

Nitrogen self-doped nanosized TiO₂ sheets with exposed {001} facets for enhanced visible-light photocatalytic activity

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Experimental

Synthesis of titania samples. The titanium nitride (TiN) powder used in this study was reagent-grade supplied by Alfa Aesar Co., Ltd. All other reagents were analytical-grade and were purchased from Shanghai Chemical Regent Factory of China without further treatment. Distilled water was used in all experiments. N-doped TiO₂ nanosheets (NTNs) were prepared by an solvothermal method using TiN as a titania precursor. In a typical synthesis, 0.2 g of TiN powder, 30 mL of absolute ethanol, 3 mL of 65 wt% nitric acid solution and 1.0 mL of 40 wt% hydrofluoric acid solution were mixed in a dried 50 mL Teflon-lined autoclave at room temperature, and then kept at 180 °C for 24 h. After cooling this autoclave to room temperature, a yellow precipitate was collected, washed with ethanol and distilled water three times, and then dried in an oven at 100 °C for 8 h. For the purpose of comparison, the N-doped TiO₂ microcrystallites (NTMs) were also prepared in pure water and all other experimental conditions were kept the same. In addition, the N-doped TiO₂ nanoparticles (NNPs) without preferential {001} facets were prepared according to the procedures reported elsewhere [S1].

Characterization. The X-ray diffraction (XRD) patterns were obtained on a D/Max-RB X-ray diffractometer (Rigaku, Japan) using Cu K α radiation at a scan rate of 0.05° 2 θ s⁻¹. The scanning electron microscopy (SEM) was performed using a Hitachi-4800-S microscope (Hitachi, Japan). The transmission electron microscopy (TEM) analysis was conducted using a JEM-2100F electron microscope (JEOL, Japan). The Brunauer-Emmett-Teller (BET) surface area and porous structure of the samples were analyzed on the basis of nitrogen adsorption isotherms measured by using a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). The UV-Vis diffuse reflectance spectra of the powders were obtained using the dry-pressed disk samples with a UV-Vis spectrophotometer (UV2550, Shimadzu, Japan). The XPS measurements were done on a VG ESCALAB 210 electron spectrometer using Mg K α radiation. The XPS data were calibrated using the binding energy of C1s (285.00 eV) as the internal standard. The percentage of {001} facets in TiO₂ crystals was estimated by using the procedure reported elsewhere [S2].

Photocatalytic H₂-production activity. The photocatalytic H₂-production experiments were performed in a 100 mL Pyrex flask at ambient temperature and atmospheric pressure, and

three openings of the flask were sealed with silicone rubber septum. A 350 W Xe arc lamp through a UV-cutoff filter (> 420 nm) was used as light source (10 cm far away from the photocatalytic reactor). The focused intensity on the flask was ca. 120 mW/cm^2 ; it was measured using a FZ-A visible-light radiometer (made in the photoelectric instrument factory of Beijing Normal University, China) with the wavelength range of 400 to 1000 nm. In a typical photocatalytic experiment, 50 mg of photocatalyst powder was suspended in 80 mL of aqueous solution containing 25% methanol scavenger in this volume. The loading of 0.5 wt % Pt co-catalyst was conducted by directly dissolving H_2PtCl_6 in the aforementioned 80 ml mixed solution. Next, the resulting suspension was stirred and illuminated using a 350 W Xe arc lamp for 20 min at room temperature. Prior to irradiation, the suspension of the co-catalyst was bubbled with nitrogen through the reactor for 40 min to completely remove the dissolved oxygen in order to achieve anaerobic conditions. Next, 0.4 mL of gas was sampled intermittently through the septum, and hydrogen was analyzed by gas chromatograph (GC-14C, Shimadzu, Japan, TCD with 5\AA molecular sieve column using nitrogen as a carrier gas). All glassware was carefully rinsed with distilled water prior to usage. The apparent quantum efficiency (QE) was measured under the same photocatalytic reaction conditions. Four low-power 420 nm-LED (3 W) (Shenzhen LAMPLIC Science Co. Ltd. China), which were positioned 1 cm away from the reactor in four different directions, were used as light sources to trigger the photocatalytic reaction. The focused intensity and areas on the flask for each 420 nm-LED were ca. 6.0 mW/cm^2 and 1 cm^2 , respectively. The QE was calculated according to the following equation:

$$\begin{aligned} \text{QE} [\%] &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ &= \frac{\text{number of evolved } \text{H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100 \end{aligned} \quad (1)$$

