

## Supplementary Information

### **Engineering N-doped TiO<sub>2</sub>@N-doped C butterfly-like Nanostructure with Long-lived Photo-generated Carriers for Efficient Photocatalytic Selective Amine Oxidation**

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## **1. Experimental detail**

### **1.1 Preparation of pure TiO<sub>2</sub> nanoparticles:**

#### **1.1.1 Preparation of potassium titanate nanowires (KTNWs):**

KTNWs as the precursor were prepared in a hydrothermal reaction between a concentrated KOH solution and P25, according to the previous report <sup>[1]</sup>. Typically, KOH (44.8 g) was dissolved in distilled water (80 mL), with subsequent addition of P25 (2 g) under magnetic stirring to form a white suspension. Equal portions of the suspension were transferred into three Teflon-lined stainless-steel autoclaves with the capability of 50 mL, and then the autoclaves were kept at 200 °C for 24 h. After reaction, the white precipitate in the autoclaved mixture was collected by centrifugation, washed with distilled water (3-4 mL) and ethanol (3-4 mL), and finally dried in an oven at 60 °C.

#### **1.1.2 Synthesis of pure anatase TiO<sub>2</sub> nanoparticles**

TiO<sub>2</sub> single nanocrystals were synthesized by a one-step hydrothermal process by using KTNMs as the starting materials. Typically, KTNMs (0.025 g) was dispersed in water (27 mL), and HF (0.02mL, 40 wt% (equal to 22.5 mol L<sup>-1</sup>)). The suspension was transferred to a Teflon-lined autoclave and heated at 180 °C for 12 h. After the autoclave cooled to room temperature naturally, samples were collected by centrifugation, thoroughly washed with distilled water and ethanol 3-4 times, and dried at 60 °C. The as-prepared pure photocatalyst was then calcined at 450 °C for 2 h under air to prepare the TiO<sub>2</sub> samples.

## 1.2 Preparation of N doped TiO<sub>2</sub> nanoparticles:

The synthesis of N-doped TiO<sub>2</sub> samples was developed a modi-fied synthesis process which reported by Chen et al.<sup>[2]</sup> Typically, 0.04 g of as-prepared pure photocatalyst was added to 2mL of ethylenediamine and stirred for 12 h at room temperature. Upon washing with deionized water and ethanol alternately and drying at 60 °C, the resultant pale-yellow material was then calcined at 450 °C for 2 h under vacuum to prepare the final N-doped TiO<sub>2</sub> samples.

## 2. Experimental results

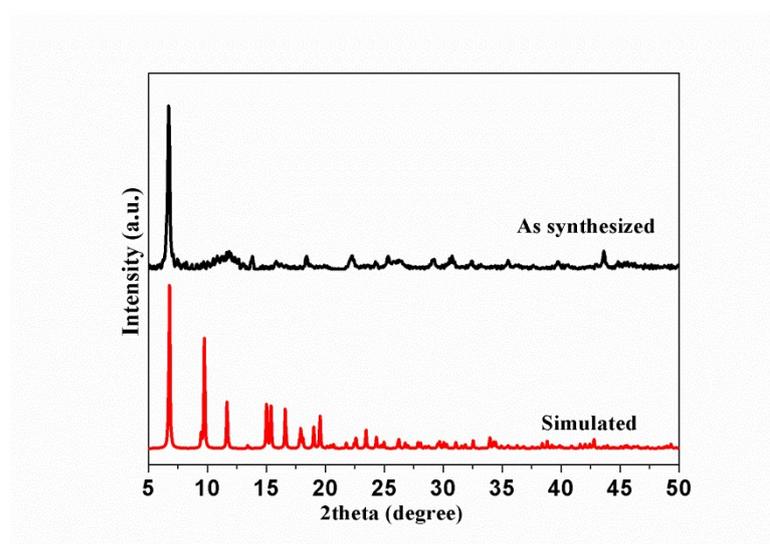


Fig. S1 XRD pattern of simulated NH<sub>2</sub>-MIL-125 (Ti) and the as-synthesized product.

