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Visible light-initiated aerobic oxidation of amines to imines over TiO₂ microspheres with TEMPO⁺PF₆⁻

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1. Experimental section

1.1 Reagents and solvents

Titanium isopropoxide (TTIP) and acetone were procured from TCI and Sinopharm Chemical Reagent Co. Ltd., China, respectively. Benzyl- α,α - D_2 -amine was supplied by CDN Isotopes, Quebec, Canada. Other reagents and solvents were purchased from commercial suppliers such as Adamas, Sigma-Aldrich, Alfa Aesar and TCI, J & K Scientific, Merck, Fischer Scientific, and Sinopharm Chemical Reagent Co. Ltd., China. All the reagents and solvents were directly used without further purification.

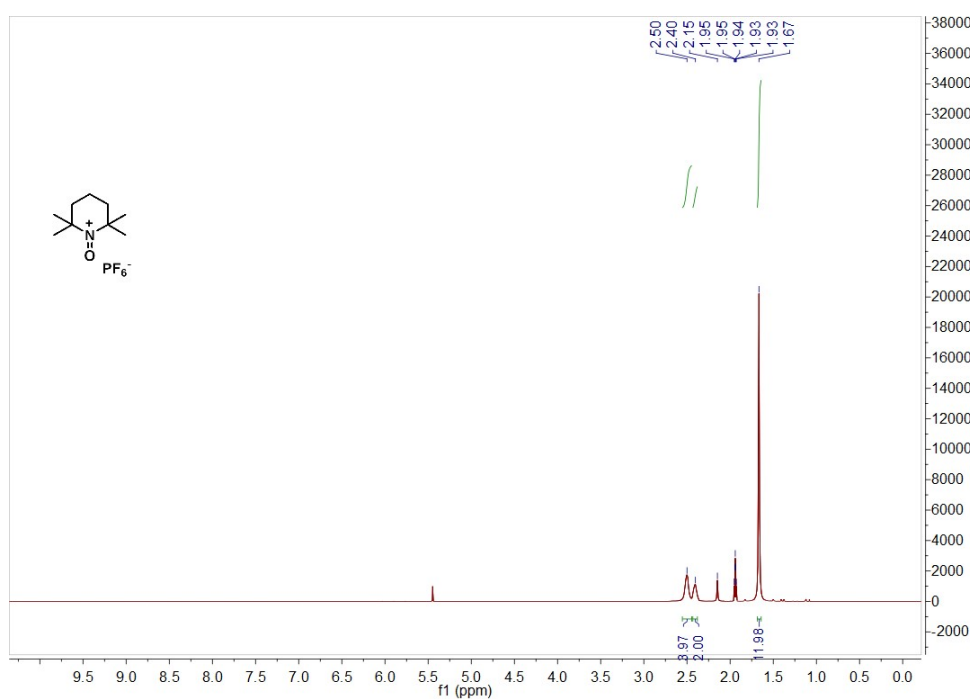
1.2 Preparation of TiO₂ microspheres

The TiO₂ microspheres were synthesized via a reported nonaqueous solvothermal method.¹ Firstly, anhydrous acetone was prepared from activated molecular sieves. Then, 2 mL of titanium isopropoxide was quickly added into 60 mL of anhydrous acetone followed by stirring for 30 min under ambient conditions. The transparent mixture was subsequently transferred to a Teflon-lined stainless-steel autoclave (100 mL volume). The solvothermal reaction was carried out in an electric oven at 200 °C for 12 hours. After synthesis, the yellowish precipitate was separated through centrifugation and washed several times with deionized water and absolute ethanol. The obtained precipitate was sent to a vacuum oven and dried at 60 °C overnight. Calcining the dried yellowish powder at 400 °C for 2 hours could remove the residual carbonate. And TiO₂ microspheres were provided.

1.3 Preparation of TEMPO⁺PF₆⁻

The TEMPO⁺PF₆⁻ was prepared according to an already reported procedure.² TEMPO (2 g, 12.8 mmol) was first transferred to deionized water (20 mL, 1.11 mol). And 60% HPF₆ (2 mL, 12.8 mmol) was added dropwise for more than one hour at room temperature. While the solution turned to an amber color, NaOCl (4.6 mL, 6.4 mmol) was added dropwise for more than one hour at an ice-water bath and stirred for another hour at an ice-water bath. The yellow crystalline precipitate was gathered via filtration and was then washed with 20 mL of 5% ice-cold NaHCO₃, 40 mL of water, and 200 mL of ice-cold Et₂O. The bright yellow TEMPO⁺PF₆⁻ (1.3 g, 4.3 mmol, 34%) was obtained by drying the solid over 24 h at 50 °C in vacuo. Anal: Calcd. for C₉H₁₈F₆NOP: C, 35.89; H, 6.02; N, 4.65 found: C, 35.67; H, 5.733; N, 4.9.

