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Communication

Visible-light photocatalytic selective aerobic oxidation of thiols to disulfides on anatase TiO_2

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ABSTRACT

This work presents the visible-light photocatalytic selective oxidation of thiols to disulfides with molecular oxygen (O_2) on anatase TiO_2. The high specific surface area of anatase TiO_2 proved to be especially critical in conferring high photocatalytic activity. Herein, surface complexation between thiol and TiO_2 gives rise to photocatalytic activity under irradiation with 520 nm green light-emitting diodes (LEDs), resulting in excellent reaction activity, substrate scope, and functional group tolerance. The transformation was extremely efficient for the selective oxidation of various thiols, particularly with substrates bearing electron-withdrawing groups (reaction times of less than 10 min). To date, the longest wavelength of visible light that this system can utilize is 520 nm by the surface complex of substrate-TiO_2. Importantly, O_2 was found to act as the electron and proton acceptor, rather than to incorporate into the substrates. Our findings regarding this surface complex-based photocatalytic system can allow one to understand the interaction between the conduction band electrons and O_2.

Disulfide bonds are prominent building blocks in molecules with multiple biological activities [1–3]. Moreover, the unique and flexible characteristics of disulfides have enabled their utilization in many fields; for example, the ability to modify an intra/intermolecular construction [4,5] highlighted the importance of disulfide bridges in self-assembled medicine. Disulfide linkages are also popular as dopants in technical rubber and polymeric materials [6,7] where they enhance the self-healing characteristic of polymers. Therefore, numerous advances in the synthesis of disulfides have been made during the past decades. Of the available strategies for the synthesis of disulfides, the oxidation of thiols still dominates this field. While classical strategies achieved the desired transformations smoothly in the presence of stoichiometric oxidants (such as H_2O_2 [8], halogens and derivatives [9], and sulfoxide [10]), they still suffered from the drawback of waste generation. This issue could be resolved by the use of air or molecular oxygen (O_2) as the terminal oxidant [11–14]. Thermally promoted pathways have been investigated to overcome the drawbacks of low activity and selectivity stemming from activation of O_2. The functional catalyst material displayed outstanding reaction activity in heterogeneous systems, but they held the disadvantage of noble material participation [15–17] or thermal deactivation of catalytic nanoparticles [18]. As for homogeneous catalysis, most of which involved organic compound catalysts [19–21], elevated temperature was necessary. However, many biologically active molecules are very sensitive to high temperature and thus, their modification with disulfide bonds should pro-

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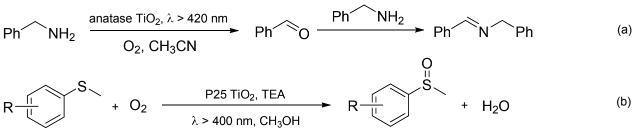
ceed at room temperature. In contrast to thermal catalysis, the visible-light photocatalytic pathway was superior in fulfilling reactions at room temperature in a green and energy-saving manner [22–24], particularly when light was introduced into heterogeneous photocatalytic schemes [25].

