

Electronic Supplementary Information

Hydroxynaphthalene–Nb₂O₅ complex photocatalysis for selective aerobic oxidation of amines induced by blue light

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1. Materials and methods

1.1 Materials

Niobium(V) chloride (NbCl_5), anhydrous *n*-butanol, Pluronic P123 and Nitric acid (65–68%) are procured from commercial suppliers. Benzyl- α,α - d_2 -amine is provided by CDN Isotopes, Quebec, Canada. No further purification was carried out for all the reagents.

1.2 Preparation of mesoporous Nb_2O_5

The mesoporous Nb_2O_5 was prepared based on a previously reported procedure, 0.01 mol of NbCl_5 is dissolved in 15 mL of anhydrous *n*-butanol followed by the addition of 1.4 mL of nitric acid (65–68%) and 2.0 g of Pluronic P123 under stirring overnight. The transparent sol was placed in a vacuum chamber at 120 °C for 6 h. Next, the as-prepared gel was calcined under 500 °C for 5 h with a programming rate of 2 °C/min.

1.3 Instrumentations

Transmission electron microscopy (TEM) and high-resolution TEM images were collected on a JEOL JEM2012–FEF operated at 200 kV. Scanning electron microscopy (SEM) images of the solid samples were measured on Zeiss Merlin Compact field emission scanning electron microscope. Powder X-ray diffraction (PXRD) measurement was carried out using a Rigaku/Miniflex 600 diffractometer with filtered $\text{Cu K}\alpha$ radiation, and the data were collected from 10° to 80°. Small-angle PXRD

measurement was carried out using a Rigaku Ultimate IV powder X-ray Cu Ka radiation diffractometer, and the data were collected from 0.5° to 10°. X-ray photoelectron spectroscopy (XPS) measurements were taken on a Thermo Scientific K-Alpha using monochromatic Al Ka radiation ($h\nu = 1486.6\text{eV}$), and the obtained spectra were calibrated using the C 1s peak at 284.8 eV. The UV-vis absorbance of 23DHN, DHNS, Nb₂O₅, 23DHN-Nb₂O₅ and DHNS-Nb₂O₅ samples were measured on 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 Micromertics system at 120 °C for 6 h prior to N₂ physisorption. The electron paramagnetic resonance (EPR) tests were executed on an EPR spectrometer (JEOL, JES-FA300). The Fourier transform infrared (FTIR) spectra of solid samples were carried out by NICOLET 5700 FTIR spectrometer with continuum IR microscope ranging from 400–4000 cm⁻¹. Gas chromatography (GC) quantitative measurements of the conversions of substrates and the selectivity of products were carried out on a gas chromatograph equipped with a flame ionization detector (GC-FID, Agilent 7890B) using high purity N₂ as the carrier gas. Gas chromatography-mass spectrometry (GC-MS) analysis was performed on an Agilent GC 8890 gas chromatograph equipped with an Agilent 5977B GC/MSD mass spectrometer. Conversion and selectivity for selective oxidation of substrates to target products 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 C_0 is the initial concentration of reactant, C_s and C_p are the concentrations of substrate and target product, respectively, at a certain time during the photocatalytic reaction.

1.4 General procedure for photooxidation of benzylamine

In the 10 mL Pyrex reactor with 0.3 mmol of benzylamine, 40 mg of mesoporous Nb_2O_5 , 1 mL of CH_3CN , 2 μmol of DHNS, 15 μmol of TEMPO were added in turn. The prepared mixture was then maintained, under ultrasonication for 10 min and stirring for 20 min in the dark, to achieve adsorption equilibrium. Then, connected to air by punching a hole in the rubber septum. Next, the Pyrex reactor was stirred at 1500 rpm under blue LEDs (light-emitting diodes, 3 W \times 4) irradiation. Finally, DHNS- Nb_2O_5 was stripped away from the reaction mixture by centrifugation. The liquid product was tested by GC-FID. The liquid products were certified by comparing the retention time of the standard sample and further certified by GC-MS.

