

Metal- and Additive-Free Oxidation of Sulfides into Sulfoxides by Fullerene-Modified Carbon Nitride with Visible-Light Illumination

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Photocatalytic selective oxidation has attracted considerable attention as an environmentally friendly strategy for organic transformations. Some methods have been reported for the photocatalytic oxidation of sulfides into sulfoxides in recent years. However, the practical application of these processes is undermined by several challenges, such as low selectivity, sluggish reaction rates, the requirement of UV-light irradiation, the use of additives, and the instability of the photocatalyst. Herein, a metal-free C₆₀/graphitic carbon nitride (g-C₃N₄) composite photocatalyst was fabricated by a facile method, and well characterized by TEM, SEM, FTIR spectroscopy, XRD, X-ray photoelectron spectroscopy, diffuse reflectance spectroscopy, and photoluminescence spectroscopy. The C₆₀/g-C₃N₄ catalyst

exhibited a high photocatalytic activity at room temperature for the selective oxidation of sulfides into the corresponding sulfoxides in the presence of other functional groups, due to the synergetic roles of C_{60} and $g-C_3N_4$. Several important parameters have been screened, and this method afforded good to excellent yields of sulfoxides under optimal conditions. The superoxide radical (' O_2^-) and singlet oxygen (1O_2) were identified as the oxidative species for the oxidation of sulfides into sulfoxides by exploring EPR experiments, and hence, a plausible mechanism for this oxidation was proposed. Moreover, the $C_{60}/g-C_3N_4$ catalyst can be easily recovered by filtration and then reused at least four times without loss in activity.

Introduction

The oxidation reaction represents one of the most vital protocols for upgrading raw starting materials into high-valueadded products in organic transformations.^[1-4] Among various types of oxidation reactions, the oxidation of sulfides into sulfoxides (sulfoxidation) is of great importance in organic synthesis,^[5] because sulfoxides are important intermediates or building blocks in the construction of pharmaceuticals, agrochemicals, and other valuable fine chemicals. For example, optically active sulfoxides are useful intermediates in medicinal and pharmaceutical chemistry to prepare therapeutic agents.^[6] Therefore, interest in the selective oxidation of sulfides into sulfoxides has attracted great interest for a long time. Traditionally, the oxidation of sulfides into sulfoxides has mainly been performed through thermal oxidation processes by the use of several kinds of oxidants, such as trifluoroperacetic acid, hydrogen peroxide, tert-butyl hydroperoxide, and iodobenzene diacetate.^[7-11] However, these methods suffer from several drawbacks, such as low selectivity, the high input of energy, and the release of highly toxic waste. Therefore, the search for new routes for the efficient and environmentally friendly oxida-

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tion of sulfides into sulfoxides has continued to be of interest in chemical research. Photocatalytic transformations, which utilize sunlight as an abundant and readily available source of energy for driving chemical reactions, have been considered to be an important pathway towards a sustainable future.^[12, 13]

Recently, the photocatalytic oxidation of sulfides into sulfoxides with high selectivity has received increasing attention because it allows oxidation reactions to occur under mild conditions through the use of solar-light irradiation. For instance, Zhang and co-workers reported the photocatalytic oxidation of the sulfides into sulfoxides over carbonyl ruthenium(II) porphyrin complexes by the use of iodobenzene diacetate (Phl(OAc)₂) as the oxygen source.^[14] An inorganic semiconductor material as a photosensitizer and a ruthenium-aqua complex as a catalyst were also reported to be robust for sulfide oxidation.^[15] Additionally, an iron(IV)-oxo species has been used to oxidize radical sulfide cations into the corresponding sulfoxides through in situ generated $[Ru^{III}(bpy)_3]^{3+}$ (bpy=2,2'-bipyridine).^[16] Nevertheless, these photocatalytic systems require a large excess of sacrificial electron acceptors, such as [Co(NH₃)₅Cl]Cl₂ and Na₂S₂O₈. From the viewpoint of green and sustainable chemistry, O22 is the most attractive oxidant because it is an environmentally friendly and readily available oxidant, with harmless water as the only byproduct generated in the reaction.^[17] However, the triplet ground state of oxygen is inactive for photocatalytic oxidation, and activation of the triplet ground state of oxygen to the oxidative species for the selective oxidation of sulfides to the corresponding sulfoxides is a challenge. There are some reports on the use of molecular



