Supplementary information

Ultrathin HNb_3O_8 nanosheets with oxygen vacancies for enhanced photocatalytic oxidation of amine under visible light irradiation

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1. Experimental Procedure.

1.1 Chemicals. Niobium chloride (99%), tetramethylammonium hydroxide solution (25%), benzylamine (99.00%), benzaldehyde (99.5%), 4-methoxybenzylamine (98%). 4-methylbenzylamine (98%), 4-chlorobenzylamine (98%), 4-fluorobenzylamine (99%), were obtained from Aladdin Chemistry Co., Ltd. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) for ESR-spectroscopy and deuterochloroform (CDCl₃, 99.96%) were purchased from Sigma-Aldrich. Acetonitrile (99.9%), absolute ethanol, methanol (99.7%), sodium sulfate anhydrous (99.0%) and other reagents were obtained from sinopharm chemical reagent Co., Ltd. Niobium acid and ammonium niobium oxalate (NH4[NbO(C2O4)2(H2O)2]nH2O was kindly supplied by CBMM.

1.2 Characterization: The N_2 adsorption-desorption isotherm was carried out on a BELSORP-MiNi II system at -196 °C. Prior to N_2 adsorption, the catalysts were evacuated under vacuum at 300 °C for 2 h. The specific surface areas (SBET) were calculated by a multipoint Braunauer-Emmett-Teller method.

The fluorescence life time spectra were recorded on a spectrophotometer (PLSP980, Edinburgh Instruments Ltd.). Decay curves were analyzed at the emission of 468 nm by a Picosecond Pulsed Light Emitting Diode (EPLED-290) with an excitation wavelength of 290 nm. The decay curves for Ur Nb₂O₅, Nb₂O₅ NR and HNb₃O₈ NS can be fitted based on the following well-known formula:¹

$$I(t) = B + \sum_{i=1}^{N} (A_i) \exp(-\frac{t}{\tau_i}) \quad (1.1)$$

where N is a number of discrete emissive species, B is a baseline correction, A_i and τ_i are pre-exponential factors. For multi-exponential decays, the average lifetime, $<\tau>$, can be formulated as:^{2,3}

$$\langle \tau \rangle = \frac{\sum_{i=1}^{N} A_i \tau_i^2}{\sum_{i=1}^{N} A_i \tau_i} \quad (1.2)$$

The photoelectrochemical tests were performed on a typical three electrode system (CHI 660B), which employed catalysts-coated-ITO as working electrode, Ag/AgCl electrode as reference electrode and a platinum (Pt) wire as counter electrode. Electrochemical impedance spectroscopy experiments were carried out in 0.1 M KCl solution containing 5 Mm Fe(CN)₆^{3–}/Fe(CN)₆^{4–}.

The apparent quantum yields (AQYs) were determined using a similar method to that for the photocatalytic performance test. Different wavelengths of visible light (420, 450, 520 and 600 nm) were obtained using 300 W Xe lamp (Beijing Perfect, Microsolar 300) by band-pass filters. The area of irradiation was ca. 6.0 cm². The light intensity was determined using a PL-MW2000 photoradiometer (Perfectlight). The **AQYs** were calculated by dividing the number of produced N-benzylidenebenzylamine molecules by the number of irradiated photons.

$$AQY(\%) = \frac{2 \times amount \ of \ N - benzylidenebenzylamine \ evolved}{number \ of \ incident \ photons} \times 100$$
(1.3)

1.3 Preparation of urchin-like niobium oxide nanospheres.

The urchin-like niobium oxide nanospheres were prepared by modified method.⁴ hydrothermal synthesis Typically, ammonium niobium oxalate (NH4[NbO(C2O4)2(H2O)2]nH2O; supplied by CBMM) containing 6 mmol Nb was dissolved in 70 mL of mixed solution containing deionized water and absolute ethanol (volumetric ratio 1:1), sealed into a 100 mL Teflon-lined stainless steel autoclave, and maintained at 180 °C for 24 h. The obtained solid was filtered, washed thoroughly with deionized water, and dried at 100 °C overnight. The obtained solids were accordingly denoted as Nb₂O₅-1-0.5, Nb₂O₅-1-1, Nb₂O₅-1-2, and Nb₂O₅-1-4. All the samples were calcined at 500 °C for 2 h in air with a ramp of 10 °C/ min prior to their use as photocatalysts.

