

Supporting Information:

Enhancing Visible Light Photo-Oxidation of Water with TiO₂ Nanowire Arrays via Co-treatment with H₂ and NH₃: Synergistic Effects between Ti³⁺ and N.

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Experimental Section

Materials. All chemicals were purchased and used without further purification including titanium (IV) isopropoxide (TTIP) (98+ %, Acros Organics), HCl (ACS Reagent Grade 36.5-38%, MP), n-hexane (Extra dry, 96+%, Acros Organics), titanium (IV) chloride, (99.0+ %, Alfa Aesar), gas mixture of H₂ and Ar (5% H₂ in Ar, Matheson Tri-gas), and ammonia (99.99 %, Matheson Tri-gas).

Hydrothermal Synthesis. Fluorine-doped Tin Oxide (FTO) coated glass substrates were first cleaned by sonication in a mixture of ethanol and water for 30 minutes, subsequently rinsed by deionized (DI) water, and finally dried in an air stream. The FTO substrates were then seeded with a thin layer of TiO₂ before growing the nanowire arrays by soaking in 0.025M TiCl₄ in n-hexane for 30 minutes. They were then taken out, rinsed by ethanol, and finally annealed in air at 500 °C for 30 minutes. The seeded FTO substrates were then placed on the bottom of a Teflon lined autoclave (125 mL, Parr Instrument), containing 50 mL n-hexane, 5 mL HCl, and 5 mL of titanium (IV) isopropoxide. The hydrothermal synthesis was conducted at 150 °C for 5 hours. After the reaction was completed and the autoclave naturally cooled down to room temperature, the TiO₂ nanowire films were taken out and cleaned by rinsing with copious amount of ethanol and water. The TiO₂ nanowire array thickness was measured as 2.6 μm ± 0.27 μm by Scanning Electron Microscopy.

Thermal treatments. To remove the contaminants and increase the crystallinity, the pristine TiO₂ nanowire sample was prepared by annealing the as-hydrothermally synthesized sample in air at 500 °C for 1 hour in a box oven. The hydrogen treatment and nitridation process were performed using a tube furnace (MTI, OTF-1200x-80). The tube was first evacuated until the pressure inside the tube was below 1 Torr. The tube was then filled with desired gases (H₂/Ar or NH₃) to atmospheric pressure. The flows of H₂/Ar (100 mL/minute) and NH₃ (100 mL/minute) were controlled by gas flow controllers during annealing time. The exhaust line was bubbled through a cup of water (the exhaust line was kept ~ 5 cm below the water surface). The hydrogen-treated sample (H-TiO₂) and the nitrided sample (N-TiO₂) were prepared by annealing the as-synthesized samples at 500 °C in H₂/Ar for 1 hour and NH₃ for 2 hours respectively. The co-treated sample (H, N-TiO₂) were prepared by first annealing in H₂/Ar at 500 °C for 1 hour, following by annealing in NH₃ at 500 °C for 2 hours.

Material Characterization. Scanning electron microscopy (SEM) was performed on a Zeiss field-emission SEM using a 10 kV focus voltage. Transmission electron microscopy (TEM) was performed on a JEOL 2010F field-emission TEM using a 200 kV focus voltage. Grazing incidence X-ray diffraction (GIXRD) patterns were collected with a Bruker D8 diffractometer. The transmittance spectra were collected using a Cary 500 UV-vis-NIR spectrophotometer attached to a Labsphere DRA-CA-5500 integrating sphere. X-ray photoelectron spectroscopy

(XPS) was performed on a Kratos Axis x-ray photoelectron spectrometer with scanning step of 0.1 eV and dwell time of 4 second/step. The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as a reference. The elemental percentages were calculated from XPS spectra using the CasaXPS computer program with specific relative sensitivity factors for the Kratos Axis XPS (Ti 2p: 2.001, O 1s: 0.78, and N 1s: 0.48). The electron paramagnetic resonance (EPR) spectra were collected at 86 K using a Bruker EMX-CW EPR spectrometer operating at the X-band frequency. The samples were first loaded in quartz glass tubes covered by aluminum foil, then baked out in an oven at 60 °C for 24 hours before EPR measurements. Five (5) scans were added for each spectrum with following scan parameters: microwave frequency = 9.47 GHz; modulation amplitude = 1 G; modulation frequency = 100 kHz; and non-saturating microwave power = 20 mW.