oxygen for the photocatalytic oxidation of sulfides into sulfoxides. Chen and co-workers reported three photocatalytic systems that achieved the aerobic oxidation of sulfides into sulfoxides by employing TiO₂ as the catalyst.^[18–20] The use of TiO₂ alone cannot promote this reaction, which requires an additional redox mediator, such as (2,2,6,6-tetramethylpiperidin-1yl)oxyl (TEMPO) and anchored organic dyes or triethylamine on the surface of TiO₂ to promote the oxidation of sulfides into sulfoxides. These processes were performed with methanol as the solvent, and methanol was also oxidized into formaldehyde. Li and co-workers performed the photocatalytic oxidation of sulfides on Pt/BiVO₄ in water under visible-light illumination, but the conversion efficiency was poor.^[21]

From the standpoint of green and sustainable chemistry, the development of metal-free catalytic systems for the oxidation of sulfides is needed because of inevitable metal residue contamination of the products through the use of a homogeneous complex or the loss of the metal component from heterogeneous catalysts.^[22,23] There is one reported case of the metal-free and photocatalytic oxidation of sulfides into sulfoxides by the use of graphitic carbon nitride (g-C₃N₄) with oxygen as the oxidant.^[24] However, two equivalents of isobutyraldehyde was required, and the real oxidant was proposed to be a peroxide radical and peracid, which were produced from the oxidation of isobutyraldehyde. Additionally, NH4HF2 was added for the preparation of mesoporous graphitic carbon nitride (mpg- C_3N_4). Clearly, the development of new photocatalytic systems for the environmentally friendly and metal-free oxidation of sulfides into sulfoxides with molecular oxygen without any additive is required.

Fullerenes (C₆₀) represent another allotrope of carbon with unique electronic properties.^[25] C_{60} is reported to be favorable for efficient electron-transfer reduction because it has a closedshell configuration, which consists of 30 bonding molecular orbitals with 60 π electrons.^[25] The unique structure of C₆₀ serves as an excellent electron acceptor, which efficiently causes rapid photoinduced charge separation and relatively slow charge recombination. Wang and co-workers have summarized recent significant advances achieved in the field of oxidation and hydrogenation as realized by g-C₃N₄-based catalytic systems;^[26, 27] they also found the combination of carbon nitride and carbon nanotubes showed synergistic effects in optoelectronic conversion.^[28] Thus, g-C₃N₄ has emerged as a class of 2D nanomaterial analogous to graphite, and its unique structure renders extensive potential use as a metal-free semiconductor for photocatalytic reactions.^[25,26] Therefore, herein, we anticipated to take advantages of the properties of fullerene and g-C₃N₄ to design a hybrid metal-free catalyst for the photocatalytic oxidation of sulfide under visible-light irradiation.

Results and Discussion

Catalyst characterization

The XRD patterns of C₆₀, C₃N₄, and 4 wt% C₆₀/g-C₃N₄ composite are shown in Figure 1. From the XRD pattern of g-C₃N₄, one characteristic XRD peak, with a strong intensity at $2\theta = 27.2^{\circ}$, is

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Figure 1. XRD patterns of C_{60^\prime} g- C_3N_4 , and 4 wt % C_{60^\prime} g- C_3N_4 composite.