¹H NMR (400 MHz, CD₃CN): δ 2.50 (s, 4H), 2.40 (s, 2H), 1.67 (s, 12H).



1.4 Characterization of the materials

Field emission scanning electron microscopy (FESEM) images of the solid samples were measured on a Zeiss Merlin Compact field emission scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were collected on a JEOL JEM-2100 operating at 200 kV. Powder X-ray diffraction (PXRD) measurement was carried out using a Rigaku/Miniflex 600 diffractometer with filtered Cu K α radiation, and the data were collected from 10° to 80°. The UV–visible absorbance of TiO₂ microspheres and benzylamine–TiO₂ microspheres samples were measured on a UV–3600 UV–vis spectrophotometer (Shimadzu, Japan) equipped with a diffuse reflectance measurement accessory. BaSO₄ was used as a reflectance standard. The specific surface areas were determined by N₂ physisorption using an ASAP automated system and the Brunauer-Emmet-Teller (BET) method. Each sample was degassed under vacuum ($< 1 \times 10^{-5}$ bar) in the Micromeritics system at 200 °C for 3 h before N₂ physisorption. X-ray photoelectron spectra (XPS) were examined on a Thermo Scientific™ K-Alpha™ (ThermoFisher). The electron paramagnetic resonance (EPR) tests were executed on an EPR spectrometer (JEOL, JES-FA 300). ¹H spectra were made on a Bruker AVANCE III HD 400 MHz NMR spectrometer. The thermogravimetric analysis (TGA) was performed by heating the TiO₂ microspheres at a rate of 10 °C min⁻¹ from room temperature to 800 °C in a nitrogen flow (NETZSCH STA2500).

1.5 Typical procedure for the selective photocatalytic oxidation of amines

Firstly, 1 mL of CH₃CN, 0.5 mmol of benzylamine, and 40 mg of TiO₂ microspheres were added into a 10 mL Pyrex reactor. Next, the mixture was dispersed via 5 min of ultrasonication and arrived at adsorption-desorption equilibrium through stirring for 30 min in the dark. Subsequently, 15 μmol TEMPO⁺PF₆⁻ was added to the reaction mixture and sonicated for 3 min. Then, the reaction system was full of aerial O₂ due to the small hole in the rubber septum of the Pyrex reactor. Under the irradiation of 460 nm blue LEDs (3 W × 4), the reaction proceeded smoothly through stirring magnetically at 1500 rpm. Finally, the photocatalysts TiO₂ microspheres were separated from the reaction mixture using centrifugation. With chlorobenzene as the internal standard, the reaction products were analyzed by gas chromatography equipped with a flame ionization detector (GC–FID, Agilent 7890B).

Conversions for oxidation of amines, yields, and selectivities to the desired imines were defined as follows:

$$\text{Conv. (\%)} = [(C_0 - C_S) / C_0] \times 100$$

$$\text{Sel. (\%)} = [C_P / (C_0 - C_S)] \times 100$$

where C₀ is the initial concentration of amines, and C_S and C_P are the concentrations of amines and imines at a specific time during the photocatalytic reaction. The products were confirmed by comparison with standard samples' retention time and further affirmed by gas chromatography–mass spectrometry (GC–MS, Agilent 5977B GC/MSD).