2. Result

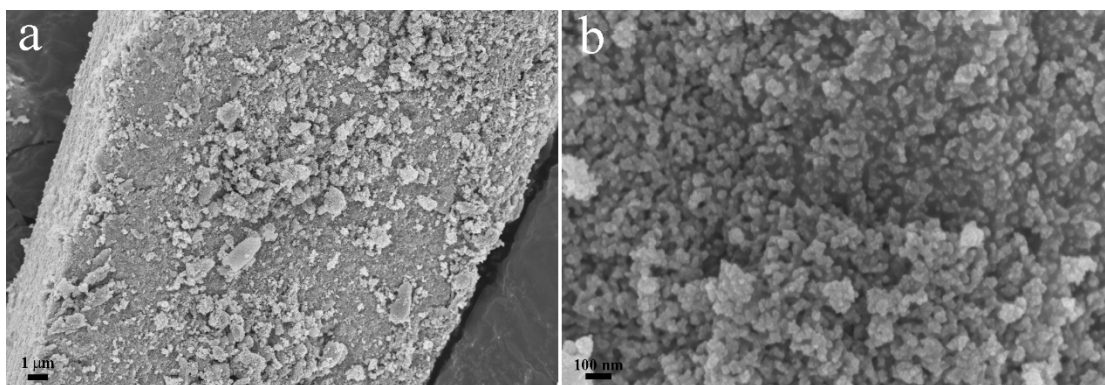


Fig. S1. (a) Low and (b) high magnification SEM images of mesoporous Nb₂O₅.

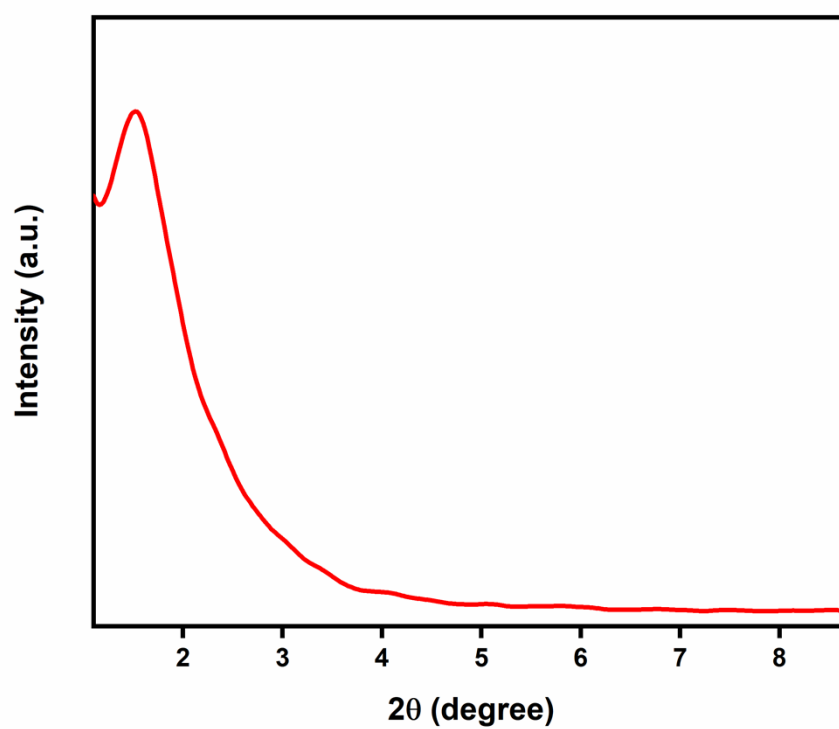


Fig. S2. Small-angle PXRD pattern of mesoporous Nb₂O₅.

