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Supporting Information

Enhancement of Aerobic Photocatalytic Benzylamine Oxidation Coupling Reaction through Light-Induced Carrier Spatial Separation

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1 Materials and Physical Measurements.

Materials

All chemicals are commercial and used without further purification. Such as zirconium tetrachloride ($ZrCl_4$), 2-aminoterephthalic acid (NH_2-BDC), palladium chloride ($PtCl_2$), N,N-dimethylformamide (DMF) and absolute ethanol (C_2H_5OH) and so on.

Physical Measurements

scanning electron microscopy (SEM) images were obtained on a field-emission scanning electron microanalyzer. After 30 minutes of ultrasound uniform dispersion in ethanol solution (1 mg/mL), a little amount of the resulting sample was deposited on a silicon wafer on a conductive substrate, dried under vacuum, and thereafter analyzed by scanning electron microscopy. Then, the morphology and microstructure of the samples were characterized by transmission electron microscopy (TEM) (JEM-2100, Japan). The N_2 desorption isotherms of the samples were measured by the BELSORP-max adsorption instrument and the pore size distribution and specific surface area of the samples were analyzed by the software of the instrument itself. The temperature of the adsorption samples was controlled at 77 K by liquid nitrogen. The ratio of substrate to product in the catalytic reaction was analyzed using 400 MHz Bruker Avance-400 nuclear magnetic resonance (NMR) spectroscopy, the chemical shift of which was calibrated with tetramethylsilane as internal standard (0 PPM). The crystallinity and purity of UiO-66-NH_2 and its composites were studied by means of Dutch PANalytical Powder X-ray Diffraction (PXRD) with wavelength of 1.5418 Å Cu Kα. The X-ray photoelectron spectroscopy (XPS) was tested on the Axis Supra instrument and the full spectra and fine spectra for each element were calibrated with vacuum carbon as internal standard (284.6 eV). The UV-vis diffuse reflectivity profile was obtained using the JASCO V-750 UV-vis spectrophotometer. Photoluminescence spectra were determined at room temperature on a Hitachi F-4600 fluorometer. The contents of Pt NPs and Cu_2O NPs in Pt@UiO-66-NH_2-OH@Cu_2O composites was measured using Optimass 9500 inductively coupled plasma emission spectroscopy (ICP-OES). Electrochemical characterizations such as impedance, transient photocurrent and Mott-Schottky (M-S) curves were tested on the Chenhua CHI 600e Electrochemical Workstation. The electrolyte tested was 0.1 mol/L sodium sulfate aqueous solution. The electron spin resonance spectra of the material were measured on the Bruker A300 Spin Resonance Spectrometer, and the superoxide free radical, singlet oxygen and hydroxyl radicals were measured by the addition of dimethylpyridine nitrogen oxides.

2 Experimental Section

Synthesis of UiO-66-NH_2-OH. The same method was used for the synthesis of UiO-66-NH_2-OH, with the difference that 2-aminoterephthalic acid (162 mg, 0.9 mmol) and 2,5-dihydroxyterephthalic acid (20 mg, 0.1 mmol) were replaced by 2-amino-terephthalic acid (171 mg, 0.95 mmol) and 2,5-dihydroxyterephthalic acid (10 mg, 0.05 mmol),respectively, and 2-amino-terephthalic acid (144 mg, 0.80 mmol) and 2,5-dihydroxyterephthalic acid (40 mg, 0.20 mmol) to obtain UiO-66-NH_2-OH (5% U), UiO-66-NH_2-OH (10%U) and UiO-66-NH_2-OH（15% U）, respectively. In the text, UiO-66-NH_2-OH is (10%U)[1].

Synthesis of Pt/UiO-66-NH_2-OH. Add UiO-66-NH_2-OH (40 mg) and polyvinylpyrrolidone (60 mg) to a mixture of ethanol and distilled water (1:1, 80 mL). Subsequently, H_2PtCl_6 (2 mL, 2.44 mM) was added and sonicated for 30 minutes. After cooling to room temperature, the products were collected by centrifugation and washed with ethanol (3×10 mL) and acetone (3×10 mL), respectively. Finally, the product was dried in a vacuum drying oven at 80°C for 12 hours to obtain gray-yellow Pt/UiO-66-NH_2-OH crystals[2].