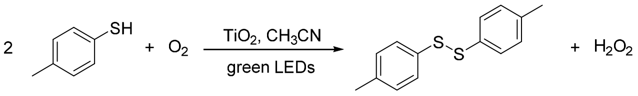
Recently, heterogeneous photocatalysis has developed into a promising route for organic synthesis [26–33]. Typically, TiO_2 has displayed great potential in heterogeneous photocatalysis [34]; specifically, TiO_2 responds to visible light as a versatile platform to realize some conversions via complexation with heteroatoms (including O, N, and S) [35]. In fact, the non-covalent interactions give rise to visible-light absorption and activation; this is a new frontier in visible-light-promoted transformations [36]. Complexation caused a reduction in the oxidation potential of TiO_2 and an upshift in its highest occupied molecular orbital (HOMO). Subsequently, under light irradiation the excited electron of the heteroatom would be efficiently injected into the conduction band of TiO_2 through weak coordination, followed by transfer to the electron acceptor, along with the release of a positive charge (h^+). Therefore, both of the highly active species are suited for the reductive or oxidative pathways in selective synthesis. In a previous report [37], we successfully realized the aerobic oxidation of amines into imines by a complexation system, in which the complex was afforded by anatase TiO_2 and amines under visible-light irradiation (Scheme 1(a)). Subsequently, we were delighted to find that the complexation strategy, occurring between P25 TiO_2 and triethylamine (TEA) to form a visible-light-harvesting surface complex, could also efficiently facilitate the aerobic oxidation of sulfides into sulfoxides (Scheme 1(b)) [38]. In these two instances, O-atom transfer from O_2 to substrates facilitates the visible-light-induced selective formation of oxidation products on TiO_2. It would be of great interest to identify new types of substrates and enrich the role of O_2 in TiO_2 visible-light photocatalysis.

Herein, we sought to establish an attractive alternative for the visible-light-promoted selective oxidation of thiols to disulfides with O_2 on anatase TiO_2. The facile formation of disulfides could be accomplished with no additives and minimal product contamination. In our two previous reports, only visible light around 400 nm could be utilized. In this work, green LEDs at 520 ± 10 nm were explored as the light source. More importantly, O_2 was found to act as the acceptor for electrons and protons rather than to incorporate into the substrates. The transformation was extremely efficient for the selective oxidation of various thiols, especially with substrates bearing electron withdrawing groups (less than 10 min). This protocol has been proven to be an energy-saving and atom-economic route to green chemistry.



Scheme 1. Visible-light-promoted photocatalytic selective aerobic oxidation of amines and sulfides on TiO_2.

Table 1
Control experiments for the visible-light photocatalytic selective oxidation of thiol to disulfide with O_2 on anatase TiO_2.



Entry	Conditions	Conv. * (%)	Sel. * (%)
1	N_2	2	> 99
2	No TiO_2	1	> 99
3	No light	3	> 99
4	Standard	92	> 99
5	CH_3OH	74	> 99

Reaction conditions: 4-methylbenzenethiol (0.6 mmol), anatase TiO_2 (ST-01, 30 mg), 520 nm green LEDs (3 W × 4), CH_3CN (1 mL), O_2 (0.1 MPa), 20 min. * Determined by gas chromatography with flame ionization detector (GC-FID) using chlorobenzene as the internal standard; conversion of thiol, Conv. (%); selectivity of the corresponding disulfide, Sel. (%).

We tested the new issue with 4-methylbenzenethiol 1a as the substrate, TiO_2 (ST-01) as the photocatalyst, and CH_3CN as the solvent, and maintained the reaction mixture at an initial O_2 pressure of 0.1 MPa. The following tests revealed that TiO_2, O_2, and visible light were all indispensable components of the reaction protocol (entries 1–3, Table 1). The results obtained after 20 min of visible-light irradiation are shown in entry 4, Table 1. It was determined that the transformation from thiol to disulfide 2a proceeded with 92% conversion and excellent selectivity under 520 nm green LED irradiation. It was hypothesized that the reaction exhibited an efficient complexation wherein the thiol substrate chemisorbed onto the surface of TiO_2 through the S atom in the initial stage, following which the application of mild visible light induced the subsequent reaction. In effect, UV-vis analysis (Fig. 1) indicated that the formation of the 4-methylbenzenethiol-TiO_2 complex could significantly shift its light absorption to the visible-light region as compared to the uncomplexed TiO_2 and thiol 1a. When CH_3OH was employed as the solvent (entry 5, Table 1), the transformation declined with a moderate conversion of 74%. This might be due to the interaction between CH_3OH and the substrate/TiO_2, resulting in a noticeable effect on the surface com-

