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Ultrathin HNb₃O₈ nanosheets (HNb₃O₈ NS) with oxygen vacancies were successfully synthesized by a simple bottom-up hydrothermal process. The obtained nanosheets were uniform with a thickness of about 3.02 nm and the surface oxygen vacancies on the HNb₃O₈ nanosheets were confirmed by electron spin resonance spectroscopy (ESR) and X-ray photoelectron spectroscopy (XPS). As compared to urchin-like Nb₂O₅ nanosphere and Nb₂O₅ nanorods, ultrathin HNb₃O₈ nanosheets showed the highest activities in the photocatalytic oxidative coupling reaction of benzylamine under visible light irradiation. The improved photocatalytic activity was attributed to the following reasons: (1) unique nanosheet structure with several molecular thicknesses that led to the effective separation of the photogenerated carriers; (2) benzylamine-HNb₃O₈ surface complex formed on the oxygen vacancies that reduced the bandgap of HNb₃O₈ NS and was profitable to harvest visible light; (3) HNb₃O₈ NS-V could efficiently chemisorb O₂ molecules and promote to activate O₂ to reactive oxygen species.

1. Introduction

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Photocatalytic oxidation of amines to imines has attracted great attention in recent years due to the versatile application of imines in fine chemicals and pharmaceuticals.1-3 Many kinds of photocatalysts, such as organometallic compounds,⁴ plasmonic precious metal (Au,⁵ Ag,⁶ Pt,⁷), semiconductor oxides (i.e. TiO₂,⁸⁻¹¹ Nb₂O₅,¹²⁻¹⁴ WO₃,^{15,16} BiVO₄,¹⁷ TiNb₂O₇.¹⁸ (Zn^{II}/Ti^{IV})LDH,¹⁹ BiOBr,²⁰ and BiOCl²¹), sulfide (WS₂,²² CdS²³), $C_3N_{4,}{}^{24}$ MOF, 25 and carbon materials 26,27 have shown high conversion of amine and excellent selectivity for imine. However, the efficiency and stability of the photocatalyst for this reaction need to be improved. Specifically, the oxidation of amine on Nb₂O₅ has been extensively investigated owing to its advantageous properties, such as high activity, nontoxicity, and good chemical stability under light irradiation. Although Nb₂O₅ cannot adsorb visible light as a wide band gap semiconductor (about 3.2 eV), it exhibited high activity under visible light irradiation. The surface complex in situ formed by amine adsorbed on the surface of Nb₂O₅, which was the ligand-tometal charge transfer (LMCT) mechanism, would conduce to harvesting visible light and enhancing the photocatalytic

activity.^{12,28} In order to increase the interaction between sensitized organic molecules and semiconductor oxides, the surficial properties of semiconductor oxides could be maneuvered by synthesis and post treatment to increase surface areas, control morphologies, form surface defects.²⁹⁻³¹

Two dimensional (2D) nanosheet materials have attracted extensive concerns owing to their special electronic structures and novel physicochemical properties, which show exciting applications such as photocatalysts, energy storage materials, sensing platforms.^{32,33} Among them, niobate and niobium oxide nanosheets showed excellent enhanced photocatalytic activities. Two- and three-layer restacked Dion–Jacobson phase niobate nanosheets prepared by exfoliation of layered perovskites exhibited enhanced photocatalytic activities of hydrogen evolution under ultraviolet irradiation (λ > 300 nm).³⁴ Exfoliated ultrathin HNb₃O₈ nanosheets displayed about 4 times higher hydrogen evolution activity than that of layered HNb₃O₈ under ultraviolet irradiation.³⁵ Nakagawa reported that single molecular sheets of niobate assembled with graphene and MoS₂ showed higher photocatalytic production of hydrogen from water.³⁶ Liang reported that monolayer HNb₃O₈ showed photocatalytic activity of selective oxidation of benzylic alcohols under visible light response irradiation.37 To the best of our knowledge, there is no report about ultrathin HNb₃O₈ nanosheets for the photocatalytic oxidative coupling of primary amines to the corresponding imines.

In this study, we have successfully prepared HNb_3O_8 nanosheet via a facile hydrothermal method. Compared with the mostly reported method by exfoliation, this method is simpler, more maneuverable and easier to obtain a uniform morphology. The prepared ultrathin HNb_3O_8 nanosheet was characterized and applied for the selective catalytic oxidation of

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benzylamine. It was proved that HNb_3O_8 nanosheet exhibited the enhanced performance in the photocatalytic oxidative coupling of benzylamine.

2. Experimental

2.1. Reagents and materials

 $NbCl_5,$ ethanol, methanol, tetramethyl ammonium hydroxide, Na_2SO_4 and acetone were in analytical grade and used without purification.

2.2 Preparation of ultrathin HNb₃O₈ nanosheets

The HNb_3O_8 nanosheets (denoted as HNb_3O_8 NS) were synthesized by a bottom-up hydrothermal method. Typically, 6 mmol of NbCl₅ was dissolved into 20 mL of absolute ethanol. Then, 20 mL of tetramethylammonium hydroxide (TMAOH) aqueous solution (15 wt%) was added dropwise into the NbCl₅ ethanol solution under magnetic stirring by metering pump with a rate of 0.6 mL/min. After TMAOH aqueous solution was added completely, the mixed solution turned into clear and transparent. The mixture was aged for 2 h at room temperature, and sealed in a 100 mL Teflon-lined stainless-steel autoclave. Hydrothermal reaction was carried out at 240 °C for 12 h. The resulted powder was separated, washed in sequence with acetone, absolute ethanol and deionized water, and dried at 60 °C under vacuum for 8 h (denoted as obtained NS). The obtained nanosheets (0.2 g) were dispersed into 400 ml 6 M $HNO_{3}\xspace$ and sonicated for 10 min. Then, the suspension solution was stirred for 12 h to ion exchange TMA cations to H⁺. The achieved powder was centrifuged and washed by ethanol and deionized water, and dried at 60 °C under vacuum for 8 h (designated as HNb₃O₈ NS). For comparison, urchin-like Nb₂O₅ (denoted as Ur Nb₂O₅) and Nb₂O₅ nanorods (denoted as Nb₂O₅ NR) were prepared according to our previously reported procedures.38,39

