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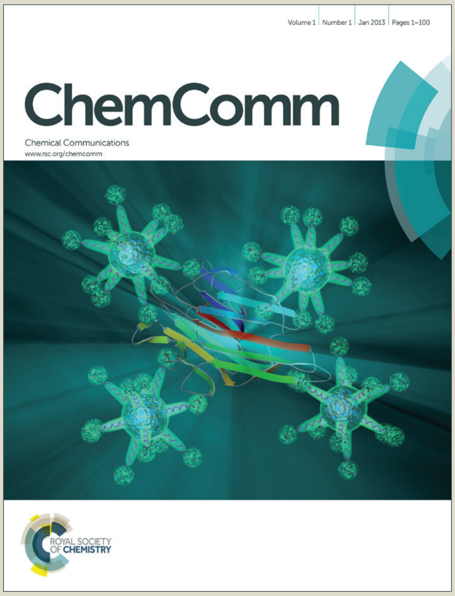

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COMMUNICATION

Photocatalytic Aerobic oxidation of amine to imine on $BiVO_4$ with visible light

Cite this: DOI: 10.1039/x0xx00000x

Bo Yuan, Ruifeng Chong, Bao Zhang, Jun Li, Yan Liu* and Can Li*

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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$BiVO_4$ was found to be an efficient photocatalyst under visible light irradiation for selective oxidation of amines to imines with high activity (99% conversion) and selectivity (up to 99%) using oxygen as oxidant.

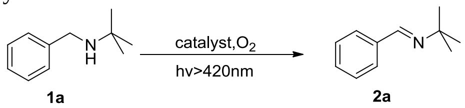
Over the years, intensive attention has been devoted to the use of light as a driving force for chemical reactions[1] because it can easily perform chemical transformation with "green" synthetic route. The exploring of low-cost and stable catalytic system with high catalytic efficiency is always a major goal in this fascinating area. Ruthenium and iridium complexes have been proven to be available visible-light photoredox catalysts in the cycloadditions as well as carbon-carbon and carbon-heteroatom bond formations.[2] However, the stability in long term operation and inclusion of precious metal restrict their practical application.[3] Inorganic semiconductors are promising photocatalytic materials due to their availabilities, chemical stabilities and diversity.[4] Among them, titanium dioxide has been widely used for the transformation of organic compounds such as alcohol oxidation[5] and nitrobenzene reduction[6]. However, TiO_2 responds only to UV light and tends to be slightly selective for many oxidation reactions. Therefore, exploring suitable visible-light photocatalysts to achieve excellent selectivity is highly desirable in synthetic chemistry.

Imine is an important synthetic intermediate because of its versatile applications in medicines or biologically active nitrogen containing organic compounds.[7] Generally, its synthesis relies on the condensation of amine and carbonyl compound. Efforts have been devoted to direct oxidation of amine to its corresponding imine.[8] Although some oxidation procedures with stoichiometric amount of oxidants such as 2-iodoxybenzoic acid or N-*tert*-butylphenylsulfinimidoyl chloride have been developed, a catalytic system using molecular oxygen as oxidant is an ideal way concerning green chemistry.[9] Several transition metal based catalytic systems have been established for this purpose, but only limited kinds of amines are oxidized to imines with expensive metals under relatively high temperature.[10] Very recently, people tried to utilize semiconductor as photocatalyst for amine transformation. Zhao et al reported a photocatalytic oxidation of primary amines on TiO_2 to prepare homo-condensed imine. Although the high selectivities were achieved, the catalytic system was not available for the secondary amines to prepare imine with the different substituted groups.[11] Shishido and Tanaka et al found that Nb_2O_5 was another efficient photocatalyst for aerobic oxidation of various amines to imines.[12] However, similar to TiO_2, it's an ultraviolet responding catalyst (light absorption edge of Nb_2O_5 is 390 nm). Other photocatalyst such as mpg-C_3N_4 (mesoporous graphite carbon nitride),[3] Au/TiO_2,[13] Ru containing MOF,[14] Ru and Rh complexes,[15] CdS[16] and LDH[17] are also reported to implement the oxidation of amine. However, most of catalytic systems are not efficient for secondary amine oxidation.