Detection experiment of active species. EPR signals were detected by a Bruker A300E spectrometer. At room temperature, 10 mg samples were dispersed in 10 mL methanol by ultrasound. Then, 30 μL suspension was added to 30 μL 50 mM DMPO (5,5-dimethyl-1-pyrroline Noxide) solution. After mixing and shaking well, the samples were put into the machine for testing $\cdot O_2^-$. In addition, testing h^+ is conducted with the similar method except replacing DMPO with TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl). All the above testing times are five minutes.

Femtosecond pump-probe TA. The femtosecond pump-probe TA measurements were performed using a regenerative amplified Ti:sapphire laser system (Coherent; 800nm, 100 fs, 7mJ/pulse, and 1kHz repetition rate) as the laser source and a HELIOS spectrometer (Ultrafast Systems LLC) as the spectrometer. The white-light continuum (475–750 nm) (WLC) probe pulse were generated by focusing the 800-nm beam (split from regenerative amplifier with a tiny portion) onto sapphire. The time delay (0-8 ns) between the pump and probe pulses were varied by a motorized optical delay line. A mechanical chopper operating at 500 Hz was used to modulate the pump pulses such that the fs-TA spectra with and without the pump pulses can be recorded alternately. The samples dispersed in dimethylsulfoxide were contained in a 2-mm quartz cuvettes under a continuous magnetic stirring condition ensuring that the photoexcited volume of the sample was kept fresh during the course of the fs-TA measurements.

3. Results

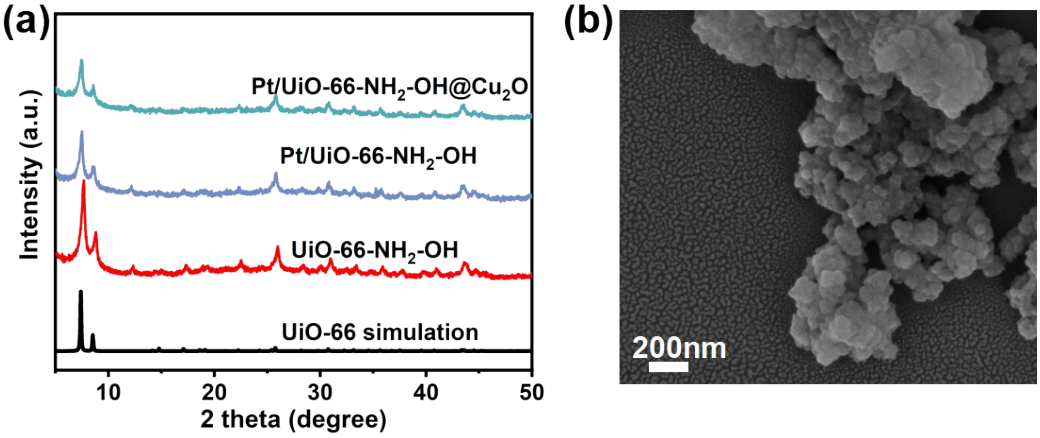


Figure S1 PXRD patterns of UiO-66-NH$_2$, Pt/UiO-66-NH$_2$-OH and Pt/UiO-66-NH$_2$-OH@Cu$_2$O; Scanning electron microscope (SEM) images of (b) Pt/UiO-66-NH$_2$-OH@Cu$_2$O.

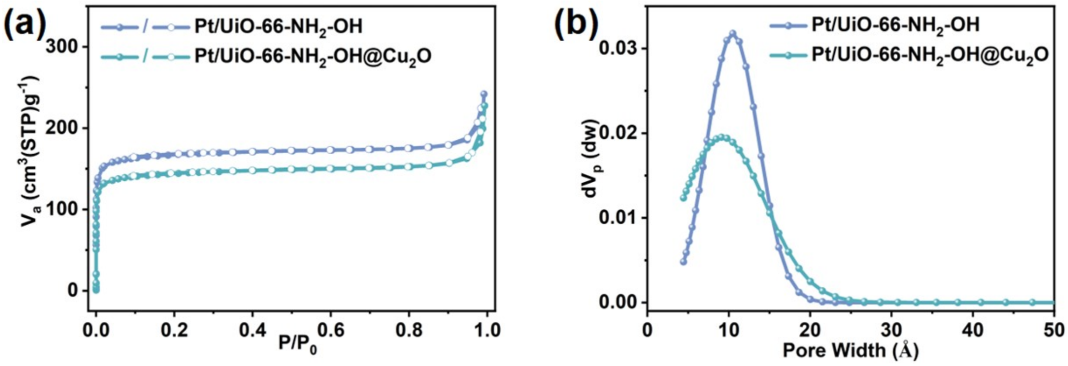


Figure S2 (a) Nitrogen adsorption-desorption isotherms and (b) pore size distributions for $Pt/UiO-66-NH_2-OH$ and $Pt/UiO-66-NH_2-OH@Cu_2O$.

