

Supporting Information
For
Band-gap tuning of N-doped TiO₂ photocatalyst for
visible-light-driven selective oxidation of alcohol to aldehydes in
water

Zizhong Zhang*, Zhishan Luo, Zhiping Yang, Shuying Zhang, Yu Zhang, Yangen

Zhou, Xuxu Wang*, Xianzhi Fu

*Research Institute of Photocatalysis, State Key Laboratory Breeding Base of
Photocatalysis, Fuzhou University, Fuzhou, China, 350002*

E-Mail: z.zhang@fzu.edu.cn; xwang@fzu.edu.cn

Tel: +86-591-83690891; fax: +86-591-83738608.

Preparation of N-doped TiO₂ samples

Titanium dioxide samples were synthesized by a sol-gel technique. A specific amount of titanium ethoxide was dissolved in redistilled ethanol to get a concentration of 0.1 mol·L⁻¹. The precursor solution was added dropwise into water to hydrolysis under vigorous stirring. The amorphous precipitates were washed with distilled water, dried at 80 °C, and then calcined at 450 °C for 20 h in a flowing O₂ to remove residual organic compounds. Fourier transformed infrared (FTIR) spectra confirmed no residual organic compounds in TiO₂ samples. The as-prepared TiO₂ was heated in pure NH₃ gas stream at 400, 450, 500, 550, 650, 700 or 800 °C for 20 h to produce a series of N-doped TiO₂ samples with various N contents.

Photocatalytic activity testing

The photoreactivity runs were performed in a test tube (45 ml) with 5 ml H₂O, 100 μmol benzyl alcohol (BA) and 20 mg photocatalysts in the presence of O₂ using a 300-W Xe arc lamp equipped with a λ ≥ 420 nm cutoff filter and an IR filter for 2 hour illumination reaction. The reaction solution was analyzed by HPLC (Waters 2487, which was equipped with an Agilent Zorbax SB-C18 column). All products were quantified using the external standard method. For the photocatalytic selective oxidation of cyclohexanol, the reaction solution was analyzed by GC with an FID detector. The conversion of alcohols and the selectivity to their corresponding aldehydes were calculated as follows:

$$\text{Conversion (\%)} = (C_0 - C_A)/C_0 \times 100\%$$

$$\text{Selectivity (\%)} = C_{AD}/(C_0 - C_A) \times 100\%$$

where C₀ is the initial concentration of alcohols, C_A and C_{AD} are the concentration of alcohols and aldehydes after photocatalytic reaction, respectively.

Figure S1. Photocatalytic oxidation of benzyl alcohol into benzaldehyde on a $\text{TiO}_{1.966}\text{N}_{0.034}$ catalyst. Benzyl alcohol conversion, benzaldehyde selectivity and the total organic carbon (TOC) with reaction time.

