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Dual modification of TiNb₂O₇ with nitrogen dopant and oxygen vacancy for selective aerobic oxidation of benzylamine to imine under green light

Zhuobin Yu,^{ab} Eric R. Waclawik,^c Zhijian Wang,^a Xianmo Gu,*^a Yong Yuan,^d and Zhanfeng Zheng*^a

TiNb₂O₇ powder was prepared by a simple hydrothermal method and subsequent heat treatment. V_o-N-TiNb₂O₇ was generated by NH₃ and ethanol treatment. The NH₃ treatment produced a new N 2p orbital band above the O 2p valance band and oxygen vacancy levels were formed by the ethanol treatment. This modified the electronic band structure of TiNb₂O₇ and resulted in a narrower band gap. The photocatytic performance of modified V_o-N-TiNb₂O₇ towards selective aerobic oxidation reactions under green light (475-600nm, peaked at 525 nm) was measured. There was a high conversion of benzylamine (above 90%) at 80 °C over 24 h and with selectivity for *N*-benzylidenebenzylamine greater than 95% under green light. V_o-N-TiNb₂O₇ was found to be an efficient photocatalyst that makes full use of visible-light. Selective aerobic oxidation of benzylamine to *N*-benzylidenebenzylamine takes place over the full visible range up to about 600 nm with high light absorption efficiency. A proposed mechanism for selective aerobic oxidation reactions by TiNb₂O₇ is put forward.

1. Introduction

The photocatalysis approach has practical advantages of economic efficiency, environmental-friendliness to drive chemical reactions in ambient conditions.¹⁻² An ideal photocatalyst is the one that can efficiently utilize the solar spectrum to drive reactions. Because it is well-known that 45% of sunlight is visible light, many researchers have paid attention to designing novel materials with a strong visible light absorption, for instance, α -Fe₂O₃ nanocolumns and CuO/Cu₂O nanorod through oblique angle deposition,³⁻⁴ WO₃ nanosheets with hydrothermal method.⁵ Efforts are also given to the modification of wide band gap photocatalysts (e.g. TiO_2) to utilize visible light.⁶⁻⁷ Recently, selective aerobic oxidation of benzylamine to imine on metal oxides has gained attention, as it offers a promising route to imine production and the light response range has red-shift due to the formation of aminemetal surface complex. Among these photocatalyst, several kinds of photocatalyst materials that function for aerobic oxidation of benzylamine to imines have recently been

reported, including WO₃,⁵ Nb₂O₅,^{2,8-9}, TiO₂,¹⁰⁻¹² BiVO₄,¹³ MnO₂,¹⁴ and layered double hydroxides.¹⁵ Nb₂O₅ can catalyse the selective photo-oxidation of benzylamine under visible light irradiation up to ca. 460 nm. Considering that imines are important intermediates used to prepare biologically active nitrogen compounds, electrophilic intermediates and pharmaceuticals,¹⁶⁻¹⁷ the development of semiconductor photocatalysts for transformation of benzylamine to its corresponding imine under light radiation and in the presence of molecular oxygen is an effective green method that can make full use of the solar energy spectrum.

 $\rm TiNb_2O_7$ has a monoclinic, layered structure and a band gap of ca. 3.2 eV, which has been recognized as a promising anode material for lithium-ion batteries (LIBs) due to the volume tolerance of the structure to accommodate Li ions.^{18-22} In the TiNb_2O_7 structure (Fig. 1), TiO_6 and NbO_6 octahedra connect each other by sharing the vertex and Ti and Nb atoms occupy the same position in the lattice structure. The



Fig. 1 (a) Crystal structure diagram and (b) band gap diagram of $TiNb_2O_7$, Nb_2O_5 , TiO_2 : valence band (VB), conduction band (CB).

^{a.} State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China. E-mail: zfzheng@sxicc.ac.cn; xianmo-001@163.com

^{b.} University of Chinese Academy of Sciences, Beijing 100049, China

 ^c School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, Brisbane, QLD 4000, Australia
^d Xi'an Thermal Power Research Institute Co. Ltd, Xi'an 710032, China

Xran Thermal Power Research Institute Co. Ltd, Xran 710032, China Electronic Supplementary Information (ESI) available: the optimized calcination times, output spectra of LED lights, UV-Vis-DR, PL, TPV, and N₂ adsorptiondesorption isotherms, recyclability, activity of oxidation of different amines using V_o-N-TiNb₂O₇, and the calculated band positions. See DOI: 10.1039/x0xx00000x

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band is composed of Ti 3d/Nb 4d orbit and the valence band formed O 2p orbital.¹⁸ The location of valence band and conduction band of TiNb₂O₇ is slightly different compared to that of anatase TiO₂ and Nb₂O₅.²³⁻²⁴ Considering the structure complicity and tolerance, the modification of layered TiNb₂O₇ could be supposed to ensure essentially homogeneous doping which may induce band structure change and may be an ideal candidate for amine selective oxidation.

