Supplementary Information

N-Doped Porous TiO_2 with Rutile Phase and Visible Light Sensitive Photocatalytic Activity

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Experimental section

1. Preparation of photocatalyst

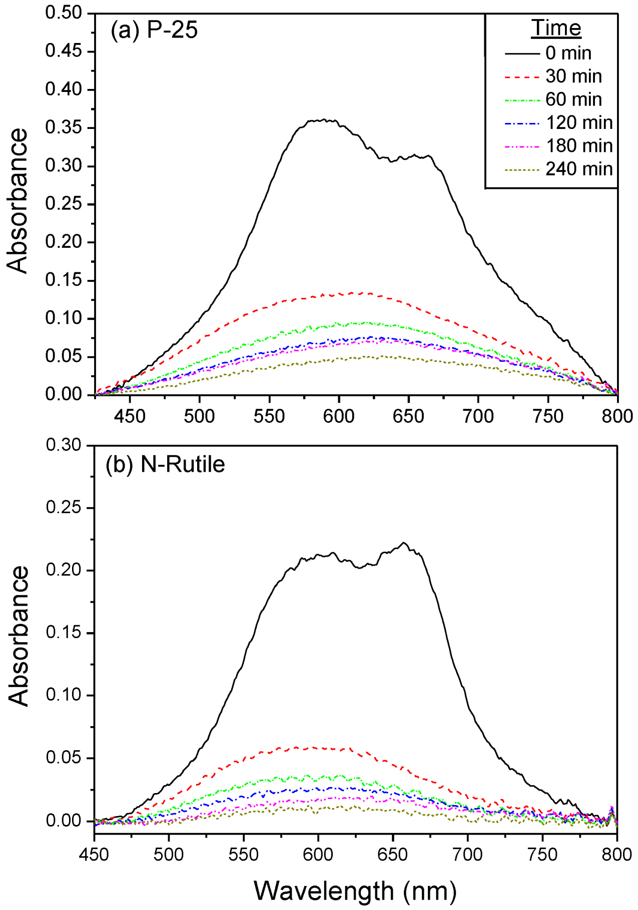
The visible light active rutile powder was prepared by hydrothermal method, with an additional annealing process. A Teflon-lined stainless steel autoclave containing 0.7 g of TiN (99 %, Strem) and 8.0 ml of 5 M HNO_3 aqueous solution was kept at 100 ^oC for 6 h. The final N-doped rutile samples were obtained after washing with deionized water, followed by annealing at 200 ^oC for 2 h in air. This procedure for preparation of N-doped rutile from TiN has been repeated using TiC (99 %, Strem) and TiS_2 (99.8 %, Strem) as precursor, but only mixed phases (anatase and rutile) were obtained.

2. Characterization

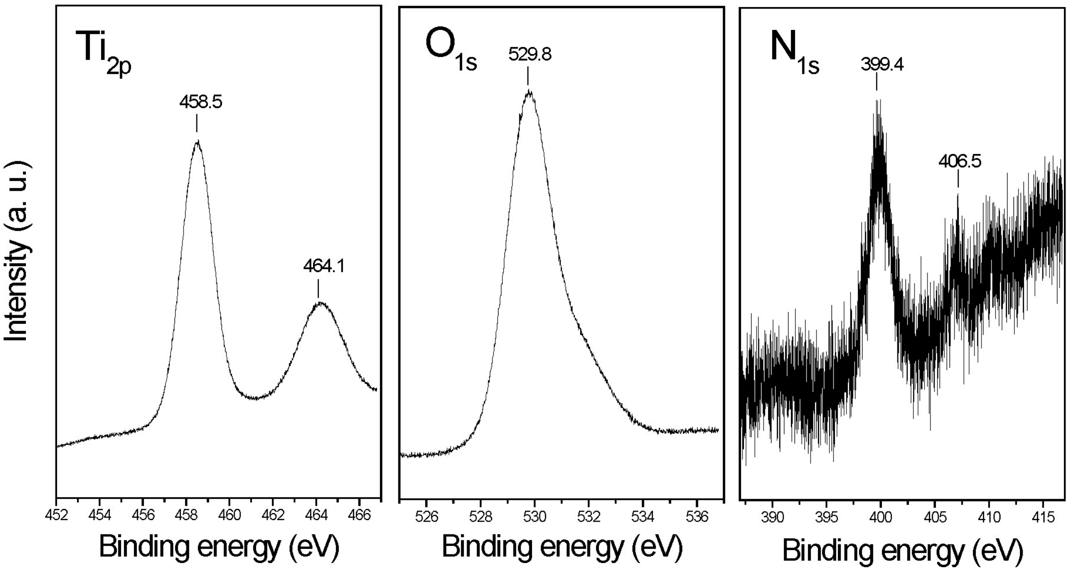
The crystalline structure of the resulting TiO_2 was determined by X-ray diffraction using a Shimadzu XD-D1 diffractometer with Cu-Kα radiation at 1.5406 Å. The nitrogen doping species of the rutile samples were examined by X-ray photoelectron spectroscopy using a Thermo VG-Scientific XPS spectrometer with an excitation beam of 1486.7 eV. The UV-Vis diffuse reflectance spectra were measured using a Hitachi U-3010 spectrophotometer. The BET area and pore volume of the N-doped TiO_2 were determined by N_2 physisorption using a Micrometrics ASAP 2010 instrument.