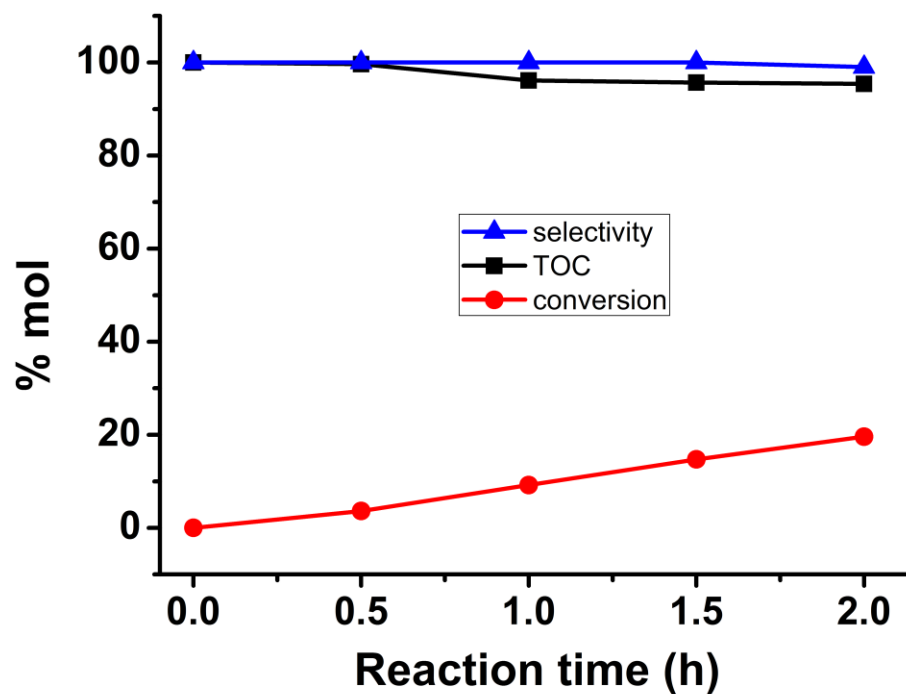


Figure S2. Wavelength dependence of the BA conversion on the $\text{TiO}_{1.966}\text{N}_{0.034}$ catalyst.

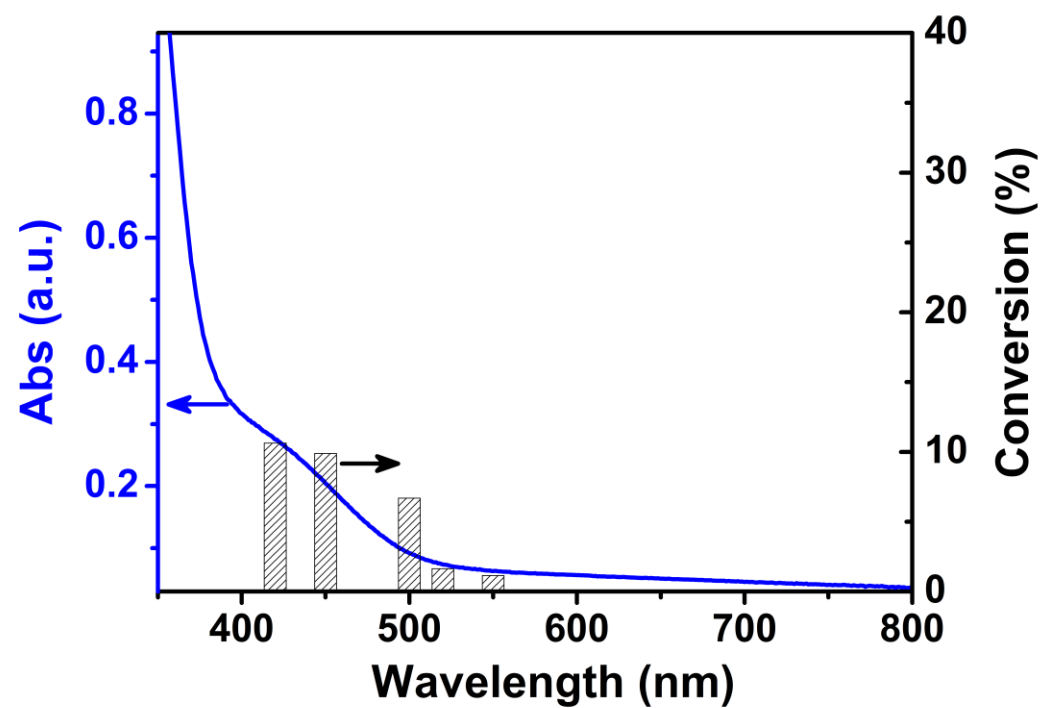


Figure S3. UV-vis absorption spectra of: (a) TiO_2 by itself; (b) TiO_2 -adsorbed BA; (c) $\text{TiO}_{2-x}\text{N}_x$ by itself; and (d) $\text{TiO}_{2-x}\text{N}_x$ -adsorbed BA.

