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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Synergistic Photocatalytic Aerobic Oxidation of Sulfides and Amines on TiO₂ under Visible Light Irradiation

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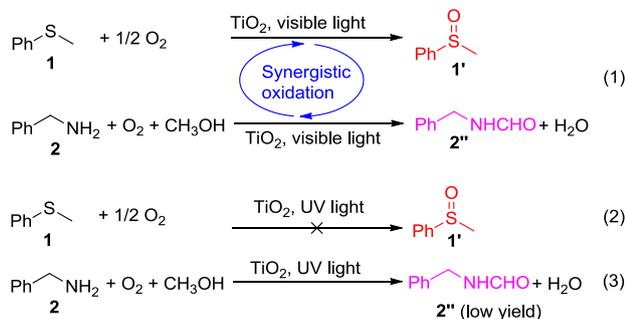
Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Selective photocatalytic aerobic oxidation, which can be conducted under ambient conditions, is of great importance towards achieving sustainable chemistry. However, its practical applications are undermined by several challenges, such as low selectivity, sluggish reaction rates, and the requirement of UV light irradiation. Herein, we report a new concept of synergistic photocatalytic oxidation, for which two seemingly irrelevant reactions can be achieved in one photocatalytic system through the synergistic interplay of reactants and catalyst. As proof of concept, two challenging reactions, the aerobic oxidation of sulfide and the aerobic oxidative formylation of amine with methanol, were employed to demonstrate such synergistic photocatalytic aerobic oxidation under visible light irradiation. This work could pave the way for highly selective photoredox catalysis via rational design based on mechanistic insight.

Introduction

The selective oxidation of organic compounds is one of the most vital transformations for upgrading raw starting materials into high value added products.¹⁻⁴ However, it is also one of the most problematic chemical reactions, as stoichiometric amounts of toxic oxidants are traditionally requires, leading to severe environmental impact and unsafe operational practices.⁵⁻⁸ O₂, the most environmentally friendly and readily available oxidant, has been used to replace toxic oxidants, but its activation necessitates transition metal based catalysts. The challenge is that most of such aerobic oxidation processes are carried out at harsh conditions such as high reaction temperature (>100 °C) and elevated O₂ pressure (several MPa).⁹⁻¹⁴ Alternatively, photocatalysis can engender a paradigm shift by enabling the organic transformation to occur at very mild conditions.¹⁵⁻²³ TiO₂ is the most widely-used metal oxide for photocatalytic reactions, such as the selective oxidation of alkanes, alcohols and amines, etc.²⁴⁻³⁰ but the large band gap (3.0-3.2 eV) only enables such reactions under UV light irradiation. In addition, the use of TiO₂ is hindered by other challenges, such as low selectivity and sluggish reaction rate.



In this work, we report a new concept of synergistic photocatalytic oxidation, which can be carried out at an accelerated rate with high selectivity of desired products under visible light irradiation. Specifically, two seemingly irrelevant reactions can be achieved in one photocatalytic system through the synergistic interplay of reactants and catalyst. As proof of concept, we demonstrated that the synergistic aerobic oxidation of two substrates, sulfide **1** and amine **2**, on the surface of TiO₂ under visible light irradiation simultaneously (eqn (1)). In contrast, the attempt to perform these two reactions individually are not successful (eqn (2) and (3)). This new strategy enables high selectivity of two valuable products, with the solvent controlling the selectivity of one product (sulfoxide **1'**) and participating in the formation of another product (*N*-benzylformamide **2''**). This finding provides a new perspective for the transformation of heteroatom-containing substrates by visible light photocatalysis via a synergistic oxidation strategy.

Results and discussion

In a typical experiment, the commercially available Degussa P25 TiO₂ was chosen as the model photocatalyst for the detailed investigation of the synergistic oxidation of two substrates. Degussa P25 TiO₂ (hereafter denoted as TiO₂ unless otherwise stated with the detailed characterization data presented in Figures S1-S4) is characterized by its ~21 nm particle size and with a surface area of 52 m²/g. It constitutes a mixture of anatase (75%) and rutile (25%) phases with the low energy {101} facet as the dominant facet. From the UV-visible spectrum (Figure 1a), it can be seen that the absorptions of thioanisole, benzylamine, or a mixture of both are well below 325 nm, indicating that no reaction can occur from the direct photochemical activation of the substrates without the involvement of a photocatalyst. However, the formation of a visible light absorbing surface complex via the

