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ARTICLE

Tertiary amine mediated aerobic oxidation of sulfides into sulfoxides by visible-light photoredox catalysis on TiO₂

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The selective oxidation of sulfides into sulfoxides receives much attention due to industrial and biological applications. However, the realization of this reaction with molecular oxygen at room temperature, which is of importance towards green and sustainable chemistry, remains challenging. Herein, we develop a strategy to achieve the aerobic oxidation of sulfides into sulfoxides by exploring the synergy between tertiary amine and titanium dioxide via visible-light photoredox catalysis. Specifically, titanium dioxide can interact with triethylamine (TEA) to form a visible-light harvesting surface complex, precluding the ensuing selective redox reaction. Moreover, TEA plays a critical role as a redox mediator in shuttling the oxidation of sulfide, whose stability was demonstrated with a turnover number of 32. This work suggests that the addition of a redox mediator is highly functional in establishing visible-light-induced reactions by heterogeneous photoredox catalysis.

Introduction

The selective oxidation of sulfides into sulfoxides, an essential chemical transformation, plays a pivotal role in accessing a series of industrially and biologically important organic compounds.¹⁻⁵ In line with the principles of green chemistry for selective oxidation, both O₂¹⁻³ and H₂O₂^{4,5} can be used as the oxidant for such specific reaction with the only side product of water. Using O₂ as the oxidant proves extremely challenging due to the difficulty of O₂ activation and its subsequent highly reactive nature once activated.⁶⁻¹⁰ These issues can be resolved by visible-light photoredox catalysis, which can ensure the activation of O₂ under mild conditions and tame the reactive oxidative species to yield sulfoxide products.¹¹⁻¹³ To this end, the reaction has been successfully carried out in homogeneous photocatalysis systems using organic dye such as Rose Bengal and [Ru(bpy)₃]²⁺ complex,¹⁴⁻¹⁷ as well as heterogeneous photocatalysis systems using metal-organic framework, CdS and metal-free organic polymers.¹⁸⁻²⁴ With so many precedents, it is odd that the quintessential photocatalyst TiO₂²⁵⁻³² was not as successful as we expected in achieving the selective oxidation of sulfides.

The low success rate of TiO₂ could be attributed to the fact that typical sulfides like thioethers contain aliphatic side chains

can be fragmented in TiO₂ induced free radical process, therefore leading to sulfoxides in low selectivity. In some reported systems, protic solvents have been employed to prevent this undesired side reaction. However, this could not be extended to a TiO₂-based system because the high oxidation potential (2.7 eV for anatase) of UV-induced hole results in the oxidation of protic solvents rather than that of sulfides. In addition, the large bandgap (3.2 eV for anatase) determines that it could not absorb visible-light directly.

To surmount the innate lack of visible-light absorption and preserve the intrinsic high activity of TiO₂, the formation of a surface complex with organic substrates could be used to enable visible-light activity and construct selective photoredox catalytic processes.³³⁻⁴² In detail, the Lewis acid sites of TiO₂ interact with the lone pair of heteroatom such as N, O and S of the substrate to form a surface complex and extend the absorption edge of TiO₂. Thus no UV-induced holes were involved in the redox process. O₂ can be activated in a tightly controlled manner only with the presence of target substrate after the occurrence of this interaction. Furthermore, the conduction band of TiO₂ also facilitates the electron transfer to O₂. This approach not only enables visible-light, which is predominant in the solar spectrum, to be efficiently utilized, but also avoids UV-initiated side reactions, resulting in high selectivity of the desired product. Recently, we have successfully demonstrated this strategy through the synergistic photocatalytic oxidation of sulfides and amines with O₂ on TiO₂ under visible-light irradiation.⁴³ In the reaction system, the oxygenation of sulfides with O₂ was aided by the presence of primary benzylic amines.

