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Improving the visible light photocatalytic aerobic oxidation of sulfides into sulfoxides on dye-sensitized TiO₂

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Abstract: Visible light-driven interfacial redox reactions during dye-sensitized TiO₂ are essential to meet the energy and environmental challenges in the form of dye-sensitized solar cell and sensitized degradation of organic pollutants. Inspired by these prior successes, it is conceivable that the underlying principles of these processes can guide us to construct selective chemical transformations in which the control of selectivity is in higher demand. We attempt to improve the selectivity for sulfoxides during the visible light-driven selective aerobic oxidation of sulfides in the merger of dye-sensitized TiO₂ photocatalysis with TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] catalysis. Thus, different factors like the TEMPO and its derivatives, initial O₂ pressures, initial sulfide concentrations, solvents, light-emitting diodes (LED) and TiO₂ were examined to

identify the critical factor for selectivity improvement. It was found that an easily synthesized anatase TiO₂, sensitized by 0.33 mol% of alizarin red S, was significant in improving the selectivity for sulfoxides at high conversions of sulfides with the aid of 2 mol% of TEMPO as a redox mediator under blue LED irradiation. This work suggests that the engineering of the TiO₂ materials can be a viable solution in improving the selectivity of visible light-driven chemical transformations by dye-sensitized TiO₂ photocatalysis.

Introduction

Oxidative organic reactions are at the core of many important chemical processes for the synthesis of fine chemicals, pharmaceuticals and industrial commodities ^[1]. In many practical oxidation processes, toxic oxidants were needed to carry out the reactions; and resultantly large quantities of undesired side products were produced, leading to undesired environmental and ecological impacts ^[2]. Moreover, many industrial oxidation reactions are energy intensive due to high operating pressure and temperature. Therefore, the operational conditions for these useful reactions are under close scrutiny because sustainable development is becoming increasingly important ^[3]. Designing innovative paradigm for selective oxidation of organic compounds becomes a subject of considerable research effort ^[4], which in turn could enlighten our understanding on detailed redox processes in addressing either environmental or energy related problems. It would be very rewarding to uncover an oxidative reaction pathway in a controlled manner yet without burdening its high redox efficiency.

To this end, one should consider the following criteria in designing a oxidative organic reaction: (1) clean oxidants like O₂ should be preferred with innocuous water as the by-product; (2) renewable energy should be favoured as a driver for the reaction; (3) inexpensive reaction

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vessel should be applied as the reaction environment; (4) the selectivity for the desired product should be improved. These criteria could resolve many oxidation related issues in a concerted fashion. Usually occurring at room temperature with atmosphere O₂ as the terminal oxidant, TiO₂ photocatalysis can meet the majority of these above criteria with the exception of selectivity factor. Under UV light irradiation, a plethora of reactive oxygen species (ROS) can be generated at both the conduction band and valence band of TiO₂ during the interfacial reduction of O₂ or the oxidation of H₂O and organic compounds ^[5].

In effect, these ROS are quite useful in mediating the degradation of toxic organic compound with O₂ on the surface of TiO₂ under UV light irradiation, one of the most wellestablished applications of TiO₂ photocatalysis. Fluctuations in the composition of ROS often lead to activity and selectivity variations in TiO₂ photocatalyst ^[6]. One can curtail the number and velocity of ROS that got involved in the photocatalytic system to get desirable results. In circumventing these issues, visible light photocatalysis derived from TiO₂ turns out to be a viable alternative. Visible light photocatalysis provides safety, robustness and environmental friendliness necessary for enabling chemical transformations in biocompatible conditions ^[7], emerging as an attractive method in performing selective oxidation reaction. In this context, we recently demonstrated the potential of visible light photocatalysis of dye-sensitized TiO₂ for selective aerobic oxidation of alcohols ^[8] and amines ^[9] in which the ROS generated at the valance band of TiO₂ were completely switched off, leading to high selectivities for the desired products of the corresponding carbonyl compounds and imines at very high conversions of benzyl alcohols and amines.

The selective oxidation of sulfides into sulfoxides with O₂ is one of very important chemical transformations ^[10] because it produces biologically active molecules that have wide

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applications in bio-related platforms. We discovered that the same system of dye-sensitized TiO₂ photocatalysis can also be applicable for the oxidation of sulfides into sulfoxides with O₂ as the terminal oxidant ^[11]. However, the selectivity for the desired sulfoxides dropped along with the increase of the conversions of sulfides. The decrease of selectivity towards the end of an organic reaction seems trivial. But eventually this leads to very unintended negative consequences, because the separation of the products from substrates and side products requires tedious workup procedures ^[12].

Recently, it was reported that the electronic properties of TiO₂ can determine the selectivity for the photocatalytic aerobic oxidation of toluene ^[13]. Meanwhile, home prepared TiO₂ can enhance the selective photocatalytic aerobic oxidation of benzyl alcohols ^[14]. These previous successes can offer valuable insights for improving the selectivity for sulfoxides by TiO₂ photocatalysis. In this regime of cooperative photocatalysis ^[15] of dye-sensitized TiO₂ with TEMPO, the surface of TiO₂ was covered with a selected dye; and electron transfer was mediated by TEMPO. At first, we did not expect the properties of TiO₂ can impact the result on product selectivity of sulfoxides for visible light-driven aerobic oxidation of sulfides. To our surprise, we found that the synthesized new TiO₂ sensitized by alizarin red S (ARS) can improve the selectivity for sulfoxides, suggesting the intriguing interfacial reaction network of ROS and the formation of products.