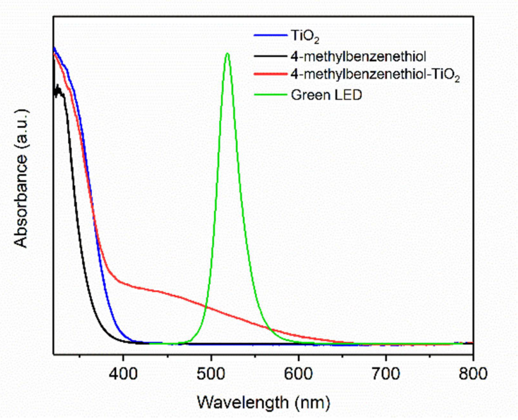


Fig. 1. UV-visible light absorbance of TiO_2 (ST-01), 4-methylbenzenethiol, 4-methylbenzenethiol-TiO_2 complex, and the relative spectrum distribution of green LED.

plexation between the substrate and TiO_2, whereas the polar aprotic solvent CH_3CN had a negligible effect on complexation.

Next, we investigated the effect of different types of TiO_2 on the conversion of thiol to disulfide (Table 2). To this end, 5 types of TiO_2 were tested; it was clear that (ST-01) TiO_2 displayed greater activity than the other types. Noël and co-workers [39] disclosed that P25 TiO_2 was applied as a photocatalyst, aided by base, for this reaction in a previous report. However, anatase TiO_2 with a high specific surface area can deliver nearly 5 times greater conversion of 4-methylbenzenethiol without the need for base. The ideal amount of TiO_2 was determined to be 30 mg (See details in Supplementary Data, the TEM characterization for P25 and ST-01 TiO_2, Fig. S1). Note that the reaction could be carried out with air as the oxidant; however, due to the odor of the substrates, O_2 with initial pressure of 0.1 MPa was selected as the oxidant so that the reaction proceeded in a closed system.

With the optimal reaction conditions established, the scope of applicable thiols was examined (Table 3). When 4-methylbenzenethiol served as the substrate, the oxidative coupling process was completed in 30 min, as monitored by thin-layer chromatography (TLC), and gave a 96% isolated yield. Other derivatives possessing electron-donating groups on the benzene ring (entries 2–7, Table 3) and benzenethiol (entry 8, Table 3) were also implemented in this protocol with excellent yields (> 90%). When considering the influence of the position of the substituent groups (entries 3–5, Table 3) on reaction efficiency, steric hindrance was the main factor necessitating prolonged irradiation time for thiol 1f. Analogous result was seen for the disubstituted thiol 1g (entry 7, Table 3). As for the thiols with electron-withdrawing groups (entries 9–12, Table 3), to our surprise, the transformations were completed in several minutes (less than 10 min) with high isolated yields and functional group tolerance. The protocol was also suitable for the hetero- and poly-aromatic thiols (entries 13 and 14, Table 3). From phenylmethanethiol, an alkyl mercaptan, (entry 15, Table 3) the disulfide 2o was obtained with an inferior isolated yield of 44% after 6 h irradiation. However, this sluggish reaction was greatly improved when triethylamine (TEA) was introduced at the beginning of the reaction as a base additive, affording the target product at a yield of 91% in 40 min.