1.3 Preparation of niobium oxide nanorods.

Niobium oxides nanorods were synthesized by a hydrothermal method from ammonium niobium oxalate (NH₄[NbO(C₂O₄)₂(H₂O)₂]·nH₂O).⁵ Typically, ammonium niobium oxalate (supplied by CBMM) containing 6 mmol of Nb was dissolved in 40 mL of deionized water and then sealed in a 60 mL Teflon-lined stainless-steel autoclave. Hydrothermal reaction was carried out at 175 °C for 3 days. The obtained solid was filtered, washed thoroughly with deionized water, and dried at 80 °C overnight.

1.4 Detection of superoxide radical anion (O2^{••}).

The detection of O_2^{-} was performed by employing 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as trapping agents. In typical experiments, 2 mg of catalyst was dispersed in 3 mL of CH₃CN which had been bubbled with oxygen for 30 min. The mixture solution was vigorously stirred at 298 K for another 30 min, followed by the addition of 30-µL DMPO solution (0.02 M in CH₃CN). The mixture was immediately analyzed by an ESR spectrometer (Bruker, Emxplus-10/12).

1.5 DRIFTS spectroscopy characterizations.

The DRIFTS measurements for benzylamine chemisorption were performed using a Bruker 70v Fourier transformation spectrometer with a Harrick diffuse reflectance accessory. The catalyst samples were first pretreated at 573 K for 2 h at Ar atmosphere, and a background spectrum was obtained from 1000 to 4000 cm⁻¹ before adsorbing benzylamine molecules. Subsequently, the sample was exposed to benzylamine vapour (95 Pa) at room temperature. The residual reactants were removed under evacuation and dry air (50 KPa) was introduced into the in situ IR cell. The time course IR spectra were recorded after Xe light irradiation.

1.6 Detection of the intermediates of the reaction mixture.

The ¹H nuclear magnetic resonance (NMR) spectra of the reaction mixture were recorded by a 600 MHz spectrometer (Bruker, AV600). After the photocatalytic oxidative coupling of amines under visible light and removal of the catalyst powder by centrifugation, the upper filtrate was analyzed in deuterochloroform solutions. For comparison, CH₃CN adding small amount of water was also analyzed in deuterochloroform solutions.



Fig. S1 Photos of an experimental set-up for photocatalysis. (A) Before, and (B) After visible light irradiation.



Fig. S2 (A) TEM images of HNb₃O₈ NS, (B) SAED image of HNb₃O₈ nanosheet, (C)(D) HRTEM image.



Fig. S3 The differential spectra before and after the adsorption of benzylamine (line) and wavelength-dependent apparent quantum yield (AQY) values (scattered spots) over HNb₃O₈ NS, Ur Nb₂O₅ and Nb₂O₅ NR.



Fig. S4 PL spectra of HNb₃O₈ NS, Ur Nb₂O₅ and Nb₂O₅ NR at the different excitation wavelengths. (A) 300 nm, (B) 310 nm, (C) 320 nm, (D) 330 nm.



Fig. S5 Simplified band diagram showing different PL emissions at 320nm excitation



Fig. S6 Electronic total charge densities for (A) benzylamine/HNb₃O₈ NS-P, (B) benzylamine/HNb₃O₈ NS-V, (C) O_2 /HNb₃O₈ NS-P, (D) O_2 /HNb₃O₈ NS-V. The isosurface value of spin charge is 0.200 e/A³.



Fig. S7 PDOS plots of benzylamine on HNb₃O₈ NS-P and HNb₃O₈ NS-V.