interaction of substrate and TiO₂ enables organic transformations under visible light irradiation.^{31, 32} When benzylamine **2** mixes with TiO₂, a red shift of the absorption spectrum can be clearly observed (Figure 1b), suggesting the formation of a surface complex through the adsorption of benzylamine **2** on TiO₂. The surface complex (Figure 1c) is akin to the donor–acceptor complex formed via the interaction of one reactant and the surface of TiO₂,^{33, 34} which enables the reaction to occur at a higher wavelength than that absorbed by individual substrates. Such surface-complex was further evidenced by the observation of an N1s peak in the XPS spectrum (Figure 1d), which was absent in the pure TiO₂ sample (Figure S3).

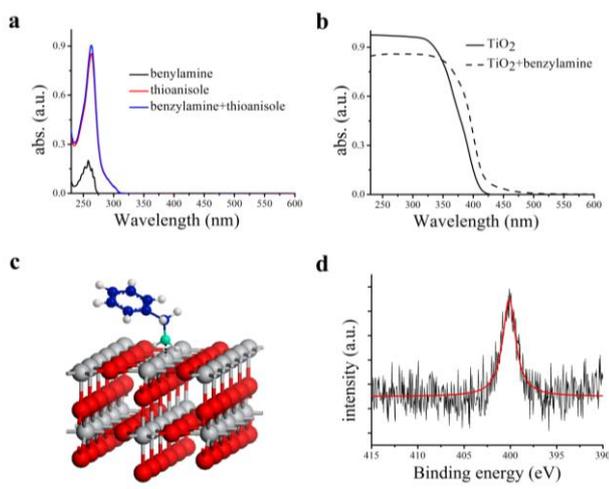


Figure 1: **a**, UV-visible absorption spectra of thioanisole **1**, benzylamine **2** and their mixture in CH₃OH; **b**, UV-visible absorption spectra of TiO₂ and after adsorption of benzylamine **2** on TiO₂; **c**, the scheme of benzylamine **2** adsorption on rutile TiO₂ (110), (the color convention thought is O atom, red; Ti atom, gray; N atom, cyan; C atom, blue; H atom, white); **d**, N 1s XPS spectrum of TiO₂ after benzylamine **2** adsorption, the red line are used to guide your eyes, a.u.: arbitrary unit.

Then, two challenging reactions, the aerobic oxidation of sulfide and the aerobic oxidative formylation of amine with methanol, were chosen to demonstrate the efficacy the synergistic photocatalytic oxidation. One reason is that the selective oxidation of sulfides to sulfoxides is very important intermediate for pharmaceuticals, but tremendous challenge of controlling product selectivity exists for heterogeneous photocatalytic systems utilizing O₂ as the oxidant.^{35–38} In addition, the aerobic oxidative formylation of amine with methanol constitutes another important yet challenging reaction.^{39–41} This is because the formation of *N*-benzylformamide demands the prior selective oxidation of methanol to formaldehyde,^{42–44} which is a difficult reaction to realize especially in the presence of a more fragile substrate, benzylamine. Both of these two oxidation reactions have never been successfully realized by TiO₂ photocatalysis under UV irradiation (eqn (2) and (3)). However, it is interesting to note that aminocatalysis is very prevalent in synthetic chemistry.⁴⁵ In particular, benzylic amines can function as organocatalysts in organic transformations.⁴⁶ Therefore, we hypothesize that the aforementioned oxidation of benzylamines could possibly serve as

the springboard in the pursuit of new selective oxidation reactions.

As a control experiment, we first identified the low selectivity and efficiency of the two individual photo-oxidations of thioanisole **1** (Table S1) and benzylamine **2** (Table S2) catalyzed by TiO₂ in the presence of O₂. Only less than 10% of thioanisole **1** was transformed into desired product sulfoxide **1'** with either the inert CH₃CN or the protic CH₃OH as the solvent. Moreover, the reaction ceased to proceed after 0.5 hour, which might be due to the deactivation of TiO₂ by thioanisole **1**. However, it is noted that the desired product could be obtained with quite high selectivity when CH₃OH is used as the solvent (Entry 2 and 4 of Table S1). Meanwhile, the photo-oxidation of benzylamine **2** (Entry 1 of Table S2) resulted in the selective formation of the undesired product imine in the presence of CH₃CN, and low selectivity of the desired product benzylformamide **2''** in the presence of CH₃OH.