Hydroxyl radicals ($\bullet\text{OH}$) testing. Measurements of $\bullet\text{OH}$ on the titania surface illuminated with visible light were performed by using terephthalic acid as a fluorescence probe according to the procedure reported elsewhere [S3, S4]. 50 mg of TiO_2 powder sample was dispersed in a 20 mL of 5×10^{-4} M terephthalic acid aqueous solution with a 2×10^{-3} M NaOH solution in a dish having diameter of about 9.0 cm. The experiment was carried out under visible-light irradiation using a 350 W Xe arc lamp with a 420 nm cutoff filter (25 cm above the dish). The average light intensity striking on the surface of the reaction solution was $\sim 75 \text{ mW/cm}^2$ as measured by visible-light radiometer. The fluorescence spectra of the generated luminescent 2-hydroxyterephthalic acid were measured on a Hitachi F-7000 fluorescence spectrophotometer. After visible-light irradiation for every 15 min, the reaction solution was filtrated to measure the increase in the fluorescence intensity at 425 nm of 2-hydroxyterephthalic acid excited by 315 nm light. The apparent quantum efficiency (QE) was measured under the same photocatalytic reaction condition. Four low-power 420 nm-LED (3 W) (Shenzhen LAMPLIC Science Co. Ltd. China), which were positioned 1 cm away from the reactor in four different directions, were used as light sources to trigger the photocatalytic reaction. The focused intensity and areas on the flask for each 420 nm-LED were ca. 6.0 mW/cm^2 and 1 cm^2 , respectively.

References

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Table S1. Physicochemical properties of NTNs, NTMs and NNPs.

Sample	Phase ^a	S_{BET} (m^2/g)	Average pore size (nm)	Pore volume (cm^3/g)	Porosity (%)	Percentage of {001} (%)
NTNs	A	87	22.7	0.35	57	67 ± 5
NTMs	A	2.8	58.7	0.06	18	60 ± 5
NNPs	A	102	7.3	0.24	47	< 10

^a A denotes anatase.