Results and discussion

In dye-sensitized TiO₂ photocatalysis for the visible light-driven selective aerobic oxidation of organic compounds, ARS was proven as one of the most resilient and efficient sensitizers based on previous report ^[11, 16]. In this work, we would not take ARS into consideration

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to improve the selectivity for sulfoxides in this regime of cooperative photocatalysis. However, the other factors would be thoroughly investigated to achieve the desirable target. In our previous report ^[11], we selected a commercial anatase TiO₂ to construct ARS-sensitized TiO₂ photocatalysis for the selective oxidation of sulfides with pressured pure O₂ of 0.1 MPa as the oxidant. The conversions of sulfides were quite good in several hours. However, towards the end of the reaction, the formed sulfoxides could be further oxidized into sulfone, resulting in lower selectivities. Thus, in that report, we could only achieve nearly 90% of selectivities at around 80% of conversions. This is an unsettled issue, prompting us to begin the current investigation.

To further prove the robustness of ARS in ARS-sensitized TiO₂, we lowered the amount of ARS to 0.33 mol% and concentration of substrate to 0.3 mol/L in performing the selective oxidation of sulfides with atmosphere O₂ under blue LED irradiation (entry 1a, Table 1). As expected, when the conversion of thioanisole was 95%, the selectivity for methyl phenyl sulfoxide dropped to 82%. Beforehand, we did not think TiO₂ can improve the selectivity for sulfoxide because it was extensively covered with dye ARS. This view was shattered when we used the benchmark photocatalyst Aeroxide P25 TiO₂ to prepare the ARS-TiO₂ photocatalyst to carry out the same visible light-driven aerobic oxidation of thioanisole. Despite the fact that 4 times of reaction time was needed, about 9% increase of selectivity for methyl phenyl sulfoxide was achieved as almost the same level of conversion (entry 1b, Table 1), suggesting the engineering of TiO₂ materials can be breakthroughs to improved selectivity.

But one cannot develop a photocatalytic system at the expanse of efficiency. Thus, we synthesized new anatase TiO_2 at room temperature to conduct the same aerobic oxidation of thioanisoles. About 10% increase of selectivity for sulfoxide was achieved at 96% conversion of thioanisole with slight longer reaction time of 1.3 h (entry 1c, Table 1). Based on PXRD result

(Figure S1), we can see that this new TiO_2 is of anatase phase with low crystallinity, which might contribute to the higher selectivity.

Table 1: The influence of TiO₂ on selectivity for sulfoxides in the oxidation of sulfides with air in the merger of visible light photocatalysis of ARS-TiO₂ with TEMPO catalysis ^[a]

$R \xrightarrow{\text{S}} + O_2 \xrightarrow{\text{ARS-TiO}_2, 2 \text{ mol}\% \text{ TEMPO}}_{\text{CH}_3\text{OH, blue LEDs}} \xrightarrow{\text{O}_{\text{H}}}_{\text{R}} \xrightarrow{\text{O}_{\text{H}}}_{\text{S}} + H_2\text{O}$							
Entry	Substrate	Product	TiO ₂	T [h]	Conv.[%] ^[b]	Sel.[%] ^[b]	
la	€ S S	S S	ST-01	1.0	95	82	
1b	C) ^S	O S S	P25	4.0	93	91	
1c	() ^{\$}		New TiO ₂	1.3	96	92	
2a	Meo	Meo	ST-01	0.7	95	86	
2b	Meo	Meo	P25	2.6	96	90	
2c	Meo	MeO	New TiO ₂	0.7	94	95	
3a	Br	Br	ST-01	1.0	90	76	
3b	Br	Br	P25	3.5	78	88	
3c	Br	Br	New TiO ₂	1.7	87	89	

[[]a] Reaction conditions: sulfide (0.3 mmol), ARS-TiO₂ (40.1 mg, containing 1×10^{-3} mmol ARS), TEMPO (0.006 mmol), 1 atm air, CH₃OH (1 mL), blue LED irradiation (3 W × 4). [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of sulfide, selectivity of sulfoxide.

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After obtaining these good results, we next verified whether it can be applied in the oxidation of other types of thioanisoles, achieving similar degree of success. The ARS-TiO₂ photocatalyst based on P25 TiO₂ (Figure S2) was used to this extension as well for comparative analysis. The results were summarized in Table 1. One can conclude that for ARS-TiO₂ (P25) always requires about 4 times of reaction times to achieve same level of conversion as that of ARS-TiO₂ (ST-01) (entries 1a, 2a and 3a *vs*. 1b, 2b and 3b, Table 1). And the photocatalytic activity of ARS-TiO₂ (new) only needs slight longer reaction time, with magnitude about 10% of increase of selectivity for sulfoxides (entries 1a, 2a and 3a *vs*. 1c, 2c and 3c, Table 1). Quite recently, anatase TiO₂ octahedrons with exposed high-index {102} was used to construct ARS-TiO₂ for the photocatalytic aerobic oxidation of sulfides in which exposed high-index facets and hollow structure was attributed to improved activity, demonstrating the potential of engineering of TiO₂ materials in improving the systems of dye-sensitized TiO₂ photocatalysis.

