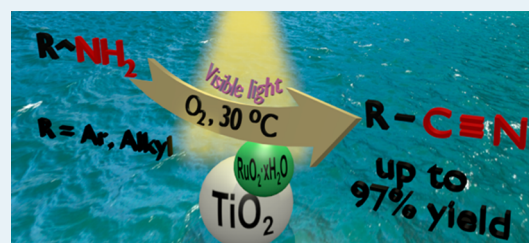


Visible-Light-Driven Aerobic Oxidation of Amines to Nitriles over Hydrous Ruthenium Oxide Supported on TiO₂Daniil S. Ovoshchnikov,^{†,‡} Baira G. Donoeva,^{*,†,§,‡} and Vladimir B. Golovko,^{*,†,§}[†]Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand[§]MacDiarmid Institute for Advanced Materials and Nanotechnology, P.O. Box 600, Wellington 6140, New Zealand

Supporting Information

ABSTRACT: Aerobic oxidation of amines to nitriles under visible light irradiation was catalyzed by supported hydrous ruthenium oxide catalyst. Both LED (blue, green, or red) and the Sun were effective light sources for the transformation of benzylic and aliphatic amines to the corresponding nitriles under atmospheric pressure of O₂. Water can be used as a solvent instead of toluene without the loss of activity and selectivity.



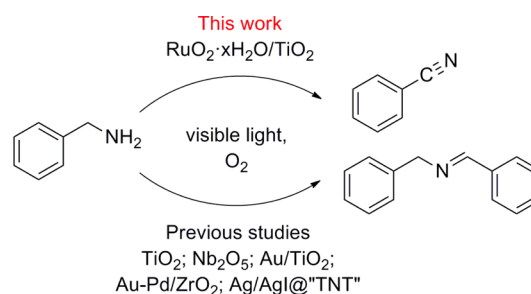
KEYWORDS: photocatalysis, amine oxidation, ruthenium, nitrile, aerobic oxidation

Utilization of sunlight as an abundant and readily available source of energy for driving chemical reactions is an important pathway toward a sustainable future. The development of catalytic systems driven by visible light is of particular interest because UV radiation represents only 5% of sunlight energy.^{1,2} Recently, various such systems were employed to catalyze alcohol oxidation,^{3–5} reduction of nitroaromatic compounds,^{6,7} Suzuki–Miyaura cross-coupling,⁸ and several other reactions.^{8–14}

Nitriles are important compounds used as intermediates for the production of agricultural chemicals, dyes, polymers, and fine chemicals.^{15,16} Additionally, compounds containing a cyano group are used as pharmaceuticals¹⁷ and functional materials.¹⁸ Traditional methods of the synthesis of nitriles, such as via Sandmeyer reaction¹⁹ or ammoxidation,¹⁶ either generate excessive waste or require high temperatures (up to 550 °C). Alternative pathways that are currently being developed include transformations of amides,²⁰ aldoximes,²¹ alcohols,²² and amines.^{23–27} In particular, supported hydrous ruthenium oxide was shown as an effective catalyst for the aerobic oxidation of amines into nitriles at temperatures around 100 °C.^{23–26} On the other hand, both ruthenium oxide and hydrous ruthenium oxide are also known for their metallic conductivity²⁸ and thus can be combined with semiconductors to form photocatalytic systems.^{29,30}

Recently, visible light driven conversion of amines to imines with high selectivity has been performed using TiO₂,^{31,32} Nb₂O₅,³³ Ag/AgI supported on titanate nanotubes (Ag/AgI@“TNT”),³⁴ Au–Pd/ZrO₂,⁸ and Au/TiO₂ photocatalysts.³⁵ In this work, we show that hydrous ruthenium oxide supported on P25 TiO₂ (RuO₂·xH₂O/TiO₂) efficiently catalyzes aerobic oxidation of amines to nitriles under visible light irradiation and ambient conditions (Scheme 1). To the best of our knowledge, this work demonstrates the first example of selective photocatalytic transformation of amines to nitriles.

Scheme 1. Photocatalytic Oxidation of Benzylamine under Visible Light Irradiation



Deposition of hydrous ruthenium oxide onto P25 TiO₂ was conducted following the procedure previously employed for the preparation of supported ruthenium oxide catalysts (see Supporting Information (SI) for details).^{26,36,37} The ruthenium content of 0.8 wt % was established using ICP-MS. X-ray photoelectron spectroscopy analysis showed a Ru 3d_{5/2} peak at 281.4 eV attributed to hydrous ruthenium oxide (RuO₂·xH₂O),³⁸ whereas a survey spectrum showed no Cl peaks, indicating complete conversion of RuCl₃ to RuO₂·xH₂O (see SI). To adequately compare the catalytic performance of RuO₂·xH₂O/TiO₂ with that of P25 TiO₂, the latter was also subjected to the conditions of the catalyst synthesis (NaOH treatment and calcination at 150 °C).

Diffuse reflectance UV–vis spectra (DR UV–vis) of RuO₂·xH₂O/TiO₂ and base-treated TiO₂ are shown in Figure 1. In contrast to base-treated TiO₂, which only absorbs in the UV region, the RuO₂·xH₂O/TiO₂ catalyst showed a continuous

Received: August 13, 2014

Revised: November 12, 2014

Published: November 16, 2014

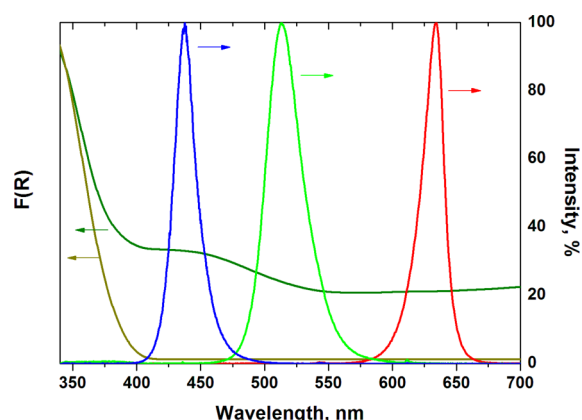


Figure 1. Diffuse reflectance spectra of $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{TiO}_2$ (dark green) and base-treated P25 TiO_2 (brown). Normalized emission spectra of blue, green, and red LEDs.

absorption across the whole visible range, with a pronounced band centered at ca. 450 nm. The absorption of light by RuO_2 in the visible range is due to the combination of interband transitions and localized surface plasmon resonance.^{39–41}

The photocatalytic oxidation of amines was performed in toluene in a Pyrex glass reactor at 30 °C under ~ 1 atm of O_2 (see [SI](#)). The mixture was irradiated using a single 50 W LED. Three different LEDs were employed in this work: blue (intensity maximum at 440 nm, Figure 1), green (513 nm), and red (634 nm). The distances between the reactor and LEDs were adjusted to obtain the same $1.5 \text{ W}/\text{cm}^2$ flux of the light supplied to the reactor. For the control experiments, reactions were carried out in the absence of light at 30 °C. Samples of the reaction mixture were collected during the reaction and analyzed using GC-FID.

Aerobic benzylamine oxidation performed in the absence of light showed conversion of only 12% in 4 h with a turnover frequency, calculated from the initial reaction rate, TOF_{Ru} of 0.7 h^{-1} (Table 1). Visible light irradiation drastically increased

Table 1. Photocatalytic Oxidation of Benzylamine^a

Catalyst	Light	Product	Conv. / Yield, ^b %	k, h^{-1}	$\text{TOF}_{\text{Ru}}, \text{h}^{-1}$
$\text{RuO}_2 \cdot x\text{H}_2\text{O} / \text{TiO}_2$	Blue		98/92	0.85	21.4
	Green		67/64	0.27	7.0
	Red		27/26	0.07	1.9
	None		12/11	0.03	0.7
$\text{RuO}_2 \cdot x\text{H}_2\text{O} / \text{MgO}$	Blue		Trace	-	-
$\text{RuO}_2 \cdot x\text{H}_2\text{O} / \text{Al}_2\text{O}_3$	Blue		8/6	-	-
	None		7/5	-	-
TiO_2	Blue		96/84	0.67	-
	Green		8/6	-	-
	Red		Trace	-	-
	None		Trace	-	-

^aReaction conditions: benzylamine (0.1 mmol), O_2 (~ 1 atm), toluene (3 mL), catalyst 50 mg (4 mol % Ru), irradiance $1.5 \text{ W}/\text{cm}^2$, 30 °C, 4 h. ^bDetermined by GC.

the rate of the reaction. The highest rate of amine oxidation was achieved under irradiation with a blue LED, with the yield of benzonitrile reaching 92% in 4 h and TOF_{Ru} of 21.4 h^{-1} . The catalyst was less active under irradiation with green or red light, with the yield of benzonitrile being 64% and 26%, respectively. The lower activity of $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{TiO}_2$ under irradiation with light of longer wavelengths could be due to the lower ability of the catalyst to absorb light in these regions (Figure 1) and/or because the electrons of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ gain less energy under irradiation with light of longer wavelengths.¹⁰ In all cases, reaction selectivity toward benzonitrile was high and exceeded 93%. The reaction exhibited a pseudo-first-order kinetics with the rate constant of 0.85 h^{-1} for the blue LED ([SI](#), Figure S2). The apparent activation energies for benzylamine oxidation performed under blue-light irradiation and in the dark were obtained from Arrhenius plots ([SI](#), Figure S3). The apparent activation energy for thermally activated process was 21.4 kJ/mol. Irradiation with blue light reduced the activation energy to 11.3 kJ/mol, giving 47% decrease in the activation energy.

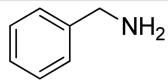
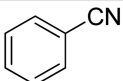
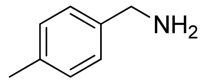
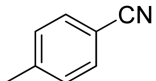
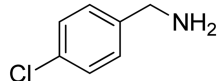
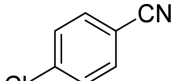
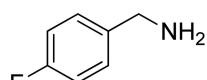
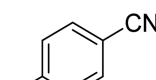
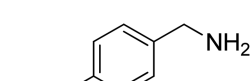
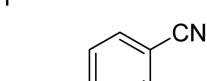
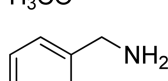
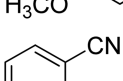
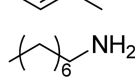
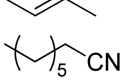
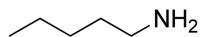
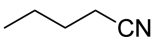
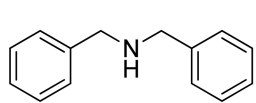
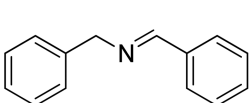
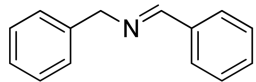
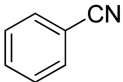
No enhancement of catalytic activity under blue light irradiation was observed over $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ supported on insulating materials MgO and Al_2O_3 (Table 1), whereas $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ gave 88% conversion (62% yield of benzonitrile) in 4 h in thermally activated reaction at 100 °C. This indicates that semiconducting support (TiO_2) is involved in the photocatalysed benzylamine oxidation over $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{TiO}_2$ and that neither direct injection of photoexcited electrons of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ into antibonding orbitals^{42,43} of the adsorbed amine nor the plasmon-induced rise of the local temperature of the catalyst is the driving force of catalysis in this case. Otherwise, activity enhancement under visible light irradiation would have been observed independently of the support type.

P25 TiO_2 , which was subjected to the conditions of catalyst synthesis (i.e., NaOH wash and calcination at 150 °C), was also active in oxidation of benzylamine under visible light irradiation. However, *N*-benzylidenebenzylamine (*N*-BBA) was formed instead of benzonitrile (Table 1) which is consistent with the previous reports.³¹ TiO_2 was only active under irradiation with blue light, whereas almost no conversion was observed under either green or red light irradiation.

Photocatalytic oxidation was further extended to various amines. Table 2 summarizes the results of aerobic amine oxidation catalyzed by $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{TiO}_2$ under irradiation with blue light. Good to excellent yields were obtained for the oxidation of both benzylic and primary aliphatic amines. Both *para*- and *ortho*-substituted benzylic amines were oxidized to the corresponding nitriles with selectivities ranging from 83% to 98%. The rate of amine oxidation was not significantly affected by either electron-withdrawing or -donating substituents. This fact is illustrated by the parameter ρ , obtained from the Hammett plot, being close to zero ([SI](#), Figure S4). The rate of oxidation of primary aliphatic amines was lower than that of benzylic amines, with conversion of pentylamine and octylamine reaching 99% in 7 and 10 h, respectively. Interestingly, photocatalytic oxidation of dibenzylamine showed much lower selectivity toward *N*-BBA than the thermal reaction reported by Yamaguchi and Mizuno (17% vs 84%),³⁶ with higher yields of benzaldehyde and benzonitrile (Table 2, entry 9). This can be explained by the fact that under visible light irradiation $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{TiO}_2$ can promote oxidation of *N*-BBA to benzaldehyde and benzonitrile (Table 2, entry 10).

Analysis of kinetic data indicates that *N*-BBA is not an intermediate in benzylamine oxidation to benzonitrile. If *N*-

Table 2. Photocatalytic Oxidation of Amines^a

N	Substrate	Product	Time, h	Light	Conv., ^b %	Yield, ^b %	TOF _{Ru} , ^c h ⁻¹
1			4	+	98	92	21.4
				-	12	11	-
2			4	+	98	84	25.4
				-	13	9	-
3			4	+	95	79	19.6
				-	12	6	-
4			4	+	93	77	16.4
				-	12	6	-
5			4	+	95	86	18.8
				-	12	9	-
6			4	+	99	97	23.2
				-	14	9	-
7			10	+	99	72	11.4
				-	12	8	-
8			7	+	99	81	12.9
				-	18	13	-
9			27	+	92	16 ^d	3.5
10 ^e			3	+	93	41 ^f	21.2

^aReaction conditions: amine (0.1 mmol), O₂ (~1 atm), toluene (3 mL), catalyst 50 mg (4 mol % Ru), blue LED, irradiance 1.5 W/cm², 30 °C. ^bDetermined by GC. ^cCalculated from the initial reaction rates. ^dOther products: benzaldehyde (yield 42%) and benzonitrile (yield 22%). ^eN-BBA (0.05 mmol). ^fOther product: benzaldehyde (51%).

BBA was an intermediate, the accumulation of N-BBA would have been observed (with the maximum yield of N-BBA exceeding 37%) because the rate constant of N-BBA oxidation is comparable to that of benzylamine oxidation (0.84 and 0.85 h⁻¹; see SI for details). However, the yield of N-BBA did not exceed 7% throughout the course of reaction (Figure S6).

Kinetic isotope effect was examined by the comparison of kinetics of oxidation of benzyl- α - α -D₂-amine and benzylamine. A small value of the ratio of rate constants $k_H/k_D = 1.3 \pm 0.1$ indicates that the cleavage of C–H bond is not involved in the rate-determining step, similarly to the oxidation of benzylic amines to imines photocatalysed by TiO₂.³¹

The catalyst RuO₂·*x*H₂O/TiO₂ is also capable of promoting amine oxidation under sunlight irradiation at near-ambient temperature (30 ± 3 °C). Catalytic setup was placed by the open window so that the reactor would be directly irradiated by the Sun for the duration of the experiment of 6 h (see SI for details). The yield of benzonitrile reached 46% with TOF_{Ru} of 5.2 h⁻¹.

Water is a solvent of choice for conducting green chemical processes.⁴⁴ However, poor selectivity of photocatalytic processes utilizing water as a solvent could be expected in some cases due to the generation of active oxygen species from the oxidation of H₂O.⁴⁵ For example, lower selectivity was

reported for the TiO₂-catalyzed oxidation of amines in water compared to that in CH₃CN.³² In order to test the suitability of water as a solvent in our system, we have conducted aerobic oxidation of benzylamine and pentylamine in water in the presence of RuO₂·*x*H₂O/TiO₂ under irradiation with the blue LED. Oxidation of both amines gave corresponding nitriles in good yields: the yield of benzonitrile reached 90% after 4 h, whereas the yield of valeronitrile was 94% after 7 h. These results show that water could be efficiently used as a solvent for the aerobic oxidation of both benzylic and primary aliphatic amines using RuO₂·*x*H₂O/TiO₂ catalyst.

The study of RuO₂·*x*H₂O/TiO₂ recyclability in water showed that catalyst retained its activity in the second catalytic cycle; however, the activity of RuO₂·*x*H₂O/TiO₂ gradually decreased in the subsequent catalytic cycles (Figure S7). ICP-MS study of the reaction mixtures (cycles 1–5) showed that in all cases the concentration of leached Ru species was below 0.5 ppm (Figure S7).

In order to better understand the mechanism of photocatalytic amine oxidation in water, we have performed a series of experiments with the addition of various radical scavengers (Figure 2). Oxidation of benzylamine in the presence of ammonium oxalate (hole scavenger)^{46–49} gave only 9% of benzonitrile, indicating the involvement of holes in the

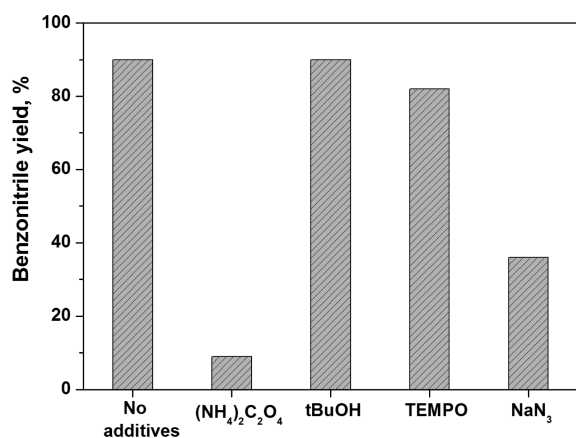
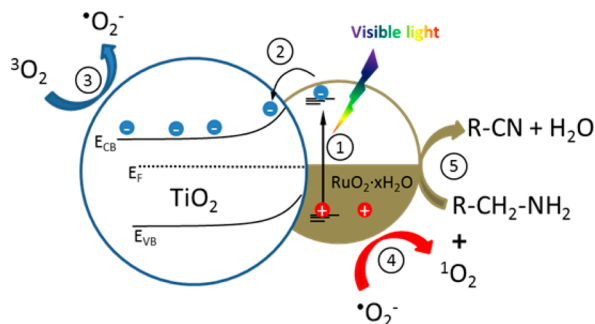


Figure 2. Effect of the addition of various radical scavengers on the oxidation of benzylamine. Reaction conditions: benzylamine (0.1 mmol), scavenger (0.1 mmol), water (3 mL), O₂ (~1 atm), RuO₂·xH₂O/TiO₂ (50 mg), blue LED 1.5 W/cm², 30 °C, 4 h.

photocatalytic process. Addition of •OH radical scavenger *tert*-butanol^{50–52} did not affect benzylamine oxidation, implying that such species are not involved in the process. Presence of either TEMPO (•O₂⁻ radical scavenger)^{53,54} or NaN₃ (scavenger of singlet oxygen, ¹O₂)^{55–57} led to the decrease of benzointrile yield to 82% and 36%, respectively, indicating the involvement of both •O₂⁻ and ¹O₂, with singlet oxygen being the predominant active species.

On the basis of these results, we can suggest a possible mechanism for the photocatalysed oxidation of amines over RuO₂·xH₂O/TiO₂. In this mechanism (Scheme 2), incident

Scheme 2. Schematic Diagram of Possible Mechanism of Amine Oxidation over RuO₂·xH₂O/TiO₂ upon Visible Light Irradiation



photons are absorbed by hydrous ruthenium oxide through interband transitions and/or the localized surface plasmon resonance (1),^{30,39–41} the photoexcited electrons are transferred into the TiO₂ conduction band (2), with subsequent formation of superoxide radicals •O₂⁻ (3), the holes remaining in RuO₂·xH₂O oxidize •O₂⁻ to form singlet oxygen^{58–60} (4) and, finally, RuO₂·xH₂O catalyzes the oxidation of amines to nitriles with ¹O₂ (5). The latter could proceed through the formation of ruthenium amide species, as was proposed earlier for thermally activated process.²³ In an alternative or parallel mechanism holes can oxidize amines, in which case superoxide radical would be directly involved in the oxidation process. In both cases, amine transformation to nitriles occurs over RuO₂·xH₂O centers as opposed to the case of pure TiO₂, where amine oxidation proceeds through the formation of positive

charge at nitrogen atom of TiO₂-amine complex with the subsequent formation of benzaldehyde and its condensation with amine to give N-BBA.^{9,31,33} The involvement of such active species as singlet oxygen and holes could be the reason for further oxidation of N-BBA in the photocatalysed process, which did not occur in the reported earlier thermally activated process (*vide supra*).

In summary, we have shown that hydrous ruthenium oxide supported on TiO₂ can promote the aerobic oxidation of wide range of amines to nitriles under visible light irradiation. Irradiation with blue light was found to be the most efficient; however, amine oxidation can also be driven by sunlight at ambient temperature. Importantly, water can be used as a solvent instead of toluene for the oxidation of both benzylic and aliphatic amines without significant loss in activity and selectivity. Preliminary mechanistic investigations indicated the involvement of singlet oxygen in the photocatalytic amine oxidation over RuO₂·xH₂O/TiO₂.

■ ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501186n.

Full experimental details, additional data (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: baira.donoeva@gmail.com.

*E-mail: vladimir.golovko@canterbury.ac.nz.

Author Contributions

‡D.S.O. and B.G.D. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Steven Graham for the help with LED assembly, Sebastian Horvath for the help with measuring characteristics of LEDs, Dr Colin Doyle from RCSMS, University of Auckland for XPS analysis, and Robert Stainthorpe for ICP-MS analysis. This work was supported by the University of Canterbury and the MacDiarmid Institute for Advanced Materials and Nanotechnology.

■ REFERENCES

- (1) Linic, S.; Christopher, P.; Ingram, D. B. *Nat. Mater.* **2011**, *10*, 911–921.
- (2) Sarina, S.; Waclawik, E. R.; Zhu, H. *Green Chem.* **2013**, *15*, 1814–1833.
- (3) Higashimoto, S.; Kitao, N.; Yoshida, N.; Sakura, T.; Azuma, M.; Ohue, H.; Sakata, Y. *J. Catal.* **2009**, *266*, 279–285.
- (4) Shiraishi, Y.; Sakamoto, H.; Sugano, Y.; Ichikawa, S.; Hirai, T. *ACS Nano* **2013**, *7*, 9287–9297.
- (5) Tanaka, A.; Hashimoto, K.; Kominami, H. *J. Am. Chem. Soc.* **2012**, *134*, 14526–14533.
- (6) Zhu, H.; Ke, X.; Yang, X.; Sarina, S.; Liu, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 9657–9661.
- (7) Tanaka, A.; Nishino, Y.; Sakaguchi, S.; Yoshikawa, T.; Imamura, K.; Hashimoto, K.; Kominami, H. *Chem. Commun.* **2013**, *49*, 2551–2553.
- (8) Sarina, S.; Zhu, H.; Jaatinen, E.; Xiao, Q.; Liu, H.; Jia, J.; Chen, C.; Zhao, J. *J. Am. Chem. Soc.* **2013**, *135*, 5793–5801.
- (9) Lang, X.; Chen, X.; Zhao, J. *Chem. Soc. Rev.* **2014**, *43*, 473–486.

- (10) Ke, X.; Sarina, S.; Zhao, J.; Zhang, X.; Chang, J.; Zhu, H. *Chem. Commun.* **2012**, 48, 3509–3511.
- (11) Gonzalez-Bejar, M.; Peters, K.; Hallett-Tapley, G. L.; Grenier, M.; Scaiano, J. C. *Chem. Commun.* **2013**, 49, 1732–1734.
- (12) Sarina, S.; Zhu, H.; Zheng, Z.; Bottle, S.; Chang, J.; Ke, X.; Zhao, J.-C.; Huang, Y.; Sutrisno, A.; Willans, M.; Li, G. *Chem. Sci.* **2012**, 3, 2138–2146.
- (13) Naya, S.-i.; Teranishi, M.; Isobe, T.; Tada, H. *Chem. Commun.* **2010**, 46, 815–817.
- (14) Naya, S.-i.; Niwa, T.; Kume, T.; Tada, H. *Angew. Chem., Int. Ed.* **2014**, 126, 7433–7437.
- (15) Fatiadi, A. J. In *Triple-Bonded Functional Groups*; Patai, S.; Rappaport, Z., Eds.; John Wiley & Sons, Ltd.: Chichester, U.K., 1983; Vol. 2, p 1057.
- (16) Pollak, P.; Romeder, G.; Hagedorn, F.; Gelbke, H.-P. In *Ullmann's Encyclopedia of Industrial Chemistry*; Bailey, J. E. et al., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000; Vol. 24, p 251.
- (17) Fleming, F. F.; Yao, L.; Ravikumar, P. C.; Funk, L.; Shook, B. C. *J. Med. Chem.* **2010**, 53, 7902–7917.
- (18) Miller, J. S.; Manson, J. L. *Acc. Chem. Res.* **2001**, 34, 563–570.
- (19) Sandmeyer, T. *Ber. Dtsch. Chem. Ges.* **1885**, 18, 1492–1496.
- (20) Zhou, S.; Junge, K.; Addis, D.; Das, S.; Beller, M. *Org. Lett.* **2009**, 11, 2461–2464.
- (21) Yamaguchi, K.; Fujiwara, H.; Ogasawara, Y.; Kotani, M.; Mizuno, N. *Angew. Chem., Int. Ed.* **2007**, 46, 3922–3925.
- (22) Oishi, T.; Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2009**, 48, 6286–6288.
- (23) Yamaguchi, K.; Mizuno, N. *Angew. Chem.* **2003**, 115, 1518–1521.
- (24) Yamaguchi, K.; Mizuno, N. *Chem.—Eur. J.* **2003**, 9, 4353–4361.
- (25) Kotani, M.; Koike, T.; Yamaguchi, K.; Mizuno, N. *Green Chem.* **2006**, 8, 735–741.
- (26) Li, F.; Chen, J.; Zhang, Q.; Wang, Y. *Green Chem.* **2008**, 10, 553–562.
- (27) Tseng, K.-N. T.; Rizzi, A. M.; Szymczak, N. K. *J. Am. Chem. Soc.* **2013**, 135, 16352–16355.
- (28) Fletcher, J. M.; Gardner, W. E.; Greenfield, B. F.; Holdoway, M. J.; Rand, M. H. *J. Chem. Soc. A* **1968**, 653–657.
- (29) Uddin, M. T.; Nicolas, Y.; Olivier, C.; Toupance, T.; Müller, M. M.; Kleebe, H.-J.; Rachut, K.; Ziegler, J.; Klein, A.; Jaegermann, W. *J. Phys. Chem. C* **2013**, 117, 22098–22110.
- (30) Bang, S.; Lee, S.; Park, T.; Ko, Y.; Shin, S.; Yim, S.-Y.; Seo, H.; Jeon, H. *J. Mater. Chem.* **2012**, 22, 14141–14148.
- (31) Lang, X.; Ji, H.; Chen, C.; Ma, W.; Zhao, J. *Angew. Chem., Int. Ed.* **2011**, 50, 3934–3937.
- (32) Li, N.; Lang, X.; Ma, W.; Ji, H.; Chen, C.; Zhao, J. *Chem. Commun.* **2013**, 49, 5034–5036.
- (33) Furukawa, S.; Ohno, Y.; Shishido, T.; Teramura, K.; Tanaka, T. *ACS Catal.* **2011**, 1, 1150–1153.
- (34) Zheng, Z.; Chen, C.; Bo, A.; Zavahir, F. S.; Waclawik, E. R.; Zhao, J.; Yang, D.; Zhu, H. *ChemCatChem* **2014**, 6, 1210–1214.
- (35) Naya, S.-i.; Kimura, K.; Tada, H. *ACS Catal.* **2012**, 3, 10–13.
- (36) Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2002**, 41, 4538–4542.
- (37) Corker, E. C.; Mentzel, U. V.; Mielby, J.; Riisager, A.; Fehrmann, R. *Green Chem.* **2013**, 15, 928–933.
- (38) Kim, K. S.; Winograd, N. *J. Catal.* **1974**, 35, 66–72.
- (39) Hu, C.-C.; Chen, W.-C.; Chang, K.-H. *J. Electrochem. Soc.* **2004**, 151, A281–A290.
- (40) Huang, L.-M.; Wen, T.-C.; Gopalan, A. *Electrochim. Acta* **2006**, 51, 3469–3476.
- (41) de Almeida, J. S.; Ahuja, R. *Phys. Rev. B* **2006**, 73, 165102–1–165102–6.
- (42) Brus, L. *Acc. Chem. Res.* **2008**, 41, 1742–1749.
- (43) Lindstrom, C. D.; Zhu, X.-Y. *Chem. Rev.* **2006**, 106, 4281–4300.
- (44) Capello, C.; Fischer, U.; Hungerbühler, K. *Green Chem.* **2007**, 9, 927–934.
- (45) Chen, C.; Ma, W.; Zhao, J. *Chem. Soc. Rev.* **2010**, 39, 4206–4219.
- (46) Li, Y.; Wasgestian, F. J. *Photoch. Photobiol. A* **1998**, 112, 255–259.
- (47) Kominami, H.; Furusho, A.; Murakami, S.-y.; Inoue, H.; Kera, Y.; Ohtani, B. *Catal. Lett.* **2001**, 76, 31–34.
- (48) Zhang, Y.; Zhang, N.; Tang, Z.-R.; Xu, Y.-J. *Chem. Sci.* **2013**, 4, 1820–1824.
- (49) Wang, J.; Yang, X.; Chen, J.; Xian, J.; Meng, S.; Zheng, Y.; Shao, Y.; Li, D. *J. Am. Ceram. Soc.* **2014**, 97, 267–274.
- (50) Minero, C.; Mariella, G.; Maurino, V.; Vione, D.; Pelizzetti, E. *Langmuir* **2000**, 16, 8964–8972.
- (51) Lv, K.; Xu, Y. *J. Phys. Chem. B* **2006**, 110, 6204–6212.
- (52) Lee, C.; Sedlak, D. L. *J. Mol. Catal. A* **2009**, 311, 1–6.
- (53) Xie, H.; Ray, P. E.; Short, B. L. *Stroke* **2005**, 36, 1047–1052.
- (54) Wang, W.; Zhang, L.; An, T.; Li, G.; Yip, H.-Y.; Wong, P.-K. *Appl. Catal., B* **2011**, 108–109, 108–116.
- (55) Foote, C. S. Quenching of Singlet Oxygen. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979, pp 139–171.
- (56) Li, M. Y.; Cline, C. S.; Koker, E. B.; Carmichael, H. H.; Chignell, C. F.; Bilski, P. *Photochem. Photobiol.* **2001**, 74, 760–764.
- (57) Zhang, D.; Qiu, R.; Song, L.; Eric, B.; Mo, Y.; Huang, X. *J. Hazard. Mater.* **2009**, 163, 843–847.
- (58) Nosaka, Y.; Daimon, T.; Nosaka, A. Y.; Murakami, Y. *Phys. Chem. Chem. Phys.* **2004**, 6, 2917–2918.
- (59) Saito, H.; Nosaka, Y. *Chem. Lett.* **2012**, 41, 1591–1593.
- (60) Hu, X.; Ji, H.; Wu, L. *RSC Adv.* **2012**, 2, 12378–12383.