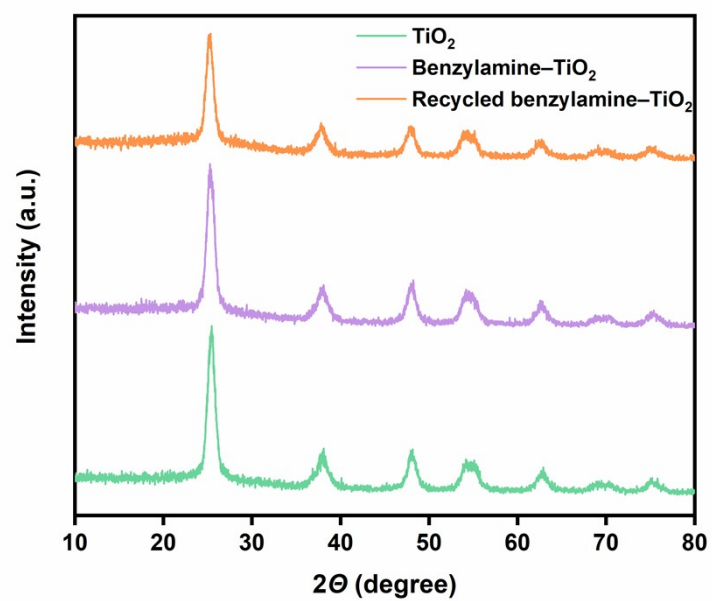


Fig. S1. The PXR D patterns of TiO₂ microspheres, benzylamine-TiO₂ microspheres, and recycled benzylamine-TiO₂ microspheres.

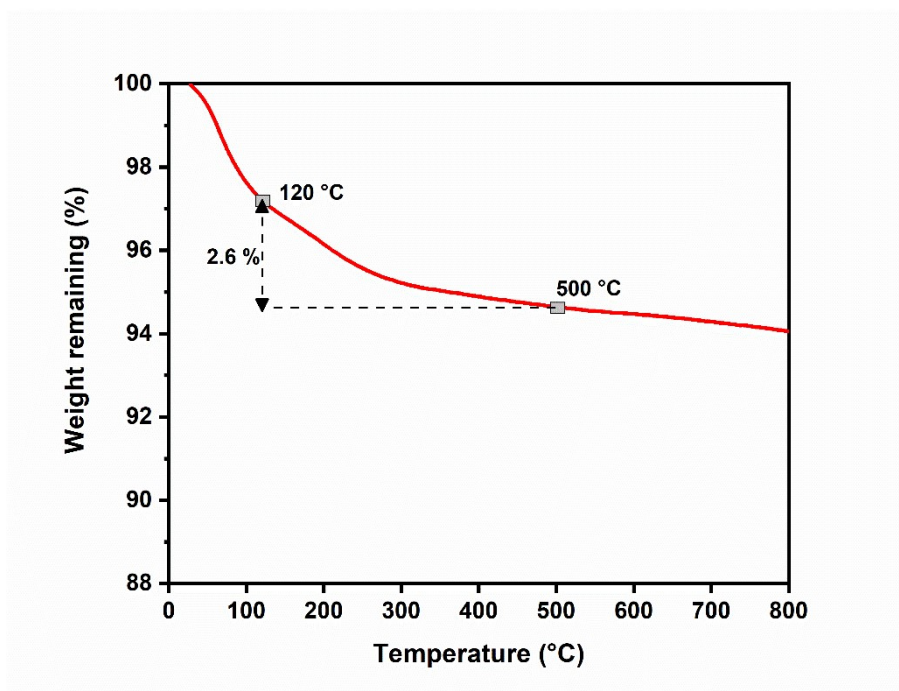


Fig. S2. TGA curve of TiO₂ microspheres recorded in a dynamic N₂ atmosphere.

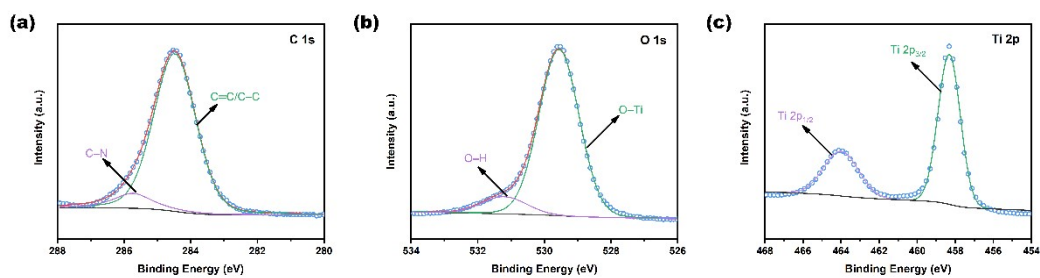


Fig. S3. High-resolution XPS spectra of (a) C 1s, (b) O 1s, and (c) Ti 2p.

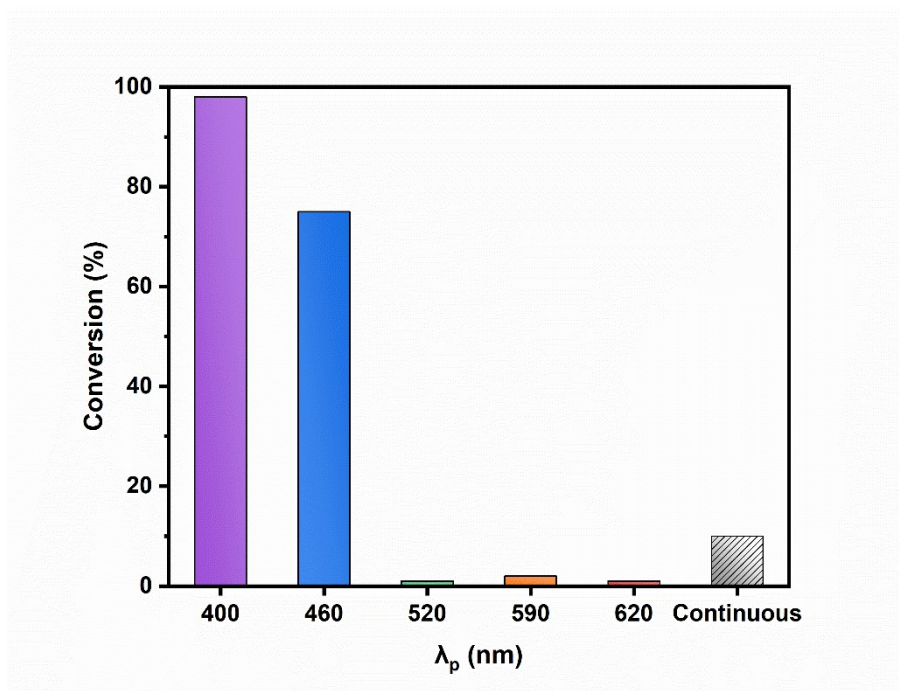


Fig. S4. The influence of different LEDs on the selective aerobic oxidation of benzylamine by cooperative photocatalysis of TiO_2 microspheres with $\text{TEMPO}^+\text{PF}_6^-$. Reaction conditions: TiO_2 microspheres (40 mg), $\text{TEMPO}^+\text{PF}_6^-$ (0.015 mmol), benzylamine (0.5 mmol), air (1 atm), CH_3CN (1 mL), LEDs (460 ± 10 nm), 0.7 h.

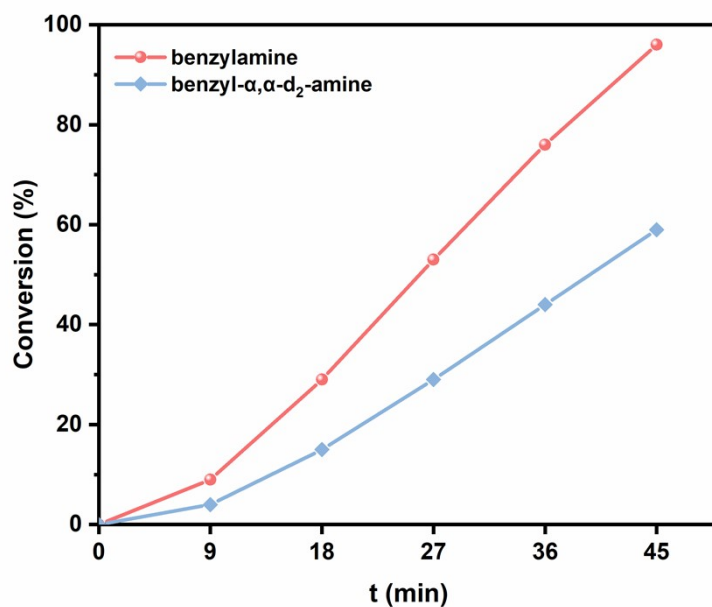


Fig. S5. Reaction kinetic plots of the selective aerobic oxidation of benzylamine and benzyl- α,α -d₂-amine by cooperative photocatalysis of TiO₂ microspheres with TEMPO⁺PF₆⁻. Reaction conditions: TiO₂ microspheres (20 mg), TEMPO⁺PF₆⁻ (0.0075 mmol), benzylamine (0.25 mmol), benzyl- α,α -d₂-amine (0.25 mmol), air (1 atm), CH₃CN (1 mL), blue LEDs (460 ± 10 nm). Conversion of benzylamine was determined by GC-FID using chlorobenzene as the internal standard.