2.3 Characterization

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Powder X-ray diffraction (XRD) patterns were recorded by a Xray diffractometer (Bruker, D8) using Cu Ka radiation (tube current: 20 mA, tube voltage: 40 kV). The morphologies were characterized by scanning electron microscope (SEM, JEOL, JSM-7001F) and transmission electron microscopy (TEM, JEOL-2010, 200 kV). The thickness of the prepared nanosheet was evaluated using a tapping-mode atomic force microscope (AFM, Nanoscope Multimode IIIa, Veeco Instruments) with Si-tip cantilever by dropping the suspension on the mica substrate. Fourier transform infrared (FT-IR) spectra were recorded using Bruker 70v FT-IR spectrometer with a resolution of 4 cm⁻¹. Raman spectra were acquired on a confocal laser micro-Raman spectrometer (HORIBA, Lab RAM HR Evolution) at a wavelength of 532 nm. Uv-vis diffuse reflectance spectra (DRS) were collected on a Uv-vis spectrophotometer (Hitachi, U-3900H) using BaSO₄ as a reference. The oxygen vacancy and chemical states of the samples were analyzed by electron spin-resonance spectroscopy (ESR, Bruker, Emxplus-10/12) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCAlab,

250Xi) equipped with a monochromatic Al K α source ($\lambda_{\overline{m}}$ 1486.7 eV). Photoluminescence (PL) emission DSpectra396887669488 samples were acquired using an Edinburgh Instruments PLSP980 spectrometer under excitation at 300 ~ 330 nm. Photocurrent measurements were carried out at room temperature with the CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) using a homemade three electrode cell with a quartz optical window containing 0.5 M Na₂SO₄ aqueous solution. The working electrodes were prepared by pasting the slurry of sample powder and ethanol onto a 1 cm² (1cm × 1cm) indium-tin oxide (ITO) glass. Pt electrode and Ag/AgCl electrode were chosen as the counter and reference electrodes, respectively. A 300 W Xe lamp (Beijing Prefect Light, Microsolar 300) with a 420 nm cutoff filter was used as a visible light source to irradiate horizontally the working electrode.

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2.4 Photocatalytic selective oxidation of amine

The photocatalytic oxidative coupling of amines under visible light was carried out in a home-made 50 mL cylindrical glass container with 300 W Xe lamp (Beijing Perfect, Microsolar 300) with 420 nm cutoff filter (Fig. S1). Typically, 20 mg catalyst was dispersed into the mixture which contains 0.25 mmol substrate and 10 mL acetonitrile. Prior to the irradiation, the mixture was continuously stirred in the dark for 0.5 h to ensure the adsorption-desorption equilibrium. The temperature of the reaction system was controlled to 25 °C by circulating water device. After removal of the catalyst powder by centrifugation, the upper filtrate was analyzed by Agilent 7890B gas chromatography to determine the change of reactant concentration.

2.5 DFT theoretical calculation

The simulations are performed on density functional theory (DFT) calculations using the Dmol3 code.40,41 The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerh (PBE) is adopted for the exchange-correlation term, and the double numerical plus polarization (DNP) basis set were chosen in all computational process. Self-consistent field (SCF) calculations were carried out with a convergence criterion of 10⁻⁶ Ha on the total energy and the electron density. The Brillouin zone is sampled by $6 \times 1 \times 3$ k-points for all the structures in the geometry optimization calculations, which produces a convergence tolerance energy of 1.0×10^{-5} Ha. The densities of states were computed with 15 k points based on the optimized structures. Perfect $\mathsf{HNb}_3\mathsf{O}_8$ (denoted as $\mathsf{HNb}_3\mathsf{O}_8$ NS-P) and HNb₃O₈ with oxygen vacancies (denoted as HNb₃O₈NS-V) layers were modeled by a 4 × 4 super cell slab, which is periodic in the x and z direction, whereas separated by a 15 Å vacuum region in the y direction to avoid the interactions with the adjacent atomic slabs. No changes were found for total energy when the vacuum was further increased.

3. Results and discussion

3.1 Characterization of HNb₃O₈ nanosheets

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As shown in Fig. 1, the XRD pattern of obtained nanosheet showed diffraction peaks at 20 of 7.39, 14.07, 17.65, 23.21, 25.54, 27.11, 28.18, 29.79, 30.73, 35.88, 46.77°, which seemed hardly to be correspond to any known phase associated with pure niobium oxides. However, the main diffraction peaks of the sample were similar to the XRD patterns of layered H₃ONb₃O₈ (JCPDS: 44-0672) and HNb₃O₈ (PDF no. 37-0833). After ion-exchanged by HNO₃, almost all the diffraction peaks of HNb₃O₈ NS slightly red-shifted to high angle, which indicated that the TMA cations were exchanged by H₃O⁺ or H⁺. Furthermore, the intensity of diffraction peaks became lower, implying that the crystallinity of HNb₃O₈ NS was lower than that of obtained nanosheet. The sharp diffraction peak at 20 of 7.39° red-shifted to 7.74°, corresponding to the characteristic peak (020) of layered H₃ONb₃O₈,⁴² which suggested the interlayer space shrank from 11.95 to 11.41 Å. The ionic radius of H₃O⁺ (about 2.82 Å) is smaller than that of hydrated forms of TMA⁺ cations (about 3.67 Å), thus the (020) diffraction peak is red shifted to the higher angle.43

