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Introduction

Nitrogen containing compounds, such as imines, nitriles and amides, are essential industrial intermediates for the synthesis of pharmaceuticals, natural products, and functional materials.¹⁻³ Conventional synthetic methods for nitrile compounds include the Sandmeyer reaction,4 the Rosenmundvon Braun reaction of aromatic halides,⁵ and the transitionmetal-catalyzed cyanation of aromatic halides.⁶ However, these methods suffer from some drawbacks, such as the usage of toxic cyanide salts as the source of cyano, and the generation of stoichiometric amounts of metal and inorganic wastes in the process. Therefore, in the past decades some methods have been developed to avoid the use of toxic cyanide, such as oxidative conversion of alcohols, aldehydes, and amines to nitriles,^{7,8} the oxidation of primary azides,⁹ and the direct transformation of methyl arenes to aryl nitriles.¹⁰ It is noteworthy that those reactions need to use stoichiometric

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Photocatalytic selective aerobic oxidation of amines to nitriles over Ru/γ -Al₂O₃: the role of the support surface and the strong imine intermediate adsorption[†]

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Hydroxyl coordinated ruthenium dispersed on the surface of γ -Al₂O₃ can be applied to the selective oxidation of amines with light irradiation and an atmospheric pressure of O₂ at room temperature. Sunlight is also an effective light source for the selective aerobic oxidation of primary amines to corresponding nitriles. The high photocatalytic activity and selectivity over Ru/ γ -Al₂O₃ originate from the adsorption of amines and imine intermediates on the abundant surface OH groups of the photocatalyst and further formation of Ru-amide species by ligand exchange of adsorbed amines and imine intermediates with adjacent exposed active Ru sites. Light is introduced to the system successfully *via* the formation of Ru-amide species, which are used as the light absorption sites of the photocatalytic selective oxidation of amines. Primary amines are directly converted to corresponding nitriles *via* a two-step oxidative dehydrogenation process.

> amounts of I2, TBHP, and PIDA as oxidants. From the perspective of sustainable chemistry, molecular oxygen is a green, cheap, and efficient oxidant. McWhinnie et al. firstly found that ruthenium catalysts may have the ability to oxidize amines under an oxygen atmosphere.¹¹ Despite all that, it was not until the pioneering study of Tang et al. that homogeneous ruthenium complex catalytic oxidation of amines with oxygen was reported.¹² Since then, a number of ruthenium complexes have been used for the oxidation of amines with oxygen.¹³⁻¹⁸ Parvulescu et al. discovered that the ruthenium terpyridyl complex functionalized with the azulenyl moiety at the 4 position of the central pyridine core exhibited a much higher reactivity for the oxidation of both aliphatic and aromatic amines with oxygen or air than other ruthenium terpyridine-based ligand complexes reported. In addition, the alkyl chain length of the reactant has a significant influence on the conversion.¹⁷ Lahiri et al. reported that ruthenium hydrido complexes can be used for the simultaneous generation of nitriles and imines by varying the catalyst. They showed that the ligand played a vital role in altering the selectivity in the oxidative dehydrogenation of primary amines. However, this system also made use of TEMPO as an electron transfer mediator.¹⁸ Meanwhile, Szymczak's group¹⁹ and Bera et al.²⁰ realized the double dehydrogenation of primary amines to nitriles under oxidant-free and acceptorless conditions by using a Ru/pyrazole system and an amide-derived Ru complex, respectively. In order to reuse the noble metal catalysts, a series of heterogeneous ruthenium catalysts have been



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reported for the oxidation of amines to corresponding nitriles with oxygen as the sole oxidant.²¹⁻²⁶ Kaneda et al. reported that a truly heterogeneous Ru/HAP catalyst (Ru loading: 17 wt%) can be used for the aerobic oxidation of both aromatic and aliphatic amines to corresponding nitriles.²¹ Later, Mizuno's group synthesized an alumina supported ruthenium hydroxide catalyst, which exhibited a much higher activity for the oxidation of both aromatic and aliphatic amines than Ru/ HAP.²² Although a slightly decreased nitrile selectivity was observed during benzylamine oxidation (82%), the catalyst also benefitted from significantly decreased metal loadings with respect to Ru/HAP, with only 1.4 wt% ruthenium being sufficient for catalytic activity. Given the efficacy of the aluminasupported ruthenium catalysts for this reaction, much work has since been performed on supported ruthenium on various metal oxides.²³⁻²⁵ Wang et al. reported that hydrated ruthenium oxide (RuO₂·xH₂O) dispersed on Co₃O₄ showed high efficiency towards the aerobic oxidation of amines to nitriles.²⁴ They discovered that the content of ruthenium and the size of Co₃O₄ particles played crucial roles in determining the catalytic performance and RuO₂·xH₂O was the active species. Additionally, Pârvulescu's group immobilized the Ru₂Cl₄(az-tpy)₂ complexes on ionic liquid dispersed silica for the oxidation of long chain linear primary amines to the corresponding nitriles.²⁶ They concluded that the conversion was strongly influenced by the alkyl chain length of the amine substrate and the choice of oxidant. However, controlling the selectivity of the oxidation of amines with molecular oxygen as the oxidant and the activation of molecular oxygen under mild reaction conditions are still an enormous challenge.²⁷ It is highly desirable to prepare these chemicals in a green manner.10