$BiVO_4$, as a visible-light-responsive photocatalyst, has been demonstrated to be active in photocatalytic[18] and photoelectrochemical water oxidation[19]. In this communication, we report our finding that $BiVO_4$ can be used as an efficient photocatalyst on a series of amine oxidation to prepare the corresponding imine with high activity and selectivity under mild conditions. Moreover, we found that the exposed surfaces of both (110) facet and (040) facet in $BiVO_4$ play an important role in the photocatalytic activity of amine oxidation. The control experiment and mechanistic studies suggested that the amine was oxidized directly involving holes generated in $BiVO_4$ irradiated with visible light and using O_2 as an electron acceptor to react with proton.

N-*t*-butylbenzylamine **1a** was chosen as the model substrate, because it could supply a synthetically useful imine product and was proved to be a tough substrate in the photocatalytic oxidation by either TiO_2[11a] or Nb_2O_5[12a]. Bi containing salts were employed as the photocatalysts and a Xe light (λ>420 nm) was used as the source of visible light. Photocatalytic activity and selectivity of **1a** oxidation over various Bi containing salts catalysts are summarized in Table 1. Bi_2MoO_6, Bi_2WO_6 and $BiVO_4$ are able to oxidize benzylamine to dehydrogenated imine. The primary results show that Bi_2MoO_6 exhibits the highest oxidation ability but moderate selectivity (Table 1, entry 1). Bi_2WO_6 has low activity and selectivity in the model photocatalytic oxidation (Table 1, entry 2). $BiVO_4$ shows excellent selectivity although the activity is poor (Table 1, entry 3). Over the past decades, exposed crystal planes of inorganic semiconductor-based photocatalyts have been verified to have great influence on catalytic activity. Recently, this group revealed that (040) and (110) facets of $BiVO_4$ play an important role in the water oxidation through spatial separation of the photogenerated electrons and holes.[18b, 20] Inspired by this finding, we envisioned that catalytic ability of $BiVO_4$ in the oxidation of amine might be improved through fine tuning of the facets. We found that $BiVO_4$ crystals with different ratios of (040) and (110) facets could be hydrothermally synthesized by treating with different pH values (Figure S3). It is worthy to note that all batches of $BiVO_4$ have almost same UV-vis diffuse reflectance, particle size and BET surface area (Figure S2, S4, S5). To our delight, $BiVO_4$ with almost 1:1 ratio of the peak intensity of XRD referring to (040) and (110) facets exhibits the highest activity in the amine photo-oxidation with 94% selectivity.

Table 1: Oxidation of N-t-butylbenzylamine over various photocatalysts ^{a}

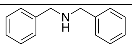
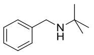
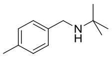
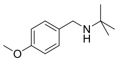
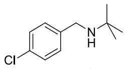
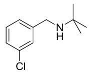
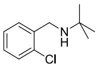
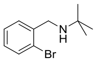
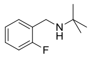
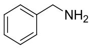
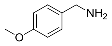
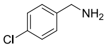
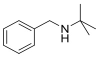
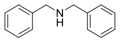
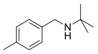
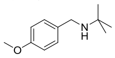
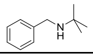


Entry	Catalyst	I(110)/I(040)	Conversion (%) ^{b}	Selectivity (%) ^{b}
1	Bi_2MoO_6		72	73
2	Bi_2WO_6		29	53
3	$BiVO_4$-1		16	94
4	$BiVO_4$-2^{c}	1.86^{d}	37	90
5	$BiVO_4$-3^{c}	1.30^{d}	40	93
6	$BiVO_4$-4^{c}	1.17^{d}	81	94
7	$BiVO_4$-5^{c}	1.48^{d}	49	93
8	$BiVO_4$-6^{c}	1.63^{d}	38	94
9 ^{e}	$BiVO_4$-4^{c}		97	91

