

Removal of malodorous organic sulfides with molecular oxygen and visible light over metal phthalocyanine

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Abstract

Organic sulfides are malodorous compounds in environment. In this work, deodorization of model substrates, methyl phenyl sulfide, 2-mercaptobenzoic acid and benzyl 2-propenyl sulfide, have been studied in an aerated methanolic aqueous solution under visible light irradiation ($\lambda > 450$ nm), using metal phthalocyanine sulfonate (MPcS, M = Al, Pd) as a photocatalyst. The result shows that all the representative sulfides could be efficiently oxidized, with concomitant formation of sulfoxide and sulfone as the main products. Kinetic study using sodium azide and benzoquinone as reactive species scavenger reveals that the sulfide oxidation is mainly initiated by singlet oxygen. It is also observed that the rate of sulfide oxidation increases with increasing the water content in the mixed solvent. Recycle experiments with immobilized PdPcS on organoclay or immobilized AlPcS on anionic resin demonstrates that the sensitizer could be repeatedly used, without significant loss in the photosensitization activity.

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1. Introduction

Sulfur-containing compounds such as hydrogen sulfide, mercaptans and organic sulfides are often emitted from sewage and wastewater treatment plants. These compounds are obnoxiously malodorous even at ppb level [1–3]. Thus, the removal of unpleasant odor is required for public healthy. Several control technologies have been used for treatment of sulfur-containing compounds, including thermal oxidation at high temperature, wet chemical scrubbing, activated carbon adsorption, and biofiltration. Although these methods have their own advantages, the operation cost is high or the process produces a large amount of wastes that require further treatment [4]. Recently TiO₂ photocatalysis has been successfully applied for destruction of organic sulfides [5–7]. However, the system needs to be excited with UV light, which occupies only about 5% in the sunlight reaching on the earth surface. Also the quantum yield developed so far is still very low (about 10% in a liquid phase [8]), that can not satisfy the requirement for practical application. Therefore, development of

a more efficient system that can utilize most of the sunlight and activate molecular oxygen with high quantum yield is desired.

Metal phthalocyanine (MPc), a class of macrocyclic complex, has been studied as sensitizer for production of singlet oxygen (¹O₂) under visible light irradiation [9]. As compared to popular sensitizer porphyrin, phthalocyanine can collect more solar light (about 50%), and is easily synthesized at a low cost. We have recently shown that through such photosensitization system, inorganic sulfide dissolved in an aerated aqueous solution can be completely oxidized to sulfate only under irradiation with visible light ($\lambda \geq 450$ nm) [10]. In this work, we intend to use MPc as a sensitizer for removal of aromatic sulfides from aqueous solution. In the literature, several works have been presented on the photosensitized oxidation of organic sulfide using organic dyes [4,11], and CoPc as the sensitizers [12]. However, the organic dyes used, such as Rose Bengal and Methyl Blue [13], absorb only part of the sunlight, and/or suffer serious bleaching during the photosensitized oxidation of organic sulfide, whereas CoPc has a very low quantum yield in ¹O₂ production (<0.1).

In this work, AlPc and PdPc have been selected as a sensitizer for oxidation of model sulfides, methyl phenyl sulfide, 2-mercaptobenzoic acid and benzyl 2-propenyl sulfide. Among

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the MPc sensitizers developed so far, the PdPc complex is the best one in terms of both photoactivity in $^1\text{O}_2$ generation and photostability against bleaching [14]. In order to increase the MPc solubility in water, the complex was sulfonated in the present study. The model sulfides were dissolved in methanolic aqueous solution. It was observed that under visible light irradiation ($\lambda > 450$ nm), these sulfides could be oxidized efficiently in the aerated solution of sensitizer. The effect of solvent composition and the reaction mechanism were examined. For easy separation and recycle, the water-soluble sensitizer was further immobilized into a commercially available resin and organoclay. Nine consecutive experiments demonstrated that the immobilized sensitizer could be repeatedly used, without significant loss in the photosensitization activity. The result is relevant to odor removal of organic sulfide simply with sunlight and molecular oxygen.

2. Experimental

2.1. Materials

The photosensitizers, aluminum (III) phthalocyaninesulfonate (AlPcS) and palladium (II) phthalocyaninesulfonate (PdPcS), were synthesized as previously described [14]. The dye was then loaded at 1.0 wt% into an anionic resin, Amberlite IRA 400 [15], or into an organoclay, cetyltrimethylammonium-pillared bentonite [16]. Methyl phenyl sulfide (MPS) and 2-mercaptobenzoic acid (MBA) were purchased from Shanghai Chemicals and used as received. Benzyl 2-propenyl sulfide (BPS) was synthesized according to the literature method [17]. ^1H NMR (CDCl_3 , δ , ppm): 7.26–7.34 (m, 5H, benzyl), 5.85 (m, 1H, $-\text{CHCH}_2$), 5.14 (m, 2H, $-\text{CH}=\text{CH}_2$), 3.69 (s, 2H, benzyl- CH_2), 3.05 (d, 2H, $\text{CH}_2-\text{C}=\text{C}$).

2.2. Procedures and analysis

Photochemical reaction was carried out in a Pyrex glass-made reactor thermostated at 20°C . The irradiation source was a Halogen lamp (500 W, Shanghai Yamin) cut off at $\lambda \geq 450$ nm. The organic substrates in solution were analyzed by HPLC (Dionex P680, Apollo C18 column, 8:2 $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ eluent) or by GC-MS (HP 5973, HP-5 column). For the heterogeneous reaction, the suspension before light irradiation was equilibrated in the dark overnight for achievement of organic adsorption. During the photoreaction, about 1 mL of the suspension was withdrawn, filtered through a membrane ($0.45 \mu\text{m}$), and analyzed by HPLC.

The catalyst stability was evaluated by consecutive experiments as follows. The suspension containing MPS (1.07 mM, 50 mL) and catalyst (PdPcS-organoclay, 25 mg) in 50% $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ was first equilibrated in the dark overnight, and then irradiated with visible light. After MPS in solution disappeared almost completely, 5 mL of MPS stock solution (10.7 mM) was supplied so as to restore its initial concentration at 1.07 mM. The suspension was then stirred for 1 h in the dark, followed by light irradiation. The reaction was monitored by HPLC as described above.

Table 1

Pseudo-first-order rate constant, k_{obs} (min^{-1}), determined from sulfide photooxidation in a homogeneous solution^a

Sensitizer	Additive	MPS	BPS	MBA
AlPcS	–	0.019	0.018	0.166
	BQ	0.018	0.015	0.142
	NaN_3	0.0009	0.0011	0.027
PdPcS	–	0.124	0.111	1.01
	BQ	0.114	0.076	0.91
	NaN_3	0.005	0.005	0.18

^a Solvent: $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (1:1). BQ presents benzoquinone. The initial concentration was $[\text{sensitizer}] = 0.020 \text{ g/L}$, $[\text{sulfide}] = 0.40 \text{ mM}$, $[\text{BQ}] = 0.20 \text{ mM}$, $[\text{NaN}_3] = 0.010 \text{ M}$.

Absorption spectra were recorded on an Agilent 8453, equipped with an attachment of Labsphere RSA-HP-53. Voltammetric experiments were performed on an electrochemical workstation (Chi660A, Shanghai Chenghua Instrument Corp) in a three-electrode compartment using a platinum plate as working electrode, a platinum wire as counter electrode, and calomel electrode as reference. The scan rate was set at 50 mV/s. The solution contained $6.0 \times 10^{-4} \text{ M}$ sulfide and 0.1 M NaClO_4 in 50% $\text{CH}_3\text{OH}-\text{H}_2\text{O}$. Quantum yield of sulfide oxidation was measured at $606 \pm 14 \text{ nm}$ (interference filter, Shanghai Haiguang). The sulfide solution contained 1.6 mM sulfide and 40 μM sensitizer in 50% $\text{CH}_3\text{OH}-\text{H}_2\text{O}$. The irradiation source was a Xenon lamp (75 W, USHIO), enclosed in an A1010 lamp housing and operated at 5.00 A with a LPS-200 powder supply (PTI). The light intensity was determined with a Reineckes salt actinometry, and it was $1.98 \times 10^{-5} \text{ einsteins/s}$ at 606 nm.