In this study, $TiNb_2O_7$ nanoparticles were prepared by a simple hydrothermal method and a subsequent sintering process. The band structure of $TiNb_2O_7$ nanoparticles were then modified by combining NH_3 treatment and ethanol treatment processes. The former process raised the edge of the valence band, while the latter lowered the edge of the conduction band. The net result was a narrower band gap that enhanced photocatalytic activity for the selective aerobic oxidation of benzylamine to *N*-benzylidenebenzylamine under green light.

2. Experimental

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2.1 Sample preparation

All chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd and used without further purification. TiNb₂O₇ was prepared by a hydrothermal process and a subsequent heat treatment. In a typical reaction, niobium oxalate $[Nb(HC_2O_4)_5, 1.35 g]$ and titanium oxysulfate (TiOSO₄•xH₂O, 0.4 g) were added to aqueous KOH solution (0.1 M, 50 mL) and kept stirring for 1 h. This solution was then transferred to a PTFE-lined autoclave (100 mL in volume) and kept at 180 °C for 24 h. After the hydrothermal processing, the white precipitate was separated by centrifugation, washed with deionized water, and dried in air at 80 °C for 12 h. The dried sample was calcined in air at 700 °C for 3 h with a heating rate of 5 °C/min (labelled as TiNb₂O₇). The TiNb₂O₇ sample was calcined in air at 700 °C for another 3 h (labelled asTiNb₂O₇-6h). The TiNb₂O₇ sample was further treated at 700 °C for 3 h under gaseous NH_3 and at 500 °C for 5 min in air (labelled as $N-TiNb_2O_7$). TiNb₂O₇ and N-TiNb₂O₇ samples (0.50 g) were dispersed in ethanol (20 ml) and stirred for 4 h. The suspension was transferred to a quartz boat and placed in a furnace at 200 °C for 3 h under Ar atmosphere (labelled as Vo-TiNb2O7 and Vo-N-TiNb₂O₇, respectively). The optimized calcination times for nitrogen doped TiNb₂O₇ in air and for TiNb₂O₇ in ethanol were based on the photocatalytic activity (Fig. S1-2⁺). In the similar manner, V₀-N-TiO₂ and V₀-N-Nb₂O₅ were prepared by combining NH₃ treatment and ethanol treatment processes for TiO₂ (anatase) and Nb₂O₅ (orthorhombic), respectively.

2.2 Characterization

The X-Ray diffraction (XRD) patterns were record on a MiniFlex II diffractometer with Cu K α radiation (λ = 1.5418 Å). The transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS) were operated 200 kV (JEM-2100F). Nitrogen sorption isotherms were carried out through an automatic adsorption instrument (Micromeritics, TriStar II

3020 analyser) operated at liquid nitrogen temperature (77 K). The UV-Vis diffuse reflectance (UV-Vis-DR) spectrometer (Shimadzu UV-3600) was used to obtain UV-Vis-DR spectra of solid samples. The X-ray photoelectron spectra (XPS) were performed using a Thermo ESCALAB 250 spectrometer with an Al K α X-ray source (hv = 1486.6 eV). The binding energy was calibrated using the C1s peak at 284.6 eV. The photoluminescence (PL) spectra were carried out on a Hitachi F-7000 FL spectrophotometer. The transient photovoltage spectra (TPV) were carried out with a home-made instrument, which was based on the pulse laser (wavelength of 355 nm and pulse width of 5 ns) from a third-harmonic Nd: YAG laser (Polaris II, New Wave Research, Inc.). The surface photovoltage spectra (SPS) were carried out by self-assembled instrument, equipped with a lock-in amplifier (SR830) synchronized with a light chopper (SR540).

2.3 Evaluation of photocatalytic activity

The photocatalytic activity for selective amine oxidation reactions were evaluated at 80 °C in an oxygen atmosphere (1 atm). Typically, the reaction system consisted of a catalyst (20 mg), benzylamine (0.04 mmol), and acetonitrile (2 mL). The products were analyzed using a Shimadzu 2014C GC equipped with а WondaCap 5 column. The imine (Nbenzylidenebenzylamine) yield and output were calculated from the following equations: (1) Imine yield = Conversion rate of benzylamine \times Selectivity to imine; (2) Imine output = Imine yield imes 0.02 mmol (benzylamine molar amount). White and single coloured LED lights (100 W COB LED lamp) including purple LED (375-430 nm, peaked at 400 nm), blue LED (425-510 nm, peaked at 455 nm), green LED (475-600 nm, peaked at 525 nm), yellow LED (585-660 nm, peaked at 585 nm), and red LED (580-665 nm, peaked at 625 nm) were used and the output spectra were shown in Fig. S3⁺.