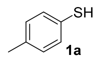
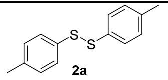
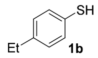
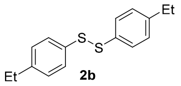
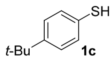
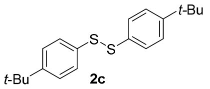
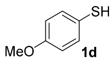
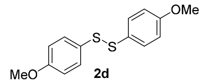
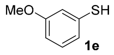
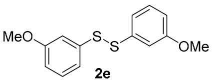
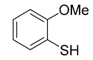
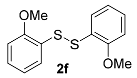
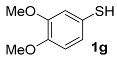
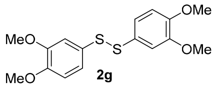
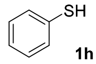
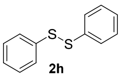
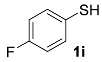
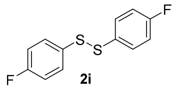
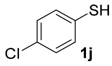
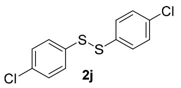
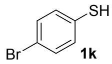
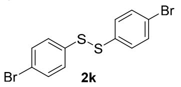
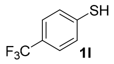
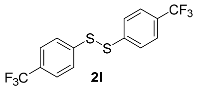
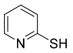
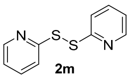
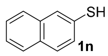
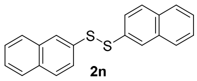
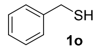
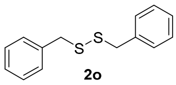
Table 2
Effect of different TiO_2 surfaces on the visible-light-induced photocatalytic selective oxidation of thiol to disulfide with O_2.

Entry	TiO_2	Supplier	BET ($m^2\cdot g^{-1}$)	Conv. * (%)	Sel. * (%)
1	ST-01	Ishihara	264	92	> 99
2	P25	Evonik	54	19	> 99
3	Rutile	Sakai	80	30	> 99
4	P90	Evonik	101	23	> 99
5	Anatase	Alfa Aesar	88	18	> 99

Reaction conditions: 4-methylbenzenethiol (0.6 mmol), TiO_2 (30 mg), 520 nm green LEDs (3 W × 4), CH_3CN (1 mL), O_2 (0.1 MPa), 20 min.
* See Table 1.

Table 3
Visible-light photocatalytic selective oxidation of thiols to disulfides with O_2 on anatase TiO_2.

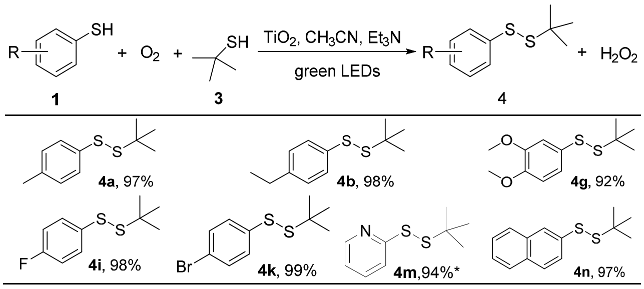
$$2\ \mathrm{RSH} + O_2 \xrightarrow[\text{green LEDs}]{TiO_2,\ CH_3CN} \mathrm{RS}^{\diagup \mathrm{SR}} + H_2O_2$$

Entry	Substrate	Product	Time (min)	Yield [a] (%)
1	 1a	 2a	30	96
2	 1b	 2b	50	96
3	 1c	 2c	50	98
4	 1d	 2d	25	91
5	 1e	 2e	25	96
6	 1f	 2f	120	92
7	 1g	 2g	120	92
8	 1h	 2h	60	93
9	 1i	 2i	10	94
10	 1j	 2j	5	98
11	 1k	 2k	5	98
12	 1l	 2l	5	97
13	 1m	 2m	10	92
14	 1n	 2n	30	98
15 [b]	 1o	 2o	40	91

Reaction conditions: thiol (0.6 mmol), anatase TiO_2 (ST-01, 30 mg), 520 nm green LEDs (3 W × 4), CH_3CN (1 mL), O_2 (0.1 MPa). [a] Isolated yields. [b] Adding 2 mmol TEA.