3. Results and discussion

3.1. Photosensitized oxidation of sulfide in the presence of sensitizer

As a green technology, the photosensitized reaction has better be performed in an aqueous solution. However, organic sulfides hardly dissolve in water. For this reason, all the photosensitized reactions were carried out in a mixed solvent of methanol-water. Fig. 1 shows the results of MPS and BPS oxidation, sensitized by PdPcS or AlPcS under visible light irradiation ($\lambda > 450$ nm) in an aerated solvent of 50% $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (1:1, v/v). The sulfide concentration continuously decreased with irradiation time, whereas the main products, sulfoxide and sulfone, increased correspondingly. Such reaction was not observed in the dark or under visible light irradiation without PdPcS or AlPcS. Thus, the observed removal of sulfide was attributed to the photosensitized reaction. In addition, the reaction sensitized by PdPcS was much faster than that sensitized by AlPcS. The reaction kinetics was well fitted to the apparent first-order rate equation. Table 1 lists the rate constants obtained with three sulfides and two sensitizers under similar conditions.

All three sulfides could be oxidized in the photosensitized systems, and the rate constant followed the order, $\text{MBA} > \text{BPS} \approx \text{MPS}$. This trend in rate constant was nearly consistent with that in the reduction potential of sulfide, which

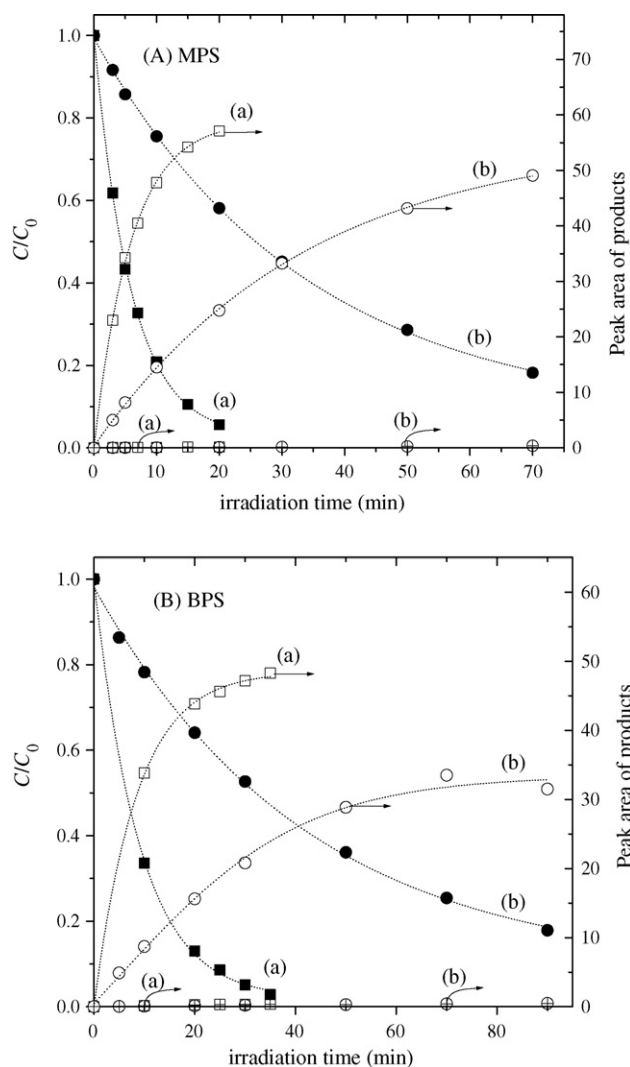


Fig. 1. Photooxidation of MPS (0.40 mM) and BPS (0.22 mM) in $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (1:1), sensitized by (a) PdPcS and (b) AlPcS (0.020 g L^{-1}). The reaction products, sulfoxide (open symbol) and sulfone (crossed open symbol), were simultaneously detected at 244 nm.

was 0.350 V for MBA, 0.397 V for BPS, and 0.408 V for MPS, respectively (versus SCE). Second, as the sensitizer, PdPcS was much more efficient than AlPcS for the oxidation of all three sulfides under similar condition. The rate constants for sulfide loss obtained with PdPcS were about one magnitude larger than those obtained with AlPcS. Similar result was also obtained with quantum yield of sulfide loss, estimated at 606 nm in 50% $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (Table 2). The quantum yields obtained with PdPcS were much higher than that with AlPcS. Since the degree of dye aggregation and thus the efficiency in the sensitized reaction are greatly influenced by solvent and dye concentration,

Table 2
Quantum yield of sulfide oxidation at 606 nm in 50% $\text{CH}_3\text{OH}-\text{water}$

Sensitizer	MPS	BPS	MPA
AlPcS	0.045	0.005	0.039
PdPcS	0.135	0.072	0.225

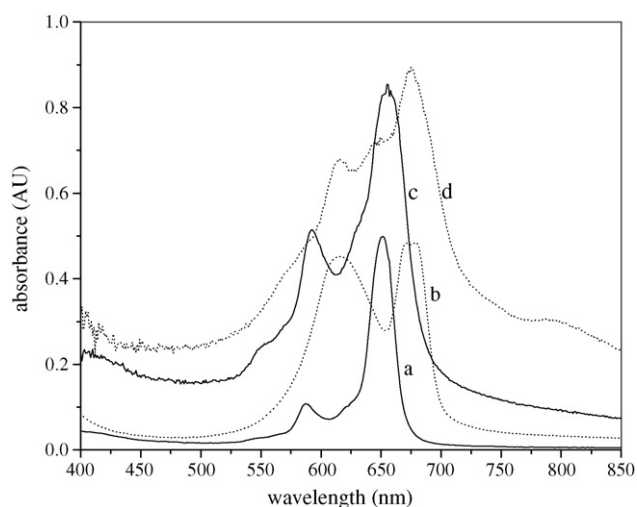


Fig. 2. Absorption spectra of (a) PdPcS, and (b) AlPcS in solution ($\text{CH}_3\text{OH}:\text{H}_2\text{O} = 1:1$), and diffuse reflectance spectra of (c) PdPcS-organoclay, and (d) AlPcS-resin in a powder form.

the data in Tables 1 and 2 only present the results under the conditions employed for the measurement.

In the literature, two types of reaction mechanisms are reported for sulfide photooxidation [4,11,13]. One is the photooxidation with superoxide radical, produced via electron transfer process. Another is the photooxidation initiated by $^1\text{O}_2$, generated via energy transfer from an electronically excited sensitizer to ground state oxygen. In order to verify the reaction pathways involved in the present work, the reactions were carried out in the absence and in the presence of different scavengers, sodium azide for $^1\text{O}_2$ and benzoquinone (BQ) for $\text{O}_2^{\cdot-}$ radicals. The results are presented in Table 1. All the reactions were almost completely depressed in the presence of NaN_3 , whereas the reactions on addition of BQ were only decreased somewhat under the present conditions. This suggests that the sulfide oxidation sensitized by PdPcS and AlPcS is mainly initiated by $^1\text{O}_2$. We have reported in a previous study that PdPcS has a higher quantum yield of $^1\text{O}_2$ production than AlPcS in dimethylformamide [14]. In the present solution, PdPcS displays a lower degree of aggregation, as compared to AlPcS (Fig. 2), and thus a higher efficiency in generation of $^1\text{O}_2$ [9,14,18]. Both the factors are responsible for the observation that PdPcS is more efficient than AlPcS for the sensitized oxidation of sulfide in an aerated solution. In all cases, the dye bleaching was not serious, and only accounted for about a few percentages after 1 h of the sensitized reaction.

3.2. Photosensitized oxidation of sulfide over the immobilized sensitizer

For practical use, the water-soluble sensitizer (AlPcS and PdPcS) needs to be fixed on a proper support. For this concern, AlPcS and PdPcS were immobilized into anionic resin and organoclay, respectively, as described previously [15,16]. Fig. 2 shows the diffuse reflectance spectra of the immobilized sensitizers. The absorption spectra on the heterogeneous catalyst showed a notably enhanced degree of dye disaggregation,

as compared to those in a homogeneous alcoholic solution. The band of AlPcS monomer in solution was centered at 675 nm, and this band was a little higher than the corresponding aggregate band at 615 nm (Fig. 2b). After immobilized on anionic resin, the dye monomer band was significantly enhanced (Fig. 2d). Such spectral feature would favor the generation of $^1\text{O}_2$ upon visible light irradiation, and thus would enhance the sulfide oxidation. This was confirmed by the photosensitized oxidation of MBA (0.91 mM) in $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (1:1, v/v). The rate constant obtained with 1.0 wt% AlPcS-resin (0.50 g L^{-1}) was 0.15 min^{-1} , whereas the data was only 0.016 min^{-1} with unsupported AlPcS in solution (0.020 g L^{-1}). Note that the supported sensitizer was firmly immobilized onto the support. No bleaching of dye was found from the solid into the solution after the photoreaction. PdPcS-loaded organoclay also showed a remarkable improved performance, as compared to free PdPcS in solution. Therefore, the immobilized sensitizer was better than the unsupported for the photosensitized oxidation of organic sulfides.

3.3. Effect of solvent on the photosensitized oxidation of sulfide

For practical use, the green solvent should be water. But the organic sulfides (MPS, BPS and MBA) have a relatively low solubility in water. Thus, it is necessary to examine the effect of solvent. As a trial, methanol was used as a dissolving organic solvent. Table 3 summarizes the apparent rate constant of sulfide oxidation over AlPcS-loaded resin and PdPcS-organoclay. In all cases, the rate constant increased with the amount of water present in the reaction medium. In both types of reaction mechanisms, peroxysulfoxide is proposed as the intermediate for sulfide oxidation [4,11,13]. In this regard, the polar intermediate would be more stable in a more polar solvent. On the other hand, the life time of $^1\text{O}_2$ is shorter in water ($3.1 \mu\text{s}$) than in methanol ($9.5 \mu\text{s}$), disfavoring the sulfide oxidation in a more polar solvent. However, due to small difference in the life time of $^1\text{O}_2$, the faster sulfide oxidation in a more polar solvent was observed, as compared to those in a less polar solvent. Similar explanation has been also given to the aromatic sulfide oxidation by peroxomonophosphoric acid [19] and *N*-chlorosuccinimide [20] in a mixed solvent of $\text{CH}_3\text{CN}-\text{H}_2\text{O}$. Whatsoever, this is a good result for practical application. It is highly possible that the sulfide photooxidation can be carried out in almost pure water,

only with trace amount of organic solvent for dissolving the aromatic sulfide.

3.4. Recycling experiment

The catalyst stability is another factor that needs to be addressed. After several times of use, the immobilized sensitizer may be partially desorbed into the solution or decomposed into some fragment. Secondly, the sensitization ability may be deactivated by the reaction intermediates or products formed during the sulfide oxidation. Thus, the recycling experiments were performed by using MPS oxidation as an example over 1.0 wt% PdPcS-organoclay (0.50 g L^{-1}). Fig. 3A showed that the composite sensitizer was recyclable for the consecutive photooxidation of MPS, whereas the reaction products of sulfoxide and sulfone gradually accumulated in the solution phase (Fig. 3B). However, the rate constant of MPS loss decreased slowly from one run to another. Interestingly, such a rate decay as