3 Results and discussion

3.1 Physicochemical properties of TiNb_2O_7 and modified TiNb_2O_7 samples

TiNb₂O₇ powders have a white colour, which indicates that light absorption is not in the visible light range. However, the colour changed progressively to grey, yellow, and dark vellow after further modification of the TiNb₂O₇ with ethanol at 200 °C, under gaseous ammonia at 700 °C, and modification under gaseous ammonia at 700 °C followed by treatment with ethanol at 200 °C, respectively. The UV-Vis diffuse reflectance (UV-Vis-DR) spectra of the TiNb₂O₇ and modified TiNb₂O₇ samples are shown in Fig. 2. It is found that there is a strong absorption band in the UV region for $TiNb_2O_7$ and V_0 - $TiNb_2O_7$. The absorption edges of N-TiNb₂O₇ and V_0 -N-TiNb₂O₇, the nitrogen doped samples, are about 540 and 570 nm, which is a significant red-shift compared to that of TiNb₂O₇ and V_o-TiNb₂O₇. There is a two-step absorption edge for V_o-N-TiNb₂O₇, which should result from original structure band and the new band created by nitrogen doping, respectively.^{22,25} As for an indirect band gap semiconductor, the relationship between the

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absorption coefficient (α) and the optical band gap energy (E_g) near the band edge follows the formula: $\alpha hv=R(hv-Eg)^2$, where hv and R are the photon energy and a constant, respectively.²² The calculated band gaps of TiNb₂O₇, V_o-TiNb₂O₇, N-TiNb₂O₇, and V_o-N-TiNb₂O₇ are 3.10, 3.04, 2.30 and 2.18 eV, respectively (Table 1). These results indicate that ammonia treatment and ethanol treatment in TiNb₂O₇ is an effective method to narrow the band gap and induces visible light absorption. This is consistent with reported literatures that nitrogen doping in TiO₂ is an effective method to narrow the

Materials	S _{BET} (m²/g)	Average pore size (nm)	Band gap (eV)	Crystallite size (nm)
TiNb ₂ O ₇	32.48	26.87	3.10	16.0
V _o -TiNb ₂ O ₇	31.14	26.95	3.04	16.1
N-TiNb ₂ O ₇	39.72	25.95	2.30	15.8
V_0 -N-TiNb ₂ O ₇	34.05	25.20	2.18	15.2

band gap.^{24,26}

Although TiNb₂O₇ and the modified TiNb₂O₇ samples exhibit very different light adsorption, they have the similar X-Ray diffraction (XRD) patterns. The patterns can be indexed using a monoclinic system (space group C2/m, lattice parameters a = 17.686 Å, b = 3.801 Å, c = 11.890 Å), which matches well with the published data (ICDD PDF Card no. 39-1407) and no other diffraction peaks from other phases such as TiO₂, Nb₂O₅ and TiNb₁₀O₂₉ are observed. The characteristic diffraction peaks of V₀-TiNb₂O₇, N-TiNb₂O₇, and V₀-N-TiNb₂O₇ are the same as that of TiNb₂O₇ except that the samples treated at 700 °C for extended time exhibit increased diffraction peak intensity. This indicates that the crystal structure of TiNb₂O₇ is well retained after ethanol treatment



Fig. 3 TEM and HRTEM images of $TiNb_2O_7$ (a, e), V_0 - $TiNb_2O_7$ (b, f), N- $TiNb_2O_7$ (c, g), and V_0 -N- $TiNb_2O_7$ (d, h).

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and NH₃ treatment. The crystallite sizes of TiNb₂O₇, V_o-TiNb₂O₇, N-TiNb₂O₇, and V_o-N-TiNb₂O₇ are 16.0, 16.0, 15.8 and 15.2 nm, respectively, calculated from the broadening of the (020) peak. It is found that there seems to be little change in terms of grain size. These materials have a similar specific surface area at 32.5, 31.1, 39.7 and 34.1 m²/g corresponding to TiNb₂O₇, V_o-TiNb₂O₇, N-TiNb₂O₇, and V_o-N-TiNb₂O₇, respectively (Fig. S4⁺). The structure parameters of these samples are listed in Table 1.

The transmission electron microscope (TEM) and high resolution TEM (HRTEM) images of TiNb₂O₇, and modified TiNb₂O₇ samples are shown in Fig. 3. It is found that the particles aggregate with single particle size less than 100 nm. There is no significant difference in morphology among TiNb₂O₇, V_o-TiNb₂O₇, N-TiNb₂O₇, and V_o-N-TiNb₂O₇ samples. Based on the high-resolution TEM images in Fig. 3, the lattice spacing is about 0.37 nm, 0.42 nm, corresponding to the (T10) and (T303) planes of TiNb₂O₇, respectively. It is found that there is no difference in the lattice spacing corresponding to the (T10) and (T303) planes of V_o-TiNb₂O₇, N-TiNb₂O₇, and V_o-N-TiNb₂O₇. This is consistent with XRD results, which further confirms that there is no obvious change in the crystal structure of TiNb₂O₇ after ethanol or NH₃ treatment.