Recently, the photocatalytic process has attracted great attention for the preparation of nitrogen containing compounds starting from amines. It is found that the condensation compound imine (e.g. N-benzylidenebenzylamine from benzylamine) is generally obtained on a large number of solid surfaces. A number of semiconductors, such as TiO₂,^{28,29} Nb₂O₅,^{30,31} CdS,³² mpg-C₃N₄,³³ LDH,³⁴ BiOCl,³⁵ BiOV₄,³⁶ and a recently reported TiO₂-complex,^{37,38} have been successfully used for the photocatalytic oxidation of amines to imines. Zhao et al.29 and Tanaka et al.30 reported the efficient catalytic oxidation of amines to imines under visible light and oxygen conditions by using TiO₂ and Nb₂O₅, respectively. They found that the visible-light response of such systems was caused by the formation of a surface complex through the adsorption of benzylamine on the surface of TiO₂ or Nb₂O₅. Novel material MOFs NH₂-MIL-125(Ti)³⁹ and 2D Por-sp²c-COF⁴⁰ were also effective catalysts for the photocatalytic oxidation of amines to imines. Several transition metal based catalytic systems have been established for this transformation under light irradiation (e.g. Ag/AgI supported on titanate nanotubes,⁴¹ Au-Pd/ZrO₂,⁴² and Au/TiO₂,⁴³). Tada's group reported that a Au/TiO₂ photocatalyst exhibited a high visible-light activity for aerobic oxidation of amines to yield the corresponding imines with high selectivity (>99%).⁴³ They suggested that the reaction proceeded *via* the localized surface plasmon resonance-excited electron transfer from Au nanoparticles to TiO₂. When a supported Ru catalyst was used for the photocatalytic oxidation of amines, the high selectivity products were nitriles.⁴⁴ Golovko *et al.* demonstrated the first example of the photocatalytic aerobic oxidation of amines to nitriles by using hydrous ruthenium oxide supported on TiO₂ under visible light irradiation.⁴⁴ They proposed that the photons were absorbed by hydrous ruthenium oxide through interband transitions and/or the localized surface plasmon resonance and the photoexcited electrons were transferred into the TiO₂ conduction band to activate molecular oxygen.

However, the detailed reaction mechanism of the oxidation of amines to corresponding nitrile products over supported Ru catalysts with light irradiation is still unclear. Therefore, it is highly desirable to understand the surface adsorption and interaction between Ru species and amines, how the reaction is initialised, and what is the surface catalytic pathway for the high selectivity to nitriles.

Herein, we report that the highly dispersed and hydroxyl coordinated ruthenium photocatalyst, Ru/y-Al₂O₃, is efficient for the oxidation of amines to nitriles with molecular oxygen under mild reaction conditions (33 °C, 1 atm) under UV or visible light irradiation. The abundant surface OH groups and highly dispersed electron-deficient Ru active sites on the Ru/γ-Al₂O₃ photocatalyst are responsible for the high activity and selectivity of photocatalytic aerobic oxidation of amines. The abundant surface OH groups of the photocatalyst play an important role for the adsorption of amines and imine intermediates, which are favourable for the formation of Ru-amide species by ligand exchange with the adjacent exposed highly dispersed electron-deficient Ru active sites. The surface adsorption of reactants and intermediates and formation of Ru-amide species ensure that the reaction proceeds by two-step oxidative dehydrogenation to form nitriles instead of condensation. Both aromatic amines and aliphatic amines can be converted to their corresponding nitriles efficiently.

Experimental

Materials

All chemical reagents were used as received without any further purification. RuCl₃ (99%) and benzotrifluoride (98%) were purchased from Energy Chemical. γ -Al₂O₃ (10 nm, 99.99%), γ -Al₂O₃ (20 nm, 99.99%), Al(OH)₃ (99.6%), SiO₂ (99%), ZrO₂ (99.99%), 4-fluorobenzylamine (99%), and *n*-amylamine (98%) were purchased from Aladdin. *N*-Benzylidenebenzylamine (99%) and *n*-hexylamine (99%) were purchased from Sigma-Aldrich. All the other chemicals were from Sinopharm Chemical Reagent Co. Ltd.

Synthesis of photocatalysts

 $Ru/\gamma-Al_2O_3$ was prepared by an impregnation method. $RuCl_3$ (0.3099 g) was placed in a beaker and dissolved in deionized water (60 mL). $\gamma-Al_2O_3$ (10 nm, 2.0 g) was dispersed in the

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resulting precursor solution and stirred at room temperature for 2 h. The resulting slurry was evaporated to dryness at 80 °C. Then, the solid was added to deionized water (30 mL), and the pH value of the suspension was adjusted to 13.2 by the addition of NaOH aqueous solution (1 mol L^{-1}). After stirring at room temperature for 24 h, the solid was separated by filtration, washed with deionized water and dried at 60 °C in a vacuum oven for 12 h. Various ruthenium-based photocatalysts were prepared by the same method with different supports.

Synthesis of $Ru(OH)_x$

 $RuCl_3$ (0.3099 g) was placed in a beaker and dissolved in deionized water (60 mL). Then, the pH value of the solution was adjusted to 13.2 by the addition of NaOH aqueous solution (1 mol L⁻¹). After stirring at room temperature for 24 h, the solid was separated by filtration, washed with deionized water and dried at 60 °C in a vacuum oven for 12 h.

γ -Al₂O₃ treated with water

 γ -Al₂O₃ (10 nm, 2.0 g) was dispersed in deionized water (30 mL) and stirred at room temperature for 24 h. The resulting slurry was separated by filtration and dried at 60 °C in a vacuum oven for 12 h.

Chemical titration of hydroxyl groups on $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$

2 g benzoic anhydride and 50 mg Ru/ γ -Al₂O₃ were dissolved in 50 mL of CHCl₃. After stirring under N₂ protection at 60 °C for 24 h, the solid was separated by centrifugation, washed with ethanol and dried at 60 °C in a vacuum oven for 12 h.

Characterization

The X-ray diffraction (XRD) patterns were recorded on a MiniFlex II diffractometer with Cu K α radiation (λ = 1.5418 Å). The photocatalysts were analyzed by transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin) and diffuse reflectance UV-vis (DR UV-vis) spectroscopy (Hitachi UV-3900). Inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements were performed using a Thermo iCAP6300 spectrometer. The X-ray photoelectron spectra (XPS) were recorded 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. In situ Fourier transform infrared spectra (FT-IR) of the samples before and after light irradiation were recorded on a Bruker Tensor II IR spectrometer equipped with a MCT detector. The photocatalytic products were analyzed using a Bruker SCION SQ GC-MS spectrometer and a Shimadzu 2014C GC with a WondaCap 5 column. Ru K-edge XAFS spectra were recorded in fluorescence mode at the beam line 14W1 station in the Shanghai Synchrotron Radiation Facility with an attached Si (311) monochromator. The spectra of Ru foil and RuO₂ references were recorded in transmission mode. The acquired EXAFS data were extracted and processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages. The structural parameter fitting was performed using the ARTEMIS module with a fitting range of 1.10–2.20 Å.

Photocatalytic performance evaluation

The photocatalytic activity for selective oxidation of amines to corresponding nitriles was evaluated at 33 °C in an oxygen atmosphere (1 atm) for 3 h. Typically, the reaction system consisted of 1 mL of benzotrifluoride, 0.2 mmol of benzylamine and 40 mg of photocatalyst. A 300 W highpressure xenon lamp (CEL-HXF 300, Beijing Aulight Co. Ltd., 320-700 nm) was used and the output spectra are shown in Fig. S1a.† The light source was mounted on the top of the reactor. The intensity of irradiation light was changed by adjusting the distance between the light source and the reaction liquid. The light intensity was measured at the crosssection of the light and the upper liquid surface using an optical power meter (Model 1918-R, Newport). Single coloured LED lights (100 W COB LED lamp) include a purple LED (375-430 nm, peaked at 400 nm), blue LED-430 (400-475 nm, peaked at 430 nm), blue LED-455 (425-510 nm, peaked at 455 nm), green LED (475-600 nm, peaked at 525 nm), and red LED (580-665 nm, peaked at 625 nm) (output spectra shown in Fig. S1b[†]).

Procedure for the light-promoted electron transfer from 1,4-bis(dimethylamino)benzene to molecular oxygen

40 mg of Ru/γ -Al₂O₃ and 0.1 mmol of 1,4bis(dimethylamino)benzene were dispersed in 1 mL benzotrifluoride and irradiated with the xenon lamp in an O₂ atmosphere (1 atm) at 33 °C for 1 h. The resulting reaction mixture was analyzed qualitatively by UV-vis.

Photocatalytic performance evaluation using the Sun as a light source

The photocatalytic oxidation of benzylamine using the Sun as a light source was conducted at 33 °C in an oxygen atmosphere (1 atm) for 6 h. The reaction system consisted of 1 mL benzotrifluoride, 0.2 mmol benzylamine and 40 mg photocatalyst. The photocatalytic setup was placed outside the laboratory (latitude 37°51' north, longitude 112°33' east) so that the reactor would be directly irradiated by the Sun for the duration of the experiment (10 a.m.–4 p.m. 18/05/2017, summer in the Northern hemisphere).

Photoelectrochemical test

Transient photocurrent measurements were conducted on an electrochemical workstation (CHI 760D, CH Instruments, Shanghai, China) using a 300 W high-pressure xenon lamp (CEL-HXF 300, Beijing Aulight Co. Ltd., 320–700 nm) as the light source. A conventional three-electrode with an applied bias of 0.9 V including the work electrode, a Ag/AgCl

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electrode (saturated KCl) was used as a reference electrode and a Pt wire was used as the counter electrode. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass. The catalyst (5 mg) was dispersed in 1 mL of mixture solution of water and ethanol (water:ethanol = 2:3) and 10 μ l Nafion (DuPont, 5 wt%) to form a slurry solution by ultrasonication. 20 μ L of the slurry was coated on the FTO glass and dried at ambient temperature for 12 h. The transient photocurrent measurements were performed under illumination conditions and the working electrodes were immersed in 0.1 mol L⁻¹ Na₂SO₄ aqueous solution with the pH maintained at 6.8.

Results and discussion

Characterization of Ru/γ -Al₂O₃

The structure of supported Ru/ γ -Al₂O₃ was studied in detail to understand the structure of Ru active sites. The Ru content of Ru/ γ -Al₂O₃ was 3.9 wt%, as confirmed by inductively coupled plasma (ICP) analysis. The X-ray diffraction (XRD) patterns (Fig. S2, ESI†) and transmission electron microscopy (TEM) images of Ru/ γ -Al₂O₃ (Fig. S3, ESI†) showed no Ru structures and Ru-containing particles, indicating the high dispersion nature of Ru species on the supports.

X-ray photoelectron spectroscopy (XPS), Ru K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were conducted to further verify the electronic properties and local coordination environment of the Ru species in Ru/ γ -Al₂O₃. The Ru K-edge XANES spectra (Fig. 1a) show that the energy absorption threshold value of Ru/ γ -Al₂O₃ is higher than that of Ru foil and lower than that of RuO₂. Additionally, as shown in Fig. 3a and S4,† the binding energies of Ru 3p_{3/2} and Ru 3p_{1/2} in Ru/ γ -Al₂O₃ are 463.6 eV and 485.8 eV, respectively, which are similar to that of RuCl₃(m) while higher than the value of 461.8 eV for Ru(0) 3p_{3/2} and 463.1 eV for RuO₂(nv) 3p_{3/2}.⁴⁵ These facts reveal that the Ru species is in the +3 oxidation state.

The Ru K-edge EXAFS Fourier transformed (FT) K^3 weighted $\chi(k)$ function spectra are shown in Fig. 1b. The main peak of Ru/ γ -Al₂O₃ appears at around 1.60 Å attributed to the Ru–O bond. The weak peak observed at 2.20 Å is assigned to the Ru–O–Al bonds.^{46,47} Compared with Ru foil, the absence of a peak at around 2.35 Å means that there is no Ru–Ru bond. The absence of the Ru–O–Ru bond (3.15 Å) excludes



Fig. 1 Structure characterization of $\text{Ru}/\gamma-\text{Al}_2\text{O}_3$. (a) Ru K-edge XANES spectra and (b) Ru K-edge EXAFS Fourier transformed (FT) K^3 -weighted $\chi(k)$ function spectra of $\text{Ru}/\gamma-\text{Al}_2\text{O}_3$ and reference samples.



Fig. 2 The IR analysis of surface OH groups over different photocatalysts. (a) IR spectra of Ru/γ -Al₂O₃ and Ru/γ -Al₂O₃ treated with different amounts of benzoic anhydride. (b) IR spectra of ruthenium-based photocatalysts with different supports.

the existence of RuO₂. Curve-fitting analysis for Ru/ γ -Al₂O₃ was performed, and the fitting results are shown in Fig. S5 and Table S1.† The first shell was well-fitted by the use of one longer Ru–O (2.09 Å) and five short Ru–O (2.04 Å). These facts reveal that a monomeric Ru species with five hydroxyl groups was anchored onto an oxygen atom originating from the hydroxyl group on the surface of γ -Al₂O₃.

Photocatalytic performance of Ru/γ-Al₂O₃

The effect of metal loading for the Ru/γ -Al₂O₃ photocatalyst in the photocatalytic oxidation of benzylamine was studied (Table S2†). The Ru/γ -Al₂O₃ photocatalyst with 3.9 wt% Ru content exhibited the highest activity for the photocatalytic oxidation of benzylamine with O₂ (1 atm) at 33 °C. 99% of benzylamine was consumed in 3 h with 86% selectivity for benzonitrile under light irradiation (entry 1, Table 1).

For comparison, the control reaction was conducted in the dark and all the other reaction conditions were kept identical. The conversion of benzylamine was 39% with 84% selectivity to benzonitrile. The catalytic activity and selectivity under light irradiation were much higher than those in the dark reaction, indicating the influence of light on the reaction.



Fig. 3 Identification of the presence of Ru-amide complexes and reaction intermediates. (a) XPS spectra of Ru(OH)_x, Ru/ γ -Al₂O₃, and Ru/ γ -Al₂O₃ with adsorbed benzylamine. (b) DR UV-vis spectra of Ru/ γ -Al₂O₃ before and after benzylamine adsorption. (c) Time profile of oxidation of benzylamine under light irradiation. Reaction conditions: benzylamine (0.2 mmol), Ru/ γ -Al₂O₃ (40 mg), benzotrifluoride (1 mL), O₂ (1 atm), 33 °C, xenon lamp and light intensity 0.87 W cm⁻². (d) *In situ* FT-IR spectra obtained when Ru/ γ -Al₂O₃ was exposed to vaporous benzylamine (BA) for 15, 35, and 55 min; N₂ was introduced to the system for 6, 15, and 30 min; O₂ was introduced to the system in the dark and under light irradiation.

	Table 1	Catalytic activity for	or the selective	oxidation of	f benzylamine to	nitriles over	different catal	ysts ^a
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Catalyst	N
O ₂ (1 atm), 33 °C	

Entry	Catalyst	Incident	$\operatorname{Conv.}^{b}(\%)$	Sel. ^b (%)
1	Ru/γ - Al_2O_3	Visible	99	86
		Dark	39	84
2	γ -Al ₂ O ₃	Visible	8	0
		Dark	No detection	_
3 ^c	$Ru(OH)_x$	Visible	2	11
		Dark	1	5
4^d	Physical mixture of $Ru(OH)_x$ and γ -Al ₂ O ₃	Visible	5	61
		Dark	2	24
5	No catalyst	Visible	No detection	_
		Dark	No detection	—

^{*a*} Reaction conditions: benzylamine (0.2 mmol), catalyst (40 mg), benzotrifluoride (1 mL), O₂ (1 atm), 33 °C, 3 h, xenon lamp and light intensity 0.87 W cm⁻². ^{*b*} Selectivity to nitriles. Conversion and selectivity were determined by gas chromatography (GC). ^{*c*} Ru(OH)_{*x*} (8 mg, five times the amount of Ru in the supported Ru/ γ -Al₂O₃ photocatalyst). ^{*d*} Ru(OH)_{*x*} (8 mg), γ -Al₂O₃ (40 mg).

The influence of light intensity on the photocatalytic oxidation of benzylamine was studied. The yield increased as the light intensity was raised, which demonstrates that the reactions are driven by light (Fig. S7†).^{48,49} The light contribution was calculated as the contribution of the irradiation effect in the reaction, and defined as $[(Y_{\text{Light}} - Y_{\text{Dark}})/Y_{\text{Light}}] \times 100\%$, where Y_{Light} and Y_{Dark} are the product yields under irradiation and dark conditions, respectively.⁴² With the increase of light intensity, the light contribution gradually increases. The higher the incident light intensity, the more electrons in the photocatalyst can be excited to facilitate the improvement of photocatalytic activity.

When the reaction was conducted in the presence of argon instead of O₂, 7% benzylamine was transformed with 44% selectivity to benzonitrile, indicating that the reaction may undergo an oxidative dehydrogenation pathway. In addition, there is no benzonitrile either in the presence of γ -Al₂O₃ or in the absence of the Ru/ γ -Al₂O₃ photocatalyst (entries 2 and 5, Table 1), suggesting that Ru species are vital active sites in the reaction. The catalytic activities of Ru(OH)_x as well as a mixture of Ru(OH)_x and γ -Al₂O₃ are extremely lower than that of the Ru/ γ -Al₂O₃ photocatalyst (entries 3 and 4, Table 1). These facts reveal that Ru species anchored on the surface of γ -Al₂O₃ are indispensable in achieving high photocatalytic activity and selectivity.

The role of the γ -Al₂O₃ support

The electronic environment of Ru in Ru/ γ -Al₂O₃ was investigated by XPS analysis. The binding energy of Ru 3p_{3/2} (463.6 eV) in Ru/ γ -Al₂O₃ is higher than the value of 463.0 eV for the unsupported Ru(OH)_x (Fig. 3a), which indicates the formation of electron-deficient Ru species due to the strong interaction of Ru and γ -Al₂O₃.

The role of surface OH groups on Ru/γ -Al₂O₃ was explored according to a reported method.⁵⁰ Benzoic anhydride was chosen as the titrant to deactivate the OH groups on Ru/γ -Al₂O₃.

The infrared spectra (IR) of Ru/ γ -Al₂O₃ (benzoic anhydride) exhibit a decrease of the O–H signal at about 3450 cm⁻¹ with the increase of benzoic anhydride amount (Fig. 2a). The bands appeared at 3063 and 2953 cm⁻¹, combined with the vibration at 1604, 1561, 1494, and 1433 cm⁻¹ owing to the presence of a benzene ring after titration and the strength gradually increases with the increase of benzoic anhydride amount, indicating the successful reaction between benzoic anhydride and hydroxyl groups on Ru/ γ -Al₂O₃. The conversion and selectivity gradually decreased to 15% and 25% with the increase of benzoic anhydride amount (Table S5†), demonstrating that the surface OH groups on Ru/ γ -Al₂O₃ facilitate the high activity and selectivity of photocatalytic oxidation of amines.

To further explore the reasons for the high activity and selectivity of photocatalytic oxidation of amines over the Ru/ γ -Al₂O₃ photocatalyst, the photocatalytic activities of other Rubased photocatalysts with different supports were tested. Apart from Ru/SiO₂ and Ru/ZrO₂, Ru/ γ -Al₂O₃ (10 nm), Ru/ γ -Al₂O₃ (20 nm), and Ru/Al(OH)₃ exhibit higher selectivity (Table S3†). As shown in Fig. 2b, the band appearing at 3450 cm⁻¹ can be attributed to the stretching vibration of OH groups. The band intensity of the OH groups in Ru/ γ -Al₂O₃ (10 nm), Ru/ γ -Al₂O₃ (20 nm), and Ru/Al(OH)₃ is significantly greater than that of Ru/SiO₂ and Ru/ZrO₂, indicating that there are more OH groups on the surface of Ru/ γ -Al₂O₃ (10 nm), Ru/ γ -Al₂O₃ (20 nm), and Ru/Al(OH)₃. The surface OH groups are conducive to the adsorption of imine intermediates to achieve the high selectivity of the reaction. Additionally, the XPS binding energy of various Ru photocatalysts is similar (Fig. S6†), which indicates that the coordination and electronic environment of ruthenium is similar in different Ru photocatalysts, and the achievement of high activity relies on the adsorption of amines on the surface OH groups and the highly dispersed active Ru sites on the surface of the photocatalyst. Compared with the other supports, γ -Al₂O₃ (10 nm) ensures high activity and selectivity owing to the abundant OH groups and high dispersion of active Ru sites on its surface.

In contrast to reported studies, 22,44 our work reveals that the high photocatalytic activity and selectivity over Ru/ γ -Al₂O₃ (10 nm) presumably originate from the adsorption of amines and imine intermediates over the abundant surface OH groups of the photocatalyst and further formation of Ru-amide species by ligand exchange of adsorbed amines and imine intermediates with adjacent exposed active Ru sites.

Photocatalytic mechanism of Ru/γ-Al₂O₃

To verify our hypothesis and further understand the reaction, we studied the mechanism of photocatalytic oxidation of benzylamine over the Ru/γ -Al₂O₃ photocatalyst. Previous reports of photocatalytic oxidation of primary amines are different from our system.^{28,51} Nitriles were obtained in the reaction rather than secondary imines. There are two major processes for the formation of secondary imines: an oxygenation pathway [eqn (a)] and a dehydrogenation pathway [eqn (b)]. The absence of aldehydes and no accumulation of secondary imines indicate that the reaction in our system may not be carried out through pathways (a) and (b). Inspired by the above mentioned pathways of the oxidation of primary amines, we can hypothesise a reasonable two-step oxidative dehydrogenation process for the production of nitriles [eqn (c)].

$$R \xrightarrow{\text{Catalyst}} R \xrightarrow{$$

$$R \sim_{NH_2} \xrightarrow{Catalyst} R \sim_{NH} \xrightarrow{+ Ph \sim_{NH_2}} R \sim_{N} R \qquad (b)$$

$$R \xrightarrow{\text{Catalyst}} R \xrightarrow{$$

The interaction of Ru/γ -Al₂O₃ and benzylamine was investigated by XPS analysis and diffuse reflectance UV-vis (DR UVvis) spectroscopy. The binding energy of Ru $3p_{3/2}$ and Ru $3p_{1/2}$ decreased to 463.0 eV and 485.3 eV, respectively, after adsorption of benzylamine, indicating the formation of Ruamide species and the increase of the electron density of Ru because of the electrons partly transferring from nitrogen to Ru (Fig. 3a). γ -Al₂O₃ has no absorption in the visible light region (Fig. 3b).⁵² The absorption in the visible range is due to the Ru species, and the two main absorption bands at 405 and 460 nm can be assigned to the metal-to-ligand charge transfer transition (MLCT, d- π *) of Ru species.⁵³ The differential spectrum before and after benzylamine adsorption

exhibits a broad absorption band centred at 430 nm. Because benzylamine does not absorb light with a wavelength longer than 300 nm,³⁰ the new absorption band can be attributed to the formation of a Ru-amide surface complex. As shown in Table S4,† different single coloured LED lights can drive the reaction, indicating that the reaction can be conducted not only under UV, but also under visible light irradiation. Meanwhile, the photocatalytic activity under different single coloured LED lights coincided with the differential spectrum before and after benzylamine adsorption, further demonstrating that the Ru-amide species are the light absorption sites. Ru/γ -Al₂O₃ can also promote the oxidation of benzylamine under simulated sunlight irradiation. The experiment was conducted under sunlight irradiation for 6 h, where the conversion reached 83% with 88% benzonitrile selectivity. The photocatalyst could be used for the photocatalytic oxidation of amines without obvious activity loss after three times.

The reaction kinetic data of the photocatalytic oxidation of benzylamine and *N*-benzylidenebenzylamine (*N*-BBA) were obtained to demonstrate that *N*-BBA is not an intermediate in the oxidation of benzylamine under light irradiation (see the ESI† for details). If *N*-BBA was an intermediate, the accumulation of *N*-BBA would exceed 37% because the rate constant of benzylamine oxidation ($k_1 = 1.3812 \text{ h}^{-1}$, Fig. S8†) is larger than that of the *N*-BBA oxidation ($k_2 = 0.2681 \text{ h}^{-1}$, Fig. S9†). As shown in Fig. 3c, the yield of benzonitrile increases gradually when the reaction time is prolonged and the reaction profile exhibits a pseudo first-order reaction feature. Meanwhile, no such accumulation of *N*-BBA is observed, indicating that *N*-BBA is not an intermediate in the reaction.

To understand the surface reaction pathway, we investigated the surface adsorption of the reactant and the reaction process by in situ Fourier transform infrared (FT-IR) spectra (Fig. 3d). When Ru/γ -Al₂O₃ was exposed to vaporous benzylamine at room temperature, the intensities of bands at 3333 and 3256 cm⁻¹ (NH₂ stretching vibration, $v_{\rm NH_2}$), 1391 cm^{-1} (CH₂ bending vibration, ω_{CH_2}), and 1271 cm^{-1} (C–N stretching vibration, v_{C-N}) were observed and gradually increased (Fig. 3d, BA adsorption 15, 35, and 55 min).⁵⁴ After flowing N₂ to the system (Fig. 3d, flowing N₂ 6, 15, and 30 min), the bands related to $v_{\rm NH_2}$ (3333 and 3256 cm⁻¹) gradually disappeared with time, while a peak appeared at 1649 cm⁻¹ in the region of the N-H bending vibration ($\delta_{\rm N-H}$). These results indicate the dissociative adsorption of benzylamine on the surface of the photocatalyst to form Ruamide species, which coincided with the results of the XPS and DR UV-vis spectra (Fig. 3a and b). After flowing O₂ to the system in the dark, no obvious changes were observed (Fig. 3, dark). When light was introduced to the system with flowing O₂ (Fig. 3, light), the intensity of the C-N stretching vibration (v_{C-N}) at 1271 cm⁻¹ gradually decreased until it disappeared, implying the consumption of the reactant. Meanwhile, the band at 2272 cm⁻¹ indicates the formation of benzonitrile. And two bands appeared at 3277 cm⁻¹ (N-H stretching vibration of primary imine, $v_{\rm N-H}$) and 1650 cm⁻¹ (C=N stretching vibration of primary imine, $v_{C=N}$),⁵⁴ demonstrating the formation and adsorption of primary imine intermediates on the surface of Ru/γ -Al₂O₃. The formation of Ruamide on the surface of Ru/γ -Al₂O₃ and the production of the primary imines under light illumination were observed by *in situ* FT-IR spectroscopy, which verify our hypothesis and provide sufficient evidence for demonstrating the mechanism.

To gain more insight into the reaction mechanism of the photocatalytic system, we studied the compatibility of Ru/γ-Al₂O₃ with different substituted aromatic and aliphatic amines under the optimised reaction conditions. Such a photocatalytic system can be successfully applied to aromatic and aliphatic amines with good to excellent conversions (Table 2). Electron-drawing substrates such as 4-fluorobenzylamine gave 4-fluorobenzonitrile in 95% conversion and 4-chlorobenzylamine in 97% conversion, both of which were suitable substrates (entries 2 and 3, Table 2). Electron-donating substrates were also studied under identical reaction conditions; 4-methylbenzylamine and 4-methoxybenzylamine were converted to the corresponding nitriles with 98% and 99% conversions, respectively (entries 4 and 5, Table 2). Not only aromatic amines, but also less reactive aliphatic amines could be converted to the corresponding nitriles (entries 6 and 7, Table 2). Interestingly, the oxidation of primary aliphatic amines can be achieved with a better conversion rate and selectivity than aromatic substrates, which differs from the other reaction systems. This phenomenon indicates that the formation of Ru-amide complexes is beneficial to the activation of aliphatic amines. Moreover, it has been reported that N radicals are generated during the reaction process,³¹ and the Ru-amide complexes may play an important role in stabilizing the adjacent N radical. N-Benzylidenebenzylamine was converted to benzonitrile as the main product (entry 8, Table 2). Secondary amines are suitable our system (entries 9 and 10, Table 2), and for N-methylbenzylamine can be transformed to corresponding N-benzylidenemethanamine as the main product. Dibenzylamine afforded the corresponding N-benzylidenebenzylamine as the main product, together with benzaldehyde (32%), benzonitrile (14%), and benzylamine (2%). This demonstrates that the reactant will not remain as imine and can be converted to benzonitrile over the Ru/γ -Al₂O₃ photocatalyst owing to the adsorption of imine and the formation of Ru-amide complexes. Because the secondary dehydrogenation of these imines is more difficult, the reaction rate is slower than that of primary amines.

It is reported that radicals were not involved in the oxidation of primary amines.²² In this study, 1,4-benzoquinone as a superoxide scavenger was added to the reaction to confirm the presence of O_2 ⁻⁻ radicals (Fig. 4a).⁵⁵ The yield of benzonitrile gradually decreased to 0.8% with the increase of the amount of 1,4-benzoquinone, indicating the presence of O_2 ⁻⁻ radicals. In order to investigate whether the Ru/ γ -Al₂O₃ photocatalyst can mediate electron transfer from electron-donating amines to oxygen to generate O_2 ⁻⁻ radicals under light irradiation, 1,4-bis(dimethylamino)benzene was employed as the indicator.^{51,56} As shown in Fig. 4b, blue coloured cationic radical

 Table 2
 Photocatalytic oxidation of various amines^a

Entry	Substrate	$R_1 = \frac{1}{h} + O_2 - \frac{1}{hv, 33 \circ C}$ Product	$R = N + H_2O$	Conv. ^b (%)	Sel. ^b (%)
1	NH ₂	CN CN	3	99 (39)	86 (84)
2	F NH2	- CCN	6	95 (52)	86 (83)
3	CI NH2		6	97 (58)	72 (45)
4	Me NH ₂	CN N	6	98 (51)	80 (75)
5	MeO NH ₂	MeO	4	99 (42)	82 (75)
6 ^{<i>c</i>}	NH ₂	CN	6	88 (38)	93 (93)
7	~~~NH ₂	CN CN	3	91 (24)	93 (93)
8 ^{<i>d</i>}		CN CN	24	96 (33)	63 (47)
9 ^e			24	89 (19)	45 (30)
10 ^{<i>f</i>}	ſ)́́́́́́́́́́́́́	€ N	36	48 (7)	85 (71)

^{*a*} Reaction conditions: amine (0.2 mmol), Ru/ γ -Al₂O₃ (40 mg), benzotrifluoride (1 mL), O₂ (1 atm), 33 °C, xenon lamp and light intensity 0.87 W cm⁻². ^{*b*} Conversion and selectivity were determined by gas chromatography (GC); the values in parentheses are the results in the dark. ^{*c*} Solvent was acetonitrile. ^{*d*} *N*-Benzylidenebenzylamine (0.1 mmol), other products: benzaldehyde (28%) and benzylamine (8%). ^{*e*} Dibenzylamine (0.1 mmol), other products: benzaldehyde (4%), benzonitrile (3%).

species of 1,4-bis(dimethylamino)benzene were obtained in the presence of the Ru/γ -Al₂O₃ photocatalyst and the obvious absorption bands can be observed in the UV-vis spectra. These results reveal the presence of O₂⁻⁻ radicals in the photocatalytic oxidation of primary amines and the Ru/γ -Al₂O₃ photocatalyst can mediate the electron transfer from amines to oxygen under light irradiation.