However, when these two seemingly irrelevant reactions are mixed in one photocatalytic system under visible light irradiation simultaneously using CH₃OH as the solvent, the desired products can be clearly observed. The reaction kinetics for the conversions of two substrates thioanisole **1** and benzylamine **2** with a ratio of 3:1 in CH₃OH and the selective formation of their respective products is illustrated in Figure 2. It can be observed that the steady conversion of thioanisole **1** to sulfoxide **1'** proceeds with high selectivity. The conversion of thioanisole **1** almost follows zero-order reaction kinetic with reaction constant of $k=12.45 \text{ mol}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$. The selectivity for **1'** decreases slightly along with the progress of time, possibly due to the minor overoxidation of **1'** to sulfone which also follows zero-order reaction kinetic. In comparison with the conversion of thioanisole **1**, the conversion of benzylamine **2** was much more complicated and it includes an induction period (0–1 h) and product formation period (1–4.5 h). Since CH₃OH is a redox active solvent, the selective aerobic oxidation of CH₃OH to HCHO, is achieved along with the formation of **1'**. HCHO then undergoes condensation with benzylamine **2** to form an intermediate. With the progress of time, the intermediate can be further transformed into *N*-benzylformamide **2''**, an industrially important product. The corresponding reaction process for the plots in is listed in Figure S5.

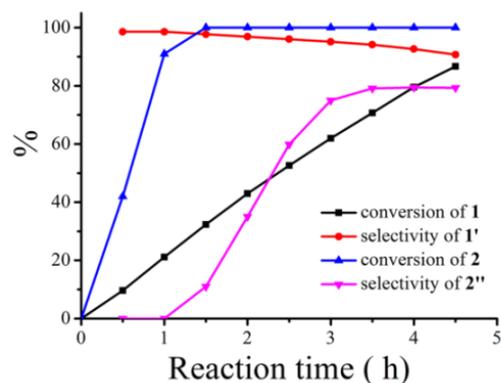
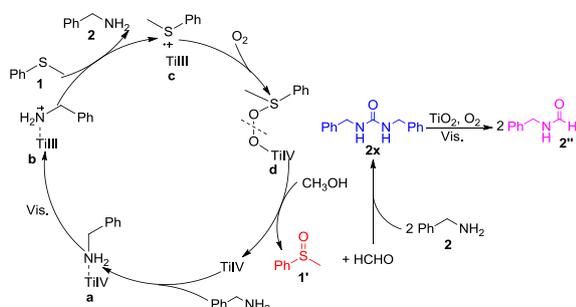


Figure 2. Reaction kinetic plot for the synergistic photocatalytic oxidation of sulfide and amine with O₂ on TiO₂ under visible light irradiation. Reaction conditions: 0.3 mmol of thioanisole **1**, 0.1 mmol of benzylamine **2**, 40 mg of TiO₂, 300 W Xe lamp, $\lambda > 400 \text{ nm}$, 5 mL of CH₃OH, 0.1 MPa of O₂.

As a control experiment, when CH₃OH is replaced by the inert organic solvent, such as CH₃CN, benzo-trifluoride, ethyl acetate, and dichloromethane, the synergistic oxidation of thioanisole **1** and benzylamine **2** only resulted in the oxidation of benzylamine **2** to imine, with thioanisole **1** remaining almost intact in all cases (Table S3). This suggests that an additional redox player is required to associate the two reactions. Here, we propose that the protic solvent CH₃OH may act as the additional redox player required to enable the desired synergistic reaction due to the following reasons. Firstly, it is typically used as a h_ν⁺ scavenger to quench other oxidation reactions in TiO₂ photocatalysis. It is also a protic solvent, which has been reported to substantially increase the oxidation reaction rate.⁴⁷ The selective oxidation of sulfides to sulfoxides indicated the necessity of protons in assisting the formation of products, protic solvents might be helpful for the aerobic oxidation of sulfides under visible light irradiation,³⁵⁻³⁸ even though they have been rarely used in TiO₂ photocatalytic selective transformations.

It is of interest to note that the synergistic oxidation reaction is extremely robust. It is able to proceed under even milder conditions, such as with 0.1 MPa of air as the oxidant, albeit at a slightly slower reaction rate. The trend of reaction for 0.1 MPa of air is the same as that for 0.1 MPa of O₂ (Figure S6). This phenomenon was ascribed to the decrease in amount of benzylamine **2** adsorbed on TiO₂ in CH₃OH compared with that in CH₃CN (Table S7). Thus, this finding might be limited as only a fraction of the entire visible light range could be used.



Scheme 1 Proposed mechanism for the synergistic selective oxidation of thioanisole **1** and benzylamine **2** with O₂ on TiO₂ under visible light irradiation.

Consequently, we propose the mechanism for the selective synergistic aerobic oxidation of thioanisole **1** and benzylamine **2** as shown in Scheme 1. The adsorption of benzylamine **2** on TiO₂ leads to the formation of surface complex **a**, which shows activity under visible light irradiation, thus facilitating electron transfer from the adsorbed benzylamine **2** to TiO₂. This results in a positive charge at the surface bound complex **b**, which could induce the oxidation of thioanisole **1** via single electron transfer. As a result, the surface bound S centered positive free radical would be formed at the surface of TiO₂ as complex **c**. In this stage, the C(sp³)-S bond cleavage could occur with respect to low selectivity to the desired product. This could be avoided by employing CH₃OH instead of CH₃CN as the solvent. The concerted incorporation of O-atoms to complex **c** forms complex **d**. The cleavage of **d**

requires additional protons which could be provided by the solvent, CH₃OH, in order to ensure the highly selective formation of **1'**. The protons from CH₃OH could also prevent the oxidation products from blocking the reactive TiO₂ surface, ensuring the sustainable oxidation of both substrates. The contribution of protons from alcohol have also been demonstrated in other oxygenation reactions in which free radical intermediates are involved. As the protons from CH₃OH were consumed in the cleavage of **d**, HCHO was formed as the side product, which would in turn undergo condensation with benzylamine **2** to form intermediate **2x** which was confirmed by the GC-MS peak of m/z 242. As the disappearance of benzylamine **2** did not deter the selective formation of **1'**, this indicated that **2x** or other unknown species could also co-catalyze the oxidation of **1**. The nitrogen in the condensation product **2x** could coordinate with the Ti-atoms of TiO₂ to initiate visible light activity for the oxidation of thioanisole **1**, as well as its own decomposition to the final product **2''** in the presence of HCHO. The transfer of electron to O₂ would restore the TiO₂, thus completing the photocatalytic cycle. In this way, the selective synergistic aerobic oxidation of thioanisole **1** and benzylamine **2** to **1'** and **2''** could be achieved.

To prove the above mechanism, we further study the influence of solvent in the synergistic oxidation. Based on the prior observation that the proton coupled electron transfer could control the reaction of free radicals, different protic solvents, i.e. different alcohols, were employed for the synergistic reactions. In all cases, the oxidation of thioanisole **1** to sulfoxide **1'** was unable to proceed under visible light irradiation in the absence of benzylamine **2** (Table S4), which was consistent with the reaction mechanism. However, when benzylamine **2** was added as the synergistic substrate, the oxidation of thioanisole **1** was significantly improved, with CH₃OH delivering the best results due to it being the strongest organic protic solvent. Although benzylamine **2** was consumed in all three protic solvents, only CH₃OH yielded the desired amide product, *N*-benzylformamide **2''**, while IPA and C₂H₅OH afforded imine as the product (Table S4). From these results, it can be seen that the choice of solvent plays an influential role in the mechanism of the reaction.