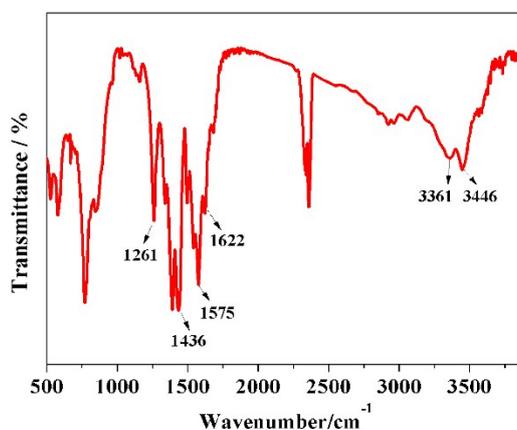


Fig. S2 FTIR spectrum of precursor.

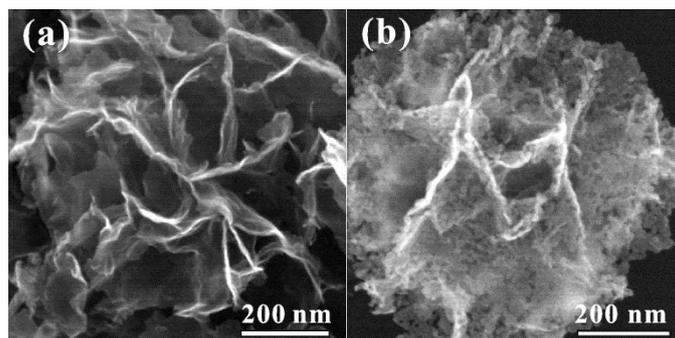


Fig. S3 Typical high-magnification SEM images of  $\text{NH}_2\text{-MIL-125(Ti)}$  precursor (a), (b) TNPC particles.

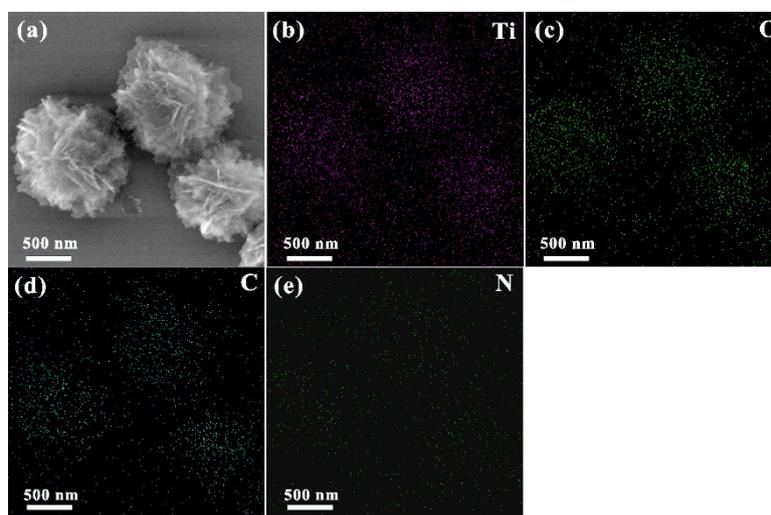


Fig. S4 Element mapping of as-obtained  $\text{NH}_2\text{-MIL-125(Ti)}$  precursor.