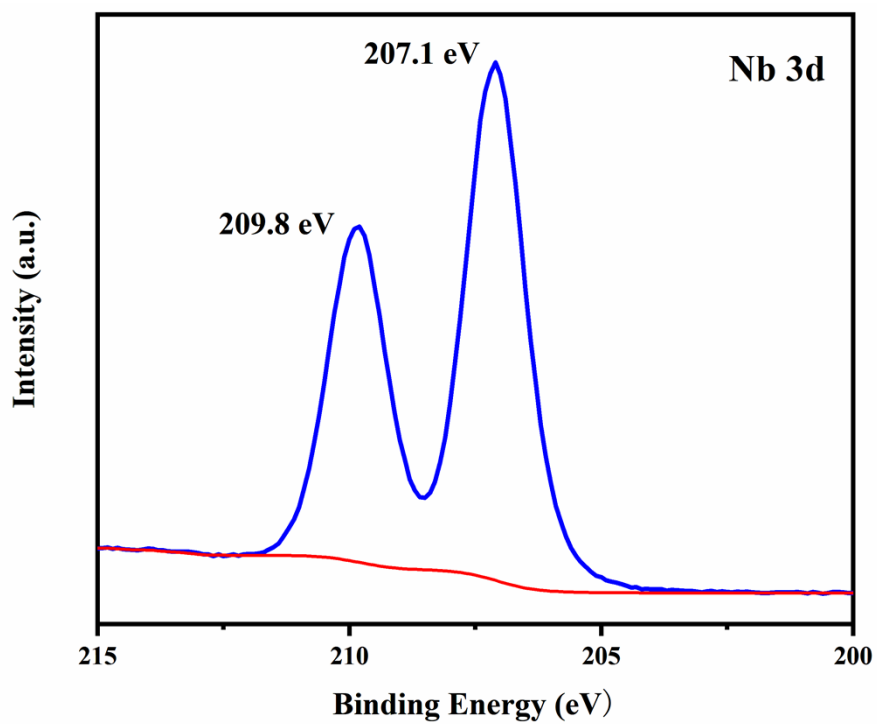


Fig. S3. XPS spectra of mesoporous Nb₂O₅.

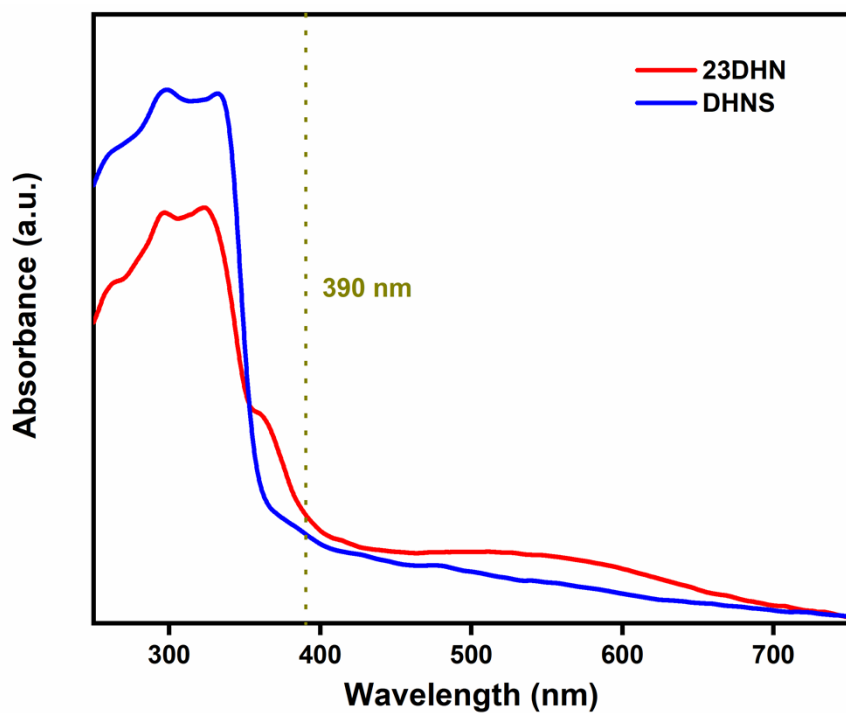


Fig. S4. Diffuse reflectance UV-visible spectra of 23DHN, DHNS.

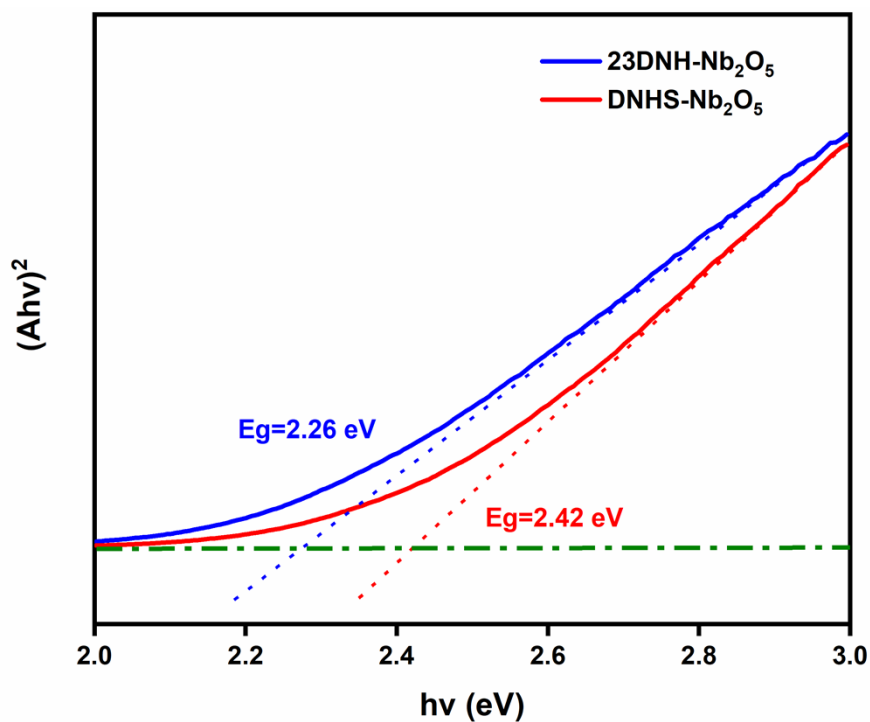


Fig. S5. Optical bandgaps confirmed by the Kubelka–Munk transformed reflectance spectra.