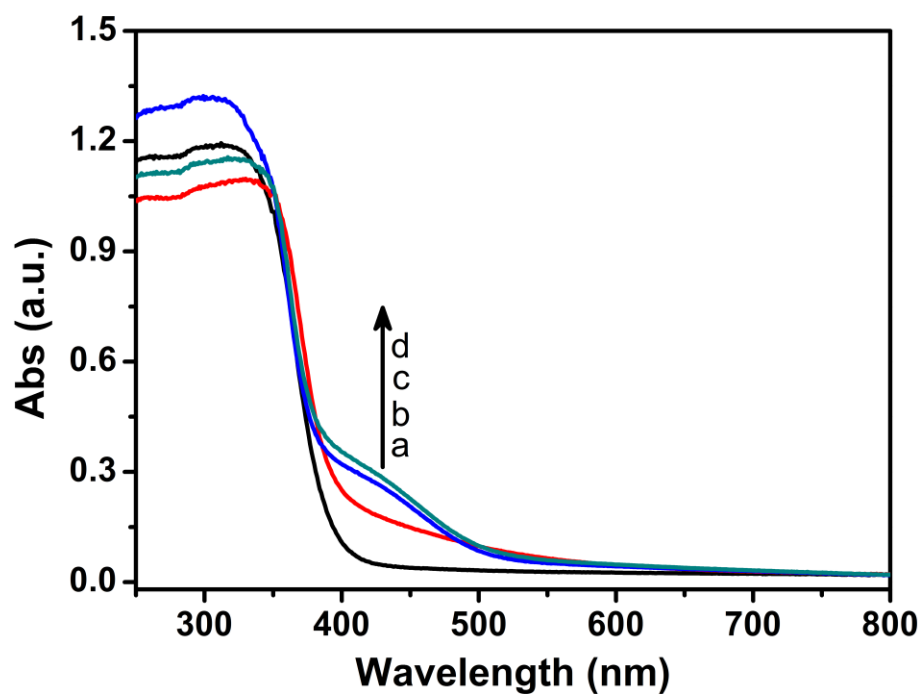


Figure S4. UV visible diffused reflectance spectrum of various $\text{TiO}_{2-x}\text{N}_x$ samples: a, $x = 0$; b, $x = 0.025$; c, $x = 0.034$; d, $x = 0.036$.

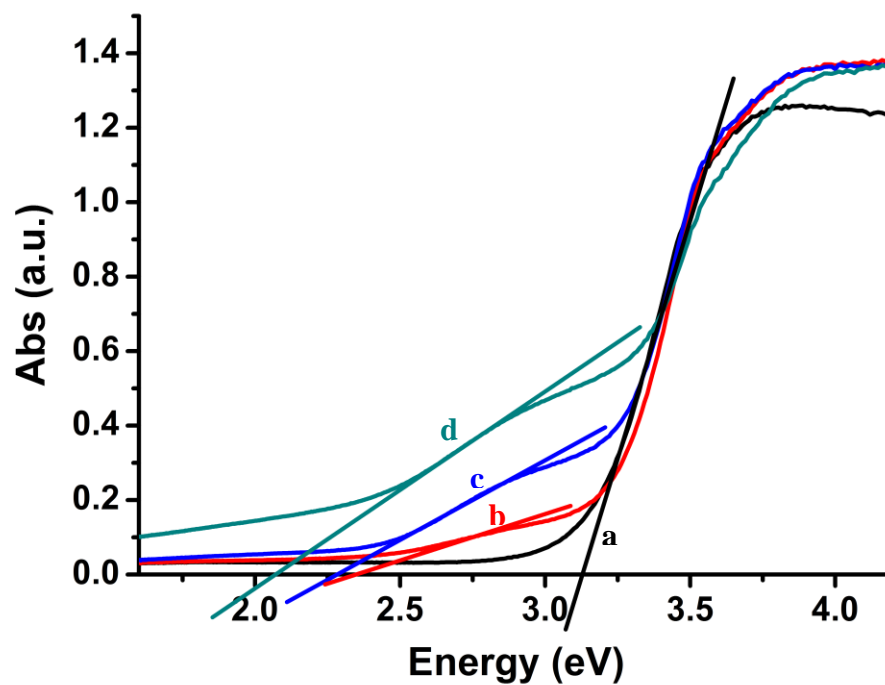


Figure S5. The intensity of DMPO-OOH/O₂^{•-} signals in EPR spectra with irradiation time over various TiO_{2-x}N_x samples: a, x = 0.020; b, x = 0.025; c, x = 0.034; d, x = 0.036; e, x = 0.101.