Fig. S8 ¹H NMR spectra of the reaction mixture for the oxidative coupling reaction of benzylamine photocatalyzed by HNb_3O_8NS , showing the peak of $NH_2OH(1.73 \text{ ppm})$ formed as a byproduct during the reaction.

Cat AQY(%) WL (nm)	HNb3O8 NS	Ur Nb ₂ O ₅	Nb ₂ O ₅ NR	Nb ₂ O ₅ ^{6,7}	Ni/CdS ⁸
420	6.57	2.32	0.82	2.19	11.0
450	4.12	1.32	0.69	1.25	11.2
500	1.78	0.42	0.28	0.5	5.9
600	0.50	0.28	0.08	0.4	0.1

Table S1. Comparisons of apparent quantum yield (AQY) values of different catalysts for benzylamine oxidation under visible light irradiation.

WL (wavelength)

Table S2. Parameters of the time-resolved photoluminescence decay curves according to a single-exponential decay for Ur Nb_2O_5 and Nb_2O_5 NR and a double-exponential decay for HNb_3O_8 NS.

Sample	$\tau_1(ns)$	A_1 (%)	$\tau_2(ns)$	$A_2(\%)$	χ^2	$<\tau>(ns)$
Nb ₂ O ₅ NR	0.76	100	-	-	0.9758	0.76
Ur Nb ₂ O ₅	0.85	100	-	-	0.9686	0.85
HNb ₃ O ₈ NS	0.94	98.3	5.13	1.7	0.9923	1.30

Entry	Catalyst	Atmosphere	Conv. (%)	Sel. (%)
1	HNb3O8 NS	O_2	95.0	99.7
2	HNb ₃ O ₈ NS	Air	94.5	99.7
3	HNb ₃ O ₈ NS	Ar	14.0	88.9
4 ^a	HNb ₃ O ₈ NS	O_2	5.0	86.5
5	No catalyst	O_2	< 1	-

Table S3. Comparisons of photocatalytic benzylamine oxidation over HNb₃O₈ NS under different reaction conditions.

Reaction conditions: substrate (0.25 mmol), CH₃CN (10 mL), O₂ pressure (1 atm), 0.02 g catalyst, Xe lamp (>420 nm) irradiation, 25 $^{\circ}$ C. ^aNo light.

Table S4. Textural Properties and reaction rate constants of the HNb_3O_8 NS, Ur Nb_2O_5 and Nb_2O_5 NR.

Sample	S _{BET}	V _{total}	Kapparent	Normalized Kapparent		
	(m^2g^{-1})	(cm^3g^{-1})	$(\times 10^{-3} \text{ mol } L^{-1} h^{-1})$	$(\times 10^{-5} \text{ mol } \text{L}^{-1} \text{ h}^{-1} \text{g m}^{-2})$		
HNb ₃ O ₈ NS	79.7	0.1984	4.45	5.58		
Ur Nb ₂ O ₅	86.4	0.2671	3.89	4.50		
Nb ₂ O ₅ NR	176.0	0.4578	2.66	1.51		

Table S5. The calculated adsorption energies, bond lengths, and Mulliken charge transfers of benzylamine and O_2 adsorbed on the surface of HNb₃O₈ NS-V and HNb₃O₈ NS-P, respectively.

	Benzylamine adsorption				O ₂ adsorption			
	E_{ads}	$\delta q \left(e ight)$	bond	distance	E_{ads}	$\delta q (e)$	bond	distance
	(eV)			(Å)	(eV)			(Å)
HNb ₃ O ₈ NS-V	-2.59	-1.011	N-Nb	2.266	-4.08	-1.163	Oa-Ob	1.394
			N-H	1.050			Oa-Nb	1.856
			H-Os	1.808			Ob-H	1.032
HNb ₃ O ₈ NS-P	-1.23	-0.838	N-H	1.030	-0.47	-0.299	Oa-Ob	1.273
			N-Hs	1.408			Oa-Hs	1.569

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