Since TiO₂ materials play an important role in determining both the selectivities and conversions for the visible light-driven aerobic oxidation of sulfide. Thus, we performed experiments to synthesize several ARS-TiO₂ photocatalysts with same amount of ARS and varied amounts of new TiO₂. The obtained photocatalysts were used to carry out the visible light-driven aerobic oxidation of thioanisole. We thought that the amounts of TiO₂ might have further impact on the selectivity for sulfoxide. Our considerations for the rational design of these experiments are that ARS can be chemically adsorbed onto TiO₂ but differed in the amount of TiO₂, resulting in different coverage of the surface of TiO₂. These difference in coverage of TiO₂ by ARS might give rise to varied selectivity due to differed interfacial redox reaction pathways. However, we found that the amount of TiO₂ as 80 mg, 60 mg, 40 mg and 20 mg does not influence selectivities which

were around 95% for methyl phenyl sulfoxide but conversions decreased with reducing the amounts of TiO₂ to be as 81%, 75%, 68% and 63% respectively.

Solvents are used pervasively in studies of visible light-driven selective aerobic oxidation of sulfides to enhance selectivities for sulfoxide and kinetics for conversions of sulfide. Thus, we took a survey of literature reports on this particular subject and submitted their preferred solvent to the merger of dye-sensitized TiO₂ with TEMPO to evaluate whether the selectivities could be further improved to let solvent take some control over the reaction outcome. For porous organic photocatalysts like C₃N₄ ^[17] or carbazolic conjugated polymer ^[18], CH₃CN was selected as a solvent; for Pt/BiVO₄ photocatalyst ^[19], a mixture of CH₃CN/H₂O (2:1) was chosen as the reaction medium; for a flavin photocatalyst ^[20], ethanol/water (95:5, *v/v*) was adopted as the medium; for Rose Bengal or immobilized Rose Bengal photocatalysts including CdS/C₃N₄ ^[22], TiO₂ ^[10], boron-dipyrromethene (BODIPY) dyes ^[23], thioxanthone ^[24] and metal organic framework ^[25], CH₃OH was utilized as the reaction medium. Except in the case of CH₃CN, the other reaction mediums were containing protic solvent in one form or another, necessitated by protons in aiding the formation of sulfoxides.

According to the results in Table 2, the reaction performed well in CH₃OH (entry 1, Table 2). However, CH₃CN was not suitable to be a solvent in our present system in terms of both conversion and selectivity (entry 2, Table 2). With a mixture of CH₃CN/H₂O (2/1, v/v), the conversion of thioanisole deteriorated significantly (entry 3, Table 2). When adding HCl to ethanol, color change was observed for ARS-TiO₂ photocatalyst due to the change of absorption of ARS in different pH values. Even though the conversion of thioanisole dropped, the selectivity of sulfoxide is excellent (entry 5, Table 2), affirming the indispensable role of protons in the

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formation of sulfoxide. Since H₂O is the most protic amongst common solvents. Adding some amount of it into ethanol can result in conversion and selectivity (entry 5, Table 2) comparable to that in CH₃OH (entry 1, Table 2).

Table 2: The influence of solvent on the selective oxidation of thioanisole with air in the merger of visible light photocatalysis of ARS-TiO₂ with TEMPO catalysis

Entry	Solvent	Conv.[%]	Sel.[%]
1	CH ₃ OH	68	96
2	CH ₃ CN	16	88
3	CH ₃ CN/H ₂ O (2/1, <i>v</i> / <i>v</i>)	3	99
4	C ₂ H ₅ OH (0.05 mol/L HCl)	41	99
5	C ₂ H ₅ OH/H ₂ O (95:5, <i>v/v</i>)	63	96

[a] Reaction conditions: thioanisole (0.3 mmol), ARS-TiO₂ (40.1 mg, containing 1×10^{-3} mmol ARS), TEMPO (0.006 mmol), 1 atm of air, CH₃OH (1 mL), blue LED irradiation (3 W × 4), 40 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of thioanisole, selectivity of methyl phenyl sulfoxide.

In response to the growing importance of photocatalysis and organocatalytic in chemical transformations, the merger of visible light photocatalysis with TEMPO catalysis has produced very exciting results in implementing chemical transformation ^[26]. One unique advantage of TEMPO is its tunability in oxidation potentials and electron transfer capability. We selected a series of 4-substituted derivatives of TEMPO (Figure 1) to figure out whether these redox mediators can further improve the photocatalytic oxidation of sulfide by ARS-sensitized TiO₂ photocatalysis apart from the two factors like TiO₂ materials and protic solvent in improving the selectivity for sulfoxide.



Figure 1: The molecular structures of TEMPO and its derivatives

Table 3: The influence of TEMPO derivatives on the selective oxidation of thioanisole with air in the visible light photocatalysis of ARS-TiO₂ ^[a]

Entry	TEMPO or derivatives	Conv.[%]	Sel.[%]
1	ТЕМРО	68	96
2	HO-TEMPO	64	97
3	CH ₃ O-TEMPO	61	97
4	Oxo-TEMPO	22	98
5	NH ₂ -TEMPO	68	96
6	CH ₃ CONH-TEMPO	67	97
7	PhCOO-TEMPO	60	97

[a] Reaction conditions: thioanisole (0.3 mmol), ARS-TiO₂ (40.1 mg, containing 1×10^{-3} mmol ARS), TEMPO or derivatives (0.006 mmol), 1 atm of air, CH₃OH (1 mL), blue LED irradiation (3 W × 4), 40 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of thioanisole, selectivity of methyl phenyl sulfoxide.

TEMPO is a organocatalyst that can be commonly used in mediating the oxidation of alcohols and amines with O₂ ^[27]. But it is not so common to applying TEMPO into the aerobic oxidation of sulfides. Only several reports were found and reported quite recently ^[11, 28]. TEMPO

and its 4-substituted derivatives can all be commercially procured to test their influence on the visible light-driven aerobic oxidation of thioanisole (Table 3). From these results we can conclude that TEMPO is one of the best redox mediator that gave one of the best conversion of sulfide. And 4-substituted derivatives of TEMPO show only comparable conversions and improvement of selectivies cannot be observed in the present study (entries 2-7, Table 3). Notably, CH₃CONH-TEMPO was reported as an efficient co-catalyst for oxidation of alcohols in catalytic systems ^[29] or oxidative functionalization of alcohols in photocatalytic system ^[30]. However, the activity CH₃CONH-TEMPO (entry 6, Table 3) was only comparable with that of TEMPO.

Table 4: The influence of the amount of TEMPO on the selective oxidation of thioanisole with air in the merger of visible light photocatalysis of ARS-TiO₂ with TEMPO catalysis ^[a]

Entry	TEMPO [µmol]	Conv.[%] ^[b]	Sel.[%] ^[b]
1	0	33	98
2	3	63	96
3	6	68	96
4	9	67	96
5	12	66	96
6	15	65	96
7	18	65	96

[a] Reaction conditions: thioanisole (0.3 mmol), ARS-TiO₂ (40.1 mg, containing 1×10^{-3} mmol ARS), 1 atm of air, CH₃OH (1 mL), blue LED irradiation (3 W × 4), 40 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of thioanisole, selectivity of methyl phenyl sulfoxide.

We arrived at a conclusion that TEMPO itself was the best co-catalyst in terms of selectivity for the visible light-driven aerobic oxidation of thioanisole by ARS-sensitized TiO₂

photocatalysis. Next, more thorough studies were carried on to decide the amount of TEMPO on the selective photocatalytic aerobic oxidation (Table 4). With the synergistic effect of new TiO₂ and CH₃OH, the selectivity is very good even without the presence of TEMPO (entry 1, Table 4). But significant increase of conversion was achieved after adding 1mol% of TEMPO (entry 2, Table 4). These results accord well with the results in Table 3 in which TEMPO derivatives do not influence the selectivity for sulfoxide but have direct effect on conversion of sulfide. Nevertheless, the benefit of further increase of TEMPO amounts do not appear (from entry 3 to entry 7, Table 4). Thus, a redox mediator is an accurate description of the role of TEMPO in the system of cooperative photocatalysis.

Table 5: The influence of initial O₂ pressure on the selective oxidation of thioanisole in the merger of visible light photocatalysis of ARS-TiO₂ with TEMPO catalysis ^[a]

Entry	Initial O ₂ pressure [atm]	Conv.[%]	Sel.[%]
1	0.2	68	96
2	0.5	80	94
3	1.0	88	93
4	1.5	88	93
5	2.0	87	93
6	2.5	87	93

[a] Reaction conditions: thioanisole (0.3 mmol), ARS-TiO₂ (40.1 mg, containing 1×10^{-3} mmol of ARS), TEMPO (0.006 mmol), CH₃OH (1 mL), blue LED irradiation (3 W × 4), 40 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of thioanisole, selectivity of methyl phenyl sulfoxide.

In photo-induced interfacial events at TiO₂, the time scale of electron transfers from conduction band electron (e_{cb} ⁻) to O₂ is about 10-100 µs ^[31], much longer than other redox events.

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Thus, prompting the efficient electron transfer from e_{cb} to O_2 is crucial in improving the overall dye-sensitized photocatalytic efficiency in which the valence band holes induced events are irrelevant. More importantly, the consequential superoxide radical (O_2^{-1}) is active in participating in the formation of sulfoxide which might have some leverage on the selectivity for the sulfoxide. Therefore, we studied the impact of initial O_2 pressure on the visible light-driven aerobic oxidation of thioanisole (Table 5). The selective photocatalytic aerobic oxidation proceeds smoothly with atmosphere O_2 as the oxidant (entry 1, Table 5). With the elevation of initial O_2 pressures, the conversion of thioanisole increases without influencing the selectivity for sulfoxide (entries 2-3, Table 5). This momentum lost with the further increase of initial O_2 pressures to the limit of our common glass apparatus of 2.5 atm (entries 4-6, Table 5), suggesting the elevation of O_2 pressure in prompting the e_{cb}^- transfer might not be a wise option in the dye-sensitized TiO₂ photocatalysis.

According to conventional wisdom, a photochemical reaction should be carried out under a diluted solution to ensure a high efficiency ^[32]. Moreover, ARS in ARS-TiO₂ preferred a diluted condition to avoid the aggregation-caused weakening or quenching of fluorescence of ARS at high concentrations. Whilst the fluorescence property of a dye is proportional to its photocatalytic activity. Most of the reported photocatalytic systems based on TiO₂ were applied in dealing with organic pollutants in very diluted conditions. This might not be a critical issue in aqueous condition. This turns out to be an issue of major concern because most photocatalytic chemical transformations are performed in organic solvent. In this manner, large amount of organic solvent is used which is disadvantageous in terms of environmental impact. We carried out the reaction at a very high concentration of thioanisole (0.30 mol/L) in CH₃OH for the photocatalytic oxidation (68% conversion, 96% selectivity, 40 min). Based on the reasons listed above, we would envision that diluting the photocatalytic systems with increase the amount of CH₃OH would improve the

visible light-driven oxidation of thioanisole. Against the conventional wisdoms, it was discovered that conversions of thioanisole decrease to be 53%, 44%, 38%, 33% respectively with the dilutions of thioanisole as 0.15 mol/L, 0.10 mol/L, 0.075 mol/L and 0.06 mol/L with slight variations of selectivities for methyl phenyl sulfide from 96% to 99%. It should mention that this phenomenon is substrate-dependent. In our previous report, in the merger of eosin Y-sensitized TiO₂ with TEMPO for visible light-driven selective oxidation of alcohols, the dilution of alcohol can have positive effect with quite similar experimental setup ^[8a], differing from the present work. We cannot fully understand the characteristics underpinning this phenomenon at this stage. But it was an unexpectedly good result in terms of environmental friendliness of the present system.

 Table 6: The influence of different LED on the selective oxidation of thioanisole with air in the

 merger of visible light photocatalysis of ARS-TiO2 with TEMPO catalysis ^[a]

Entry	LED	$\lambda_{max} \ [nm]$	Conv.[%] ^[b]	Sel.[%] ^[b]
1	Blue	460	68	96
2	Green	510	55	97
3	Yellow	590	22	>99
4	Red	630	15	>99
5	Violet	400	45	97
6	White	Continuous	41	97

[a] Reaction conditions: thioanisole (0.3 mmol), ARS-TiO₂ (40.1 mg, containing 1×10^{-3} mmol ARS), TEMPO (0.006 mmol), 1 atm of air, CH₃OH (1 mL), LED irradiation (3 W × 4), 40 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of thioanisole, selectivity of methyl phenyl sulfoxide.

After the consideration of the above internal factors of photocatalysis, we take one important external factor into account for the sake of further improving selectivity for sulfoxide.

One technological breakthrough is the invention and dissemination of inexpensive LED ^[33], emitting high-energy light at certain wavelengths that can be used for dye-sensitized TiO₂ photocatalysis. For visible light LED, there are emitting three-primary colors, i.e. red, green and blue. LED emitting other colors are synthesized from these three-primary colors. Blue LED is quite powerful in driving the selective aerobic oxidation of thioanisole (entry 1, Table 6). With the increase of maximum emitting wavelengths, the conversions decreased (from entry 2 to entry 4, Table 6). We also considered a more powerful 400 nm LED to drive this oxidation reaction with lower conversion of 45% (entry 5, Table 6). The might ascribe to this range is near to the absorption edge of TiO₂ that leads to the partial oxidation of solvent CH₃OH and slows down the oxidation of substrate thioanisole. Meanwhile, white LED, whose spectrum contains peaks the same as the blue ones, can also be suitable as a driver for this oxidation reaction (entry 6, Table 6).



Figure 2: The correlation between photocatalyst and light sources, (a) the UV-visible light absorbance of TiO₂, ARS and ARS-TiO₂; (b) the relative spectrum distribution of blue LED

For a photochemical reaction, the light absorption and consequential photo-induced redox reactions are interrelated. Thus, we want to establish relationship between the visible light absorption of the photocatalyst and the applied light sources (Figure 2). TiO₂ is a photocatalyst

that does not absorb visible light (TiO₂, Figure 2a); and the visible light absorbance of ARS-TiO₂ was caused by the sensitizer ARS (ARS, Figure 2a). Moreover, there is red-shift of absorbance (ARS-TiO₂) due to the interaction catechol motifs of ARS and TiO₂. In this fashion, large amount of light of visible range could be captured by be ARS-TiO₂. This property underpins the results of Table 6 in which different LED can be used to perform the reaction. There is very large overlap between the absorbance of ARS-TiO₂ and the relative spectrum distribution of blue LED. One can envision that green LED might be a better light sources because there are more overlap between green LED ^[8b] and the absorbance of ARS-TiO₂. This should be the case if the output energy of green and blue LED were near to each other. However, in this case, the output energy of blue radiation energy is about twice to that of green LED. The technological side of blue LED caused higher conversion of thioanisole.