HNb₃O₈ NS were examined by FT-IR and Raman spectroscopy in order to gain additional structural information. FT-IR spectra of the obtained NS and HNb₃O₈ NS are shown in Fig. 2A. The IR absorption in the range of 400-1000 cm⁻¹ was corresponded to the vibration of the Nb₃O₈- host slice.⁴⁴ The IR absorptions at 917 and 826 cm⁻¹ of the obtained NS could be related to the octahedral vibrations of NbO₆ in layered niobates.^{45,46} As for HNb_3O_8 NS, the peak at 917 cm⁻¹ blueshifted to 913 cm⁻¹ and its intensity decreased. The absorption bands around 684 and 628 cm⁻¹ of the obtained NS were attributed to the characteristic symmetric and antisymmetric stretch vibration modes of the Nb-O-Nb bridge bond in the corner-shared NbO₆ octahedron, while the absorption band of $HNb_{3}O_{8}$ NS shifted to 678 $\mbox{cm}^{\text{-1}}$ and became broad. The absorption band at 547 cm⁻¹ and weak absorption bands at461 cm⁻¹ for the obtained NS belonged to bending vibrations and librational modes of NbO₆, respectively. Obviously, the peaks of HNb_3O_8 NS at this region became weak. The IR weak absorptions at 3016 and 1416 cm⁻¹ of the obtained NS were





assigned to stretching and bending vibration of C-H in CH₃ of TMA⁺.⁴⁴ The band at 1485 cm⁻¹ was attributed to the CH₃ bending vibration of TMA cations. These peaks nearly disappeared in the HNb₃O₈ NS, which indicated that the TMA cations were substituted by H_3O^+ or H^+ . The bands at 3390 and 1636 cm⁻¹ were assigned to the stretching and bending vibrations of hydroxyl groups. It could be inferred that (CH₃)₄N⁺ and water intercalated into the Nb₃O_{8⁻} slice could be replaced by H_3O^+ or H^+ and HNb_3O_8 NS was synthesized by this simple bottom-up hydrothermal process. Raman spectra were shown in Fig. 2B. The peaks in the Raman shift range of 800-1000 cm⁻¹ could be assigned to the stretching mode of the terminal Nb-O bond striking out into the interlayer.⁴⁷ The characteristic strong and broad peaks at 902 and 946 cm⁻¹ for layered compounds implied that many terminal Nb=O bonds were exposed to the outer surface.46 However, the broad peak at 888 cm-1 with a shoulder peak at 957 cm⁻¹ of HNb₃O₈ NS might be due to the formation of NbO₄-H₂O adducts.⁴² The peaks at 458, 476, 537, 629, 670 cm⁻¹ of the obtained NS were assigned to the stretching mode of O-Nb-O linkage,47 while there was a broad Raman band centred at 666 cm⁻¹ for HNb₃O₈ NS similar with the Nb₂O₅·nH₂O nanosheet.⁴² The peaks in the ranges of 200 - 300 cm⁻¹ for the obtained NS were ascribed to the bending mode of the Nb-O-Nb linkage, while there was a wider peak for HNb₃O₈ NS. Meanwhile, the Raman band at 147 cm⁻¹ range could be attributed most likely to the strong interactions of the TMA+ cations with the intercalated water molecules.⁴⁸ Specially, the



Fig. 1 XRD patterns of obtained Nanosheet and HNb₃O₈ Nanosheet.



Fig. 3 SEM images of (A) obtained Nanosheet, (B) HNb $_3O_8$ NS, (C) AFM images, and (D) the corresponding roughness profiles for the HNb $_3O_8$ nanosheet.

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peak centered at 755 cm⁻¹ should be assigned to the stretching mode of the C_4N^+ group in TMA⁺.⁴⁹ These two peaks disappeared in the HNb₃O₈ NS. Raman spectra also confirmed that the initial synthesized nanosheet was transformed to HNb₃O₈ NS.

SEM images of the obtained NS and HNb₃O₈ NS are shown in Fig. 3A–B. It can be observed that the obtained NS with microflower morphology was composed of two dimensional interleaving nanosheets. After treated by HNO₃, the 3D hierarchical structure remained. Fig. 3C shows AFM images of layered HNb₃O₈ nanosheet. It revealed that the 2D nanosheets were spread out on the surface of mica plate with a lateral scale about several hundred nanometres. From the roughness profile shown in Fig. 3D, the thickness range of HNb₃O₈ nanosheet was from 2.82 to 3.23 nm. As it was reported that the single layered HNb₃O₈ slab along b axis is about 0.9 ~ 1.05 nm,⁴² we speculate that our HNb₃O₈ NS might be composed of three layers of single HNb₃O₈ slabs.

In addition, the HNb₃O₈ NS was further investigated by TEM (Fig. 4). The low-magnification TEM images (Fig. 4A) manifested that the typical morphology was microflower composed of well-defined aggregated nanosheets. The side-view TEM image of HNb₃O₈ NS (Fig. 4B) showed that the distance between the two single sheets was estimated to be 1.03 nm, which was slightly less than that evaluated by XRD ($2\theta = 7.74^{\circ}$, d = 1.14 nm). Moreover, Fig. 4B also showed that the layer number of HNb₃O₈ nanosheet was 2-5, which was in consistent with the results of AFM. The high-resolution TEM(HRTEM) images of HNb₃O₈ NS (Fig. 4C and Fig. S2C, D) showed that the lattice fringes were discontinuous and chaotic, implying structural distortion, which might arise from the occurrence of defects that was always produced with unsaturated Nb and O atoms. The corresponding selected area electron diffraction pattern (SEAD) displayed a



Fig. 4 (A) Typical TEM images of HNb_3O_8 microfowers, (B) Side view, (C) HRTEM image, (D) SAED image of HNb_3O_8 nanosheet.