Table S1. The influence of the different photocatalyst on the blue light-initiated selective aerobic oxidation of benzylamine ^a

| Entry | Photocatalyst | Crystal phase | Conv. (%) ^b | Sel. (%) ^b |
|-------|---|----------------|------------------------|-----------------------|
| 1 | TiO ₂ microspheres | Anatase | 75 | 99 |
| 2 | P25 TiO ₂ | Anatase/rutile | 54 | 99 |
| 3 | Alfa Aesar TiO ₂ | Anatase | 53 | 99 |
| 4 | TiO ₂ | Rutile | 44 | 99 |
| 5 | TiO ₂ /SiO ₂ (1:1) ³ | -- | 9 | 99 |

^a Reaction conditions: photocatalyst (40 mg), TEMPO⁺PF₆⁻ (0.015 mmol), benzylamine (0.5 mmol), air (1 atm), CH₃CN (1 mL), blue LEDs (460 ± 10 nm), 0.7 h. ^b Determined by GC-FID using chlorobenzene as the internal standard, conversion of amines, and selectivity of corresponding imines.

Table S2. The influence of solvent on the selective aerobic oxidation of benzylamine by cooperative photocatalysis of TiO₂ microspheres with TEMPO⁺PF₆⁻ ^a

| Entry | Solvent | Conv. (%) ^b | Sel. (%) ^b |
|-------|----------------------------------|------------------------|-----------------------|
| 1 | CH ₃ CN | 75 | 99 |
| 2 | Cyclohexane | 67 | 99 |
| 3 | C ₂ H ₅ OH | 34 | 86 |
| 4 | CH ₃ OH | 19 | 76 |

^a Reaction conditions: TiO₂ microspheres (40 mg), TEMPO⁺PF₆⁻ (0.015 mmol), benzylamine (0.5 mmol), air (1 atm), solvent (1 mL), blue LEDs (460 ± 10 nm), 0.7 h. ^b Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine.

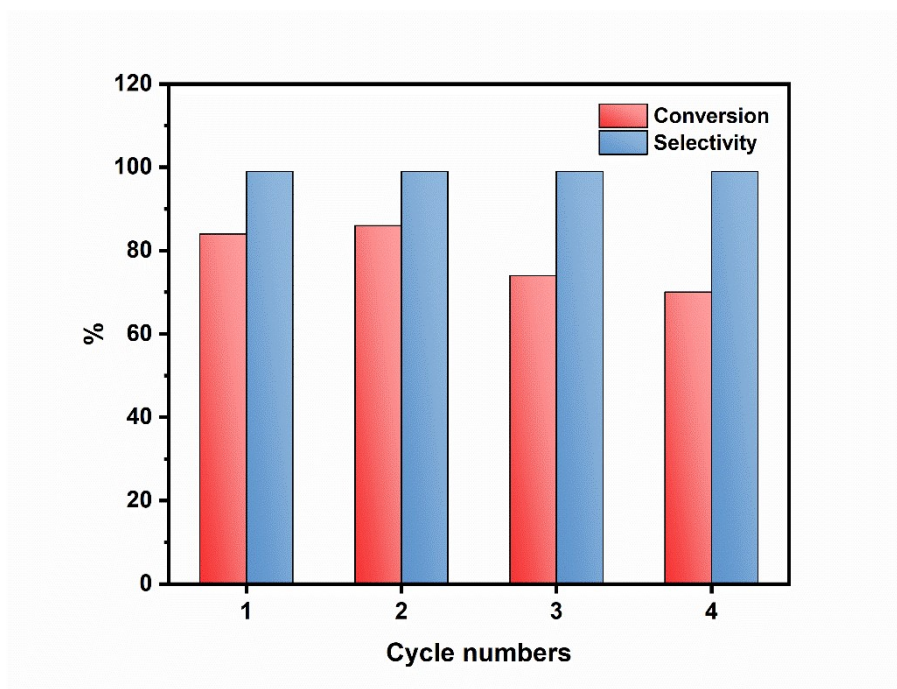


Fig. S6. Recycling experiments for the blue light-initiated selective aerobic oxidation of benzylamine by cooperative photocatalysis of TiO₂ microspheres with TEMPO⁺PF₆⁻. Reaction conditions: TiO₂ microspheres (40 mg), TEMPO⁺PF₆⁻ (0.015 mmol), benzylamine (0.5 mmol), air (1 atm), CH₃CN (1 mL), blue LEDs (460 ± 10 nm), 0.8 h.

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