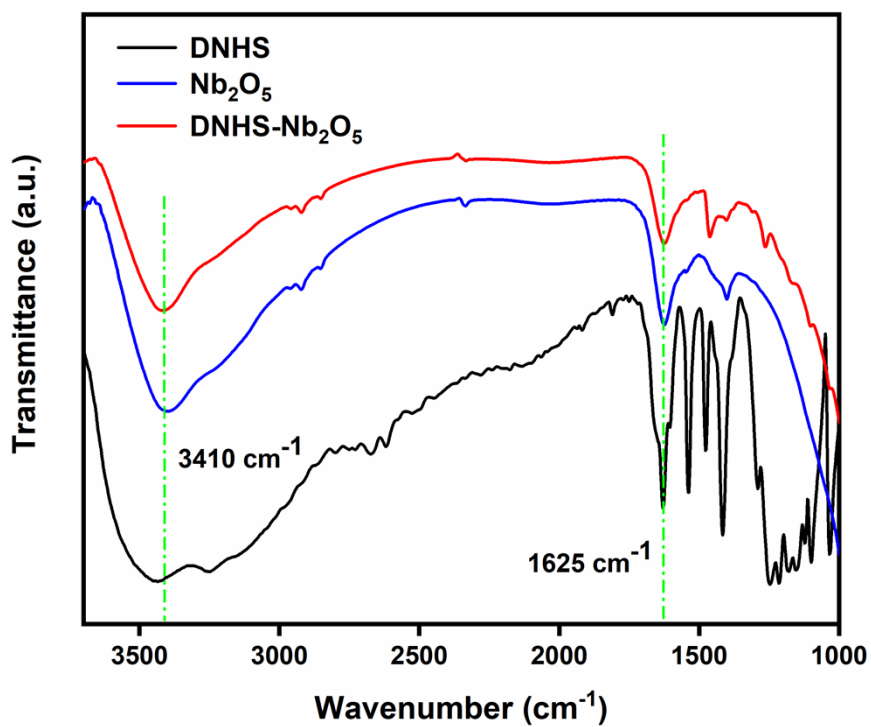


Fig. S6. The FTIR spectra of Nb_2O_5 , DNHS, DNHS– Nb_2O_5 .