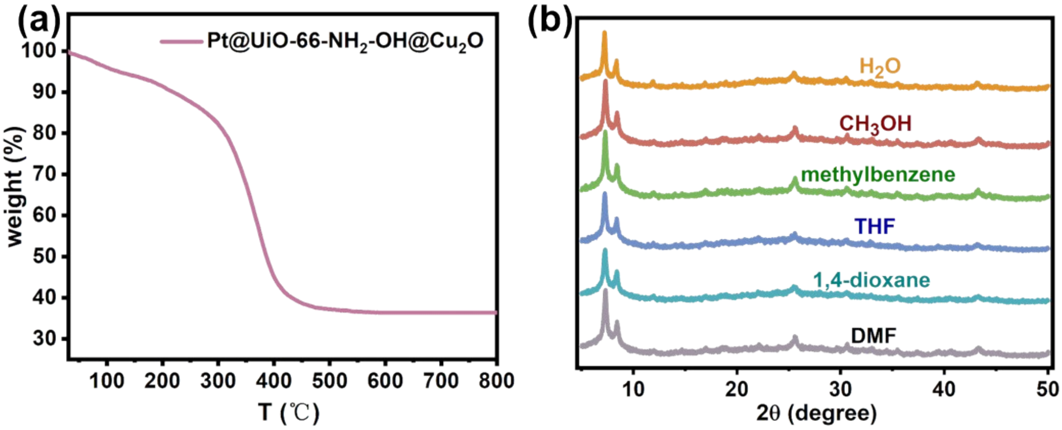
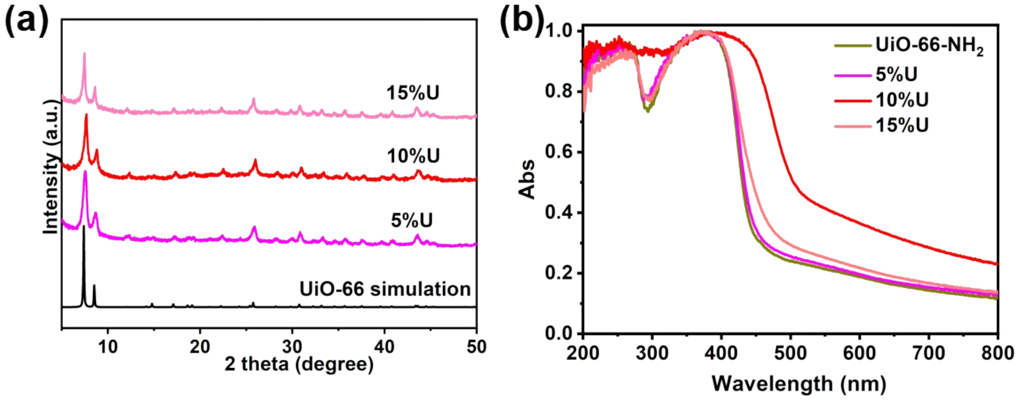
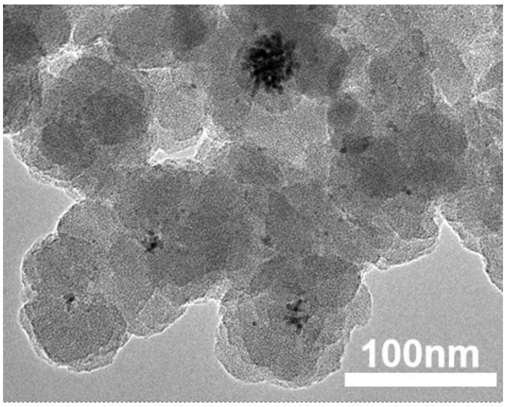


Figure S3 (a) Thermogravimetric analysis (TGA) curve of $Pt@UiO-66-NH_2-OH@Cu_2O$, and (b) PXRD patterns of $Pt@UiO-66-NH_2-OH@Cu_2O$ after immersion in various organic solvents for 24 hours.