Fig. 5 (A) Room-temperature ESR spectra of HNb₃O₈ NS, Ur Nb₂O₅ and Nb₂O₅ NR. (B), (C) High-resolution Nb 3d and O 1s XPS spectra of HNb₃O₈ NS, Ur Nb₂O₅ and Nb₂O₅ NR. (D) UV-vis spectra of HNb₃O₈ NS, Ur Nb₂O₅ and Nb₂O₅ NR and the corresponding benzylamine-adsorbed niobium oxide catalysts.

series of dispersive diffraction rings which indicated the polycrystalline characteristics of the HNb_3O_8 NS (Fig. 4D and Fig. S2B).

Room-temperature electron spin resonance (ESR) spectroscopy and X-ray photoelectron spectroscopy (XPS) are both conducted to identify the oxygen vacancy and chemical states of the samples (Fig. 5). As compared with Ur Nb_2O_5 and Nb₂O₅ NR, HNb₃O₈ NS exhibited an intense ESR signal at g = 2.003 which could be assigned to the envelope of the hyperfine structure of Nb⁴⁺ species.⁵⁰ The intensity of ESR signal of HNb₃O₈ NS was higher than those of Ur Nb₂O₅ and Nb₂O₅ NR, which revealed that the density of oxygen vacancies in the HNb₃O₈ NS was much higher than that in the Ur Nb₂O₅ and Nb₂O₅ NR.⁵¹ This is not in accordance with the HNb₃O₈ nanosheets prepared by exfoliation process.³⁵ As shown in Fig. 5B, the binding energies of Ur Nb₂O₅ and Nb₂O₅ NR centered at 207.1 and 209.9 eV, could be ascribed to Nb $3d_{5/2}$ and Nb $3d_{3/2}$, respectively, and the spin orbit separation was 2.8 eV, which suggested the totally existence of Nb5+.38,51 Whereas for HNb3O8 NS, besides the characteristic peaks at 209.9 eV and 207.1 eV corresponding to the Nb⁵⁺ ions, the peaks located at 209.2 eV and 206.3 eV were also presented and well corresponded to the Nb4+ ions. The percentage of Nb⁴⁺ in HNb₃O₈ NS was about 19.9%, which indicated HNb₃O₈ NS possessed abundant oxygen vacancy sites. The binding energies of O1s could be deconvoluted into two peaks (shown in Fig. 5C). The peaks at 530.3 eV originated from the characteristic lattice oxygen of niobium oxide, while the peaks at 531.68 eV arose from surface adsorbed oxygen or oxygen vacancies.⁵¹ The percentage of surface adsorbed oxygen or oxygen vacancies were 14.7%, 15.3% and 27.8% for Nb₂O₅ NR, Ur Nb₂O₅ and HNb₃O₈ NS, respectively. This indicated that the surface of HNb₃O₈ NS had more oxygen vacancies than those of Nb₂O₅ NR and Ur Nb₂O₅. These results are in agreement with the HRTEM results.

Uv-vis spectra of HNb_3O_8 NS, Ur Nb_2O_5 and Nb_2O_5 NR and the corresponding benzylamine-adsorbed niobium oxide

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catalysts are displayed in Fig. 5D. The bandgaps of HNb₃O₈ NS, Ur Nb₂O₅ and Nb₂O₅ NR were 3.40, 3.20 and 3.19 eV, respectively, calculated by the Tauc method, which implied that all the three samples did not exhibit any visible-light absorption. However, Uv-vis spectra of the benzylamine-adsorbed Ur Nb₂O₅ and Nb₂O₅ NR were slightly red-shifted to visible-light region, while Uv-vis spectrum of the benzylamine-adsorbed HNb_3O_8 NS was greatly shifted to red light region (λ = 650 nm). The differential spectra before and after the adsorption of benzylamine and wavelength-dependent apparent guantum yield (AQY) values towards N-benzylidenebenzylamine evolution over the three catalysts are shown in Fig. S3. Obviously, the adsorption intensity of the benzylamineadsorbed HNb_3O_8 NS was higher than that of HNb_3O_8 NS, which indicated that the surface complex in situ formed by benzylamine adsorption was conducive to harvesting visible light and enhancing the photocatalytic reaction. In addition, HNb₃O₈ NS exhibited a higher AQY value of 6.57% at 420 nm, which was 8.01, 2.83 and 3.00 times of Ur Nb₂O₅, Nb₂O₅ NR, Nb₂O₅ reported in the literatures (Table S1),^{12,14} respectively. Since HNb₃O₈ NS possessed larger fraction of unsaturated surface metal sites (verified by ESR and XPS results), the amount of adsorbed benzylamine on the HNb₃O₈ NS was higher than that of the reported Nb₂O₅,¹³ which would lead to HNb₃O₈ NS possessed higher photocatalytic activity for amine oxidation.