Electrochemical and Photoelectrochemical (PEC) Characterizations.

The PEC measurements were performed using a three-electrode electrochemical cell with the FTO supported nanowire arrays as the working electrode, a Ag/AgCl (saturated KCl) reference electrode, a platinum wire counter electrode, and 1 M KOH electrolyte (pH = 13.5). The working electrode with exposed area of 0.205 cm² was illuminated from the back side (through the FTO substrate – TiO₂ nanowire interface) by a solar simulator (Newport, Model 9600, 150 W xenon lamp) equipped with an AM 1.5 G filter (Newport, Model 81094). The light intensity was measured as 100 mW/cm² using a thermopile detector with the spectrum response from 0.19 to 10.6 μm (Newport, 818P-020-12). A CHI 660D electrochemical station was used for linear sweep voltammetry (I-V) and chronoamperometry (I-t) measurements.

Incident photon to current conversion efficiencies (IPCEs) were calculated from chronoamperometry measurements using a motorized monochromator (Oriel Cornerstone 130 1/8 m). The monochromator slit size was adjusted to 0.75 mm x 2 mm providing monochromatic wavelengths with a bandwidth of ~ 5 nm and a power density which could be adjusted from 8 to 4000 μW/cm² for wavelengths from 320 to 600 nm. A typical light power density spectrum used for IPCE can be found in Figure S6. Light power was measured using a handheld optical power meter with a UV enhanced silicon photo-detector (Newport). IPCE values were calculated using the following equation:

$$IPCE(\lambda) = \frac{1240 j_p(\lambda)}{\lambda E_\lambda(\lambda)}$$

where $j_p(\lambda)$ is the measured photocurrent density (mA/cm²) and $E_\lambda(\lambda)$ is the incident light power density (mW/cm²) for each wavelength, λ (nm).

The measured potentials vs. the Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale *via* the Nernst equation

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + E_{\text{Ag/AgCl}}^{\circ} \quad (2)$$

where E_{RHE} is the converted potential vs. RHE, $E_{\text{Ag/AgCl}}$ is the experimental potential measured against Ag/AgCl reference electrode, and $E_{\text{Ag/AgCl}}^{\circ} = 0.1976 \text{ V}$ at $25 \text{ }^{\circ}\text{C}$.

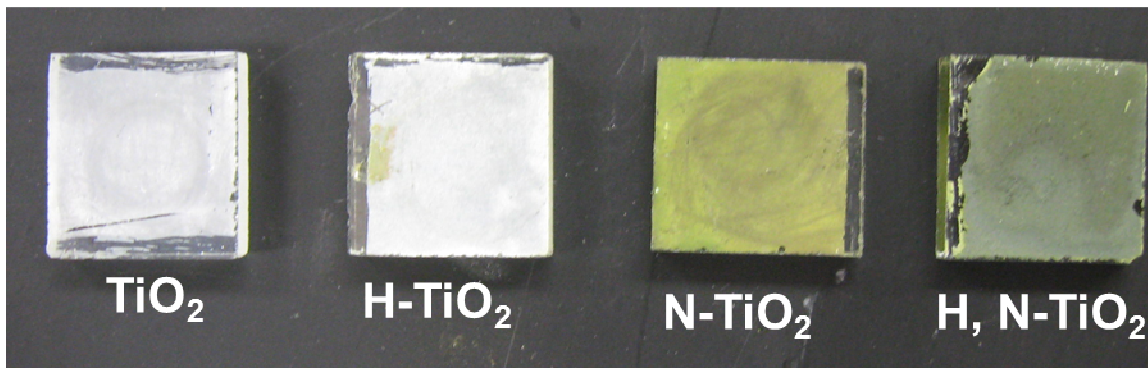


Figure S1. Digital images of TiO_2 , H-TiO_2 , N-TiO_2 , and H, N-TiO_2 nanowire arrays.

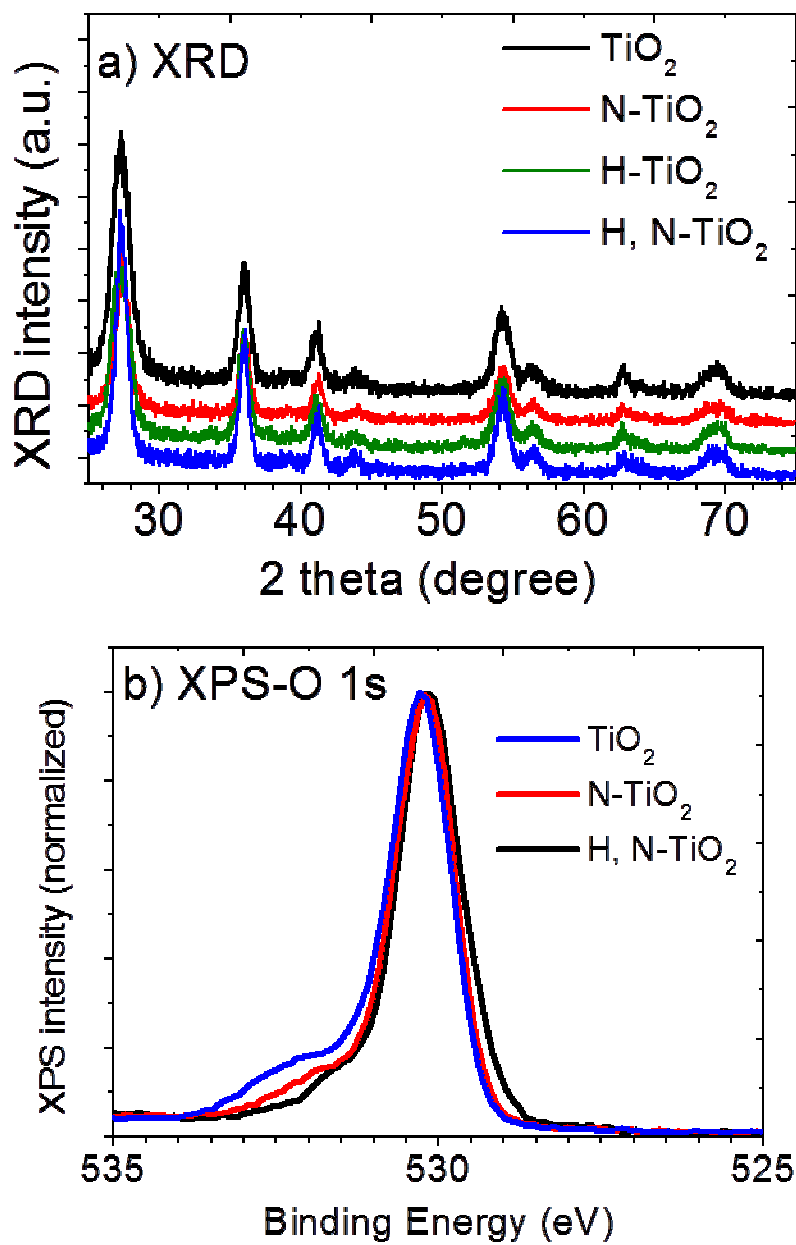


Figure S2. (a) Grazing incidence XRD patterns of TiO₂, N-TiO₂, H-TiO₂, and H, N-TiO₂. All peaks are indexed to rutile TiO₂ phase (JCPDS #88-1175) and (b) Core O 1s XPS spectra of the TiO₂, N-TiO₂, and H, N-TiO₂.