Figures S4. (a) PXRD patterns of 5%U, 10%U($UiO-66-NH_2-OH$), and 15%U; (b) UV-visible diffuse reflectance patterns of $UiO-66-NH_2$, 5%U, 10%U($UiO-66-NH_2-OH$), and 15%U.



Figures S5 TEM of 1.5Pt@UiO-66-NH$_2$-OH

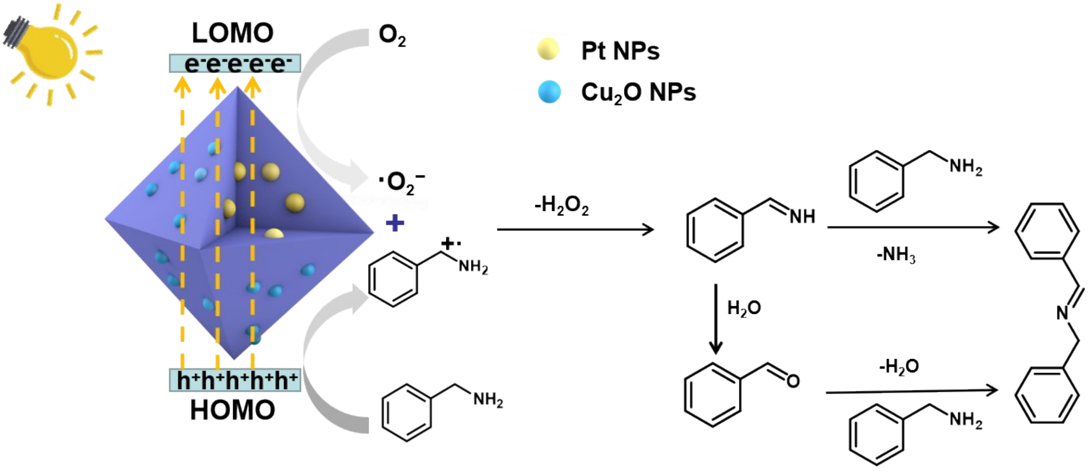


Figure S6 Proposed mechanism on Pt@UiO-66-NH$_2$-OH@Cu$_2$O for the photocatalytic oxidation of benzylamine.

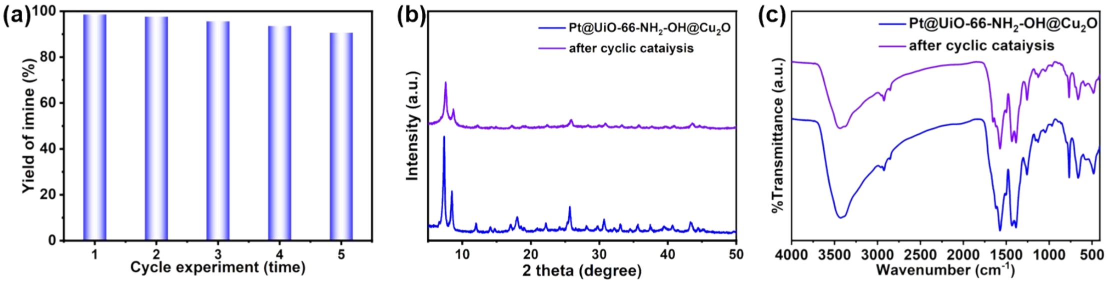


Figure S7 (a) Recycling photocatalytic experiments of Pt@UiO-66-NH$_2$-OH@Cu$_2$O. (b) PXRD pattern and (c) FT-IR spectra of Pt@UiO-66-NH$_2$-OH@Cu$_2$O after cyclic cataiysis.