Table 1: The influence of ratio of substrates on the synergistic photocatalytic oxidation of thioanisole **1** and benzylamine **2**

$$\text{Ph-S-Ph} + \text{Ph-NH}_2 + \text{O}_2 + \text{CH}_3\text{OH} \xrightarrow[\text{O}_2, \text{CH}_3\text{OH}]{\text{TiO}_2, \lambda > 400 \text{ nm}} \text{Ph-S(=O)-Ph} + \text{Ph-NH-C(=O)-Ph} + \text{H}_2\text{O}$$

Entr y	Benzylamine (mmol)	Ratio	Thioanisole		Benzylamine	
			Con1. (mol%) ^[a]	Sel1. (mol%) ^[a]	Con2. (mol%) ^[b]	Sel2. (mol%) ^[b]
1	0.05	10:1	41	97	100	72
2	0.10	10:2	51	96	100	81
3	0.15	10:3	57	96	100	77
4	0.20	10:4	56	95	100	46
5	0.25	10:5	51	96	100	14

Reaction conditions: 0.5 mmol of **1**, 0.1 MPa of O₂, 40 mg of TiO₂, 300 W Xe lamp, λ > 400 nm, 5 mL of CH₃OH, 4 h. [a] Determined by GC using chlorobenzene as the internal standard, conversion of **1**, selectivity of **1'**. [b] Determined by GC using chlorobenzene as the internal standard, conversion of **2**, and selectivity of **2''**.

To better understand the essence of the synergistic effect, the amount of thioanisole **1** was fixed and the amount of benzylamine **2** varied, the results of which were summarized in Table 1. It can be seen that the formation of sulfoxide **1'** was almost the same for all ratios of thioanisole **1** to benzylamine **2**, except the slight drop of conversion of thioanisole **1** with 0.1 equiv. of benzylamine **2** (entry 1, Table 1). This suggests that benzylamine **2** acts as an organocatalyst for the aerobic oxidation of thioanisole **1** on TiO₂; reaction could not proceed at all without benzylamine **2**. Although the conversion of benzylamine **2** was a very rapid process, able to achieve 100% conversion in merely 4 hours or less, the formation of *N*-benzylformamide **2''** from the resultant intermediate does not occur as rapidly. This leads to a difference in selectivities among entries 2-5 (Table 1), which could be enhanced with the prolonging of reaction time. The ratio of 3:1 between thioanisole **1** and benzylamine **2** furnished good selectivities for both desired products at good conversions for both substrates. These results are in good agreement with the kinetics study in Figure 2 and the proposed mechanism in Scheme 1.

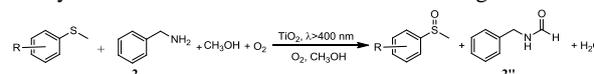
In addition, it is noted that the scale-up of the synergistic reaction could be high valuable. Thus, a study was conducted on the effect of substrate concentrations on the outcome of the synergistic reactions while maintaining the optimal of 3:1 between two substrates. It was discovered that generally, the concentrations of both substrates could be simultaneously increased or decreased without a dramatic change in the conversions and selectivities of both **1'** and **2''** (Table S5). However, it was also observed that an overly high concentration of benzylamine **2** could result in a low selectivity of **2''** due to side reactions (Table S5).

More rigorous control experiments were carried out to prove the essential photocatalytic aerobic nature of the synergistic reaction system (Table S6). It was observed that the synergistic oxidation reaction ceased to proceed when a $\lambda > 420$ nm longpass filter was applied (entry 5, Table S6), which is different from our previous report in which the selective aerobic oxidation of amines in CH₃CN proceeded smoothly with visible light irradiation of the same wavelength range.³² In this scenario, one might suspect the results were caused by the direct irradiation of rutile TiO₂ in the used photocatalyst. If the reaction results were caused by the directed irradiation of photocatalyst, UV irradiation should lead to better results. But our control experiment (entry 1, table S6) does not support this hypothesis.

To understand the scope of reaction, different types of thioanisoles were employed in the reaction while keeping benzylamine **2** constant. Table 2 revealed that the oxidation of substituted thioanisoles **1b-k** to the corresponding sulfoxides **1b'-k'** proceeded smoothly with very high selectivities, and that the conversions varied only slightly with the different substituted groups (entries 2-8, Table 2). However, very strong electron withdrawing group such as NO₂ may significantly reduce the conversion rate of sulfide **1i** to sulfoxide **1i'** (entry 9, Table 2), resulting in a much longer time needed to obtain a higher conversion of **1i**. Besides the aforementioned electronic effect, the NO₂ groups of **1i** could be easily adsorbed on the surface of TiO₂ which could partially block the adsorption of **2**, contributing to the observed sluggish reaction rate. This would also cause the oxidation of **2** to yield benzaldehyde as the final product, rather than the desired *N*-benzylformamide **2'**. Meanwhile, changing the

methyl group of **1** to ethyl as in the sulfide **1j** would not greatly influence the reaction rate of sulfide **1j** to sulfoxide **1j'** (entry 10, Table 2), but a phenyl group as in **1k** would result in lower reaction rate and selectivity for (entry 11, Table 2) in the conversion to **1k'**. Nevertheless, the summation of our results showed that the reaction is applicable to a large scope of thioanisoles, generally producing high conversions and selectivities for the product of sulfoxides.

Table 2. The selective aerobic oxidation of sulfides and benzylamine on TiO₂ in CH₃OH under visible light irradiation



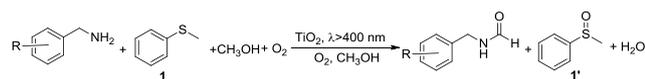
Entry	Substrate (Sulfide)	Product (Sulfoxide)	Sulfide		Benzylamine	
			Con1. (mol%) ^[a]	Sel1. (mol%) ^[a]	Con2. (mol%) ^[b]	Sel2. (mol%) ^[b]
1			83	92	100	77
2			81	99	100	75
3			81	94	100	81
4			91	92	100	76
5			86	93	100	76
6			75	90	100	66
7			80	88	100	72
8			75	90	100	76
9			48	91	100	12 ^[c]
10 ^[d]			84	86	100	57
11			40	88	100	41

Reaction conditions: 0.3 mmol of sulfide, 0.1 mmol of **2**, 0.1 MPa of O₂, 40 mg TiO₂, 300 W Xe lamp, 5 mL of MeOH, $\lambda > 400$ nm, 4 h. [a] Determined by GC using chlorobenzene as the internal standard, conversion of sulfide **1**, selectivity of sulfoxide **1'**. [b] Determined by GC using chlorobenzene as the internal standard, conversion of **2**, selectivity of **2''**. [c] Selectivity for benzaldehyde **1e**. [d] 0.1 mmol of 4-chlorobenzylamine. Me, methyl; Et, ethyl.

Finally, the scope of reaction with regards to benzylamines was investigated by testing different types of amines in reaction while fixing sulfide as thioanisole **1**, while were tested in the reaction (Table 3). It was observed that different primary benzylamines could yield high selectivities in the oxidation of thioanisole **1** to sulfoxide **1'** (entries 1-8, Table 3), but the conversion of thioanisole **1** for the substituted benzylamines is lower than that of benzylamine **2**. In addition, the selectivities for the corresponding *N*-benzylformamides of substituted benzylamines were all lower

than that of benzylamine **2**. This is because, for the electron donating groups, the oxidation of amines led instead to the formation of imine products, which could not induce the oxidation of thioanisole **1**, thus resulting in the lower conversion of thioanisole **1**. Meanwhile, for the electron withdrawing groups, the slower reaction rates were due to the relative difficulty in donating the electron to the conduction band of TiO₂, and could be compensated by allowing longer reaction times. The selectivities for corresponding formamides could be improved with longer reaction time. It could also be seen that the existence of heteroatom in the aromatic rings of amines only led to slight drop in the selectivity of formamides (entries 6-8, Table 3). For secondary benzylamines, no corresponding formamides were formed; benzaldehyde **2y** was the only product formed in the oxidation of secondary benzylamines **2j** and **2k** (entries 9 and 10, Table 3). This is in part because condensation between secondary benzylamines and HCHO to form the corresponding formamide is much more difficult than its primary counterpart. In addition, secondary benzylamines are not stable in the reaction conditions. The breakage to C-N bond and ensuing oxidation led to the benzaldehyde **2y** as the main observed product.

Table 3: The selective aerobic oxidation of amines and thioanisole on TiO₂ in CH₃OH under visible light irradiation



Entry	Substrate (Amine)	Product (Formamide)	Amine		Thioanisole	
			Con2. (mol%) ^a	Sel2. (mol%) ^b	Con1. (mol%) ^b	Sel1. (mol%) ^b
1 ^k			100	49	70	95
2			100	63	70	94
3			100	56	61	95
4			100	59	56	95
5			100	73	78	93
6			100	70	57	95
7			100	41	54	95
8			100	15	64	96
9			100	23	67	95
10			67	55	64	95

Reaction conditions: 0.1 mmol of amine, 0.3 mmol of thioanisole **1**, 0.1 MPa of O₂, 40 mg TiO₂, 300 W Xe lamp, 5 mL of CH₃OH, λ>400 nm, 4 h. [a] Determined by GC using chlorobenzene as the internal standard, conversion of amine, selectivity of corresponding formamide. [b] Determined by GC using chlorobenzene as the internal standard, conversion of **1**; selectivity of **1'**. [c] imine (15%) as another product. Me,

methyl; Et, ethyl, *t*-Bu, tert-butyl; MeO, methoxyl.