clearly observed, and there is also a weak XRD peak at 2θ = 13.0°. The two peaks are characteristic XRD peaks of graphitelike g-C₃N₄, corresponding to the (100) and (002) planes, and suggest that g-C₃N₄ was successfully prepared. For C₆₀, it exhibits four diffraction peaks at 2θ = 10.7, 17.7, 20.7, and 21.7°, corresponding to the (111), (220), (311), and (222) planes, respectively, and can be indexed to the cubic phase of C₆₀ (JCPDS no. 44-0558).^[25] For the C₆₀/g-C₃N₄ composite, the intensity and position of the characteristic peak at 2θ = 27.2° barely changes relative to those of bare g-C₃N₄, which suggests that the deposition of C₆₀ on the surface of g-C₃N₄ does not influence the lattice structure of g-C₃N₄. More importantly, characteristic peaks for C₆₀ were also clearly observed in the XRD pattern of the 4 wt% C₆₀/g-C₃N₄ composite, which suggested that C₆₀ had been successfully immobilized on the surface of g-C₃N₄.

Representative SEM and TEM images of $g-C_3N_4$ and 4 wt % $C_{60}/g-C_3N_4$ composite are shown in Figure 2. As observed from Figure 2 a, C_3N_4 shows clear mesopores in lamellar structures. In Figure 2 b, there are some dark spots with lower transmis-



Figure 2. TEM images of a) $g-C_3N_4$ and b) 4 wt% $C_{60}/g-C_3N_4$ composite. SEM images of c) $g-C_3N_4$ and d) 4 wt% $C_{60}/g-C_3N_4$ composite (scale: 1 μ m).



sion that indicate perturbation of C₆₀ nanoparticles, without changing the porous structure of C_3N_4 , because C₆₀ nanoparticles are so small and easy to wrap in g-C₃N₄ nanosheets.

In Figure 2 c, the SEM image of C_{60}/g - C_3N_4 composite also displays a 2D lamellar structure, which is in good agreement with the TEM observation. Additionally, the SEM image of the C_{60}/g - C_3N_4 composite shows more mesopores than those in the SEM image (Figure 2 d); this may be due to ultrasonic treatment.^[29]

X-ray photoelectron spectroscopy (XPS) measurements were performed to determine the chemical composition and valence state of various species. The peak positions in all XPS spectra are calibrated with C1s at 284.6 eV. Figure 3a displays the XPS survey spectra of $g-C_3N_4$ and the 4 wt % $C_{60}/g-C_3N_4$ composite.

There are only carbon and nitrogen elements in the two samples, which suggest that there are no impurities in the two samples. The C1s XPS spectrum can be fitted into two peaks with different binding energies at 284.6 and 287.9 eV (Figure 3 b). The peak with the binding energy at 287.9 eV is attributed to sp²-bonded carbon (N–C=N),^[30] whereas the other weak peak located at 284.6 eV can be assigned to the C–C bond. By comparing the C1s XPS spectrum of g-C₃N₄ with that of 4 wt% C₆₀/g-C₃N₄, the binding energy for the sp²-bonded carbon (N–C=N) peak shifted from 287.9 eV for g-C₃N₄ to 287.7 eV for the 4 wt% C₆₀/g-C₃N₄ catalyst, which suggested that there was an interaction between C₆₀ and g-C₃N₄.

As far as the high-resolution N1s XPS spectrum of q-C₃N₄ is concerned, the N1s peak can be deconvoluted into three peaks at 398.1, 398.8, and 400.2 eV, which correspond to C=N-C, N-(C)₃, and N-H, respectively (Figure 3 c); the very weak peak at 404.2 eV corresponds to π excitation.^[30,31] Similarly, the peaks also shifted to a lower binding energy for the $4 \text{ wt \% } C_{60}/g$ - C_3N_4 catalyst. As a hybrid photocatalyst, the change in the light absorption of the UV/Vis region is a direct way to check the efficiency of the hybrid photocatalyst. Therefore, the samples of $g-C_3N_4$ and $4 wt \% C_{60}/g-C_3N_4$ composite were further characterized by UV/Vis diffuse reflectance absorption spectroscopy. As shown in Figure 4, both g-C₃N₄ and the C_{60}/g - C_3N_4 composite exhibit a sharp and wide absorption edge at $\lambda \approx 435$ nm, which are assigned to the intrinsic band gap absorption of g-C_3N_4.^{[32]} According to the equation $E_g\!=\!$ 1240/ $\lambda_{\rm g}$ (in which $E_{\rm g}$ is the band gap energy of the semiconductor and $\lambda_{\rm g}$ is the optical absorption edge of the semiconductor), the band gap of $g-C_3N_4$ is estimated to be 2.85 eV. As shown in Figure 4, the absorption bands of the C_{60}/q - C_3N_4 composites in the visible region become stronger with an increase in the loading of C_{60} from 1 to 5 wt%, which suggests that C₆₀ enhances the light absorption of g-C₃N₄; this is beneficial for photocatalytic reactions. The difference in absorption is significant for a larger difference in the amount of C_{60} , for example, by comparing the spectra for 1 and 5 wt%, but the indistinctive overall change may be due to the small amount of C₆₀.

