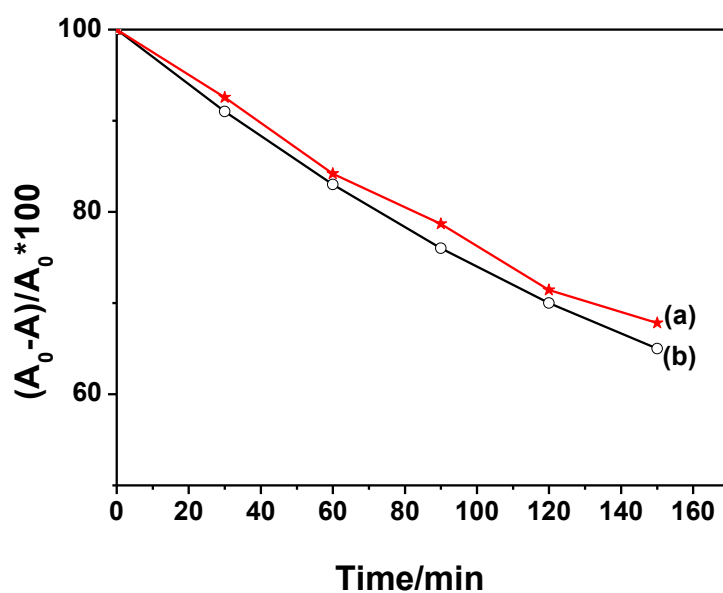


Figure S5 Photocatalytic activities of samples in visible light irradiation: (a) N-doped anatase
TiO₂ without dominant (001) facets; (b) N-P25

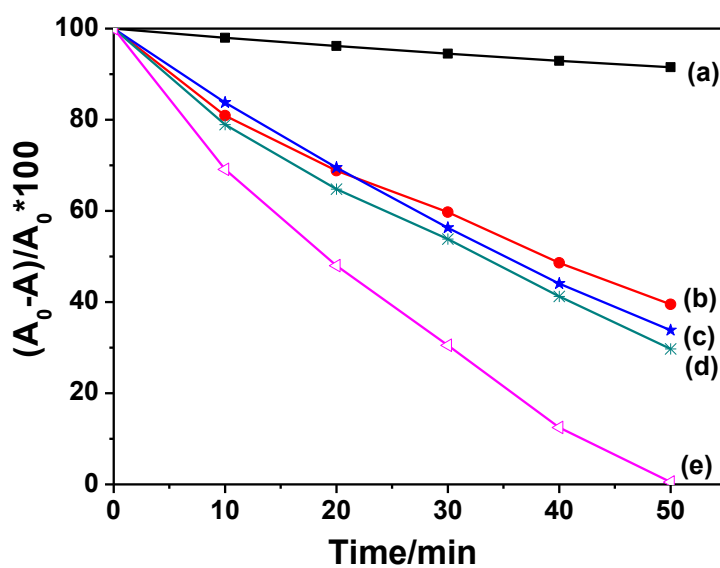


Figure S6 Photocatalytic activities of samples in UV-visible light irradiation: (a) no catalyst;
(b) P25; (c) N-P25; (d) raw NT-001; (e) raw NT-001 after annealing at 500 °C for 2h.

Supplementary references

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- S2. M. Sathish, B. Viswanathan, R. P. Viswanath, Chinnakonda S. Gopinath, *Chem. Mater.*, 2005, **17**, 6349.
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