[a] Reaction conditions: λ>420 nm, catalyst (100 mg), N-t-butylbenzylamine (0.1 mmol), CH_3CN as a solvent (8 mL), irradiation time : 5 hours, oxygen balloon (1 atm); [b] Determined by gas chromatography analysis using 1,4-diisopropylbenzene as the internal standard; [c] Related to different batches of catalyst, $BiVO_4$-1 prepared by calcination, $BiVO_4$-2, 3, 4, 5, 6 prepared by a hydrothermal method at 160 °C for 12 hours; [d] $BiVO_4$-2,3,4,5,6 samples prepared by hydrothermal at pH values of 2.26, 2.51, 3.11, 3.64, 4.52 ; [e] irradiation time : 7 hours .

The oxidation of various amines including primary, secondary amine derivatives were also examined, and the results are listed in Table 2. Dibenzyl amine exhibits high reactivity and selectivity (Table 2, entry 1). To verify the oxidative activity of our catalyst system, we investigated different substituted N-t-butyl amines which were demonstrated to have poor reactivities in the other photocatalytic systems.[11a, 12a] We found that the high activity of this photocatalytic system can be extended for the oxidation of different substituted N-t-butyl amines. As listed in Table 2, variation of the substituent on the different positions of phenyl moiety of the amine has little impact on the selectivities of the reaction (Table 2, entries 2-9). Various substituted N-t-butyl imine could be obtained with high conversion (93-97%) and selectivities (90-99%). However, the oxidation of amine carrying the electron-donating group on the phenyl (Table 2, entries 3 and 4) proceeded more efficiently than those amines with electron-withdrawing substituted group (Table 2 entries 5-9). Moreover, higher reaction rates for para-substituted substrates relative to the *meta* and *ortho* isomers reveal the presence of a steric effect (Table 2, entries 5 VS 6-7). Primary amine could also undergo oxidative coupling to the corresponding homo-imine with high conversion and selectivity (Table 2, entries 10-12). To prove the practicality of this reaction system, the reactions were carried out with lower catalyst loadings (Table 2 entries 12-15) and larger scale of substrates (Table 2 entry 16). Prolonging the reaction time, high conversions and selectivities could also be achieved.

Table 2: Oxidation of amine over photocatalyst ^{a}

Entry	Substrate	Reaction time/h	Conversion (%) ^{b}	Selectivity (%) ^{b}
1		6	99	99
2		7	97	91
3		10	97	99
4		7	93	90
5		16	96	93
6		18	96	95
7		20	97	91
8		14	96	>99
9		16	95	92
10 ^{e}		16	89	89
11 ^{e}		12	93	86
12 ^{e}		20	85	89
13 ^{c}		17	92	92
14 ^{c}		13	92	90
15 ^{c}		20	90	95
16 ^{c}		21	91	90
17 ^{d}		48	79	92

[a] Reaction conditions: λ>420 nm, $BiVO_4$-4 (100 mg), amine (0.1 mmol), CH_3CN as a solvent (8 mL), oxygen balloon (1 atm); [b] Determined by gas chromatography analysis using 1,4-diisopropyl benzene as the internal standard; [c] $BiVO_4$-4 (20 mg); [d] $BiVO_4$-4 (100 mg), amine (1.5 mmol); [e] $BiVO_4$-4 (20 mg), amine (0.35 mmol);

After the reaction, solid $BiOV_4$ could be easily separated after a simple filtration and reused. We did not observe significant deterioration of activity and selectivity in the recovered catalyst even after seven times of use (Figure S6).