The samples were further characterized by FTIR spectroscopy (Figure 5). The absorption band at $\tilde{\nu} = 1627 \text{ cm}^{-1}$ should be ascribed to the stretching vibration modes of the C=N bond, whereas the four strong bands at $\tilde{\nu} = 1253$, 1328, 1419, and

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Figure 3. XPS spectra of $g-C_3N_4$ and the 4 wt% $C_{60}/g-C_3N_4$ composite: a) XPS survey spectrum, b) high-resolution C1s spectrum, and c) high-resolution N1s spectrum.

1574 cm⁻¹ are attributed to aromatic C–N stretching vibration modes.^[33] In addition, a sharp band was also observed at $\tilde{\nu}$ = 812 cm⁻¹, which was attributed to the *s*-triazine ring system.^[34] The stretching modes of terminal N–H groups at the defect sites of the aromatic ring exhibit a shoulder band near $\tilde{\nu}$ = 3170 cm^{-1,[32]} For C₆₀, the FTIR spectrum is weak, but some characteristic bands at $\tilde{\nu}$ = 578, 1172, and 1427 cm⁻¹ are visible; these are attributed to the internal modes of the C₆₀ molecule.^[35] After the deposition of C₆₀, there is no apparent structural difference between g-C₃N₄ and 4 wt% C₆₀/g-C₃N₄. However, the characteristic bands for g-C₃N₄ from $\tilde{\nu}$ = 1200 to



Figure 4. UV/Vis diffuse reflectance absorption spectra of $g\text{-}C_3N_4$ and $C_{60}/g\text{-}C_3N_4$ with different compositions.



Figure 5. FTIR spectra of g-C_3N_4, C_{60}, and the 4 wt % C_{60}/g-C_3N_4 composite.

1700 cm⁻¹ are shifted, which suggests that there is an interaction between $g-C_3N_4$ and C_{607} which may benefit electron transfer and enhance the photocatalytic activity of composite materials.

It has been reported that the delocalized 60 π -electron structure of C₆₀ facilitates the separation of photoinduced electrons because it can serve as an excellent electron acceptor.^[35] C₆₀ has a 2D π -conjugated structure, which is a good electron-accepting material that effectively hinders electron-hole recombination.

Photocatalytic oxidation of sulfides

The photocatalytic activity of the C₆₀/g-C₃N₄ catalysts was evaluated by the oxidation of methyl phenyl sulfide (**1a**) as the model reaction. The photocatalytic reactions were performed under continuous illumination with visible light from a 300 W xenon lamp equipped with a $\lambda = 400$ nm cutoff filter under an oxygen balloon. First, the catalytic activity of the series C₆₀/g-C₃N₄ catalysts was investigated. It was observed that the conversion of **1a** increased with increasing C₆₀ weight percentage from 1 to 4 wt% (Table 1, entries 1–4). However, the photocatalytic performance of the C₆₀/g-C₃N₄ catalyst decreases upon further increasing the weight percentage of C₆₀ to 5 wt%



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[a] Reaction conditions: **1a** (0.2 mmol), catalyst (30 mg), CH₃OH (5 mL), oxygen balloon, room temperature, Xe lamp (1 W cm⁻², λ > 400 nm) irradiation for 2 h. [b] Without catalyst. [c] In the dark. [d] Filled with N₂. [e] In air, with irradiation for 2 h. [f] In air, with irradiation for 10 h. [g] C₆₀ and C₃N₄ were added in amounts corresponding to those of entry 9.