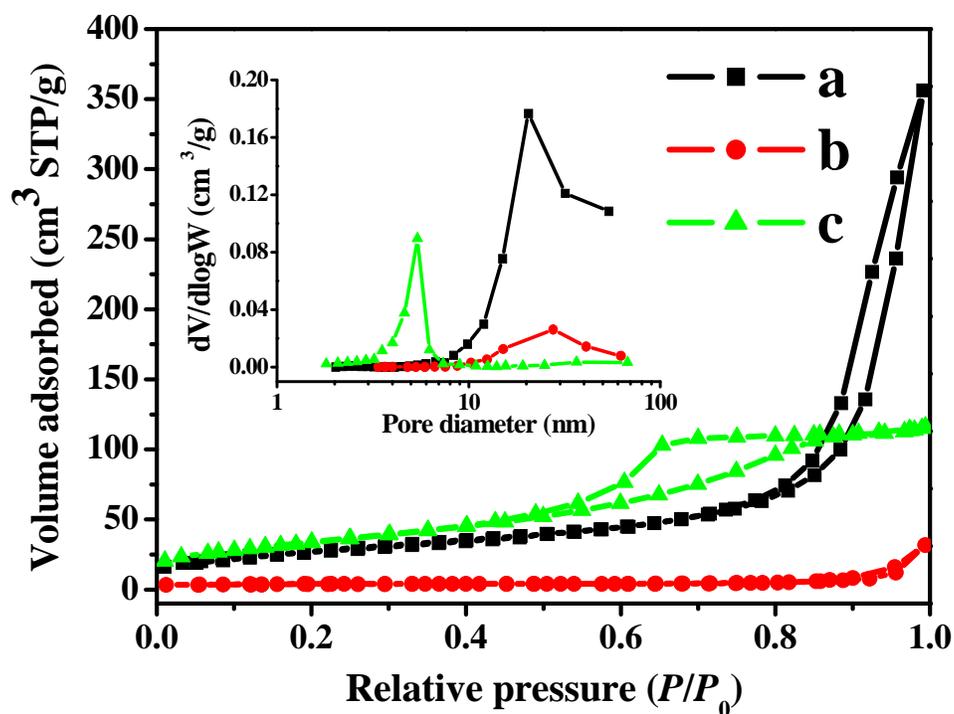


Fig. S1. N_2 adsorption-desorption isotherms and the corresponding pore size distributions (inset) for NTNs (a), NTMs (b) and NNPs (c).