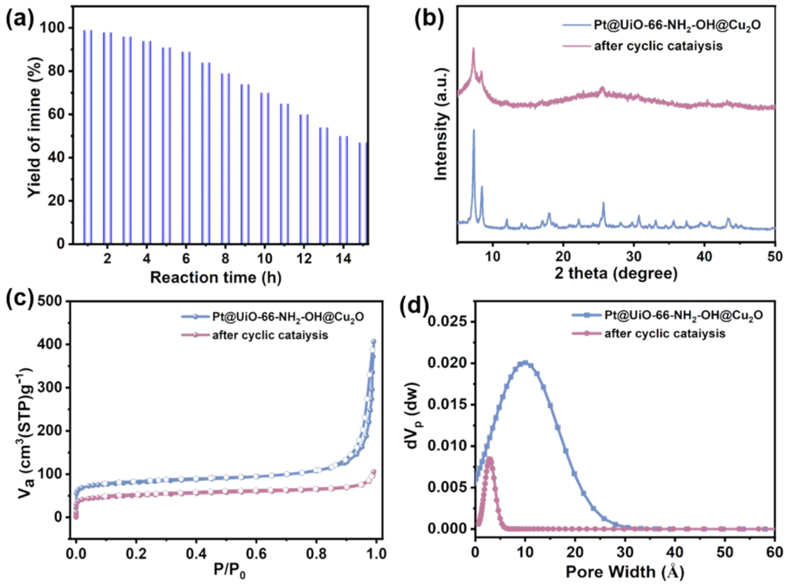


Figure S8 (a)The long-time (15 h) recycling performanceof Pt@UiO-66-NH_2-OH@Cu_2O, (b) XRD patterns, (c) N_2 adsorption-desorption isotherms, and (d) pore size distribution curves of Pt@UiO-66-NH_2-OH@Cu_2O before and after long-term catalytic cycles.

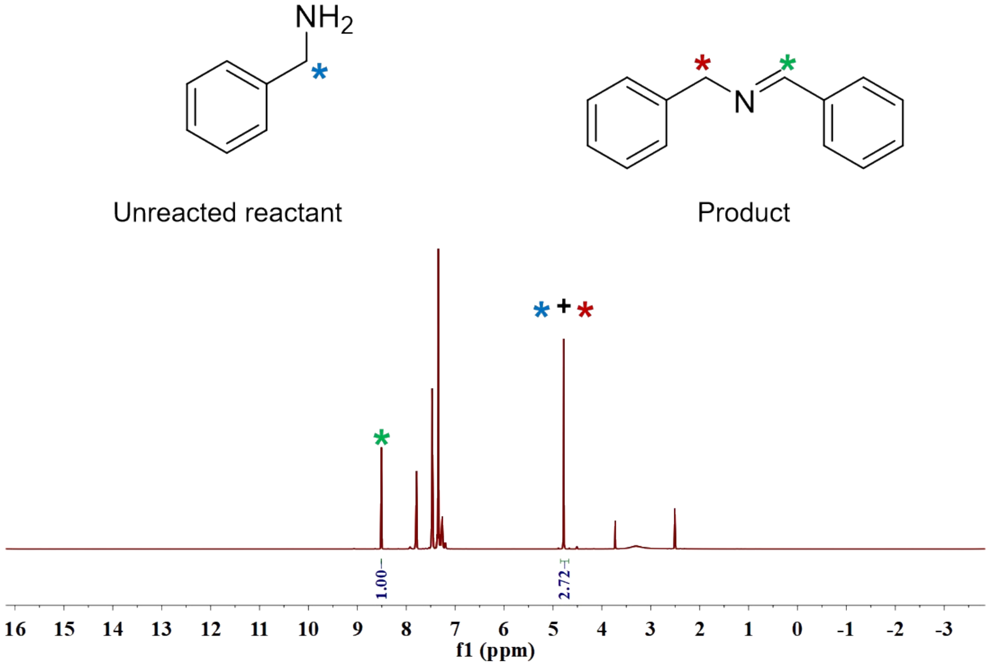


Figure S9 ^1H NMR spectra of the solution of the product without H_2O in the reaction system

Table S1 Performance of visible-light-induced self-coupling of benzylamine using photocatalysits.

Entry	Catalyst	Reaction Condition	Recyclable	Time (h)	Yield (%)	Ref. No.
1	F70-TiO_2(1:20)	Air balloon, MeCN, λ > 400 nm	5	12	97.6	6
2	Ti-MOF/g-C_3N_4	Air, 300 W Xe lamp	5	3	88	7
3	$Cu_2WO_4(OH)_2$	O_2, MeCN, 300 W Xe lamp	4	8	88.84	8
4	$Bi_2O_2CO_3$/g-C_3N_4	Air balloon, DMF, 300W Xe lamp	4	3	93.3	9
5	HPM/Cu_X-MCS-s	DMF, H_2O and 25℃, LED	4	1	98	10
6	This work	MeCN, 100 W LED lamp	5	1	99	

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