(Table 1, entry 5). These results suggested that C₆₀ played a crucial role in the photocatalytic activity of the C₆₀/g-C₃N₄ catalysts. With increasing C₆₀ content, a larger number of active catalytic sites are provided, but, once a limiting value is reached, the adsorption of substrate molecules and light will be restrained.

Furthermore, the reactions were conducted in different solvents to study its influence on the photocatalytic oxidation of **1 a** (Table 2). Interestingly, the solvent had a great effect on the photocatalytic activity of the 4 wt% C_{60}/g - C_3N_4 catalyst towards the oxidation of **1 a**. No reaction took place in THF (Table 2, entry 1), and the reactions in ethanol and benzotrifluoride produced low conversions of 22.5 and 30.4% (Table 2, entries 2 and 3), respectively. Acetonitrile is considered to be the best solvent for photocatalytic reactions in some cases,^[36,37] and it also produced a high conversion of 83.9% (Table 2, entry 4); however, the selectivity of methyl phenyl sulfoxide (**1 b**) was poor. It has been reported that Pt/BiVO₄ systems exhibit excel-

Entry	Solvent	t	Conversion	Selectivity [%]	
		[h]	[%]	1b	1c
1	THF	6	<1	_	-
2	CH ₃ CH ₂ OH	6	22.5	36.1	63.9
3	benzotrifluoride	6	30.4	47.8	53.2
4	CH₃CN	6	83.9	68.3	31.7
5	H ₂ O	6	99.5	55.7	44.3
6	CH₃OH	6	99.9	100	0
[a] Reaction conditions: 1a (0.2 mmol), 4 wt % C_{60} /g- C_3N_4 (30 mg), solvent (5 mL), oxygen balloon, room temperature, Xe lamp (1 W cm ⁻² , $\lambda > 400$ nm)					

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lent performance for the oxidation of sulfides in water, compared with in organic solvents.^[21]

In our catalytic system, a quantitative conversion of 1 a was observed in water after 6 h, but the reaction in water produced an almost equal mixture of 1b and methyl phenyl sulfone (Table 2, entry 5). Pleasingly, methanol was found to be the best solvent because 1a was quantitatively transformed into **1b** after 6 h in methanol under visible-light irradiation (Table 2, entry 6). Therefore, methanol was the best solvent for the photocatalytic oxidation of 1 a, and could stabilize the oxidation product of 1b to prevent further oxidation. Compound 1b in water could be further oxidized into methyl phenyl sulfone; this was possibly because 1b could easily dissolve in water, as a result of its polarity, to promote further oxidation. In addition, the huge difference between ethanol and methanol in the activity of the C₆₀/g-C₃N₄ catalyst was possibly because the hydrophilic C_{60}/g - C_3N_4 catalyst could be much better dispersed in methanol. According to the experimental results, the 4 wt% C₆₀/g-C₃N₄ catalyst was the best choice for the photocatalytic oxidation of sulfides.