3. Photocatalytic activity measurement

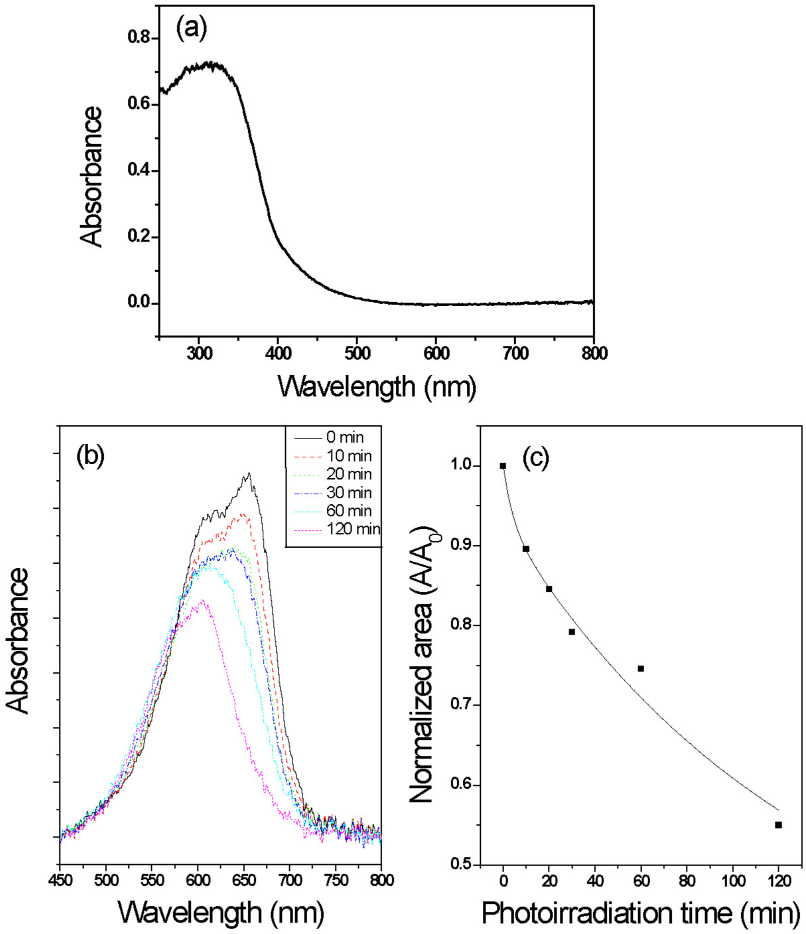
In the study of methylene blue decolorization of air-TiO_2 systems, 0.5 g of TiO_2 powder was added in a 10 ml of MB aqueous solution of 500 ppm to create a submonolayer dye coverage of TiO_2 particle. The suspension was stirred and then kept in a 50 % humidity environment overnight in the dark. The MB-coated TiO_2 powder was pressed into an indented circular area (Φ=19.4 mm, 0.5 mm in depth) in a glass plate for subsequent photoirradiation and reflectance measurement. The MB coverages on Degussa-P25 (40 m^2 g^{-1}) and N-doped rutile (77 m^2 g^{-1}) samples were calculated to be $2.00x10^{12}$ and $1.04x10^{12}$ molecules/cm^2, respectively. An Oriel mercury lamp, with or without a filter, was used in the MB photocatalytic decolorization experiments. The light below 410 nm could be removed by the filter. The irradiation power on the TiO_2 sample at wavelengths > 410 nm was measured to be ~15 mW cm^{-2}.



Supporting Figure 1 Change of the absorbance of methylene blue on (a) P-25 and (b) N-doped rutile with the time of photoirradiation using the full wavelength range from the light source.



Supporting Figure 2 Ti_{2p}, O_{1s} and N_{1s} X-ray photonelectron spectra of the mixed phases of anatase and rutile from TiC transformation.



Supporting Figure 3 (a) UV-Vis diffuse reflectance spectrum; (b) change of the absorption of methylene blue with photoirradiation time; (c) normalized MB peak area as a function of photoirradiation time of the mixed phases of TiO_2 (anatase + rutile) from TiC transformation.