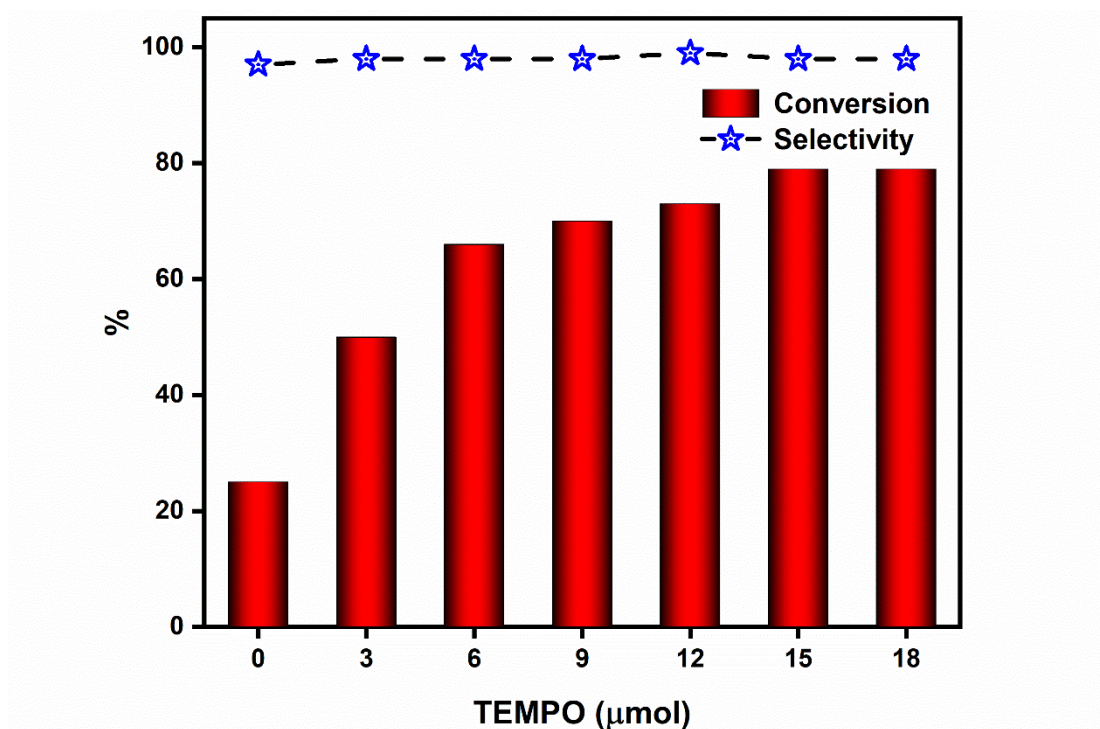


Fig. S7. The influence of applied quantity of TEMPO for photocatalytic selective aerobic oxidation of benzylamine. Standard reaction conditions: benzylamine (0.3 mmol), mesoporous Nb_2O_5 (40 mg), TEMPO (15 μmol), DHNS (2 μmol), blue LEDs (460 ± 10 nm), aerial O_2 , CH_3CN (1 mL), 50 min. Determined by GC–FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine.

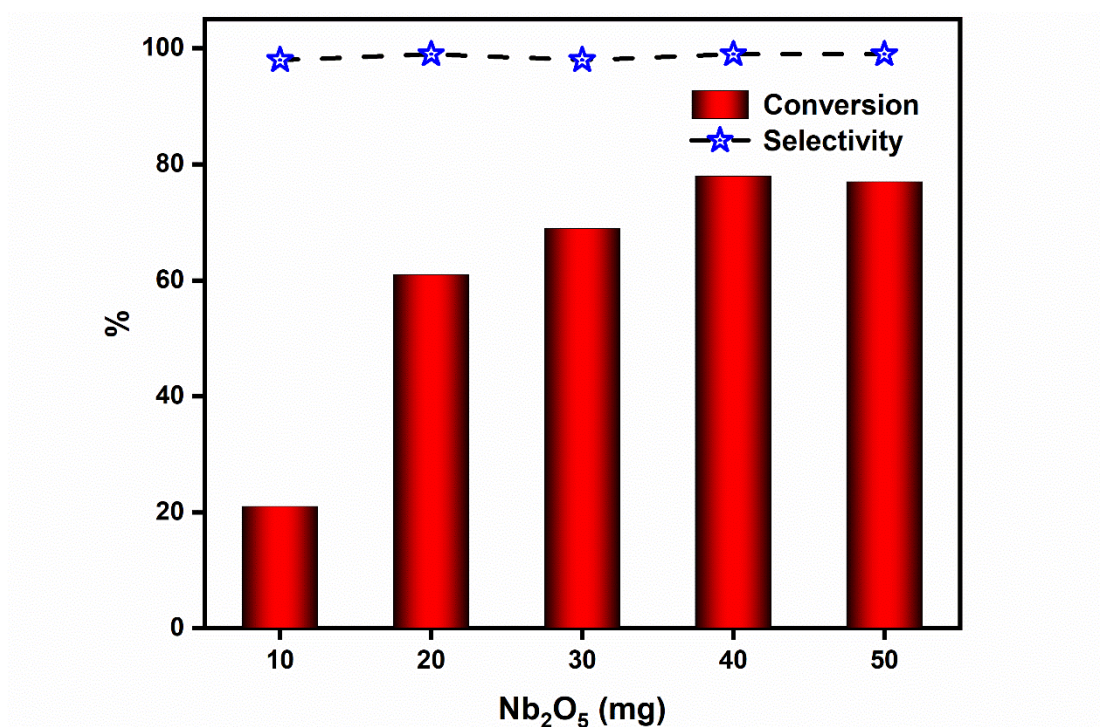


Fig. S8. The influence of applied quantity of mesoporous Nb₂O₅ for photocatalytic selective aerobic oxidation of benzylamine. Standard reaction conditions: benzylamine (0.3 mmol), mesoporous Nb₂O₅ (40 mg), TEMPO (15 μmol), DHNS (2 μmol), blue LEDs (460 ± 10 nm), aerial O₂, CH₃CN (1 mL), 50 min. Determined by GC–FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine.