



Supporting Information

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Spaced Titania Nanotube Arrays Allow the Construction of an Efficient N-Doped Hierarchical Structure for Visible-Light Harvesting

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Experimental Section

Growth of TiO₂ nanotubes: Titanium foils (Advent Research Materials, 0.125 mm thickness, 99.6+% purity) were degreased by sonication in acetone, ethanol and deionized water, followed by drying in N₂ gas stream. The TiO₂ nanotubes were formed by anodizing titanium foils in triethylene glycol electrolyte containing NH₄F (0.3 M) and H₂O (3 M), at 60 V for different times at 60 °C. The DC potential was applied by using a VLP 2403 pro, Voltcraft power supply. Right after the anodization, the samples were immersed in ethanol, and then dried under N₂ gas stream. Subsequently, the TiO₂ nanotubes were annealed at 450 °C in air for 1 h using a Rapid Thermal Annealer (Jipelec Jetfirst 100 RTA), with a heating and cooling rate of 30 °C min⁻¹.

Nanoparticle decoration: For TiCl₄ treatments, aqueous TiCl₄ solutions (0.1 M) was prepared under ice-cooled conditions. The TiO₂ nanotube layers were then treated in a closed vessel at 70 °C for 30 min. Afterwards, the samples were washed with distilled water and rinsed with ethanol and finally dried in a N₂ gas stream; and this process was repeated several times. After these treatments, the samples were annealed again at 450 °C for 10 min to crystallize attached nanoparticles.

Nitrogen doping: TiO₂ samples were annealed in a pure NH₃ gas flow at 450 °C for different duration times. Before and after annealing, the chamber was flowed with N₂ gas.

Characterization of the structure: Field-emission scanning electron microscope (FE-SEM, Hitachi S4800) was used to characterize the morphology of the samples. The chemical composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5600, US). X-ray diffraction (XRD) performed with a X'pert Philips MPD (equipped with a Panalytical X'celerator detector) was employed to examine the crystallographic properties of the materials. High-resolution transmission electron microscopy (HRTEM, FEI TITAN G2 60-300) was used for TEM image, HAADF and EDS mapping.

Photoelectrochemical spectra: Photoelectrochemical spectra were conducted in 0.1 M Na₂SO₄ under an applied potential of 0.5 V (vs. Ag/AgCl) in a three-electrode system using 150 W Xe-lamp (Oriel 6365) equipped with a Oriel Cornerstone 7400 1/8 m monochromator (illuminated area=0.785 cm²).

Photoelectrochemical measurements: The photoelectrochemical experiments were carried out under simulated AM 1.5G (100 mW cm⁻²) illumination provided by a solar simulator (300 W Xe with optical filter, Solarlight) equipped with a 420 nm cut-off filter. 0.1 M Na₂SO₄ was used as an electrolyte. Photocurrent vs. voltage (I–V) characteristics were recorded by scanning the potential from –0.6 to 1.1 V (vs. Ag/AgCl (3 M KCl)) with a scan rate of 1 mV s⁻¹ using a Jaissle IMP 88 PC potentiostat.

IMVS and IMPS: Intensity modulated photovoltage and photocurrent spectroscopy (IMVS and IMPS) measurements were carried out using modulated light from a high power LED (λ =530 nm).

Photocatalytic measurements: Photodegradation of acetaldehyde was performed in a 15 mL quartz cell. 20 μ L of acetaldehyde was injected in liquid form using a micropipette. Before irradiation, the reaction vessel was kept in the dark for 30 min. The exposure area was 1 cm². Gas chromatography (GCMS-QO2010SE, Shimadzu) was used to determine the concentration of CO₂. Photocatalytic methylene blue (MB) decomposition runs were performed in a magnetically stirred quartz cuvette. The initial concentration of MB was 0.01 mM. The samples were immersed in the cuvette in the dark for 30 min to establish the dye adsorption/desorption equilibrium. In order to measure the decomposition rates of MB, the absorbance of the testing solutions was measured periodically every 30 min using a UV/Vis spectrometer at wavelength $\lambda = 662$ nm. All photocatalytic measurements were conducted under visible light provided by a solar simulator AM 1.5 (300W Xe, 100 mW cm⁻², Solarlight) equipped with a 420 nm cut-off filter.

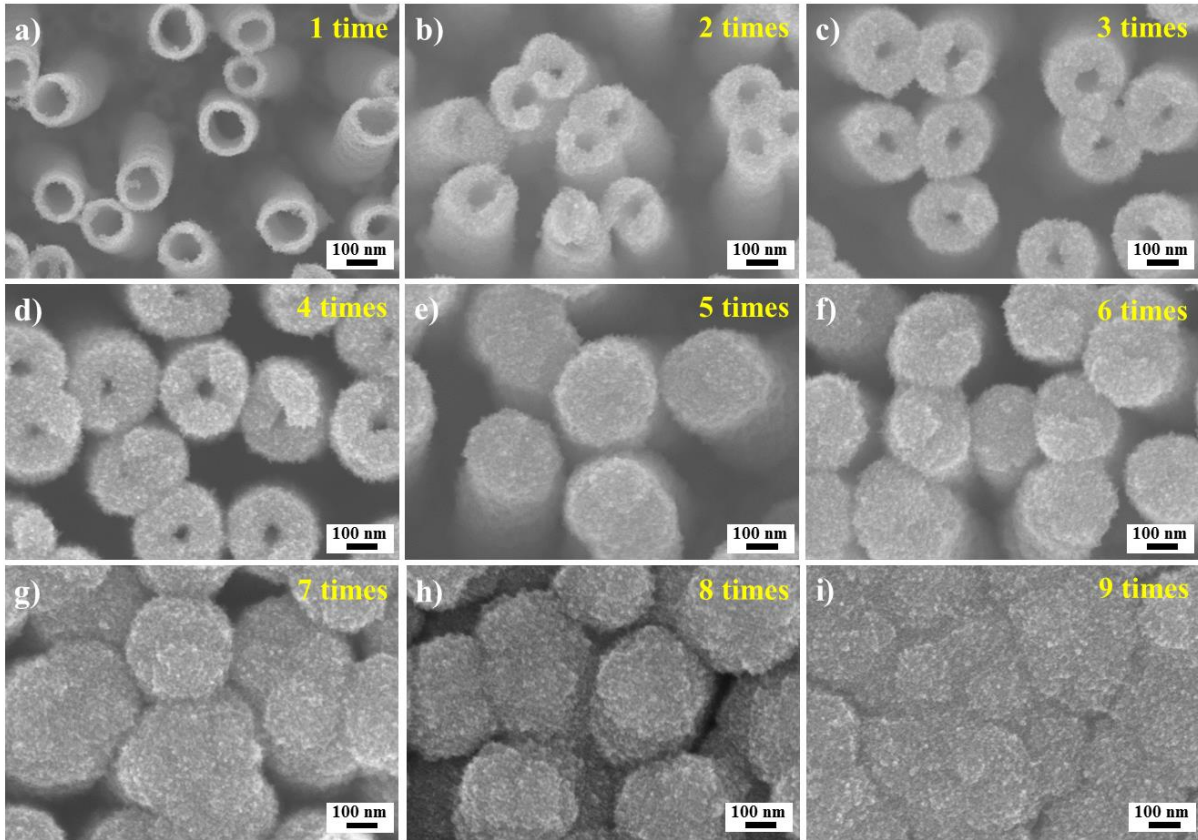


Figure S1. SEM images of spaced TiO₂ nanotubes decorated with different layers of TiO₂ nanoparticles (1-9 layers).

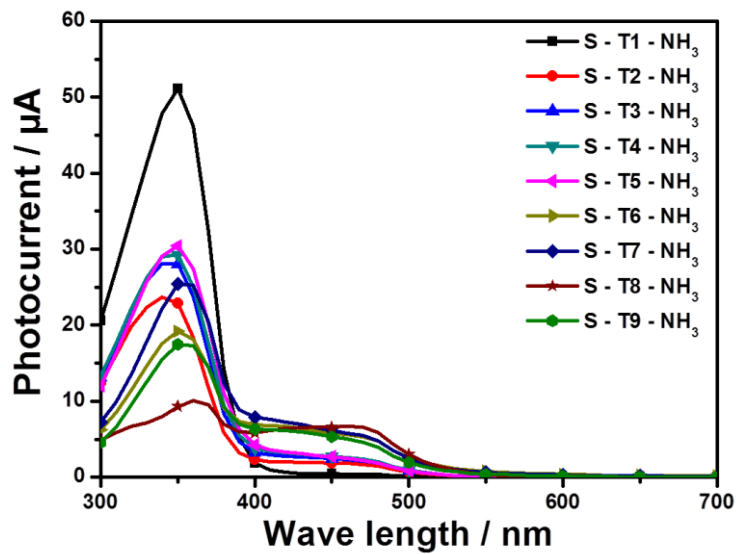


Figure S2. Photocurrent spectra of N-doped spaced TiO₂ nanotubes decorated with different layers of TiO₂ nanoparticles.

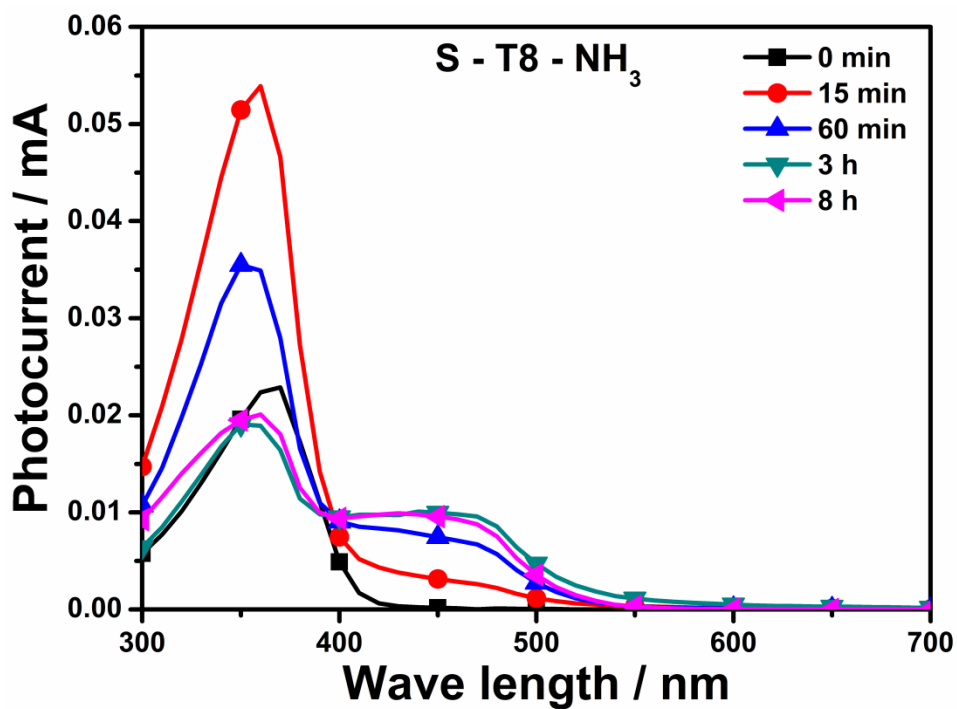


Figure S3. Photocurrent spectra of N-doped spaced TiO₂ nanotubes decorated with different layers of nanoparticles at 450°C for different times.