The survey and high resolution X-ray photoelectron spectra (XPS) of TiNb₂O₇ and modified TiNb₂O₇ samples are shown in Fig. 4. The characteristic peaks of Nb $3d_{3/2}$ and Nb $3d_{5/2}$ for TiNb₂O₇ at approximately 210.0 and 207.0 eV are in accordance with Nb⁵⁺ band.²⁷ The characteristic peaks of Ti $2p_{1/2}$ and Ti $2p_{3/2}$ for TiNb₂O₇ at approximately 464.0 eV and

458.1 eV can be indexed to Ti⁴⁺ band.²⁷ The N 1s at 396 eV can be attributed to N-Ti.²⁸⁻²⁹ The amount of N in N-TiNb₂O₇ and V_0 -N-TiNb₂O₇ is 1.99 wt% and 0.91 wt%, respectively. The results indicate N has been incorporated in the structure in N- $TiNb_2O_7$ and V_0 -N-TiNb_2O_7 samples. The O 1s peak of $TiNb_2O_7$, consists of three characteristic peaks at about 529.5, 531.6, and 533.0 eV, which attributes to O-M (M=Ti or Nb) bond, O²⁻ in the oxygen deficient regions, and loosely bound oxygen on the surface, respectively.³⁰⁻³¹ It is found that the intensity of O 1s at 531.6 eV is enhanced while the intensity of O 1s at 529.5 eV decreases when TiNb2O7 or N-TiNb2O7 is treated by ethanol to form V_0 -TiNb₂O₇ and V_0 -N-TiNb₂O₇, which indicates that oxygen vacancy levels can be increased by ethanol treatment.³⁰ For N-TiNb₂O₇ sample, the O 1s band at 529.5 eV is very high compared with the bands at 531.6 and 533.0 eV, this may due to that the longer heat treatment at 700 °C induces better crystallinity. A control experiment was devised for the $TiNb_2O_7$ precursor which was treated in air for 6 h instead of 3 h. This sample exhibited a similar O 1s band to N-TiNb₂O₇ and the XRD pattern indicated it had better for V₀-N-TiNb₂O₇ crystallinity also (Fig. S5⁺). In addition, according to EDS analysis, the O/Ti ratio decreased from 6.68 for $TiNb_2O_7$ to 4.45 for V₀-N-TiNb₂O₇ providing evidence for the formation of O vacancy. Therefore, it was concluded that ethanol treatment is an effective method to create surface oxygen vacancies.

The density of states (DOS) of the valence band of $TiNb_2O_7$ and the modified samples was measured by valence band XPS spectroscopy (Fig. 5a). There is an obvious difference



Fig. 4 XPS spectra of TiNb₂O₇, V_o-TiNb₂O₇, N-TiNb₂O₇, and V_o-N-TiNb₂O₇.

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Fig. 5 (a) Valance-band XPS spectra, (b) SPS spectra in oxygen atmosphere and (c) schematic diagram of the DOS of V_0 -TiNb₂O₇, N-TiNb₂O₇, and V_0 -N-TiNb₂O₇.

in the valance band maximum energy among $TiNb_2O_7$ and modified $TiNb_2O_7$ samples, which is 0.8 eV and 0.21 eV more negative for N-TiNb_2O_7, and V_o-N-TiNb_2O_7 than $TiNb_2O_7$, respectively, furthermore, the valence band of V_o-TiNb_2O_7 is

the same as that of TiNb₂O₇.³² Combing the results of UV-Vis-DR spectra and the valance band XPS spectra, the schematic diagram of the DOS of TiNb₂O₇ and the modified samples is drawn (Fig. 5c). The NH₃ treatment of TiNb₂O₇ generates a new N 2p orbital above the O 2p valance band.¹⁸ The ethanol treatment brings about the formation of oxygen vacancy, with an energy level just below the conduction band. The combination of these two treatments thus narrows the band gap and may create catalyst for working under long wavelength visible light. The difference of values in valence band position between N-TiNb₂O₇ and V₀-N-TiNb₂O₇ and in the conduction band between $V_{o}\mbox{-}TiNb_{2}O_{7}\,and\,\,V_{o}\mbox{-}N\mbox{-}TiNb_{2}O_{7}$ were attributed to the high content of nitrogen and of oxygen vacancies therefore.^{19,28,33} The photoluminescence (PL) spectra of $TiNb_2O_7$ and $V_0-N-TiNb_2O_7$ is shown in Fig. S6⁺, the luminescence peak centred at 540 nm resulted from TiO₆ units while the luminescence centred at 630 nm may be attributed to defects such as oxygen deficiency or cation vacancies.³⁴⁻³⁵



Fig. 6 The conversion, imine (*N*-benzylidenebenzylamine) selectivity, and yield (mmol/mmol_{catalyst}) over TiNb₂O₇ and modified TiNb₂O₇ photocatalysts (a), TiO₂, Nb₂O₅ and modified samples (b). Reaction conditions: catalyst (20 mg), benzylamine (0.04 mmol), acetonitrile (2 mL), green LED (100 mW/cm²), 80 °C, 12 h.