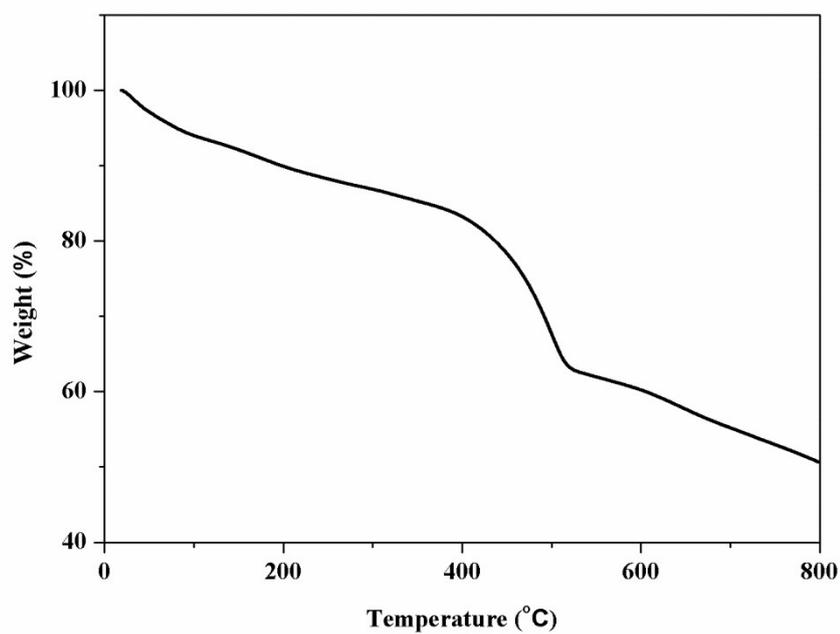


Fig. S5 TGA curves of the as-obtained NH<sub>2</sub>-MIL-125(Ti) precursor.

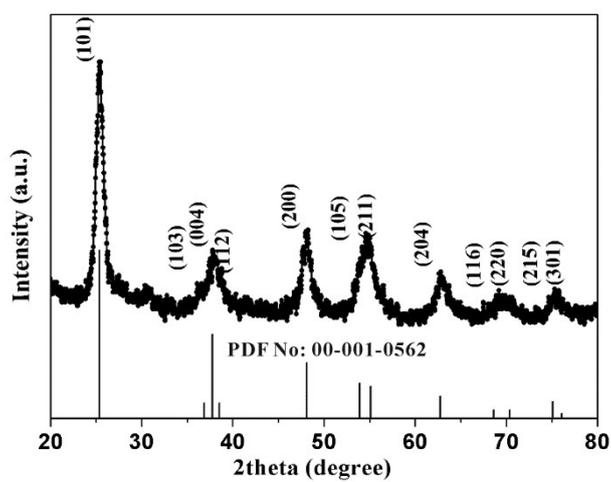


Fig. S6 The XRD pattern of TNPC particles.

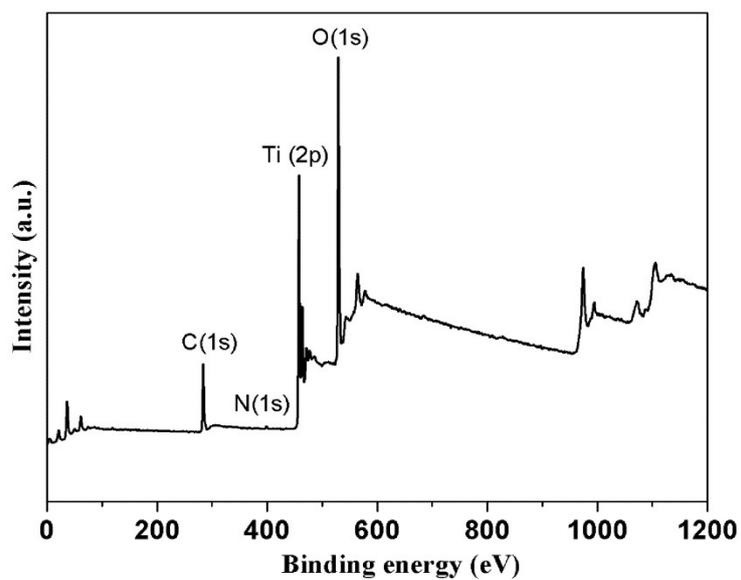


Fig. S7 XPS survey spectrum of TNPC nanoparticles.

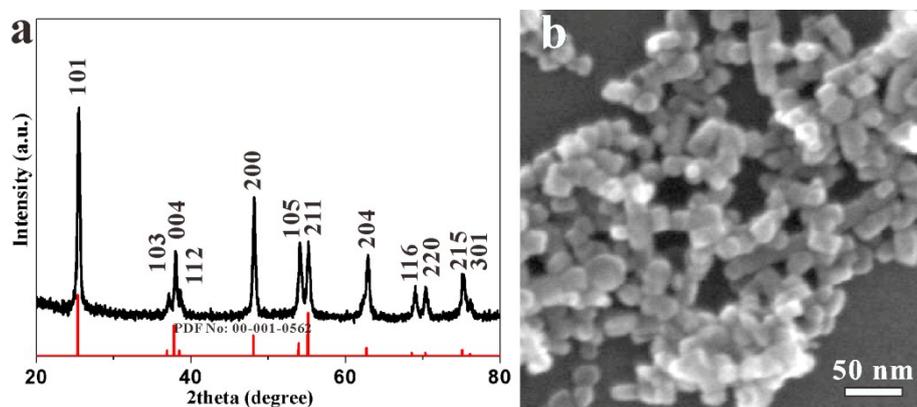


Fig. S8 (a) XRD pattern of pure  $\text{TiO}_2$ , (b) SEM image of pure  $\text{TiO}_2$ .