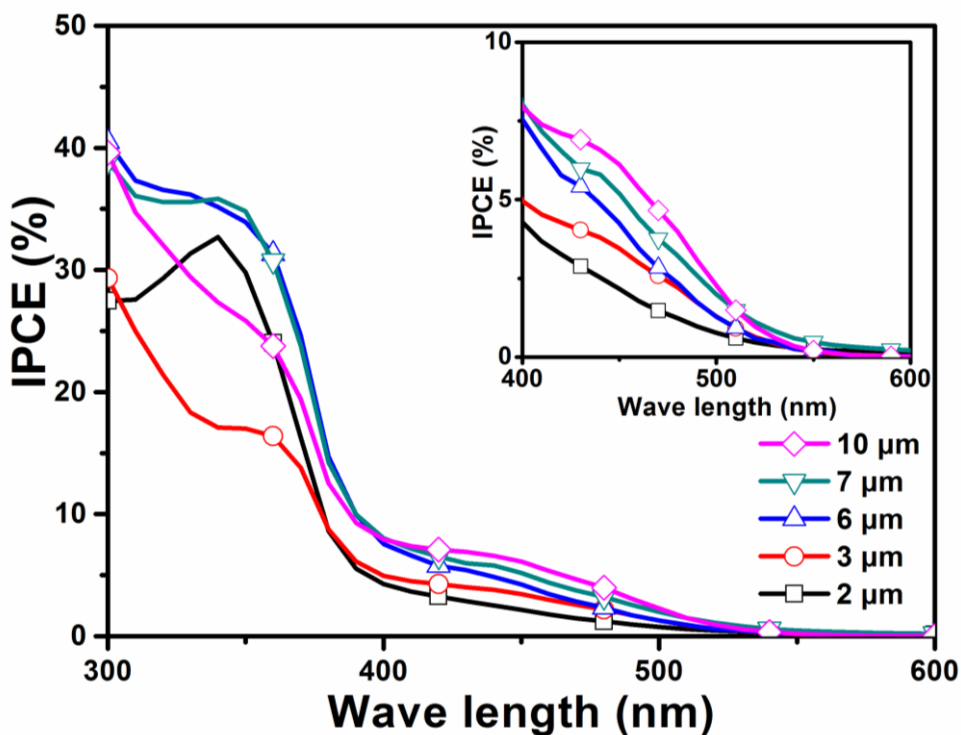


Figure S4. IPCE of N-doped hierarchical spaced TiO₂ nanotubes (eight layers of TiO₂ NPs) of different thicknesses.

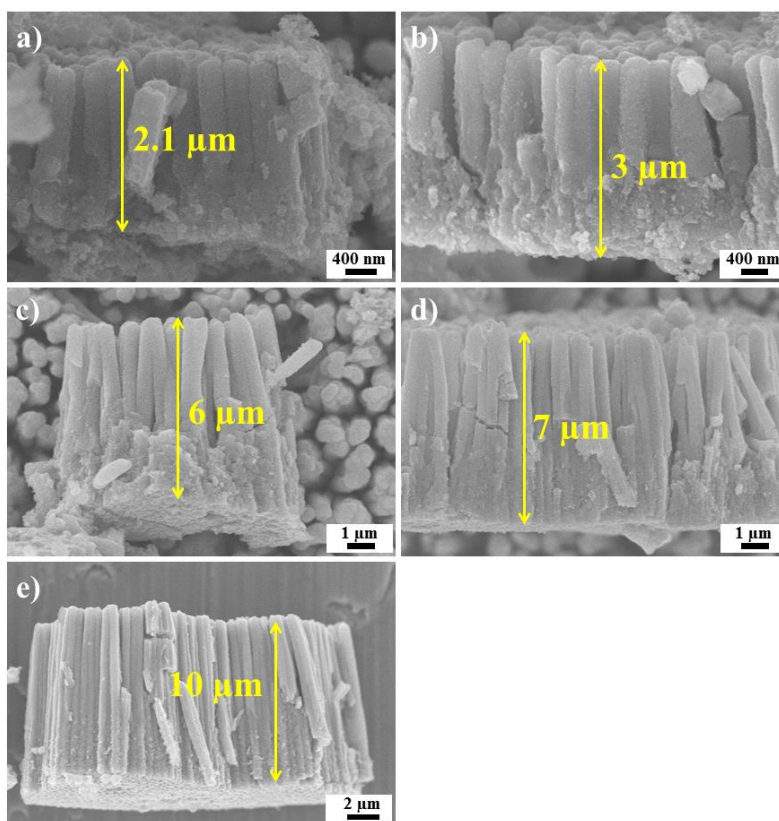


Figure S5. Cross-section SEM images of different thicknesses of spaced TiO₂ NTs decorated with 8 layers of nanoparticles; a) 2, b) 3, c) 6, d) 7 and e) 10 μm.