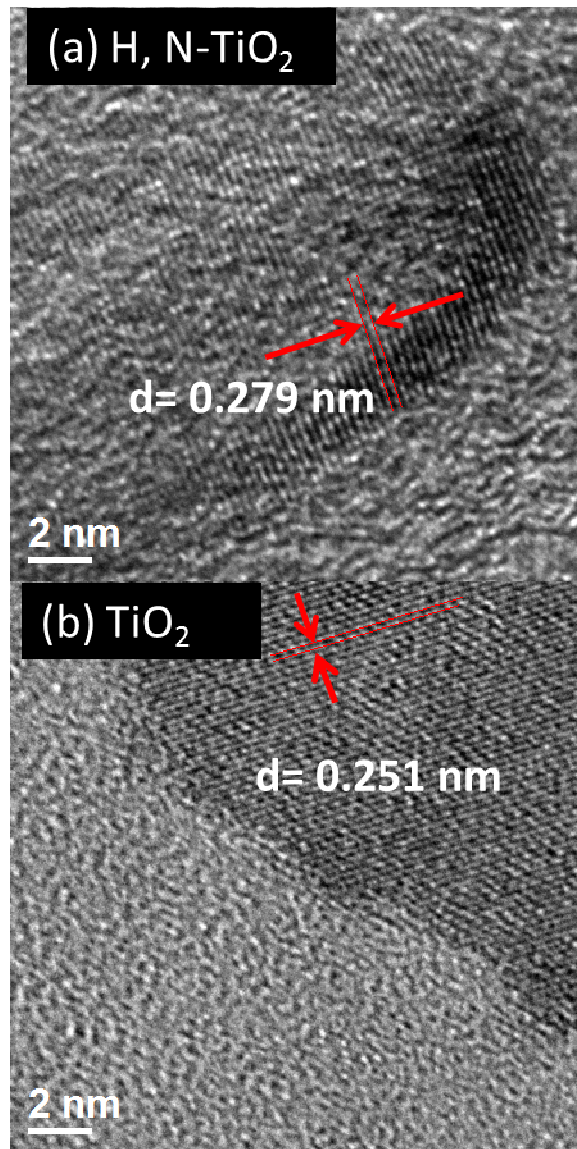


Figure S3. High resolution TEM images of (a) H, N-TiO₂ and (b) TiO₂ samples.

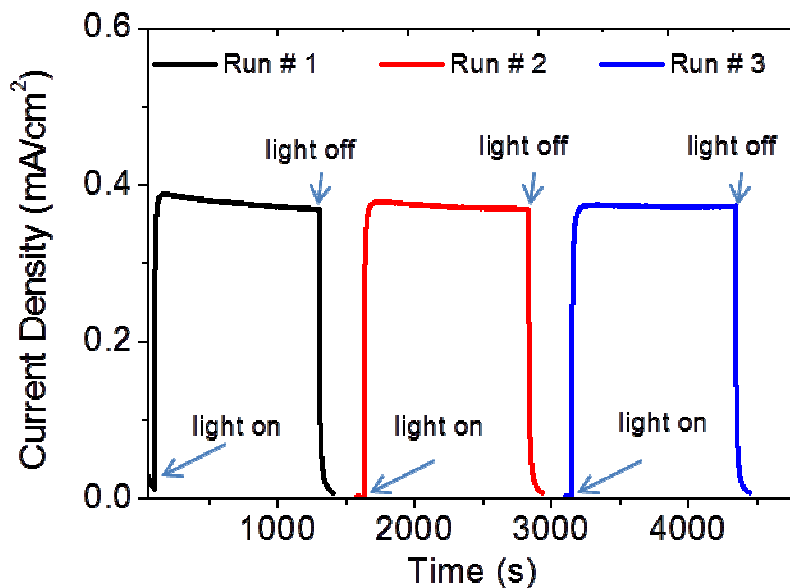


Figure S4. Chronoamperometry (CAM) measurement at 1.23 V_{RHE} of the H, N-TiO₂ sample. The measurement was performed using a three-electrode electrochemical cell with a Ag/AgCl reference electrode, a Pt wire counter electrode, and 1 M KOH electrolyte. A solar simulator (Oriel 96000) coupling with an AM 1.5 G filter was used as the light source with light intensity of 100 mW/cm² measured by a thermopile detector (Newport, 818P-020-12). The measurement was performed in 3 sequential runs: run #1, run #2, and run #3. After each run, we used a pipet to flush out bubbles forming on the H, N-TiO₂ photoanode.