To verify the oxygen vacancies and the charge carrier dynamics (separation, trap, transfer and recombination), roomtemperature steady state and time-resolved photoluminescence (PL) spectroscopies were conducted. As shown in Fig. 6A and Fig. S4, all the spectra displayed a series of emission peaks located at ~410, ~419, ~450, ~468, ~473, ~481, ~492, ~540 and ~620 nm. On the whole, the shapes of the PL spectra looked similar for three different samples though their morphologies were widely divergent. More intriguingly, HNb₃O₈ NS possessed higher PL intensity compared with Ur Nb₂O₅ and Nb_2O_5 NR, suggesting their higher concentration of oxygen vacancies and defects. The defect concentration increased the number of charge recombination centers, which might hamper the photoactivity.⁵² On the other hand, oxygen vacancies and defects also contribute to activate oxygen molecules and benzylamine. Similar to PL spectra of TiO₂^{53,54} and ZnO⁵⁵, the peaks centered at 410 nm (3.02 eV) and 419 nm (2.96 eV) were ascribed to the strong excitonic emission. The blue emissions at ~450 (2.76 eV), ~468 (2.65 eV), ~473 (2.62 eV), ~481 (2.58 eV), and ~492 (2.53 eV) nm were attributed to the radiative recombination of electrons from the local defect level of shallow donor centers with holes at the valence band (VB). The broad green emissions at 540 nm (2.29 eV) corresponded to the radiative transition from the shallow donor levels to the oxygen vacancy related trap states. In addition, HNb₃O₈ NS showed the higher intensity of the peak at 540 nm than those of Ur Nb₂O₅ and Nb₂O₅ NR, implying that there were abundant oxygen vacancy sites in the surface of HNb₃O₈ NS. The peak at 620 nm was not reported earlier, though it was likely to be related to an intrinsic defect. According to the above analysis, the simplified band diagram with different levels involved in the emission was displayed in Fig. S5. Additionally, time-resolved PL spectra of



Fig. 6 (A) PL spectra of HNb_3O_8 NS, Ur Nb_2O_5 and Nb_2O_5 NR. (B) The corresponding decay curves. (C) Transient photocurrent responses and (D) Electrochemical impedance spectroscopy (EIS) of HNb_3O_8 NS, Ur Nb_2O_5 and Nb_2O_5 NR.

HNb₃O₈ NS, Ur Nb₂O₅ and Nb₂O₅ NR were illustrated in Fig. 6b to get more information on the influences of oxygen vacancies on the lifetimes of charge carriers. The PL peak decay spectra of Ur Nb₂O₅ and Nb₂O₅ NR were fitted well to a single-exponential function (I = $A_1 e^{-t/\tau 1}$), whereas the PL peak decay spectrum of HNb₃O₈ NS was fitted more reasonably by a double-exponential model (I = $A_1 e^{-t/\tau 1} + A_2 e^{-t/\tau 2}$), revealing two radiative lifetimes $(\tau_1 \text{ and } \tau_2)$ with different corresponding magnitudes (A₁ and A₂). The calculated results were summarized in Table S2. The fast decay (τ_1) was originated from the radiation emission of direct interband exciton recombination, while the slower decay (τ_2) was generated from the indirect recombination of trapped electrons with VB holes.^{56,57} Since HNb₃O₈ NS had two emissive states with τ_1 = 0.94 ns and τ_2 = 5.13 ns, the calculated average lifetime of HNb₃O₈ NS was 1.30 ns, which was greater than that of Ur Nb_2O_5 (0.85 ns) and Nb_2O_5 NR (0.76 ns), respectively, indicating that oxygen vacancies on the surface of HNb₃O₈ NS as trapping sites for the photoinduced electron acceptor prominently prolonged the lifetime of charge carriers. Therefore, HNb₃O₈ NS would exhibit higher photocatalytic performance than other two samples.

Transient photocurrent measurements and electrochemical impedance spectroscopy (EIS) were further carried out to verify the separation of photoinduced charge carrier. Fig. 6C showed that the photocurrent of HNb₃O₈ NS was 2.2 and 5.3 times of Ur Nb₂O₅ and Nb₂O₅ NR, respectively, in the presence of benzylamine. However, the photocurrents of the three samples were almost similar without benzylamine in the electrolyte (not shown). Photocurrent generated from the transmission of photoinduced electrons to the surface of ITO, meanwhile benzylamine (hole acceptor) in the electrolyte accepted the photogenerated holes. Due to the ultrathin nanosheet structure, the photo-induced carriers were engendered on the surface of the nanosheet to directly enter into the reaction, which enormously avoided recombination of photo-electron and photo-holes during the electron transmission. In contrast, above phenomenon often unavoidably happened for the traditional bulk material. Thus incident photon-to-electron

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conversion efficiency is enhanced as a result of the nanosheet structure. That is to say, a higher photocurrent density often means a higher ability in separating the photo-generated electrons and holes. Fig. 6D showed that The charge transfer resistances (R_{ct}) of HNb₃O₈ NS, Ur Nb₂O₅ and Nb₂O₅ NR were 60.3, 63.5, and 71.2 Ω , respectively. As is known, the smaller charge transfer resistance, the higher the charge transfer efficiency.⁵⁸ From the results of transient photocurrent response and EIS spectra, we could speculate that the asprepared HNb₃O₈ nanosheet could improve the activity of photocatalytic reaction through the more efficient separation of the photo-induced electrons and photo-induced holes.

3.2 Catalytic Performance

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To verify the photocatalytic performances of the prepared catalysts, the oxidative coupling of amines was performed. The blank reaction was conducted in the absence of the catalyst for 12 h under visible light irradiation. Nevertheless, no product was detected. Similarly, to demonstrate the effect of visible light on reaction, control experiments were carried out in the dark with other conditions identical. The control reaction was testified to be very slow and few products were obtained in the presence of photocatalysts (Table S3). But in the presence of visible light under identical conditions, excellent conversion to N-benzylidenebenzylamine was observed. Fig. 7A showed the time-dependent catalytic conversion over HNb₃O₈ NS, Ur Nb₂O₅ and Nb₂O₅ NR, respectively. Apparently HNb₃O₈ NS showed excellent photocatalytic activity for the oxidative coupling reactions of benzylamine under visible light irradiation compared to Ur Nb₂O₅ and Nb₂O₅ NR. The conversions of benzylamine were monotonically increasing with reaction time for the three samples. They exhibited a typical zero-order kinetic reaction character (shown in Fig. 7B). The apparent reaction rate constant (k) for the oxidation of benzylamine were 4.45×10^{-3} mol L⁻¹ h⁻¹ for HNb₃O₈ NS, which was 1.14 and



Fig. 7 Catalytic performances in selective oxidation of benzylamine. (A) Timedependent catalytic conversion. (B) The kinetic rate plots and calculated kinetic rate constants. (C) Performances of HNb₃O₈ NS, Ur Nb₂O₅ and Nb₂O₅ NR for the selective oxidation of benzylamine under visible light. (D) Recyclability and stability of HNb₃O₈ NS in the benzylamine oxidation reaction.