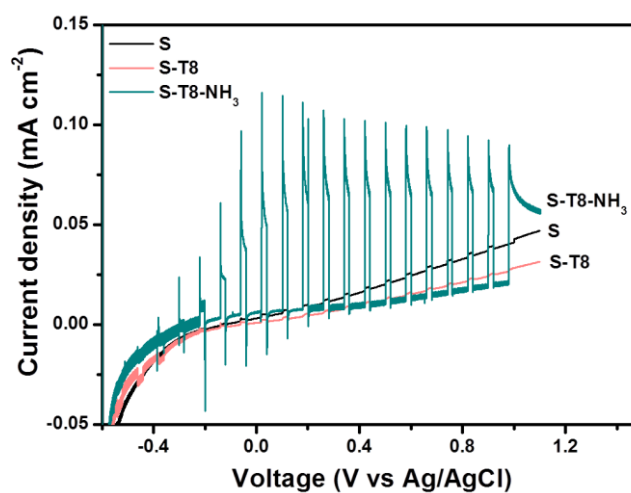


Figure S6. Photocurrent density vs. potential curves under chopped visible light (AM 1.5, 100 mW cm⁻², 420 nm cut-off filter) illumination of spaced TiO₂ nanotubes (S), spaced TiO₂ nanotubes decorated with 8 layers of nanoparticles (S-T8) and N-doped spaced TiO₂ nanotubes decorated with 8 layers of nanoparticles (S-T8-NH₃).

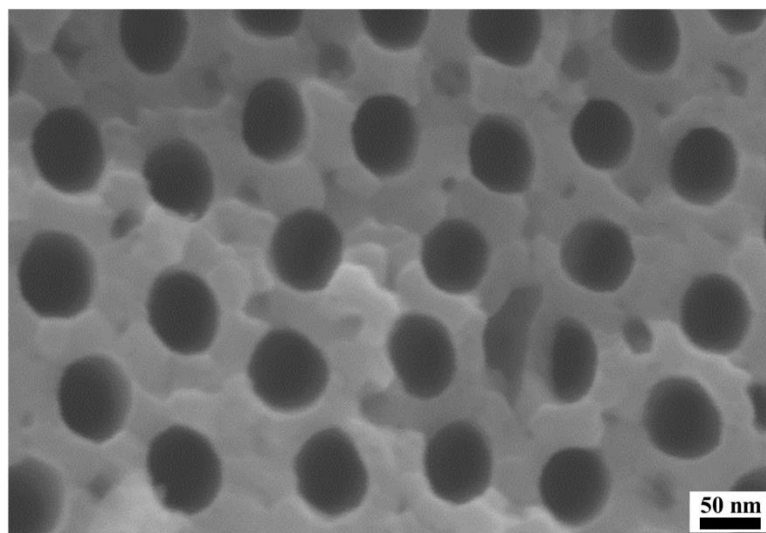


Figure S7. SEM image of conventional close-packed TiO₂ nanotubes.

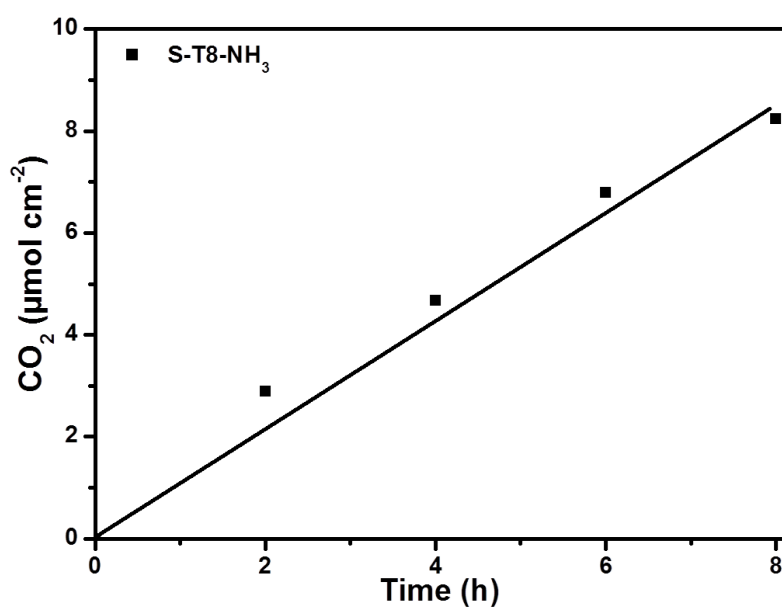


Figure S8. Photocatalytic CO₂ evolution rate during the photodegradation of acetaldehyde (AM 1.5, 100 mW cm⁻², 420 nm cut-off filter).