Figure 3: Control experiments for the selective oxidation of thioanisole in the merger of visible light photocatalysis of ARS-TiO₂ with TEMPO catalysis. **a**, blank reaction; **b**, TiO₂ only; **c**, ARS only; **d**, TEMPO only; **e**, without ARS; **f**, without TiO₂; **g** without TEMPO; **h**, standard conditions;

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i, without blue LED irradiation; **j**, without O₂; **k**, adding 0.5 equiv. of DABCO (1,4diazabicyclo[2.2.2]octane); **l**, adding 0.5 equiv. of *p*-BQ (*p*-benzoquinone). Reaction conditions: of thioanisole (0.3 mmol), ARS-TiO₂ (40.1 mg, containing 1×10^{-3} mmol ARS), TEMPO (0.006 mmol), 1 atm of air, CH₃OH (1 mL), blue LED irradiation (3 W × 4), 40 min, yield of methyl phenyl sulfoxide was determined by GC-FID.

In order to gain more insights on the reaction mechanism, we further carried out a series of control experiments. Since thioanisole cannot absorb light of visible range in CH₃OH ^[10a], no reaction was observed under blank reaction (Figure 3, **a**), suggesting the importance of photocatalytic components. There are three constituted components namely, ARS, TiO₂ and TEMPO in this regime of cooperative photocatalysis. We can find that none of the three constituted components can independently carry out the photocatalytic reactions (Figure 3, **b-d**). Next, we excluded one component out of the three to further verify the essential reaction factors. With the absence either ARS or TiO₂, the visible light photocatalytic reactions almost stopped (Figure 3, **e** and **f**), indicating these two components underpins the photochemical reaction. Without TEMPO, the selective oxidation of thioanisole can still be carried on (Figure 3, **g**), implying TEMPO is not an essential part of the photochemical reaction.

The standard condition result reinforces that the catalysis of TEMPO can significantly improve the outcome (Figure 3, **h**) in a cooperative catalytic manner. Without blue LED irradiation, there is almost no yield of sulfoxide (Figure 3, **i**), affirming the photocatalytic nature of the reaction. Several further control experiments were performed to establish the nature of ROS in this reaction regime. With the reaction atmosphere was filled with N₂ rather than air, the reaction ceased to proceed (Figure 3, **j**). When we added 1 equiv. of DABCO, a trap of singlet oxygen, into the reaction system, there is some drop in the yield of sulfoxide (Figure 3, **k**). We attributed this drop

of yield phenomena to the competitive oxidation of DABCO and thioanisole, demonstrating energy transfer is not the deciding factor in formation of this product. However, further experiment is needed to prove this point. Furthermore, we added 0.5 equiv. of *p*-BQ to act as a scavenger for O_2^{-} . It was found that the formation of sulfoxide disappeared after adding *p*-BQ (Figure 3, I), revealing O_2^{-} is indispensable ROS in the photocatalytic reaction.



Figure 4: Reaction kinetics plots for the selective oxidation of thioanisole with air in the merger of visible light photocatalysis of ARS-TiO₂ with TEMPO catalysis (**a**) in 1 mL of CH₃OH; (**b**) in 1 mL of CD₃OD. Reaction conditions: thioanisole (0.3 mmol), ARS-TiO₂ (40.1 mg, containing 1×10^{-3} mmol ARS), TEMPO (0.006 mmol), 1 atm of air, blue LED irradiation (3 W × 4). Taking a sample at regular intervals of 10 minutes and concentration of thioanisole was determined by GC-FID.

After gaining some mechanistic understanding based on control experiments, we made further efforts in kinetics studies to get more insights on the detailed reaction processes. We first establish the relation between conversions of thioanisole and selectivity for sulfoxide (Figure S5). Although the selectivity for sulfoxide have been apparently improved compared with our previous report, there are some sulfone formed if one wants to achieve 100% conversion of thioanisole,

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leaving room for future improvement. The kinetics plot follows C=C₀-kt for the photocatalytic aerobic oxidation of thioanisole (Figure 4, **a**). A zero-order reaction relationship was established, suggesting that the oxidation reaction rate does not dependent on the concentration of thioanisole. Next, we carried out the reaction using CD₃OD as the solvent (Figure 4, **b**). The reaction constant in CH₃OH is $k_{\rm H}$ =0.0044 mol·L⁻¹·min⁻¹; while the reaction constant in CD₃OD is $k_{\rm H}$ =0.0042 mol·L⁻¹·min⁻¹. The reaction constants in CH₃OH and CD₃OD is almost the same excluding some experimental variations. The purpose of these results can be two-fold. In the above control experiments, we thought that energy transfer of singlet oxygen does not contribute to the formation of sulfoxide. Since the lifetime of singlet oxygen is significantly longer in deuterated solvent, it should be much faster in CD₃OD than in in CH₃OH. This prediction contradicts result in Figure 4, implying electron transfer is the sole pathway for formation of sulfoxide. This kinetics studies demonstrate that even though the protons from CH₃OH is helpful in the formation of sulfoxide, abstraction of protons from CH₃OH is not the rate-determining step of overall process. Otherwise, the reaction should become much slower in CD₃OD.