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	Reactant	Product	Con.	Sel.	Yield	
_			(%)	(%)	(%)	
	NH ₂	$\bigcirc \frown \bigcirc \bigcirc$	95.0	98.9	94.0	
	CR/O	CH,O	95.3 ся,	75.0	71.5	
	CH ₂ NH ₂		96.5 Ia	92.4	89.2	
	NH2		95.5	81.2	77.5	
	CI NH2		89.4	78.2	69.9	

Table 1. Photocatalytic oxidation of various benzylic amines to imines over HNb₃O₈ NS

Reaction conditions: HNb_3O_8 NS (20 mg), benzylamine (0.25 mmol), acetonitrile (10 mL), in air, Reaction time 6 h, Temperature 25 °C.

1.97 times of Ur Nb₂O₅ (3.89 × 10⁻³ mol L⁻¹ h⁻¹) and Nb₂O₅ NR (2.66 × 10⁻³ mol L⁻¹ h⁻¹), respectively. As shown in Table S4, the normalized rate constant of HNb₃O₈ NS was still the highest in the three samples. This demonstrated that the morphology of niobium oxide had a great influence on the photocatalytic performance in the selective oxidation of benzylamine.

The conversions of benzylamine and selectivity to Nbenzylidenebenzylamine on the catalysts of layered HNb₃O₈ NS, Nb₂O₅ NR and Ur Nb₂O₅ are shown in Fig. 7C. All the photocatalysts showed very high selectivities to Nbenzylidenebenzylamine, which were 98.9%, 98.8% and 97.5% for HNb₃O₈ NS, Nb₂O₅ NR and Ur Nb₂O₅, respectively. HNb₃O₈ NS exhibited the highest conversion of benzylamine (95.0%) while the other counterparts showed 88.8% and 60.3% benzylamine conversion for Ur Nb₂O₅ and Nb₂O₅ NR, respectively. Fig. 7D showed the recyclability of HNb₃O₈ NS. In the five recycled experiments, there was no obvious change in photocatalytic efficiency. The product yield was comparable to the fresh sample. Hence, it is reasonable to believe that the asprepared HNb₃O₈ NS is perfectly stable and recyclable.

The catalytic activity of HNb₃O₈NS was further inquired into various amine derivatives with electron-donating groups (CH₃O– and CH₃) and electron- withdrawing groups (–F and –Cl). The substituents on the benzene ring had a less influence on the reaction conversion (89.4% - 96.5%) (Table 1), nevertheless, the selectivity to the corresponding imines was affected by different substituents. When the substituents were CH₃O- and -Cl, the selectivity to the corresponding imines was 75.0% and 78.2%, respectively. It was reported that during the oxidation process, benzylamine (or benzyl alcohol) was adsorbed on the uncoordinated Nb atom near the surface complex by the adsorption band formed by lone pairs of N (or O) filled the vacant 3d orbital of Nb atom.^{12,37} Therefore, we speculated that when the substituent was CH₃O-, there were two adsorption models, that is, CH₃O- or -NH₂ might be adsorbed on the uncoordinated Nb atom. The results indirectly manifested that the surface complex formed by amine adsorbed on the surface of HNb₃O₈NS by LMCT mechanism promoted the photocatalytic activity of benzylamine oxidation under visible light.

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Fig. 8 (A) Photocatalytic selective oxidation of benzylamine over HNb₃O₈ NS with different radical scavengers under visible light irradiation for 4 h. AO = ammonium oxalate, IPA = isopropyl alcohol and BQ = benzoquinone. (B) Room-temperature ESR spectra of the HNb₃O₈ NS, Ur Nb₂O₅ and Nb₂O₅ NR.

3.3 Mechanism Investigation

To get more insight into the role of photogenerated radical species in photocatalytic oxidation of benzylamine, the

scavenger measurements were performed on HNb_3O_8 NS catalyst, where K₂S₂O₈, ammonium oxalate (AO), benzoguinone (BQ) and isopropyl alcohol were added into the photocatalysis system to selectively eliminate photogenerated electrons, holes, O₂^{•-} radicals, and hydroxyl radicals (•OH), respectively.⁵ The results are illustrated in Fig. 8A. Obviously, the additions of AO and K₂S₂O₈ both led to significant decreases in the activities for the photocatalytic oxidation of benzylamine, which clearly demonstrated that both photogenerated holes and electrons were essential drivers for the photocatalytic reactions. In the different reactive oxygen species, O2+- radicals showed significant suppression of benzylamine oxidation, whereas hydroxyl radicals (•OH) executed negligible influences on the conversion of benzylamine. Therefore, O2+- radicals could be determined to be the dominating reactive oxygen species in the photocatalytic molecular oxygen activation of HNb₃O₈NS.

Upon identifying the generation of $O_2^{\bullet-}$ radicals on the surface of HNb₃O₈ NS with oxygen vacancies, ESR spin-trapped technique with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin-trapping agent was carried out. As displayed in Fig. 8B, the four characteristic peaks of DMPO-O₂ adduct were evident in the mixed CH₃CN dispersion with 2 mg of HNb₃O₈ NS and [DMPO] at 2×10^{-5} M under visible light irradiation for 20 s, verifying the generation of $O_2^{\bullet-}$.¹⁶ Meanwhile, no ESR signal was detected over Ur Nb₂O₅ and Nb₂O₅ NR at the same condition, demonstrating that the amount of $O_2^{\bullet-}$ radicals was inappreciable over Ur Nb₂O₅ and Nb₂O₅ NR. Hence, the existence of surface oxygen vacancies was the vital factor to activate molecular oxygen to $O_2^{\bullet-}$ radicals over HNb₃O₈ NS under visible light irradiation.