Conclusions

To sum up, our novel concept of the synergistic aerobic photocatalytic reactions is extremely advantageous as it allows the following to be achieved: 1) high selectivity for the two desired products; 2) reaction at high substrate concentrations; 3) clean reaction with O₂ under visible light irradiation; and 4) long lifetime of the commercially available TiO₂ photocatalyst. The present report represents a successful example in selective organic transformation with TiO₂ photocatalyst, which could pave the way for new discoveries of selective oxidation of organic compounds with an inexpensive metal oxide photocatalyst. Owing to the inspiration from the recent progress both in organocatalysis and the techniques for the surface modification of semiconducting transition metal oxides, it is expected that more synergistic redox reactions can be achieved by judiciously selecting a pair of substrates and an appropriate solvent. In parallel, the functions of metal oxide nanomaterials are determined with specific surface area and texture,⁴⁸ hierarchical structure⁴⁹ and exposed crystal phase.⁵⁰ The tunability of TiO₂ in these aspects is one of the best among metal oxide materials. Thus photocatalytic activity could also be improved to deliver better results.

Experimental section

The reaction was irradiation with an Asahi Spectra MAX-303 300 W Xenon light source using a UV-VIS mirror model. In this mirror model, the irradiating wavelength range is 270 nm-650 nm, thus the possible heating of the reaction medium the infrared light is completely excluded. Additional Asahi Spectra longpass cutoff filters (>400 nm) are used to control irradiation wavelength range during the reaction. The reaction medium was maintained at room temperature throughout the experimental process.

All of the reagents used were obtained from commercial suppliers of the highest purity without further purification. In a typical reaction, 40 mg of TiO₂, 0.3 mmol of thioanisole and 0.1 mmol of benzylamine were added to 5 mL of CH₃OH in a Pyrex vessel. After the reaction mixture was stirred for 30 min in dark to reach adsorption equilibrium, O₂ was purged into the Pyrex vessel to raise the initial pressure to 0.1 MPa. The reaction mixture was magnetically stirred at 800 r/min and illuminated with λ>400 nm visible light irradiation in an air-conditioned room to warrant the reaction temperature constantly at 25 °C.

At the end of reaction, the TiO₂ photocatalyst particles were separated from the reaction mixture by filtration and the products were quantitatively analyzed by gas chromatography (GC) equipped with a flame ionization detector (FID) using chlorobenzene as the internal standard. The structure of products were confirmed by comparison with the retention time with standard samples and further confirmed by gas chromatography-mass spectrometry (GC-MS).

The quantitative measurements of conversions of substrate and selectivities of products were made on an GC (Agilent 7890A) equipped with a flame ionization detector (FID) and Agilent Technology 19091J-413 capillary column (30 m×0.32 mm×0.25 μm) using high pure N₂ as the carrier gas. Standard analysis conditions: injector temperature 250 °C, detector temperature 300

°C, column temperature program: 50 °C (hold 1.5 min) raised up to 300 °C (hold 3 min) at a rate of 20 °C/min. GC-MS analysis was performed on a Shimadzu GC 2010 gas chromatograph equipped with a Shimadzu GCMS-QP2010 Ultra mass spectrometer in selected ion monitoring using a Restek (Rxi®-5Sil MS) capillary column (30 m×0.25 mm×0.25 µm), coupled with an electron ionization mass spectrometer with high pure He as the carrier gas.

Full experimental details are provided in the Supplementary Information.

10 Acknowledgment

Final support from the Singapore National Research Foundation (CREATE Programme of Nanomaterials for Energy and Water Management and Singapore-Berkeley Research Initiative for Sustainable Energy (SinBeRISE)) is gratefully acknowledged.

15 Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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