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The PL intensity of V_o-N-TiNb₂O₇ is much weaker than TiNb₂O₇, which indicates charge separation is enhanced and is an advantage that can improve photocatalytic activity.³⁶

3.2 Photocatalytic activity for selective aerobic oxidation of benzylamine to imine over $TiNb_2O_7$ and modified $TiNb_2O_7$ samples under green light

It is noted that TiNb₂O₇ and modified TiNb₂O₇ high selectivity photocatalysts exhibit towards Nbenzylidenebenzylamine during the aerobic oxidation of benzylamine under green light (475-600 nm, peaked at 525 nm, Fig. 6). V_0 -N-TiNb₂O₇ exhibits the highest activity (with Nbenzylidenebenzylamine yield benzylamine under green light (475-600 nm, peaked at 525 nm, Fig. 6). Vo-N-TiNb2O7 exhibits the highest activity (with N-benzylidenebenzylamine yield of 450 mmol/mol_{catalvst}), much higher than TiNb₂O₇ (37 mmol/mol_{catalvst}), V_o-TiNb₂O₇ (162 mmol/mol_{catalvst}) and N-TiNb₂O₇ (255 mmol/mol_{catalvst}) in terms of Nbenzylidenebenzylamine yield. The high activity of Vo-N-TiNb₂O₇ indicates that the combination of ethanol treatment and NH₃ treatment on TiNb₂O₇ effectively improves the Nbenzylidenebenzylamine yield by increasing the light absorption efficiency (by utilizing more green light). Furthermore, the N-benzylidenebenzylamine yield of V_o-N-TiO₂ is 83 mmol/mol_{catalyst} with low selectivity (55%) while the Nbenzylidenebenzylamine yield of V_0 -N-Nb₂O₅ is 172 mmol/mol_{catalyst} with high selectivity (95%). At the same time, it is clearly observed that the benzylamine conversion and Nbenzylidenebenzylamine yield increase in the order of Vo-N- $TiO_2 > TiO_2$ and $V_0 - N - Nb_2O_5 > Nb_2O_5$, respectively. The low Nbenzylidenebenzylamine selectivity for TiO₂ should attribute to its lower selectivity for partial oxidation products.² Therefore, the results indicate that Vo-N-TiNb2O7 has better catalytic performance than Vo-N-TiO2 and Vo-N-Nb2O5 in terms of yield and selectivity for selective aerobic oxidation of benzylamine to imine under green light. The reason should result from the uniformly distributed nitrogen dopant and oxygen vacancy in



Fig. 7 Benzylamine conversion, N-benzylidenebenzylamine selectivity and yield of V_0 -N-TiNb₂O₇ photocatalyst under single-coloured LED lights. Reaction conditions: catalyst (20 mg), benzylamine (0.04 mmol), acetonitrile (2 mL), light intensity (100 mW/cm²), 80 °C, 12 h.

the whole TiNb₂O₇ particles while only within a subsurface region in TiO₂ and Nb₂O₅ particles thanks to their difference in structure.²⁴ V_o-N-TiNb₂O₇ exhibits good catalytic activity and high V_o-N-TiNb₂O₇ exhibits good catalytic activity and high selectivity under white and single coloured (purple, blue and green) LED illumination, while benzylamine conversion rate dramatically decreases when performed under either yellow or red LED light (Fig. 7). The conversion rate of benzylamine over V_o-N-



Fig. 8 (a) Light intensity (80 °C, 12 h), (b) time profile (80 °C, 100 mW/cm²) and (c) temperature influence (6 h, 100 mW/cm²) on selective oxidation of benzylamine over V_0 -N-TiNb₂O₇ photocatalyst under green light.

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TiNb₂O₇ is 98%, 98%, 88% and 68% under white, purple, blue and green light, respectively. The selectivity for the oxidation of benzylamine to *N*-benzylidenebenzylamine over V₀-N-TiNb₂O₇ is 98% (green LED) while the selectivity is 91% (white LED), 82% (purple LED), 90% (blue LED). The conversion rate of benzylamine over V₀-N-TiNb₂O₇ is 8% and 6% under yellow and red light, respectively. Control experiment shows that the conversion rate of benzylamine is negligible over V₀-N-TiNb₂O₇ in the absence of light, which confirms that the oxidation of thenzylamine over V₀-N-TiNb₂O₇ is a light-driven reaction. Therefore, given that V₀-N-TiNb₂O₇ has the outstanding catalytic performance, ideal selectivity (98%), and, moderate yield of *N*-benzylidenebenzylamine (68%, 12 h, green LED) of the materials investigated, the photocatalytic performance of V₀-N-TiNb₂O₇ under green light was studied in detail.