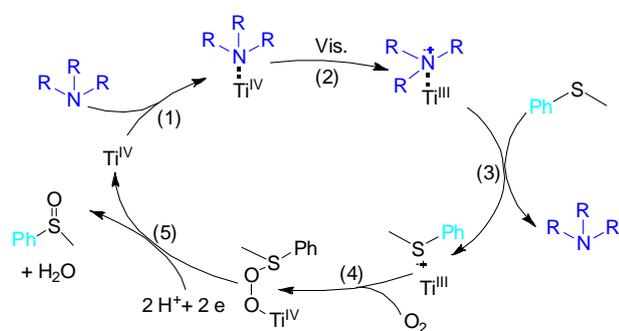
In the aforementioned system, the primary benzylic amines were also reacted, which could potentially complicate the separation of products and perplex the understanding the

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reaction mechanism. Because the participation benzylic amines further reaction bewilders the mechanistic understanding; and the relative large molecule makes the computational effort much more time-consuming. In contrast, tertiary amine will not undergo further condensation reaction, we hypothesized that non-benzylic aliphatic tertiary amine (tertiary amine) might be stable in the catalytic cycle to further mediate the oxidation of sulfides. Thus only a catalytic amount of tertiary amine would be needed to execute the oxidation process. Using a small molecular tertiary amine is also recommended in practice to facilitate the easy separation of catalyst and product. Not only that, if the tertiary amine remains intact at the end of the reaction, the in-depth understanding of the photochemical mechanism could be mapped out more precisely since no assumption is needed to figure out computationally plausible mechanism at as high a level of theory as practically possible. As a result, it is of interest to study the photoredox synergistic catalysis by TiO₂ and tertiary amine in the selective oxidation of sulfides with O₂.



Scheme 1. Proposed mechanism for the aerobic oxidation of thioanisole on TiO₂ with tertiary amine as redox mediator under visible-light irradiation

Trimethylamine (TMA) and triethylamine (TEA) are small molecular tertiary amines which are widely used as reductants in visible-light-induced reduction reactions.⁴⁴ They have also been used as model pollutants to investigate the TiO₂ photodegradation process.^{45,46} They are not considered stable under oxidation conditions, and thus are rarely used as co-catalysts in aerobic oxidations. The problem of instability of TMA or TEA can be circumvented by the reaction environment, such as the solvent used. The selection of nitrogen-containing molecule to enable visible-light photoredox reaction is quite reasonable considering that nitrogen-doping is the most successful method to sensitize TiO₂ to visible-light photocatalysis.⁴⁷ We should clarify that “surface adsorption” and “bulk doping” are totally different tactics to achieve visible-light activity. But the underpinning conclusions might be drawn from each other. Some even propose that “surface adsorption” as “*in-situ* doping”.⁴⁸ This is reinforced by the suggestion that the nature of nitrogen-doping might have originated from the formation of surface complex on the surface of TiO₂.⁴⁹ The hypothesized photoredox synergistic catalysis can be simply described in Scheme 1: (1) the tertiary

amine interacts with the Ti vacant sites on the surface of TiO₂ to form a visible-light absorbing surface complex; (2) single electron transfer from amine to conduction band of TiO₂ occurs under visible-light irradiation, leaving the hole localized on amine to form cationic free radical; (3) the amine cationic free radical is captured by sulfide to produce a sulfide cationic free radical, restoring the amine; (4) oxygen-atom transfer to sulfide, replenishing the Ti^{IV} state; and (5) further electron and proton transfers aided in the formation of product, which would leave the Ti site and thus complete the entire photoredox catalytic cycles.

Results and discussion

To confirm the aforementioned mechanism, the interaction between amine and TiO₂ (evidenced by XPS, Figure S1), which is crucial to the observed visible-light activity in Scheme 1, should be identified. We employed first-principles calculations based on density functional theory to investigate the absorption of amine on the Degussa P25 TiO₂ surface, which consists of 25% of rutile and 75% of anatase. For computational expediency, simulations were based on a model of the smaller TMA molecule on both the (110) surface of rutile and the (101) surface of anatase, which constitute the most stable surfaces for rutile and anatase TiO₂, respectively.^{50,51}

Table 1: The calculated adsorption energies E^{ad} (eV) of TMA on anatase (101) and rutile (110) surface

Surface	1 (O-2c)	2 (Ti-5c)	3 (O-3c)
Rutile (110)	-0.04	-0.43	-0.09
Anatase (101)	2.20	-0.28	-0.04

With the setup of the surface models (see supporting information for details), the adsorption of TMA can be calculated in a straightforward way. The adsorption energy E^{ad} was calculated according to the following equation:

$$E^{\text{ad}} = E^{(\text{TMA}/\text{slab})} - E^{(\text{slab})} - E^{(\text{TMA})}$$

where $E^{(\text{TMA}/\text{slab})}$, $E^{(\text{slab})}$ and $E^{(\text{TMA})}$ are the total energy of the slab with TMA, the slab, and TMA, respectively. Negative adsorption energy indicates that the TMA can be absorbed on the slab surface. We have examined three adsorption sites for TMA on rutile (110) and anatase (101) surfaces; **1** O-2c site, **2** Ti-5c site and **3** O-3c site (Figures 1a and 1b). The calculated adsorption energies are listed in Table 1. From the results in Table 1, we can see that the Ti-5c site of both surfaces (Figure S3) are more favorable for the adsorption of TMA molecule, which is in excellent agreement with step 1 proposed in Scheme 1. The adsorption energy of TMA on the **2** Ti-5c site of rutile (110) surface is -0.43 eV, which is smaller than that on the anatase (101) surface (-0.28 eV), indicating that the adsorption of TMA on rutile (110) is preferable to that on the anatase (101) surface. The distances from the N atoms to the nearest Ti atoms are 2.79 Å for the rutile (110) surface and 2.44 Å for the anatase (101) surface, respectively, indicating

that TMA is physically adsorbed on these two surfaces. The binding force between TMA and TiO_2 is Lewis base and acid interaction. Thus, the visible-light absorption of the surface complex is in a quite narrow range; and the desorption of TMA from the TiO_2 surface occurs easily. This result agrees well with step 3 proposed in Scheme 1 in which the N-centered cationic radical could be replaced by the S-centered cationic radical.

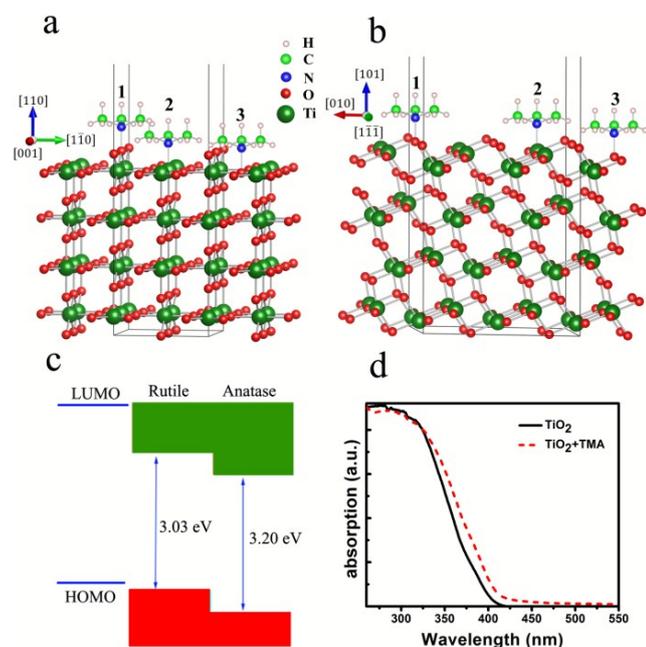


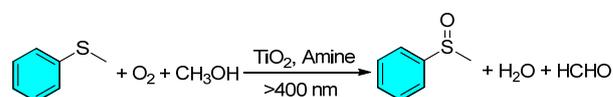
Figure 1. The formation of surface complex of TiO_2 and its implications. **a** and **b**, the possible adsorption sites of TMA on rutile (110) and anatase (101) surface of TiO_2 ; **c**, schematic (not to scale) of the band alignment of TMA on the surface of Degussa P25 TiO_2 ; **d**, UV-visible absorbance spectroscopy of Degussa P25 TiO_2 and complex of TMA and TiO_2 .