Figure 5: Hammett plot for the aerobic oxidation of *para*-substituted thioanisoles in the merger of visible light photocatalysis of ARS-TiO₂ with TEMPO catalysis. Reaction conditions: sulfide (0.3 mmol), ARS-TiO₂ (40.1 mg, containing 1×10^{-3} mmol ARS), TEMPO (0.006 mmol), 1 atm of air, CH₃OH (1 mL), blue LED irradiation (3 W × 4).

After the establishment of electron transfer rather energy transfer pathway governing the formation of product, the electronic effect of substituted groups in thioanisole and its derivatives was considered. Thus, we carried out the kinetics studies for the oxidation of thioanisole and its *para*-substituted derivatives. The oxidation of all these sulfides obey the zero-order reaction plot. After obtaining the reaction constant, a Hammett plot can be constructed to determine the value of ρ (Figure 5). Based on the ρ value of -0.70, we can conclude mechanisms involves the formation of positive charge after the electron transfer. This result agrees well with the mechanism we proposed that TEMPO⁺ (2,2,6,6-tetramethylpiperidine-1-oxoammonium) accepting electron from thioanisole, leaving the positive charge at the radical cation of thioanisole.

We did not delve into the special effect of ARS sensitizer in implementing this photocatalytic aerobic reaction. The electron ejection from ARS to conduction band of TiO₂ of ARS-sensitized TiO₂ belongs to the type II pathway ^[34] due to the fact that ARS is a catechol dye. Type II sensitizer shows strong new absorption band in the longer wavelength region which is in good agreement with UV-visible absorbance of ARS-TiO₂ (Figure 2, **a**). Under visible light irradiation, type II dye does not experience pathway from the ground HOMO state to the excited LUMO state of dye*. In contrast, the direct injection of electron from HOMO of type II dye to the conduction band of TiO₂ occurs. Both the broadening of wavelength absorption and direct electron injection pathway are all due to the bidentate mononuclear chelating linkage of the catechol motif of ARS and the Brønsted acid sites of TiO₂. Recently, we found that catechol-TiO₂ complex could be an efficient photocatalytic system for selective oxidation reaction, implying the merit of this linkage^[35].



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Figure 6: The proposed mechanism for the selective oxidation of sulfide into sulfoxide with air in the merger of visible light photocatalysis of ARS-TiO₂ with TEMPO catalysis

The mechanism can be tentatively rationalized in Figure 6. Under blue LED irradiation, ARS will directly inject electron to the conduction band of TiO₂, without undergoing an excited state of ARS*. Resultantly, ARS radical cation ARS⁺⁺ was generated in this step. ARS⁺⁺ can further drive the conversion of TEMPO to TEMPO⁺, returning to its ground state of ARS. Then TEMPO⁺ will be restored to TEMPO by interaction with thioanisole, engendering radical cation of thioanisole. This was supported by the Hammett plot relationship. In addition, we synthesized a stable salt of TEMPO⁺BF₄⁻ to replace TEMPO as a starting redox mediator to merge with the visible light photocatalysis of ARS-TiO₂. We found that 93% conversion of thioanisole was achieved after photocatalytic reaction of 2 h. This result is inferior to that of TEMPO, 1.3 h, for the same conversion, which might be caused the difficult of abstracting electron from sulfide. In order to keep the stability of TEMPO, bulky side groups existed in TEMPO. Thus, it is not a good catalyst for steric hindered substrates, verifying this predication in expanding the scope of substrates. At the conduction band of TiO_2 , O_2^{-} will be produced by reduction of O_2 . The newly generated O_2^{-} will attack radical cation of thioanisole, supported by the *p*-BQ trapping control experiment. Protons from solvent assist the formation of sulfoxide, supported by different protoncontaining solvent experiments (Table 2).



Figure 7: The ESR signals of superoxide captured by DMPO (DMPO-·OOH) (a) and TEMPO(b)

Spectroscopic studies would give more direct evidence to the reaction pathways. Therefore, we carried out ESR investigation to understand the essential roles of ROS and TEMPO in managing the oxidation outcome. Since there is overlap of ESR signals between the spin trapping of superoxide radicals (O_2^{-r}) with DMPO (5,5-dimethyl-1-pyrroline n-oxide) of DMPO-·OOH and TEMPO. We can only obtain the ESR signals of DMPO-·OOH on ARS-TiO₂ without TEMPO under visible light irradiation. The signals agrees well with the hyperfine coupling constant of radicals of DMPO-·OOH (AN=13.7G, AH=11.2G) and TEMPO (AN=17.1G), tracing the time course of DMPO-·OOH and TEMPO (Figure 7) ^[36]. The signal of DMPO-·OOH increased with time from 0 min to 10 min (Figure 7 **a**), giving further evidence to the proposed mechanism in Figure 7 that O_2^{-r} is the essential ROS in the formation of sulfoxide. After adding TEMPO into the reaction system, the ESR signals of TEMPO becomes weaker and weaker under visible light irradiation from 0 min to 4 min (Figure 7 **b**). This is in good agreement that the occurrence of TEMPO to TEMPO⁺, transforming ESR active species into a silent one. It is very evident that all the *in situ* ESR results support the mechanism in Figure 6.