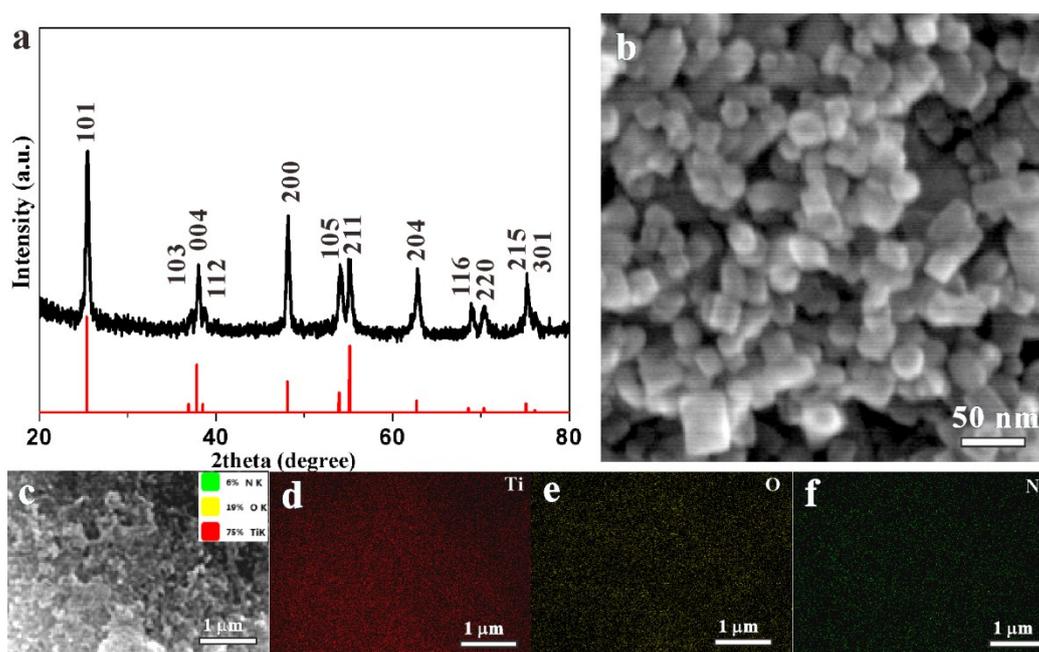


Fig. S9 (a) XRD pattern of pure N doped anatase TiO<sub>2</sub>, (b) SEM image of N doped anatase TiO<sub>2</sub>, (c-f) Corresponding elemental mapping.

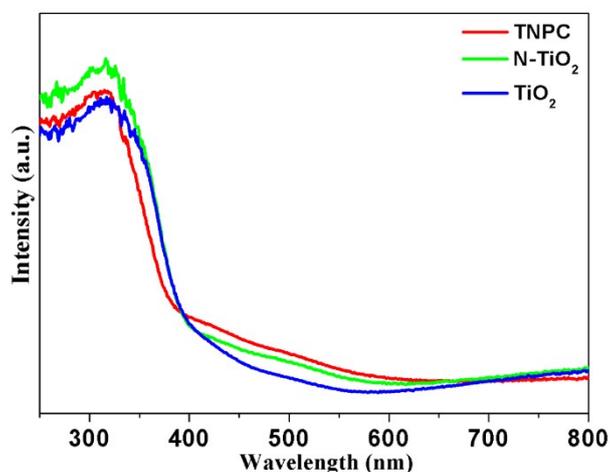


Fig. S10 Uv-vis absorption spectra of TNPC, N-TiO<sub>2</sub> and pure TiO<sub>2</sub> nanoparticles.