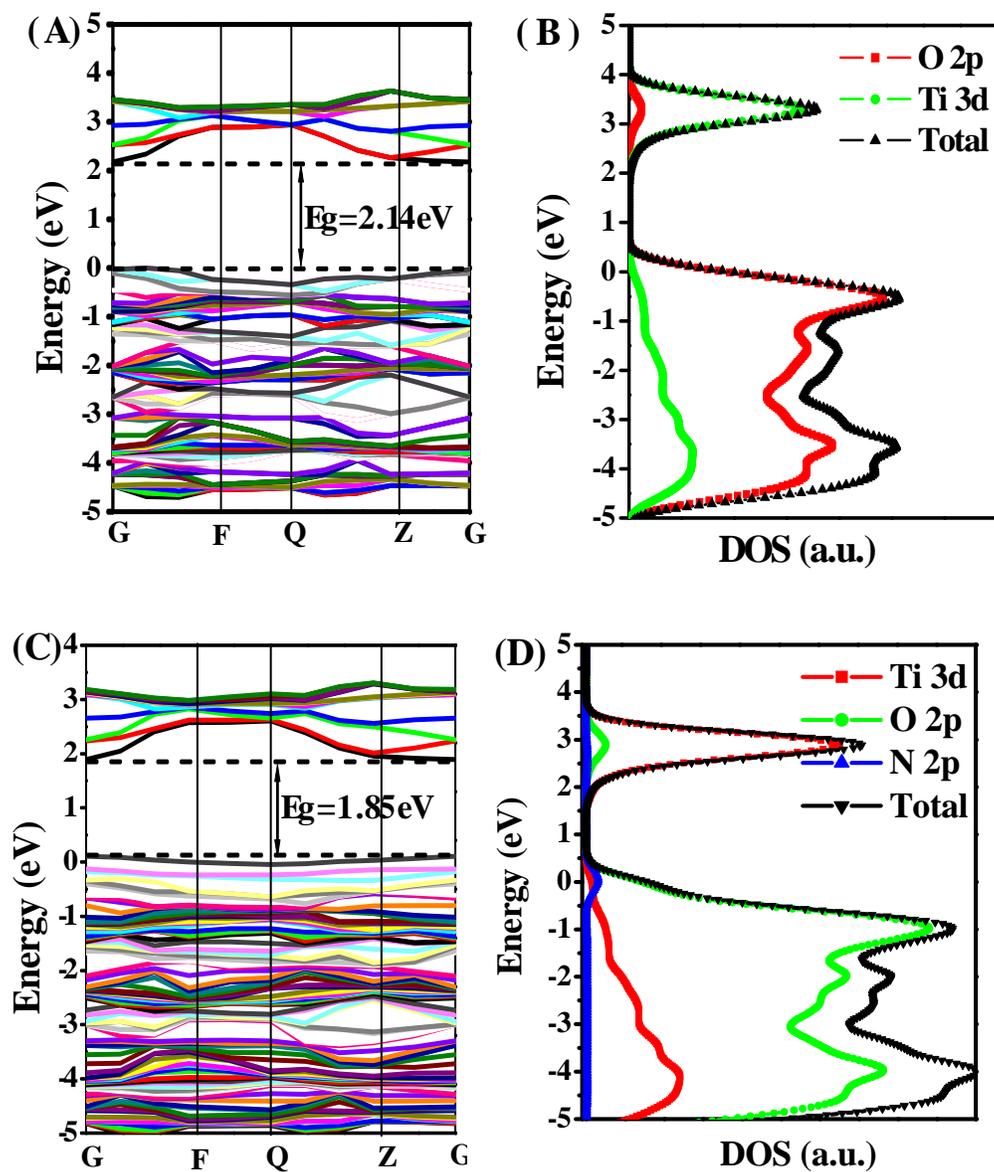


Fig. S2 Band structure plots (A, C) and total density of states (B, D) for pure TiO₂ (A, B) and N-doped TiO₂ at 2.08 at. % doping levels (C, D). The energy is measured from the top of the valence band of pure anatase TiO₂.

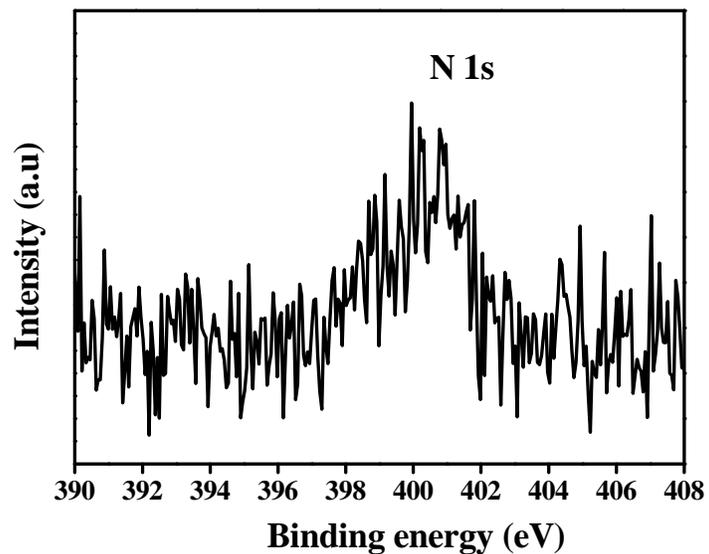


Fig. S3. High-resolution XPS spectrum of N 1s for the NTN sample.

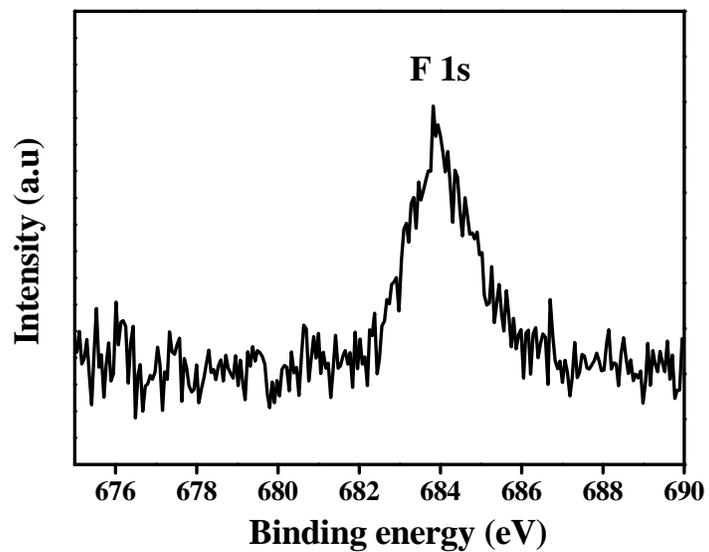


Fig. S4. High-resolution XPS spectrum of F 1s for the NTN sample.