The photocurrent response of Ru/y-Al2O3 before and after benzylamine adsorption was compared under intermittent light irradiation to evaluate the separation ability of photoelectron-hole pairs. As shown in Fig. S10,† a photocurrent response was generated immediately when light irradiation was switched on, and then decreased quickly to zero when light irradiation was switched off. The Ru/y-Al2O3 adsorbed with benzylamine displayed higher photocurrent density than Ru/γ-Al₂O₃, indicating the formation of a surface Ru-amide complex can effectively separate photoelectron-hole pairs and extend the electron-hole distances by electron transfer thereby from nitrogen to Ru restraining charge recombination.57,58

To further prove the electron transfer between Ru and amines in the Ru–amide complex under light irradiation, 1,4-bis(dimethylamino)benzene was employed as the substrate because the blue coloured cationic radical species of 1,4-bis(dimethylamino)benzene can indicate the occurrence of the electron transfer.^{51,56} Fig. S11† shows the photographs and UV-vis absorption spectra of the cationic radical species of 1,4-bis(dimethylamino)benzene generated under different conditions with xenon light irradiation. When the reaction was conducted in the presence of $Ru/\gamma-Al_2O_3$ and oxygen, a dark blue solution was obtained (Fig. S11a⁺) and the obvious absorption bands can be observed in the UV-vis spectra (Fig. S11b[†]). A light blue solution was obtained in the absence of oxygen (the reaction system was degassed by three freeze-pump-thaw cycles) and the intensity of the absorption bands in the UV-vis spectra was much weaker than that in the oxygen atmosphere, indicating that more blue coloured cationic radical species of 1,4-bis(dimethylamino)benzene were produced in the presence of oxygen. For comparison, control experiments were carried out in the absence of Ru/y-Al2O3 under different atmospheres. No obvious change of the solution and no corresponding absorption bands in the UV-vis spectra were observed. These facts reveal the electron transfer from nitrogen to Ru in the Ru-amide complex and the formation of the corresponding nitrogen radicals. When the reaction was conducted in the presence of oxygen under light illumination, the electrons derived from nitrogen were trapped by Ru(III) to generate Ru(Π), then the oxygen can be converted to O_2^{-} by Ru(Π). The reaction can proceed continually and produce a large number of nitrogen radicals in the presence of oxygen. However, no electron transferred from Ru(II) to oxygen in the argon atmosphere, which leads to the formation of the electron-rich Ru species and no sufficient Ru(III) can trap the electrons derived from nitrogen so only a small amount of nitrogen radicals was obtained.



Fig. 4 Reaction mechanism over the Ru/ γ -Al₂O₃ photocatalyst. (a) Influence of 1,4-benzoquinone on the photocatalytic oxidation of benzylamine. (b) UV-vis absorption spectra and photograph of the cationic radical species of 1,4-bis(dimethylamino)benzene generated by Ru/ γ -Al₂O₃ using a xenon lamp in the presence of oxygen. (c) Proposed mechanism for the photocatalytic oxidation of benzylamine on the Ru/ γ -Al₂O₃ photocatalyst.

Based on the above analysis, we can suggest a reasonable mechanism for this reaction (Fig. 4c). At first, the primary amine is dissociatively adsorbed on the surface of Ru/γ -Al₂O₃ to form the Ru-amide surface complex (step 1). When the surface complex is irradiated under light, the photogenerated electrons derived from the N 2p orbital of the adsorbed amine species can be trapped by Ru(III) to generate Ru(II) (step 2). The adsorbed O_2 can be activated by Ru(II) to generate $O_2^{-,59}$ which can be adsorbed on the surface of the photocatalyst to form an intermediate (intermediate A) possessing a six-member-ring structure (step 3). The cleavage of the C-H bond and the Ru-N bond of intermediate A occurs to form the corresponding primary imines and ruthenium peroxide species (step 4). The primary imines adsorb on the surface OH groups by the hydrogen bond and can further be oxidised to nitriles in the same way (steps 5-8). However, some primary imines can escape from the surface of the photocatalyst and react with primary amines to generate the side product secondary imines (Scheme S1[†]). Finally, the photocatalytic cycle is completed by the regeneration of Ru sites on the surface of the photocatalyst through desorption of oxygen (step 9).

Conclusions

In summary, we have developed a light-induced green pathway for the synthesis of nitriles from oxidative dehydrogenation of primary amines under mild conditions over a γ -Al₂O₃ supported Ru photocatalyst. The large surface area of γ -Al₂O₃

allows the high dispersion of hydroxyl coordinated Ru species, which results in a strong interaction between the Ru centre and the support. The abundant surface OH groups and active Ru sites subsequently influence the reaction pathway of surface adsorbed amines. The adsorption of reactants and intermediates and the formation of Ru–amide complexes on the surface of the photocatalyst under light irradiation were identified by the detailed investigation of the reaction mechanism, which ensure that the primary amines can be directly converted to corresponding nitriles with good to excellent yields *via* a two-step oxidative dehydrogenation process. It is expected that this method can be applied for designing a new generation of heterogeneous catalysts.

Conflicts of interest

There are no conflicts to declare.

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