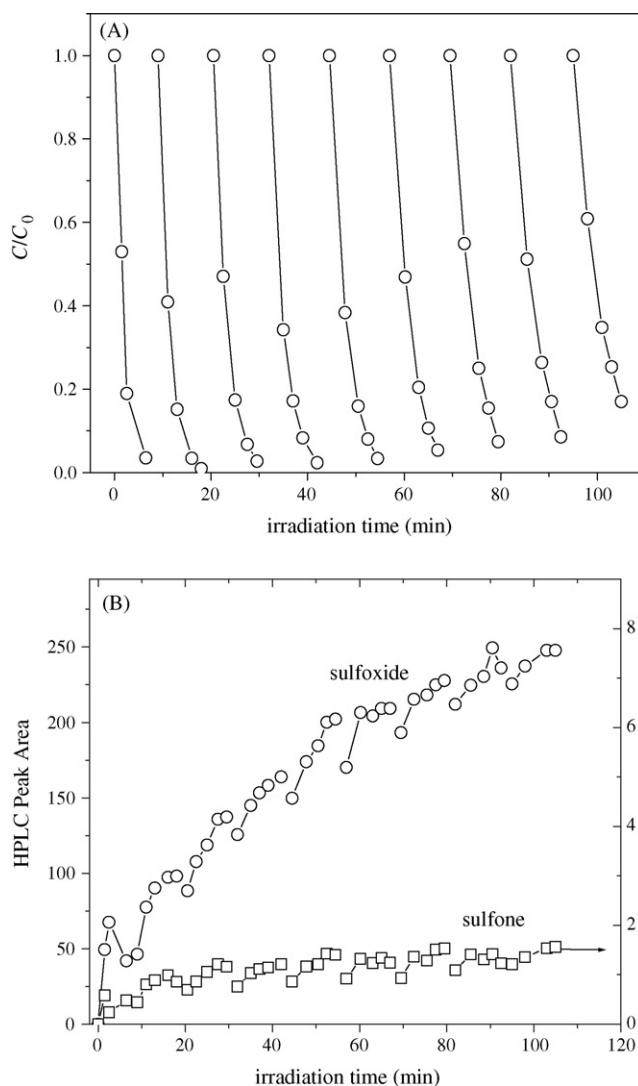


Fig. 3. (A) Cyclic photooxidation of methyl phenyl sulfide over 1 wt% PdPcS-organoclay (0.50 g L^{-1}) in $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (1:1, v/v). For each run the initial concentration of MPS was about 1.07 mM. (B) The corresponding products detected at 244 nm in the filtrate.

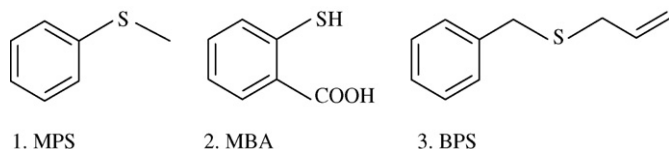
Table 3

Pseudo-first-order rate constant, k_{obs} (min^{-1}), determined from sulfide photooxidation over 1.0 wt% AlPcS-loaded resin in different solvents^a

Solvent	Organic sulfides		
	MBA	BPS	MPS ^b
$\text{CH}_3\text{OH}:\text{H}_2\text{O}$ (v:v)			
30:70	0.18	0.055	0.46
50:50	0.15	0.025	0.23
70:30	0.11	0.026	0.18

^a The catalyst was set at 0.50 g/L . The substrate concentration was: $[\text{MBA}] = 0.91 \text{ mM}$, $[\text{BPS}] = 0.15 \text{ mM}$, $[\text{MPS}] = 1.18 \text{ mM}$.

^b The reaction was with 1.0 wt% PdPcS-loaded organoclay.



Scheme 1. Molecular structures of (1) methyl phenyl sulfide, (2) 2-mercaptobenzoic acid, and (3) benzyl 2-propenyl sulfide.

a function of the number of the run was almost linear, the slope of which was 0.0433 min^{-1} per run. Two factors are responsible for such a rate decay. First, the catalyst concentration was gradually decreased, due to sample analysis (1 mL of the suspension was taken out each time). Second, the immobilized PdPcS experienced a slow bleaching during the reaction process, as observed above in a homogeneous solution. However, the latter factor seems not critical to the immobilized PdPcS. The net concentration of PdPcS present in the suspension was only 0.0050 g L^{-1} , which was much lower than free PdPcS (0.020 g L^{-1}) used in the solution study (Fig. 1A). After nine recycle runs, the heterogeneous catalyst still exhibited an excellent activity for the sulfide oxidation ($k_{\text{obs}} = 0.177 \text{ min}^{-1}$) (Scheme 1.).

4. Conclusions

This work demonstrates that AlPcS and PdPcS are both good sensitizers for the fast removal of malodorous organic sulfides, MPS, MBA and BPS, in an aerated medium of methanol and water, only with molecular oxygen and visible light. The sulfide oxidation was mainly induced by singlet oxygen, and was favorable in a polar solvent containing water. After immobilized onto anionic resin and organoclay, the sensitizers were still photoactive, and could be recycled with high photoactivity and photostability. Although the reaction products, sulfoxide and sulfone, are inodorous, they still remain as sulfur-containing compounds, which may be detrimental to the environment. Future research is needed for complete mineralization of organic sulfide, as well as for improvement of the catalyst activity and stability.

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