Based on the above calculation results, TMA should be localized on the surface of rutile TiO_2 . With the recent report on the band alignment between rutile and anatase in Degussa P25 TiO_2 ,⁵² the electron transfer between TMA and Degussa P25 TiO_2 can be described as in Figure 1c. In Degussa P25, rutile the valence band $E_{vb} = 2.31$ V (vs. NHE). With the adsorption of TMA, the band gap of rutile TiO_2 does not change, but calculations reveal an increase in electron density (Figure S4). However, the UV-visible absorption showed a redshift of about 10 nm (Figure 1d), suggesting a narrowing of the band gap by 0.08 V, which may have been too small to be reflected by the calculations. This suggests that the E_{HOMO} of the adsorbed TMA surface-complex is about 2.23 V (vs. NHE). The single electron oxidation potential of thioanisole in CH_3OH is 1.75 V (vs. NHE),⁵³ suggesting that the oxidation potentials have matched well to allow a smooth electron transfer process. Specifically, under visible-light irradiation, the electron at the HOMO of the adsorbed TMA will be excited, leaving the hole for the oxidation of thioanisole. Meanwhile, the excited electron will be injected into the conduction band of rutile, which will be further transferred to the conduction

band of anatase, and ultimately to electron acceptor, which can be either O_2 or the surface-bound peroxide in step 4 of Scheme 1.

To verify our hypothesis, we conducted the aerobic sulfide oxidation with a variety of small molecular amines with low boiling points, which would be easy to separate from the sulfoxide product. The experimental results are presented in Table 2. The conversion of thioanisole in CH_3OH was very low under visible-light irradiation (entry 1, Table 2). Interestingly, with the introduction of a catalytic amount (0.1 equiv.) of amine into the reaction system, the conversions of thioanisole were significantly boosted (entries 2-6, Table 2). Like in our previous report, primary amines can initiate the oxidation (entries 2-3, Table 2), and a decrease in the amount of amine leads to a decrease in the conversion of thioanisole (entry 7, Table 2). As expected, the tertiary amines TMA and TEA remained stable during the oxidation process, ensuring higher conversions of thioanisole (entries 5 and 6, Table 2). However, the installment of functional group in the side chain of TEA such as triethanolamine (TEOA) would make TEOA unstable in the reaction conditions. Fragmentation of TEOA dominates rather than performing the duty as a redox mediator, leading to a sharp decrease in the conversion of thioanisole (entry 8, Table 2). Thus, besides enhancing the visible-light activity, TEA plays a more significant role as a metal-free redox mediator in shuttling the oxidation of sulfide, which is analogous to how transition metal ions such as Ni^{2+} or Ru^{3+} act as redox shuttles in prompting photocatalytic reduction reaction.^{54, 55}

Table 2: The influence of amine on the selective aerobic oxidation of thioanisole under visible-light irradiation^[a]



Entry	Amine	Conv. (mol%) ^[b]	Select. (mol%) ^[b]
1	none	7	99
2	isopropylamine	30	98
3	butylamine	35	98
4	<i>tert</i> -butylamine	44	97
5	trimethylamine	50	97
6	triethylamine	58	96
7 ^[c]	<i>tert</i> -butylamine	28	97
8	triethanolamine	14	99

[a] Reaction conditions: 0.3 mmol of thioanisole, 0.03 mmol of amine additive, 40 mg of Degussa P25 TiO_2 , 300 W Xe lamp, 5 mL of CH_3OH , $\lambda > 400$ nm, 0.1 MPa of O_2 , 5 h. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of thioanisole, selectivity of methyl phenyl sulfoxide; [c] 0.015 mmol of amine.