The photocatalytic activities of Vo-N-TiNb2O7 under green light with different intensity are shown in Fig. 8a. It was found that the conversion of benzylamine increases with the increasing intensity of light as expected. The conversion of benzylamine increases from 18.4% to 68.1% when the intensity varies from 30 to 100 mW/cm². Meanwhile, it is observed that the selectivity toward product Nbenzylidenebenzylamine is above 95% in all cases. The conversion rate of benzylamine increases gradually when the reaction time is prolonged (Fig. 8b) and the reaction profile exhibits a pseudo first-order reaction feature. The conversion of benzylamine reaches to approximately 94.5% with high selectivity (> 95%) when the reaction time is 24 h. It is found that there is a small quantity of benzaldehyde in the products, which indicates benzaldehyde is an intermediate product. The generation of benzaldehyde intermediate is similar to the situation when TiO₂ or Nb₂O₅ are used as photocatalyst for benzylamine oxidation under visible light.^{2,11} As shown in Fig. 8c, the conversion rate increases gradually when the reaction temperature is increased from 30 to 80 °C and benzylamine is converted to N-benzylidenebenzylamine with a very high selectivity (> 95%) regardless of the reaction temperature. The Vo-N-TiNb2O7 photocatalyst can be readily recovered by filtration for reuse. Over time, conversion decreases slightly from 94.5% to 91.6%, while high selectivity is maintained after four successive cycles (Fig. S7⁺). Various kinds of amine derivatives including with -CH₃ group (electron donation -CI group (electron withdrawing groups, group), phenylethylamine, and n-propylamine are carried out for aerobic oxidation over V₀-N-TiNb₂O₇ under green light and the photocatalytic activity is listed in Table S1. It is found that their corresponding imines are the main products and the substituents on the benzene ring have only a weak influence on the activity.¹⁰

3.3 Proposed photocatalytic mechanism

It is well known that the alignment of the CB or VB band edge position of a semiconductor with the redox potential of a reaction determine whether a photocatalytic reaction can proceed. If the CB edge is more negative and the VB edge is more positive than the redox potentials of a reaction, it would have potential to drive the photocatalytic reaction.⁴ From consideration of the redox potential, the one-electron oxidation potential of benzylamine is -5.17 eV (vs. vacuum energy level, 0.67 V vs. NHE).³⁷ The onset of the valence band of V_0 -N-TiNb₂O₇ is -7.43 eV vs (vs. vacuum energy level), calculated from theoretical band edge and the valence band XPS result. Therefore, the redox potential difference is enough to oxidize benzylamine. Efficient excitation of electrons and holes could induce the reaction. To explain the mechanism, there are two questions that should be clarified: (1) Which structure absorbs green light? (2) What is the role of nitrogen doping and oxygen vacancy in the photocatalytic reaction?

The interaction between Vo-N-TiNb2O7 and benzylamine has been investigated. The UV-Vis-DR spectra (Fig. S8⁺) show that that adsorption of benzylamine on solids causes a redshift of the absorption band. For V_o -N-TiNb₂O₇, the differential spectrum before and after benzylamine adsorption exhibits a broad absorption band central at 530 nm (red shifted 0.25 eV). Because benzylamine does not absorb light in the region of λ > 300 nm,² the new absorption can be attributed to the formation of a surface complex analogous to that observed on large band gap metal oxides such as Nb₂O₅ and TiO₂ during selective aerobic oxidation of benzylamine to imine.⁸ The surface complex can participate in a direct electron transfer from a donor level consisting of a N 2p orbital derived from adsorbed amine species to the conduction band of Vo-N-TiNb₂O₇. The transient photovoltage (TPV) spectra of V₀-N-TiNb₂O₇ before and after benzylamine adsorption were carried out under 532 nm light irradiation (green light, Fig. S9⁺). A stronger negative signal for Vo-N-TiNb2O7 after benzylamine adsorption is observed which indicates that the formation of surface amine complex can effectively separate photoelectrons and holes, and the photo-generated electrons are accumulated at the surface. It is reported that nitrogen doping can also narrow the band gap. However, the narrow band gap due to the formation of surface complex or N doping cannot guarantee a good activity (The nitrogen doped sample, N-TiNb₂O₇ with a narrow bang gap at 2.3 eV, does not exhibit very high activity compared to Vo-N-TiNb2O7). The abundant oxygen vacancy sites produced at the surface due to ethanol treatment (confirmed by XPS and PL results) should also be taken into consideration. At these oxygen vacancy sites, conduction band electrons of V₀-N-TiNb₂O₇ are trapped and can interact with dissolved O₂, generating oxygen free radicals can transform benzylamine N- (0_2^{-}) that to benzylidenebenzylamine rapidly. The surface photovoltage spectra (SPS) of TiNb₂O₇ and modified TiNb₂O₇ samples are shown in Fig. 5b. It is found that V_0 -N-TiNb₂O₇ exhibits the strongest photovoltaic response signal in oxygen atmosphere compared to $TiNb_2O_7$, V_0 - $TiNb_2O_7$, and N- $TiNb_2O_7$. The photovoltaic response edges of V₀-N-TiNb₂O₇ is about 570 nm, which approximately agrees with corresponding absorption edges in UV-Vis-DR spectra and should attribute to the bandto-band transition.³⁸ The above phenomenon should arise as more photo-generated electrons are captured by O₂ (electron capture) and the photo-generated holes result in stronger surface photovoltage signal.38 The results indicate that the photo-generated electrons and holes for Vo-N-TiNb2O7 readily

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Fig. 9 (a) Schematic diagram of V_o -N-TiNb₂O₇ and (b) Proposed mechanism for selective aerobic oxidation of benzylamine to imine over V_o -N-TiNb₂O₇ under green light (M = Ti or Nb).

separate, which means electrons are free to interact with O_2 and generate oxygen free radicals (O_2^{-}) easily.