Unlike symmetric disulfides, asymmetric species were inherently challenging to synthesize. Additionally, the synthesis of some of the asymmetric disulfides was accomplished through this heterogeneous system with the aid of organic base (TEA). We did some investigations of this issue, employing 1a and *t*-butylthiol 3 as the reagents (Table 4). When proceeding through the above optimized conditions, symmetric disulfide 2a was the sole product. However, in the presence of TEA, the photocatalytic reaction exhibited the unique ability to selectively yield the corresponding asymmetric disulfide 4a, with a 97% isolated yield, in just 5 min. The products obtained from other starting materials, 4b, 4g, 4i, and 4k, indicated that the

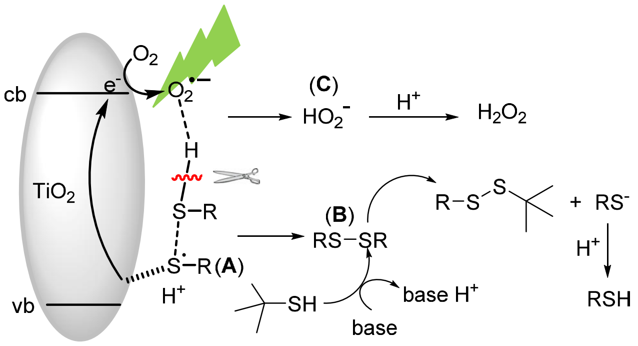
Table 4
Visible-light photocatalytic oxidative synthesis of asymmetric disulfides with O_2 on anatase TiO_2.



Reaction conditions: benzenethiol (0.6 mmol), *t*-butylthiol (1.8 mmol), TEA (2.0 mmol), anatase TiO_2 (ST-01, 30 mg), 520 nm green LEDs (3 W × 4), CH_3CN (1 mL), O_2 (0.1 MPa), 5 min. * Reaction time, 2 h.

electronic or steric effects exhibited minimal loss to the present system, as seen by their corresponding yields. In the case of 4k, we also examined 2k as a substrate under dark conditions lacking TiO_2 wherein 4k was found at 98% yield. This finding suggested that the symmetric disulfide was not thermodynamically stable and therefore could transform into the asymmetric disulfide in the presence of mercaptan 3 and base. As for product 4m, the electrical properties of the N atom had a negative effect on the nucleophilic substitution between 2m and 3. Finally, this asymmetric synthesis was also compatible with thiol 1n.

A plausible mechanism for the visible-light photocatalytic selective oxidation of thiols to disulfides on TiO_2 is depicted in Scheme 2. It was assumed that prior to photocatalysis, the thiol, a heteroatom substrate, was easily adsorbed onto the surface of TiO_2 via weak coordination at the initial stage. Then, visible-light irradiation motivated an electron from the thiol to be transferred to the conduction band (cb) of TiO_2 while circumventing the valence band (vb). At the same time, sulfur radical A and H^+ were released. The unpaired electron was easily trapped by O_2 to form the superoxide radical anion $O_2^{\bullet-}$. Subsequently, a three-component transient state, involving $O_2^{\bullet-}$, radical A, and a thiol molecule, was formed. This state then transformed into product B and anion C. It should be noted that the thiol bearing an electron-withdrawing group was beneficial for the electrophilic attack on the electron rich cloud density of radical A. Thus, it was rational that thiols bearing electron-withdrawing groups displayed greater activity than those possessing electron-donating groups. Finally, anion **C** combined with H^+ to form H_2O_2. The synthesis of asymmetric disulfides proceeded smoothly, wherein mercaptan 3 rapidly performed a nucleophilic attack on the newly formed symmetric disulfide with the assistance of TEA.



Scheme 2. Visible-light photocatalytic selective oxidation of thiol into disulfide with O_2 on anatase TiO_2.

In summary, we have developed a visible-light-induced strategy for the aerobic oxidation of thiols to disulfides. In this context, anatase TiO_2 served as a multifunctional platform, not only for complexation with thiols, but also for electron transfer to form $O_2^{\bullet-}$. When various thiols were examined, the method exhibited excellent reaction selectivity, functional group tolerance, and substrate scope with high isolated yields (> 90%). Notably, the substrates with electron-withdrawing groups could fulfil the transformation in less than 10 min. The concise design contributed to the atom-economic and energy-saving concepts of sustainable chemistry. Simultaneously, it was also an efficient strategy for the synthesis of some asymmetric disulfides with TEA as an additive.