To further prove the catalytic nature of amine, we varied the amount of TEA used in the reaction to study its effect on the selective aerobic oxidation thioanisole on TiO_2 under

visible-light irradiation in more details. And the results are summarized in Table 3. We discovered that the decreasing the amounts to TEA lead to a drop in conversion to some extent (entries 1 and 2, Table 3) in comparison with the starting result (entry 3, Table 3). Increasing TEA did not lead to an apparent increase in conversion (entries 4 and 5, Table 3). These combined results prove that TEA truly acts as a redox catalyst to aid in the photoredox process. It would be more convincing if we detect TEA free radical cation proposed in Scheme 1. However, only time-resolved electron spin resonance spectroscopy can perform this task due the fleeting nature of this free radical,⁵⁶ which is unfortunately beyond our instrumental capacity but needs special attention in the future investigation in this direction.

Table 3: The effect of the amount of TEA on the photocatalytic oxidation of thioanisole on TiO₂ under visible-light irradiation^[a]

Entry	Amount of TEA (mmol)	$n_{\text{substrate}}/n_{\text{TEA}}$	Conv. (mol%) ^[b]	Select. (mol%) ^[b]
1	0.01	30	43	98
2	0.015	20	49	97
3	0.03	10	58	96
4	0.3	1	59	96
5	0.6	0.5	62	95

[a] Reaction conditions: 0.3 mmol of thioanisole, 0.1 MPa of O₂, 40 mg of Degussa P25 TiO₂, 300 W Xe lamp, 5 mL of methanol, 5 h, $\lambda > 400$ nm. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of thioanisole, selectivity of methyl phenyl sulfoxide.

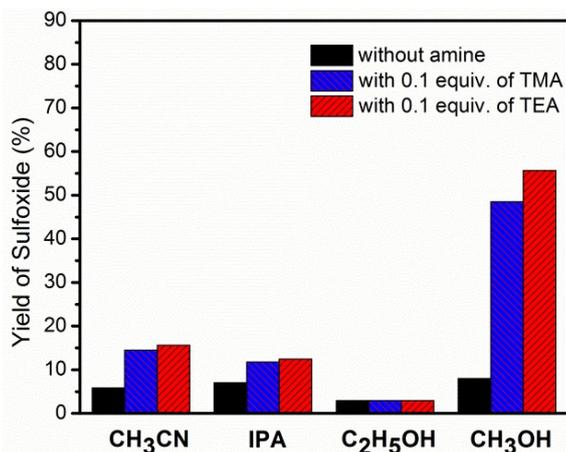
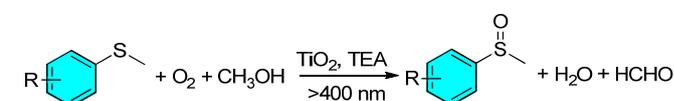


Figure 2. The influence of solvent on the visible-light-induced selective oxidation of thioanisole with O₂ on TiO₂ in the presence tertiary amine (TMA or TEA).

As previously stated, TMA or TEA are not stable molecules under typical photocatalytic aerobic oxidation conditions. However, they may be able to act as a redox mediator for the oxidation of thioanisole on TiO₂ under

visible-light irradiation due to protection by the reaction medium, CH₃OH. Moreover, the protons from CH₃OH would aid in the formation of sulfoxide and regeneration of the TiO₂ surface. To confirm this hypothesis, CH₃CN, one widely commonly used solvent in photoredox catalysis, and other protic solvents were investigated in the formation of sulfoxide, which was summarized in Figure 2. We can see that TMA and TEA can initiate the formation of sulfoxide in most of the tested solvents. However, the amine molecules were either partially (in the case of IPA and C₂H₅OH) or completely (in the case of CH₃CN) consumed during the oxidation process. The protic nature of CH₃OH is also stronger than that of IPA or C₂H₅OH, which aids in the formation of the product. The combination of these two factors enables CH₃OH to confer the best result in Figure 2.