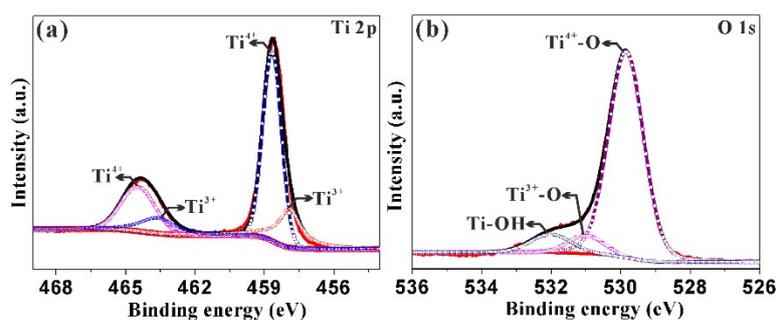


Fig. S11 High resolution XPS spectra of synthesized pure TiO<sub>2</sub> (a) Ti2p; (b) O1s.

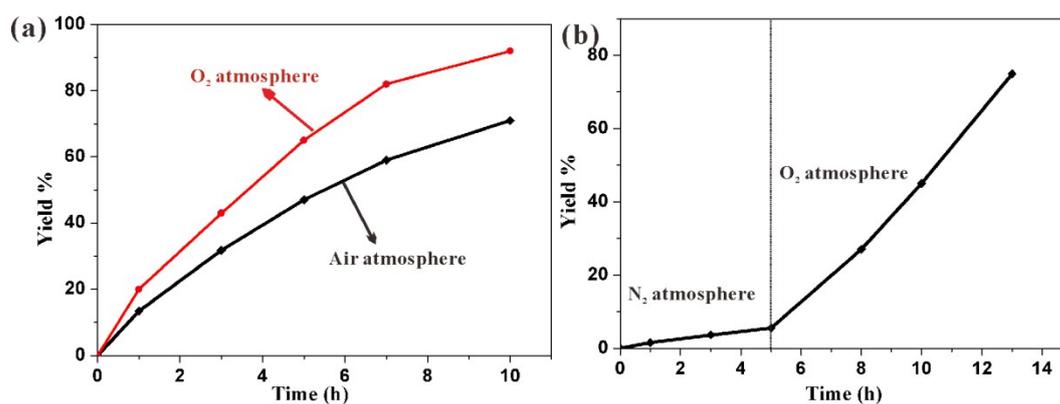


Fig. S12 Reactant conversion with respect to reaction time in the oxidative coupling of benzylamine in different atmosphere, (a) O<sub>2</sub> and air; (b) N<sub>2</sub> and O<sub>2</sub> atmosphere.

Table S1. Photocatalysis oxidation coupling of amines to imines in different reaction

conditions

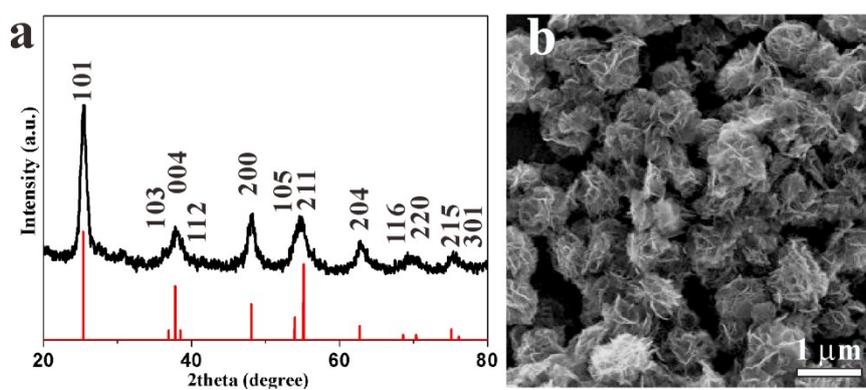
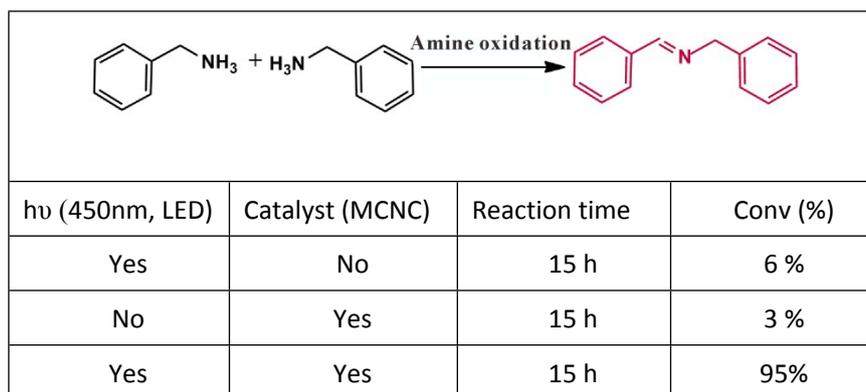