The other advantage afforded by high levels of surface oxygen vacancy in V_0 -N-TiNb₂O₇ is their ability to trap electrons and thus minimise photo-generated e⁻-h⁺ recombination. Photo-generated electrons transfer to the catalyst surface and improve the photocatalytic performance for selective aerobic oxidation of benzylamine.^{28,39} When compared to the photocatalytic performance of V_0 -TiNb₂O₇, it is clear that more electrons could be excited due to the nitrogen doping. Therefore, V_o -N-TiNb₂O₇ exhibits a better activity than V_0 -TiNb₂O₇. Based on the above analysis and the previous literature, a catalytic mechanism for selective aerobic oxidation of benzylamine to N-benzylidenebenzylamine over V_o-N-TiNb₂O₇ photocatalyst under green light is proposed (Fig. 9). Firstly, benzylamine is adsorbed on the surface of V_o-N-TiNb₂O₇, forming a surface complex (Step 1). Secondly, V₀-N-TiNb₂O₇ has a narrower band gap by generation of a N 2p band nearly above the O 2p valance band through the processes of N-doping and through amine species adsorption. Oxygen vacancies can interact with O_2 to generate (O_2^{-}) , and the photo-generated hole can abstract H^{+} from N of benzylamine while the photo-generated electron would move to the conduction band of V_{o} -N-TiNb₂O₇ (Step 2). The nitrogencentred radical of compound A would transform into a more stable carbon-centred radical of compound B by means of transferring intramolecular hydrogen.⁸ Thirdly, compound B converts to compound C via a transfer step (Step 3). Fourthly, C-N bond and O-O bond (Compound C) would break to form benzaldehyde and three-member-ring structure containing M-O-N bond (M = Ti or Nb). The intermediate benzaldehyde reacts spontaneously with unreacted benzylamine to from imine (Step 4). Finally, the catalyst surface regenerates for another reaction cycle by desorption of the NH₂–OH molecule (Step 5).

4. Conclusions

In summary, TiNb₂O₇ has been prepared by a simple hydrothermal method and subsequent heat treatment. Surface modified TiNb₂O₇, treated by NH₃ and ethanol treatment, has more outstanding photocatalytic performance for the selective aerobic oxidation of benzylamine to Nbenzylidenebenzylamine under green light. It is proposed that the ethanol treatment brings about the formation of surface oxygen vacancies while N-doping should generate a N 2p level nearly above the O 2p valance band, which results in a narrower band gap and prevents photo-generated e⁻-h⁺ exciton recombination. Therefore, it is found that photogenerated electrons transfer to the catalyst surface and improve the photocatalytic performance for selective aerobic oxidation of benzylamine. The yield of Nbenzylidenebenzylamine over Vo-N-TiNb2O7 photocatalyst reaches approximately 450 mmol/mol_{catalyst} under green light (12 h, 80 °C), which has much better photocatalytic performance than TiO₂ and Nb₂O₅ in terms of yield and selectivity of N-benzylidenebenzylamine under green light. V₀-N-TiNb₂O₇ is one of few photocatalysts that can function for of aerobic oxidation benzylamine to Nbenzylidenebenzylamine with good conversion and high selectivity under green light. The results indicates that Vo-N-TiNb₂O₇ is an efficient photocatalyst to make full use of visiblelight because it takes place even under visible irradiation up to about 600 nm that selective aerobic oxidation of benzylamine to N-benzylidenebenzylamine.

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Notes and references

- D. Cambie, C. Bottecchia, N. Straathof, V. Hessel and T. Noel, Chem. Rev., 2016, 116, 10276-10341.
- 2. S. Furukawa, Y. Ohno, T. Shishido, K. Teramura and T. Tanaka,

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ACS Catal., 2011, 1, 1150-1153.