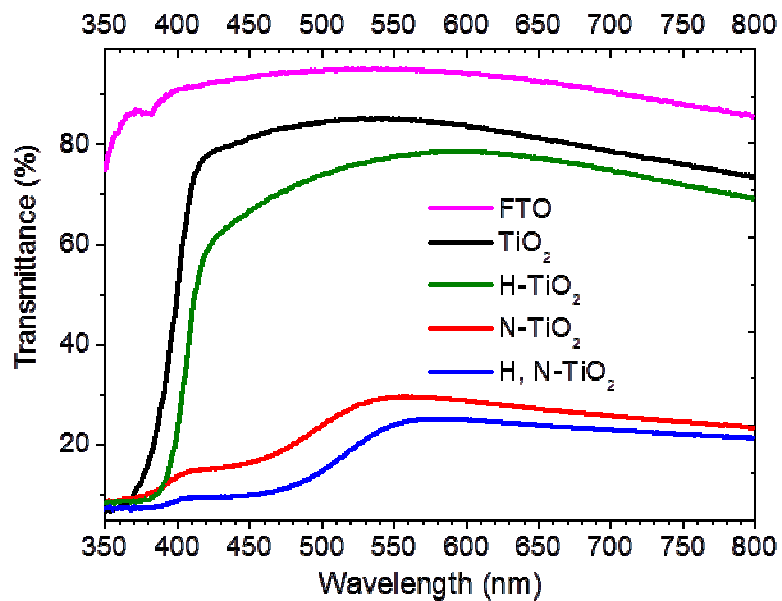


Figure S5. Raw data of the UV-vis transmittance spectra of FTO substrate, TiO₂, H-TiO₂, N-TiO₂, and H, N-TiO₂ samples.

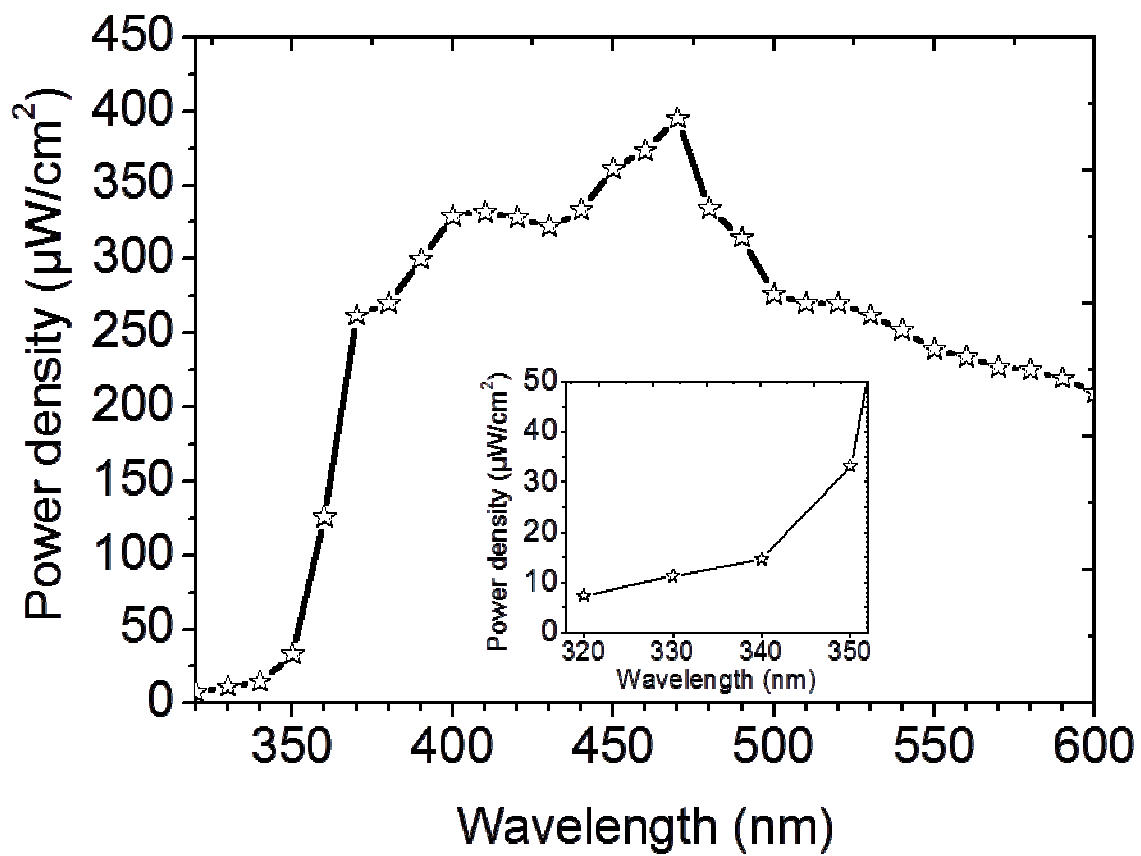


Figure S6. A typical incident light power density spectrum (from 320 nm - 600nm) used for the IPCE measurements. The inset shows the incidence power density spectrum from 320 nm - 350nm.