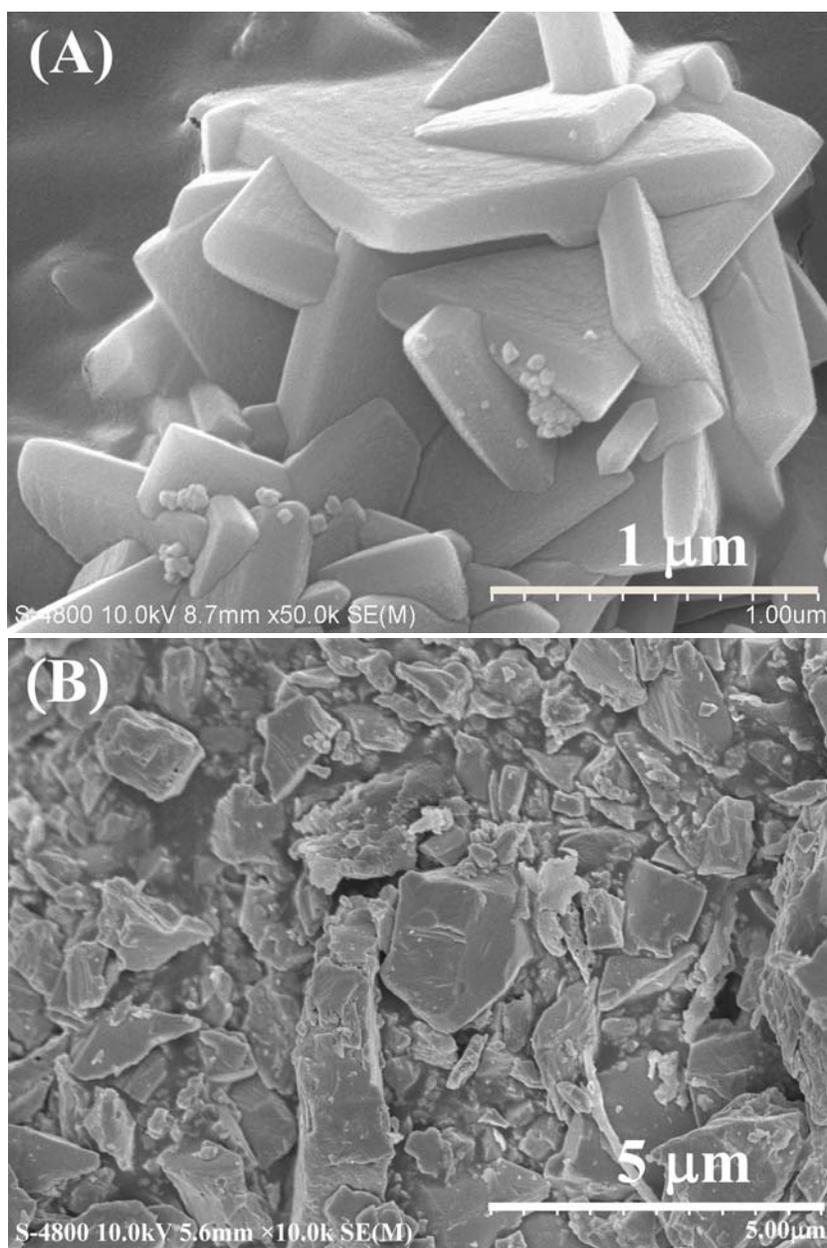


Fig. S5. SEM images of the NTMs sample (A) and TiN precursor (B). The average grain size of NTMs is ca. 1.2 μm with a thickness of ca. 310 nm and the percentage of {001} facets is ca. 60% as estimated by the method reported elsewhere [S2].