Table 4: Visible-light-induced oxidation of sulfides into sulfoxide with O₂ on TiO₂ with TEA as redox mediator^[a]



Entry	Substrate	Product	T (h)	Conv. (mol%) ^[b]	Select. (mol%) ^[b]
1 ^[c]			22	81	93
2			10	84	92
3			10	85	93
4			10	82	95
5			10	81	98
6			10	76	95
7			12	81	88
8			12	84	86
9			12	86	85
10			12	33	92
11 ^[d]			12	62	79
12			12	77	88
13			12	50	80

[a] Reaction conditions: 0.3 mmol of sulfide, 0.03 mmol of TEA, 40 mg of Degussa P25 TiO₂, 300 W Xe lamp, 5 mL of CH₃OH, $\lambda > 400$ nm, 0.1 MPa of O₂. [b] Determined by GC-FID using chlorobenzene as the internal standard conversion of sulfide, selectivity of the corresponding sulfoxide. [c] 0.6 mmol of thioanisole, 0.015 mmol of TEA. [d] 0.1 mmol of TEA.

We have established that the interaction of TEA and TiO₂ induces the visible-light activity and further mediates the selective oxidation of sulfide into sulfoxide with O₂. The choice of solvent, CH₃OH, keeps TEA stable and ensures the selective and smooth formation of sulfoxide. Having obtained the optimal conditions for visible-light-induced photocatalytic aerobic oxidation, we proceeded to explore the scope of the sulfide substrates in Table 4. The stability of TEA in the photocatalytic system is reflected by the turn over number of 32 for the oxidation of thioanisole (entry 1, Table 4) with 78% of TEA preserved. To our delight, we found that thioanisole and substituted thioanisole could be conveniently transformed into corresponding sulfoxide with high selectivities (entries 2-9, Table 4). More than 90% of TEA could be recovered after the reaction in all cases. The substituted groups did not influence the results significantly in terms of reaction time and selectivity. However, it should be noted that the reaction time is slightly shorter and the selectivities are slightly higher for electron donating group substituted thioanisoles (entries 3-6, Table 3) than that of electron withdrawing groups substituted thioanisoles (entries 7-10, Table 4). Very strong electron withdrawing groups, such as -NO₂, could make the reaction rate even slower (entry 10, Table 4). The -NO₂ group could also undermine the stability of TEA in the reaction medium. However, increasing the amount of TEA could yield a high conversion of sulfide (entry 11, Table 4). Meanwhile, replacing the methyl group to ethyl in thioanisole showed minor impact on the conversion of sulfide (entry 12, Table 4). This is surprising as the photocatalytic aerobic oxidation of aliphatic substrates on TiO₂ tended to yield undesirable selectivities due to the radical nature of reaction process. In our reaction system, the solvent CH₃OH could tame the uncontrollable aliphatic chain reaction, thus ensuring high selectivity. When the methyl group of thioanisole was replaced by phenyl group, a significant decrease in conversion was observed (entry 13, Table 4), and a much longer reaction was required to obtain a conversion comparable to that of thioanisole.

Conclusions

In conclusion, through the photoredox synergistic catalysis of TiO₂ and TEA, the visible-light-induced selective oxidation of sulfide into sulfoxide with O₂ was successfully conducted in CH₃OH. The interaction between TiO₂ and TEA gives rise to the visible-light activity in the reaction system. Computational calculations have also revealed that TEA adsorbs more favourably on the rutile surface. TEA acts as a redox mediator for the oxidation of sulfoxide, by donating electrons to the conduction band of rutile, via which to the conduction band of anatase, ultimately to the final electron acceptor. Apart from its importance in synthesis, this finding could have implications in our understanding of the unique robust photocatalytic activity of Degussa P25 TiO₂. However, we should admit that very limited visible-light was captured in the current system. Longer wavelength light ($\lambda > 420$ nm and $\lambda > 450$ nm) should also be used for reaction. We anticipate this could be achieved by anchoring dye molecule on TiO₂ with a TEA-like redox

mediator channelling the electron flow. Guided by the general strategy of photoredox synergistic catalysis, more versatile and complicated visible-light-induced organic transformations could be envisioned through adopting the surface of metal oxides as the reaction podium.

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