- 3. P. Basnet, G. Larsen, R. Jadeja, Y. Hung and Y. Zhao, ACS Appl. Mater. Interfaces, 2013, 5, 2085-2095.
- 4. P. Basnet and Y. Zhao, Catal. Sci. Technol., 2016, 6, 2228-2238.
- 5. N. Zhang, X. Li, H. Ye, S. Chen, H. Ju, D. Liu, Y. Lin, W. Ye, C. Wang, Q. Xu, J. Zhu, L. Song, J. Jiang and Y. Xiong, J. Am. Chem. Soc., 2016. 138. 8928-8935.
- 6. K. Yao, P. Basnet, H. Sessions, G. Larsen, S. Murph and Y. Zhao, Catal Today, 2016, 270, 51-58.
- 7. J. Lim, P. Murugan, N. Lakshminarasimhan, J. Kim, J. Lee, S. Lee and W. Choi, J. Catal., 2014, 310, 91-99.
- 8. Y. Zhang, L. Pei, Z. Zheng, Y. Yuan, T. Xie, J. Yang, S. Chen, J. Wang, E. Waclawik and H. Zhu, J. Mater. Chem. A, 2015, 3, 18045-18052.
- 9. S. Furukawa, Y. Ohno, T. Shishido, K. Teramura and T. Tanaka, J. Phys. Chem. C, 2013, 117, 442-450.
- 10. L. Huang, J. Jia, H. Liu, Y. Yuan, J. Zhao, S. Chen, W. Fan, E. Waclawik, H. Zhu and Z. Zheng, RSC Adv., 2015, 5, 56820-56831.
- 11. X. Lang, W. Ma, Y. Zhao, C. Chen, H. Ji and J. Zhao, Chemistry, 2012, 18, 2624-2631.
- 12. X. Lang, H. Ji, C. Chen, W. Ma and J. Zhao, Angew. Chem., Int. Ed.,, 2011, 50, 3934-3937.
- 13. B. Yuan, R. Chong, B. Zhang, J. Li, Y. Liu and C. Li, Chem. Commun., 2014, 50, 15593-15596.
- 14. Z. Zhang, F. Wang, M. Wang, S. Xu, H. Chen, C. Zhang and J. Xu, Green Chem., 2014, 16, 2523-2527.
- 15. X. Yang, B. Chen, X. Li, L. Q. Zheng, L. Wu and C. Tung, Chem. Commun., 2014, 50, 6664-6667.
- 16. L. Aschwanden, T. Mallat, M. Maciejewski, F. Krumeich and A. Baiker, ChemCatChem, 2010, 2, 666-673.
- 17. L. Aschwanden, T. Mallat, F. Krumeich and A. Baiker, J. Mol. Catal. A-Chem., 2009, 309, 57-62.
- 18. H. Park, T. Song and U. Paik, J. Mater. Chem. A, 2015, 3, 8590-8596.
- 19. H. Park, H. Wu, T. Song, X. David and U. Paik, Adv. Energy Mater., 2015, 5, 1401945-1401951.
- 20. H. Li, L. Shen, G. Pang, S. Fang, H. Luo, K. Yang and X. Zhang, Nanoscale, 2015, 7, 619-624.
- 21. X. Lu, Z. Fang, L. Gu, Y. Hu, W. Chen, Z. Wang and L. Chen, Energ. Environ. Sci., 2011, 4, 2638-2644.
- 22. S. Lou, Y. Ma, X. Cheng, J. Gao, Y. Gao, P. Zuo, C. Du and G. Yin, Chem. Commun., 2015, 51, 17293-17296.
- 23. G. Liu, L. Wang, C. Sun, X. Yan, X. Wang, Z. Chen, S. Smith, H. Cheng and G. Lu, Chem. Mater., 2009, 21, 1266-1274.
- 24. O. Lopes, E. Paris and C. Ribeiro, Appl. Catal. B-Environ., 2014, 144, 800-808.
- 25. Z. Zhai, Y. Huang, L. Xu, X. Yang, C. Hu, L. Zhang, Y. Fan and W. Hou, Nano. Res., 2011, 4, 635-647.
- 26. L. Kong, Z. Jiang, C. Wang, F. Wan, Y. Li, L. Wu, J. Zhi, X. Zhang, S. Chen and Y. Liu, ACS Appl. Mater. Interfaces, 2015, 7, 7752-7758.
- 27. L. Srisombat, S. Ananta, B. Singhana, T. Lee and R. Yimnirun, Ceram. Int., 2013, 39, S591-S594.
- 28. Y. Wang, C. Feng, M. Zhang, J. Yang and Z. Zhang, Appl. Catal. B-Environ., 2011, 104, 268-274.
- 29. J. Yuan, M. Chen, J. Shi and W. Shangguan, Int. J. Hydrogen Energ., 2006, 31, 1326-1331.
- 30. J. Wang, Z. Wang, B. Huang, Y. Ma, Y. Liu, X. Qin, X. Zhang and Y. Dai, ACS Appl. Mater. Interfaces, 2012, 4, 4024-4030.
- 31. B. Lee, H. Song and J. Jeong, Adv. Mater. Sci. Eng., 2015, 2015, 1-5.
- 32. X. Chen, P. Y. Yu and S. Mao, Science, 2011, 331, 746-750.
- 33. H. Huang, C. Wang, J. Huang, X. Wang, Y. Du and P. Yang,

Nanoscale, 2014, 6, 7274-7280.

- 34. A. Kudo, E. Kaneko, Micropor. Mesopor. Mat., 1998, 21, 615-620.
- 35. Q. Ma, Y. Zhou, M. Lu, A. Zhang and G. Zhou, Mater. Chem. Phys., 2009, 116, 315-318.
- 36. P. Wu, J. Wang, J. Zhao, L. Guo and F. Osterloh, J. Mater. Chem. A, 2014, 2, 20338-20344.
- 37. T. Łuczak, J. Appl. Electrochem., 2008, 38, 43-50.
- 38. L. Jing, S. Li, S. Song, L. Xue and H. Fu, Sol. Energ. Mat. Sol. C., 2008, 92, 1030-1036.
- 39. Y. Wang, C. Feng, M. Zhang, J. Yang and Z. Zhang, Appl. Catal. B-Environ., 2010, 100, 84-90.

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