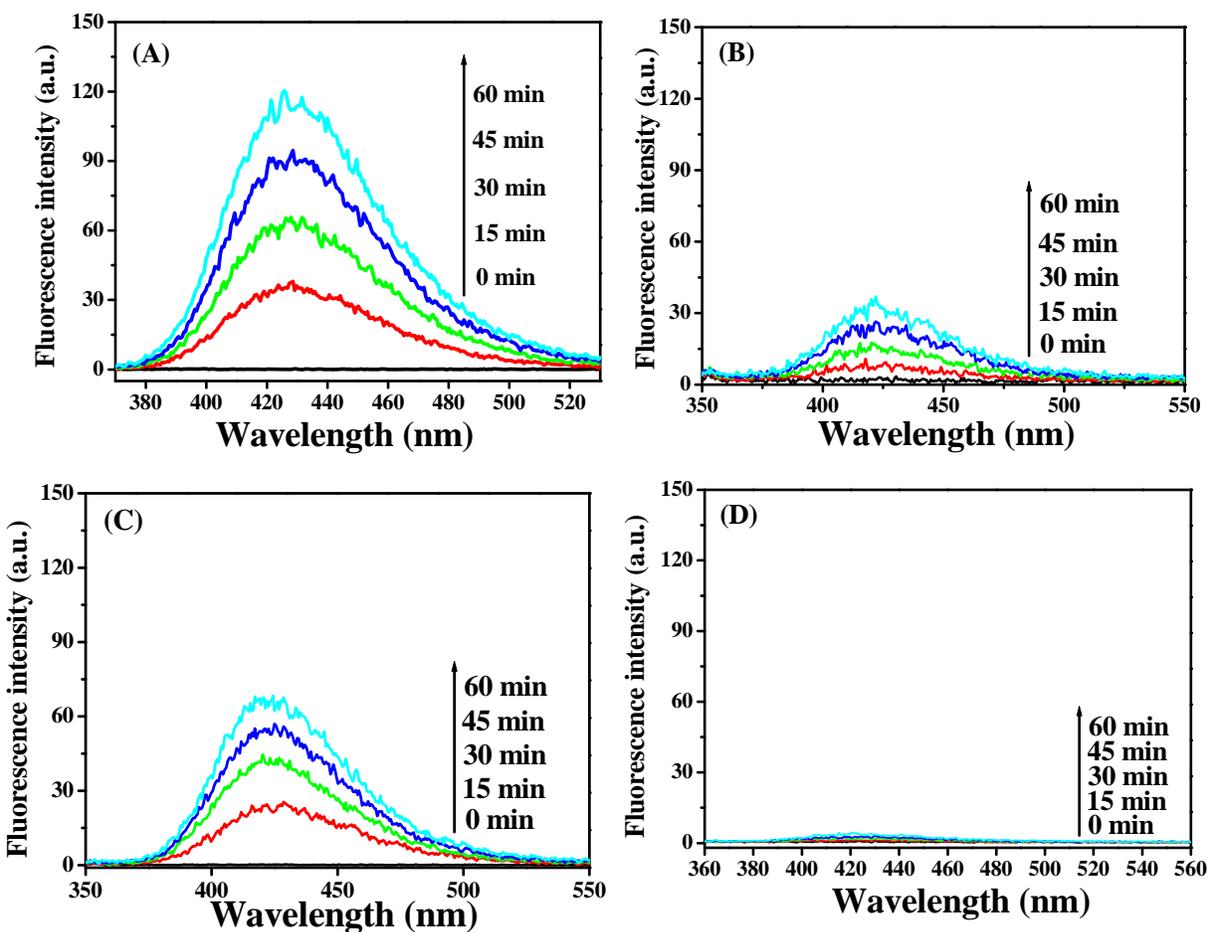


Fig. S6. Fluorescence spectra changes with visible light irradiation time for the NTNs (A), NTMs (B), N-doped TiO₂ nanoparticles (C) and P25 titania sample (D) in a 5×10^{-4} M basic solution of terephthalic acid.

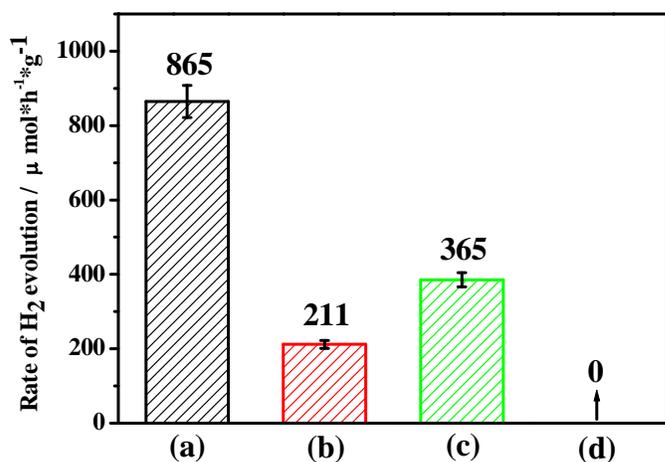


Fig. S7. Comparison of the photocatalytic H₂ production in methanol aqueous solutions for the NTNs (a), NTMs (b), N-doped TiO₂ nanoparticles (c) and P25 titania sample (d) under visible-light irradiation.