In order to investigate the mechanism of benzylamine oxidation, the surface adsorption of the reactant was studied by in situ FT-IR spectroscopy. After exposing to vaporous benzylamine at 95 Pa, the intensities of bands at 3515, 3354, and 1645 cm⁻¹ increased with time on HNb₃O₈ NS. The bands at 3515 and 3354 cm⁻¹ could be attributed to the stretching vibrations of hydroxyl groups and N-H respectively.¹² Due to the fact that the OH bending vibration, NH₂ bending vibration (1620 and 1583 cm⁻¹) and C-C stretching vibrations of an aromatic



Fig. 9 In situ FT-IR spectra of benzylamine adsorbed on HNb_3O_8 NS (A) and after irradiation under a dry air atmosphere at different time (B). Comparison of FT-IR spectra of adsorption and irradiation at different time (C).

ring(v_{C-C}, 1499 and 1525 cm⁻¹) could not be clearly distinguished, the peak centered at 1645 cm⁻¹ in the region of 1500 – 1750 cm⁻¹ was rather broad.⁵⁹ The weak and broad peaks in the region of 1280 – 1400 cm⁻¹ and 1100 – 1200 cm⁻¹ also increased in intensity with adsorption time, which might be assigned to CH₂ bending vibrations (v_{CH2}) and C–N stretching vibration (δ_{C-N}).⁵⁹ Obviously, the result obtained by the in-situ FT-IR spectra indicated that benzylamine was adsorbed on the surface of HNb₃O₈ NS in the form of molecules.

After dry air was introduced into the IR cell and irradiation with Xe lamp for various period of time, the changes in FT-IR spectra were recorded during the irradiation process as shown in Fig. 9B. The comparison of adsorption and irradiation IR spectra was displayed in Fig. 9C. After irradiated 3 min under visible light, the bands at 1651, 1413 cm⁻¹ formed and were attributed to vC=O and δ CHO, respectively.^{12,59} This means that benzaldehyde was formed firstly during the benzylamine oxidation. The bands at 1544, 1510, 1489 cm⁻¹ belonging to C–C stretching vibrations of aromatic rings increased in intensity



Fig. 10 The optimized adsorption configurations of benzylamine on HNb₃O₈ NS-P (A) and HNb₃O₈ NS-V (B). Atoms are color labeled: Nb (cyan), H (white), O (red), C (grey) and N (dark blue). PDOS plots of benzylamine on HNb₃O₈ NS-P and HNb₃O₈ NS-V (C), benzylamine (D), N atom (E), and Nb atom (F). Top, HNb₃O₈ NS-P; down, HNb₃O₈ NS-V. The Fermi level is set to zero, as shown by the dashed line.



Fig. 11 The optimized adsorption configurations of O_2 on HNb_3O_8 NS-P (A) and HNb_3O_8 NS-V (B). PDOS plots of O_2 on HNb_3O_8 NS-P (C) and HNb_3O_8 NS-V (D). Top, O_2 molecule; down, O_2 on HNb_3O_8 NS. The Fermi level is set to zero, as shown by the dashed line.

with further prolonging the irradiation time to 17 min, 60,61 which might imply that the N-benzylidenebenzylamine was produced on the surface of HNb₃O₈ NS.

To gain insights into the formation of surface complex between benzylamine and the HNb₃O₈ NS with oxygen vacancy, we investigated the adsorption of benzylamine on HNb₃O₈ NS with oxygen vacancy (HNb₃O₈ NS-V) and perfect HNb₃O₈ NS (HNb₃O₈ NS-P) using the density function theory (Fig. 10 and Fig. S6). The optimized adsorption geometry of benzylamine on HNb₃O₈ NS with oxygen vacancy (Fig. 10B, Fig. S6B) showed that the nitrogen is deeply inserted in the oxygen vacancy of defective HNb₃O₈ NS by the simultaneous formation of a -N-Nbcoordinate bond (2.27 Å, Table S5) and an -N-H-O- hydrogen bond (1.81 Å) where the O atom was the adjacent crystal lattice oxygen of HNb₃O₈ NS-V.^{12,37,62} However, for HNb₃O₈ NS-P, benzylamine was adsorbed by hydrogen bond formed through the bonding of N atoms of benzylamine to surface hydroxyl of HNb₃O₈ NS-P (Fig. 10A).¹⁶ The adsorption energy was estimated at about -2.59 eV for the HNb₃O₈ NS-V and 2.1 times of that for the HNb₃O₈ NS-P (-1.23 eV) (Table S5). The strong interactions between benzylamine and the oxygen vacancy of defective HNb₃O₈ NS led to an upward shift of p orbitals of benzylamine about 0.21 eV (Fig. 10D) and a downward shift of Nb 3d orbitals about 0.06 eV (Fig. 10F), which induced a bandgap narrowing of approximately 0.15 eV (Fig. 10C and Fig. S7). Compared with PDOS projected on N atoms adsorbed on the HNb₃O₈ NS-V and HNb_3O_8 NS-P (Fig. 10E), we could observe that the electronic density of p orbital projected on N atoms adsorbed on the HNb_3O_8 NS-V decreased dramatically at the valence-band maximum, which indicated that lone pair electrons of N atom were transferred to the adjacent Nb atom. This also could be confirmed by the electronic density of d orbital projected on Nb atoms increased and widened (Fig. 10F). These results clearly exhibited that the surface complex of benzylamine-HNb₃O₈ NS-V would reduce the bandgap of HNb₃O₈ NS and be profitable to harvest visible light.