Fig. S13 (a) XRD pattern of TNPC nanoparticles after catalytic reaction, (b) SEM image of TNPC nanoparticles after catalytic reaction.

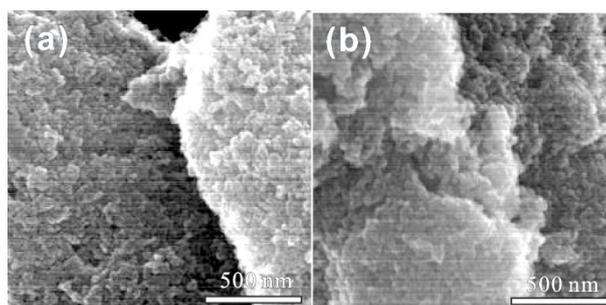


Fig. S14 SEM image of (a) Pure  $\text{TiO}_2$  nanoparticles and (b)  $\text{N-TiO}_2$  after catalytic reaction.

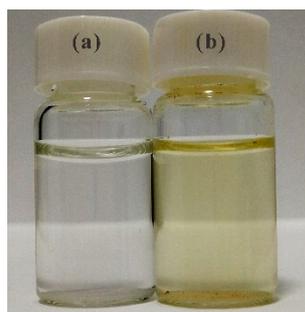


Fig. S15 Detection the  $\text{H}_2\text{O}_2$  in the selective amine oxidation to imines reaction. (a) the image of KI, aqueous acetic acid and starch, (b) the image of KI, aqueous acetic acid, starch and extracting solution of selective amine oxidation to imines.

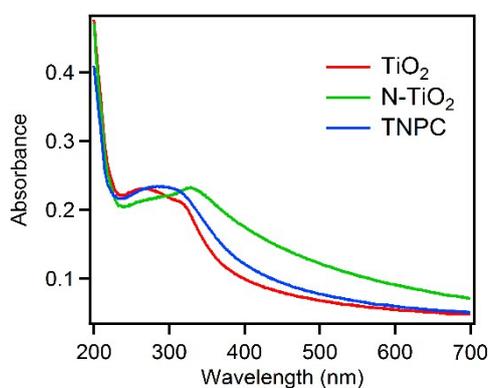


Fig. S16 UV/Vis of samples in acetonitrile solution after TA measurement.

Table S2. Fitting parameters of transient absorption kinetic at 800 nm<sup>a</sup>

800nm	$\tau_1$	$A_1$	$\tau_2$	$A_2$	$\tau_3$	$A_3$	$A_4$
$\text{TiO}_2$	$2.8 \pm 0.7\text{ps}$	25%	$96.6 \pm 20\text{ps}$	26%	$798 \pm 200\text{ps}$	19%	-30%
N- $\text{TiO}_2$	$4.0 \pm 1.2\text{ps}$	14%			$774 \pm 43\text{ps}$	39%	-47%
TNPC	$3.9 \pm 0.6\text{ps}$	21%			$222 \pm 7\text{ps}$	45%	-34%

<sup>a</sup> Raw signals were fit to the function  $A_4 + \sum_{i=1}^3 A_i \exp(-t / \tau_i)$ . Percentage amplitudes

reported in the table were then calculated as  $A_i / \sum_{i=1}^4 |A_i|$ .

### 3. Reference

[1] M. Wagemaker, A. P. M. Kentgens, F. M. Mulder, *Nature*, **2002**, 418, 397 – 399.

[2] X. B. Chen, Y. B. Lou, A. C. S. Samia, C. Burda, J. L. Gole, *Adv. Funct. Mater.* **2005**, 15, 41–49.