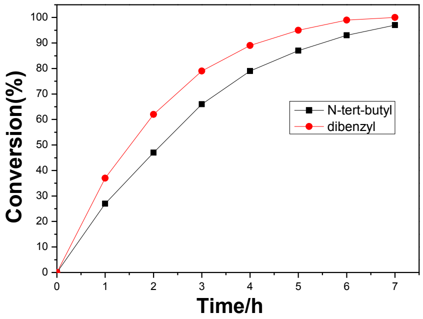


Figure 1: The comparison of the reaction conversion between the N-benzyl and N-tert-butyl benzylamine

In the photo-oxidations of amines catalyzed by TiO_2 and Nb_2O_5, the process which substrates adsorbed onto metal oxides to form amide species is regarded as the prerequisite. Because of the steric hindrance around the nitrogen atom, the bulky N-*tert*-butyl derivatives have much slower reactivities than N-benzyl derivatives in those reaction systems. In our case, we also make a comparison of the reaction rates between the N-benzyl and N-tert-butyl benzylamine. The results were described in the figure 1. The slight difference of the reactivities among these two substrates indicated that the photooxidation of amine catalyzed by $BiVO_4$ might have a different course to produce the corresponding imines.

To understand the mechanism of the present catalytic system, a series of kinetic experiments of *para*-substituted N-*tert*-butyl benzylamines (MeO, Me, H, Cl, and F groups) were conducted in the photocatalytic oxidation. The slope of the linear plot giving a ρ value close to zero indicates that the rate-determining step of this reaction doesn't involve the C_α-H activation (Figure 2).

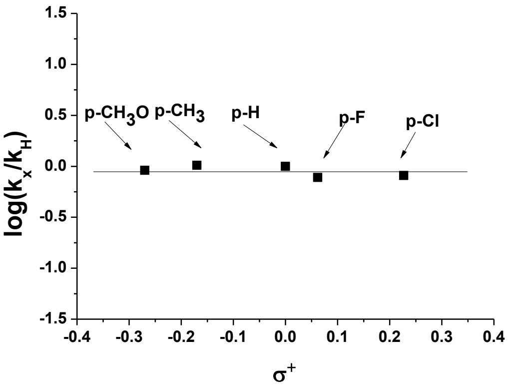
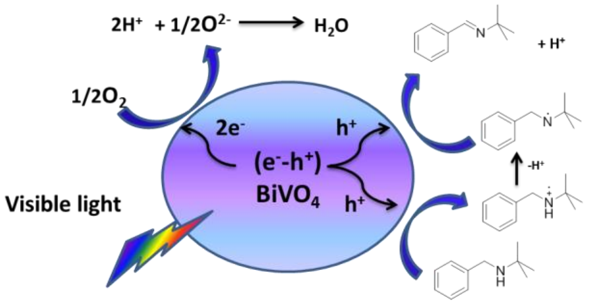


Figure 2: Hammett plots for the oxidation of substituted secondary amines with oxygen using $BiVO_4$ catalyst. Hammett plots were obtained from a ratio of conversion with reaction time of 60 min; the reaction condition was given in Table 2

Based on the above results, we propose a possible reaction mechanism as shown in figure 3: electron (e^-) and hole (h^+) pairs are generated by the irradiation of $BiVO_4$. The photogenerated electron reduces molecular oxygen to produce activated oxygen species. At the same time, amine probably loses an electron, thus forming the carbocationic-radical type intermediate. The activated oxygen species react with protons which are from the hole oxidation of amine.

Figure 3: The proposed mechanism of photooxidation of amine catalyzed by $BiVO_4$.



In order to confirm the mechanism, a reaction using $AgNO_3$ instead of O_2 as acceptor of photogenerated electron was carried out. The reaction shows even higher activity (See Figure S7). It demonstrates that photogenerated hole is an oxidative active site and O_2 is a capture of photogenerated electron.

In summary, we found that $BiVO_4$ acted as an efficient photocatalyst with visible light for the oxidation of a series of amines, forming the corresponding imines using O_2 as oxidant. Importantly, various bulky N-*tert*-butyl substituted benzylamine, which were proven to be a disfavoured type of substrates reported in the literature[11a, 12a], could also be oxidized with high selectivities (up to 99%).

We acknowledge the financial support from the National Nature Science Foundation of China (NSFC Grant No. 21322202) and the Basic Research Program of China (973 Program: 2014CB239403).

Notes and references

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.*
E-mail: *yanliu503@dicp.ac.cn*, *canli@dicp.ac.cn*

† Electronic Supplementary Information (ESI) available: [Experimental details and Figures S1-S6]. See DOI: 10.1039/c000000x/

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