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$R_{U}^{I} \xrightarrow{S} + O_{2} \xrightarrow{ARS-TiO_{2}, 2 \text{ mol}\% \text{ TEMPO}} CH_{3}OH, \text{ blue LEDs} \qquad R_{U}^{I} \xrightarrow{S} + H_{2}O$					
Entry	Substrate	Product	T [h]	Conv.[%] ^[b]	Sel.[%] ^[b]
1 ^[c]			1.6	94	92
2 ^[c]	HSCO	H,CO	1.2	98	94
3 ^[c]	B	Br	2.0	89	88
4 ^[d]	C S		5.0	87	94
5	Hochina	H ₃ C	1.0	97	92
6	F	F. C. S.	1.3	94	91
7	cr S	CI CI	1.5	88	89
8			1.5	85	85
9	O2N S	O ₂ N	4.0	37	85
10	CI S S	CI O	2.0	49	96
11	OCH3 S	OCH3 O	1.3	97	98
12	H ₆ COS_	HCO, S	1.3	94	92

Table 7: The selective oxidation of sulfides into sulfoxides with air in the merger of visible light

 photocatalysis of ARS-TiO2 with TEMPO catalysis ^[a]

13	CIS	CI	1.7	82	90
14	\$C2H5	C2H6	1.3	90	88
15	S'Ph	O S Ph	3.0	17	93
16	n-Bu∕ ^S ∕n-Bu	O Ⅱ n-Bu ^{r S} n-Bu	0.5	99	95

[a] Reaction conditions: sulfide (0.3 mmol), ARS-TiO₂ (40.1 mg, containing 1×10⁻³ mmol ARS), TEMPO (0.006 mmol), 1 atm of air, CH₃OH (1 mL), blue LED irradiation (3 W × 4). [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of sulfide, selectivity of sulfoxide. [c] Sulfide (0.4 mmol), TEMPO (0.008 mmol).
[d] thioanisole (1.5 mmol), TEMPO (0.015 mmol). Ph, phenyl; *n*-Bu, *n*-butyl.

Being scalable could be one step towards practical application, thus we attempted to scale up the amounts of sulfides to 0.4 mmol in the presence of 2 mol% of TEMPO, we found that slight prolonging the reaction time can achieve the same level of conversions and selectivities (entries 1-3, Table 7) in comparison with 0.3 mmol scale (entry 3, entries 4c and 5c, Table 1). With these results in hand, we further increase the sulfide to 1.5 mmol and decrease the amount of TEMPO to 1 mol% and less than 5 times of reaction time of 5 h, 87% conversion and 94% selectivity of sulfoxide can be obtained (entry 4, Table 7). In this manner, turnover number in terms of ARS is 1305, an indicator of the resilience of ARS in this system of cooperative photocatalysis. At 60% conversion of thioanisole, the second cycles for the oxidation can achieve conversion of 65%, further demonstrating that the robustness of the ARS-TiO₂ photocatalyst. The characterizations by XRD and DR-UV-visible spectra of the used photocatalyst suggests the slight loss of ARS part and the stability of TiO₂ part during the recycle photocatalytic reactions.

After establishing that our protocol is scalable, we want to demonstrate that our protocol is a very general one. Therefore, we carried out the selective aerobic oxidation of a series of *para*-

substituted thioanisoles (entries 5-9, Table 7). It was found that excepted for nitro substituted thioanisole (entry 9, Table 7), the selectivities for sulfoxides are quite good at high conversions of substrates (entries 5-8, Table 7). The *ortho*-substituted Cl group can be detrimental to the conversion of sulfide (entry 10, Table 7) due to steric hindrance of substrate. However, the influence of *ortho*-substituted CH₃O group in sulfide is not so apparent (entry 11, Table 7). For *meta*-substituted Cl and CH₃O group, slight longer time can guarantee very good selectivities and conversions (entries 12 and 13, Table 7). If the methyl side of thioanisole was replaced with an ethyl group, the impact on the reaction can be minor (entry 14, Table 7). In contrast, If the methyl side of thioanisole was replaced with a phenyl group, the conversion of sulfide is very unsatisfactory (entry 15, Table 7), attributing to the steric hindrance of diphenyl sulfide. Besides, the selective oxidation of aliphatic sulfide was successful with high conversion and selectivity (entry 16, Table 7).

Conclusion

In summary, we have successfully improved the selectivities for sulfoxides in the oxidation of sulfides with air in the merger of visible light photocatalysis of ARS-TiO₂ with TEMPO catalysis. In the current regime of cooperative photocatalysis, both solvent and TiO₂ can be pivotal in terms of selectivities for sulfoxides and conversions for sulfides amongst all the investigated factors. Our research demonstrates that the potential mechanistic insight guided improvement of a cooperative photocatalysis system employing the engineering of TiO₂ material. Dye-sensitized semiconductor photocatalysis for visible light-driven selective chemical transformations is an emerging area of research, whose future development can rely upon similar strategies deployed in improving dye-sensitized solar cell and sensitized degradation of organic pollutants.

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