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Graphical Abstract

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Visible-light photocatalytic selective aerobic oxidation of thiols to disulfides on anatase TiO_2

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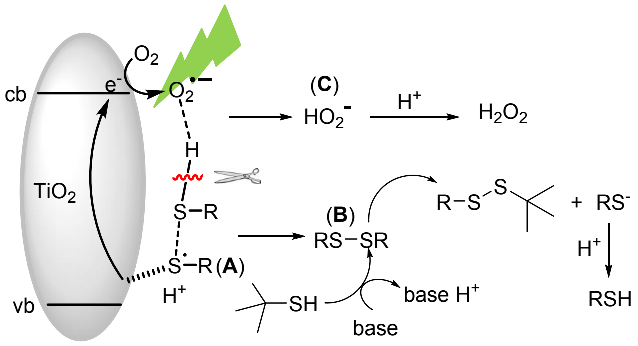

Surface complex formed between thiols and TiO_2 gives rise to visible-light photocatalytic activity, leading to excellent reaction activity, substrate scope, and functional group tolerance under 520 nm LED irradiation.

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锐钛矿TiO_2可见光催化选择有氧氧化巯基化合物到二硫化物

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摘要：二硫化物独特的化学性质使其在生物分子结构改性、药物传输、工业原材料生产中有重要的应用，因而它的合成和研究一直备受关注．在报道的众多合成方法中，最主流的仍然是硫酚的氧化合成．鉴于传统的合成条件严苛、不利于环境保护，以O_2/空气为氧化剂的光催化实现二硫化物的合成已经成为热点研究．在已报道的光催化剂中，TiO_2因为具有化学性质稳定、高效廉价、易回收等优点，在非均相光催化体系中倍受关注．但其缺陷是只能在紫外光区响应激发，这在很大程度上限制了它的应用．本文通过底物巯基化合物与TiO_2表面络合的方式吸收可见光，使其光响应拓展到可见光区．

本文以O_2为氧化剂，巯基化合物与锐钛矿TiO_2络合，可见光高效催化选择氧化生成二硫化物．同时优化了反应条件，如不同波长LED光源、不同类型TiO_2及TiO_2用量，确定硫酚(0.6 mmol)、O_2 (0.1 MPa)、绿光LED (520 nm)、CH_3CN (1mL)、锐钛矿TiO_2 (30 mg, ST-01)为反应最优条件．通过紫外-可见光吸收光谱、透射电镜、比表面积、核磁和高分辨质谱等方法对光催化剂和产物进行表征．结果表明，该反应体系对硫酚(包括杂环、多环硫酚)具有普适性，反应效率高，产率> 90%．其中含吸电子基团的底物比含供电子基团的底物更利于反应进行；同时官能团空间效应对反应速率有一定影响．反应对各

类官能团具有很好的兼容性. 对于硫醇类底物, 需要有机碱三乙胺(TEA)参与才能完成转化. 另外, 当反应有TEA参与时, 可在很短的时间内(< 5 min)生成不对称的二硫化物, 且产率极高(> 92%). 当底物与二氧化钛的表面络合物吸收可见光后, 激发产生的电子通过底物的S原子直接注入到TiO_2的导带, 得到含硫自由基和超氧自由基两个活性体. 含硫自由基与底物分子作用形成对称的二硫化物, 进而在TEA协助下生成不对称二硫化物, 而超氧自由基则最终转化成H_2O_2. 整个过程中TiO_2的作用至关重要, 包括: 与巯基化合物络合, 完成电子传输, 促进超氧自由基形成等. 该反应体系简单高效, 具有很高的原子经济性, 符合绿色化学理念.

关键词: 可见光; 光催化; 二氧化钛; 分子氧; 二硫化物

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