To further demystify O_2 activation by surface oxygen vacancies, we theoretically simulated the adsorption configurations of O_2 molecule on HNb₃O₈ NS with oxygen

vacancy and HNb₃O₈ NS-P (Fig. 11 and Fig. S6D), AFig. 11A showed that O2 molecule was physisorbed on the surface of the HNb₃O₈ NS-P surface with the slightly elongated O-O bond length of 1.27 Å (from 1.22 Å to 1.27 Å, Table S5). The calculated E_{ads} of O₂ was merely -0.47 eV and O₂ was negatively charged by 0.30 |e| according to the Mulliken charge analysis. In sharp contrast, molecular oxygen could be intensively chemisorbed on the surface oxygen vacancies of HNb₃O₈ NS-V through an end-on configuration with a significant elongation of O-O bond length of 1.39 Å (Fig. 11B and Table S5), promoting the generation of O2^{•-.63} Meanwhile, the chemisorbed O2 could receive 1.16 |e| from the HNb₃O₈ NS-V. The highly enhanced adsorption energy (E_{ads}) of -4.08 eV (about 8.7 times for that of HNb₃O₈ NS-P) indicated that the O₂ chemisorption was more favorable on the defect surface of HNb₃O₈ NS-V, which promoted efficient O₂ activation during the photocatalytic process. The PDOS plots of O2 adsorbed on HNb3O8 NS-P displayed the divergence of spin-up and spin-down peaks, which demonstrated that a non-zero magnetic dipole moment was generated by the two single electrons of the π_{2p} orbital with a ferromagnetic spin configuration, hence O2 was just physisorbed on the surface of



Fig. 12 (A) Reaction scheme for the photocatalytic oxidation of benzylamine to Nbenzylidenebenzylamine on HNb_3O_8 NS with oxygen vacancy. (B) Proposed mechanism for selective aerobic oxidation of benzylamine to imine over HNb_3O_8 NS under visible light irradiation.

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HNb₃O₈ NS-P through the hydrogen bond between O₂ and surficial hydroxyl (Fig. 11C). In contrast, the PDOS plots of O₂ adsorbed on HNb₃O₈ NS-V showed symmetric spin-up and spindown peaks without magnetic moment (Fig. 11D), which was chemisorbed O₂•-.^{63,64} The new-formed orbitals in the valence band were filled by electrons, whereas there were no electrons left in the conduction band when the O₂ molecule was adsorbed.^{65,66} Therefor, HNb₃O₈ NS-V could efficiently chemisorb O₂ molecules and promote to activate O₂ to reactive oxygen species.

Based on the above analysis and the previous reports,^{8,13,18,21,37} we proposed a possible mechanism to explain the photocatalytic oxidation of benzylamine on HNb₃O₈ nanosheets with oxygen vacancies (shown in Fig. 12). Firstly, benzylamine was adsorbed on the oxygen vacancy sites of HNb₃O₈ NS, forming a surface complex (Step 1). Secondly, the surface charge transfer complex adsorbed visible light, and charge carriers (h⁺/e⁻) were generated. The adsorbed benzylamine was oxidized by the photogenerated hole (h⁺) to form the relevant nitrogen-centered radical (intermediate A), meanwhile the abstracted H⁺ would react with the adjacent Lewis base site and form a surficial hydroxyl. Thirdly, molecular oxygen was activated by the photogenerated electron (e⁻) to produce superoxide radical anion $(O_2^{\bullet-})$ on the same oxygen vacancy site. At the same time, an intramolecular hydrogen transfer process was introduced from -CH₂ to nitrogen-centered radical of intermediate A, which would result in a more stable carbon-centred radical of intermediate B was formed. Fourthly, $O_2^{\bullet-}$ adsorbed on the oxygen vacancy site interacted with carbon radical and formed an intermediate C containing a fivemember-ring structure along with the termination of the radicals. Fifthly, benzaldehyde was produced due to the cleavage of the C-N bond of benzylamine and the O-O bond of oxygen and would react with unreacted benzylamine to yield imine via a condensation reaction. Simultaneously, a threemember-ring structure including the Nb-O-N bond was interlinked with a six-member-ring structure by the edgeshared Nb-O bond (intermediate D). Finally, the catalytic site was regenerated by desorption of the NH₂OH molecule. To verify the production of NH₂OH molecule, ¹H NMR of the reaction mixture during the middle of the photocatalytic oxidation of benzylamine reaction was conducted, and the peak for NH₂OH clearly appeared at 1.71 ppm (Fig. S8).

4. Conclusions

In summary, Ultrathin HNb₃O₈ nanosheets with oxygen vacancies were successfully synthesized by a simple bottom-up hydrothermal process. The obtained HNb₃O₈ NS-V sample exhibited excellent photocatalytic oxidation performance for the aerobic oxidation of benzylamine with molecular oxygen under visible light irradiation, far exceeding that of urchin-like Nb₂O₅ nanosphere and Nb₂O₅ nanorods. Theoretical and experimental results revealed that the oxygen vacancies on the ultrathin HNb₃O₈ nanosheets not only were favorable to forming benzylamine-HNb₃O₈ surface complex that reduced the

bandgap of HNb₃O₈ NS and was induced to harvest visible light, but also could efficiently chemisorb O₂ molecules and promote to activate O₂ to reactive oxygen species. Furthermore, unique nanosheet structure with several molecular thicknesses led to the effective separation of the photogenerated carriers. These findings deepen our knowledge about the roles of oxygen vacancies on the surface of ultrathin transition metal oxide nanosheet, also shed light on exploring defective wide-bandgap semiconductors for the photocatalytic organic synthesis.

Conflicts of interest

There are no conflicts to declare.

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