To obtain more information on the photocatalytic oxidation of 1a, additional experiments were also performed. For comparison, a control experiment was also conducted in the absence of catalyst under the same reaction conditions (Table 1, entry 6); the oxidation of 1 a did not occur, which suggested that the reaction was promoted by the catalyst. In addition, a low conversion of 20.2% was observed in the presence of g- C_3N_4 with a high selectivity of 98.1% to **1b** (Table 1, entry 7). However, the single use of C_{60} produced a very low conversion of **1 a** (Table 1, entry 8). The conversion was not increased if C_{60} was added with g-C₃N₄ (Table 1, entry 13 vs. entry 8), which indicated that the merely mixing with C_{60} had little effect on the catalytic efficiency of $g-C_3N_4$. These results suggested that C_{60} and g-C₃N₄ had a synergetic effect on the photocatalytic oxidation of $1\,a.$ The dispersion of C_{60} on the surface of $g\text{-}C_3N_4\!\text{,}$ to give rise the hybrid C_{60}/g - C_3N_4 catalyst, might enhance the absorption of visible light (Figure 4) and promote the electrontransfer ability (Figure 9, below), resulting in enhanced photocatalytic activity. In addition, no reaction took place in the dark or under a nitrogen atmosphere (Table 1, entries 9 and 10).

These results show that the C₆₀/g-C₃N₄photocatalyst, light irradiation, and oxygen are all crucial factors in the photocatalytic oxidation of sulfides into sulfoxides. Although there has been an example of photocatalytic oxidation of sulfide into sulfoxide with q-C₃N₄, this catalytic system required the use of isobutyraldehyde as an additive.^[24] To the best of our knowledge, this is the first example of the successful oxidation of sulfide to sulfoxide with a metal-free heterogeneous catalyst without any additive under mild conditions (25°C, 1 atm $(=101325 \text{ Pa}) \text{ O}_2$). Clearly, it is more sustainable to perform chemical reactions without additives. Photocatalytic oxidation in air resulted in a relatively low conversion efficiency, compared with that if the system was filled with oxygen (Table 1, entry 4 vs. entry 11); this was due to the low concentration of oxygen in the reaction solution. By prolonging the reaction time to 10 h, compound 1b was attained in a high yield of 94.4% in air (Table 1, entry 12).

The time course of the product distribution was recorded for the photocatalytic oxidation of **1a** in methanol over the 4 wt% C_{60}/g - C_3N_4 catalyst. During the reaction process, the concentration of **1a** gradually decreased, whereas the concentration of **1b** gradually increased (Figure 6). No intermediates or other byproducts were observed during the reaction process. After light irradiation for 6 h, **1a** was quantitatively converted into the target product of **1b**.



Figure 6. Time course of the products distribution for the photocatalytic oxidation of 1 a (MPS) into 1 b (MPSO).

Substrate scope

The substrate scope of the developed method was extended to a series of structurally diverse sulfides, and the reactions were performed in methanol over the 4 wt% C_{60}/g - C_3N_4 catalyst. As shown in Table 3, this method with the 4 wt% C_{60}/g - C_3N_4 catalyst exhibits a good tolerance for a wide range of sulfides. The sulfides were successfully oxidized into the corresponding sulfoxides with good to excellent yields. For all cases, the selectivity of the sulfoxides reached nearly 100%. However, the activity of the substrates was greatly influenced by their structures. The electronic properties of the substituents in the aryl sulfides played an important role in the substrate activity (Table 3, entries 1–3 vs. 4–6).

Generally, the substrates with electron-donating groups demonstrate higher activity than those substrates with electron-withdrawing groups; the latter require longer reaction times to give high yields of the corresponding sulfoxides (Table 3, entries 1-3 vs. 4-6). The substrates with electron-donating groups more easily donate electrons to sulfur atoms than the substrates with electron-withdrawing groups, which would be beneficial for the oxidation reactions. Additionally, the steric hindrance of the groups also showed a great influence on the substrate activity (Table 3, entries 1 vs. 7, 5 vs. 6, and 8 vs. 9). The large steric hindrance of the substrates caused them difficulties in accessing the active sites. For example, diphenyl sulfide, with two aromatic rings connected by a sulfur atom, has a high electron density on the sulfur atom, but it demonstrated the lowest activity of all tested substrates (Table 3, entries 8 and 9), owing to the greatest steric hin-



Table 3. Substrate scope of the oxidation of sulfides into sulfoxides. ^[a]				
Entry	Sulfide	<i>t</i> [h]	Conversion [%]	Selectivity [%]
1	SMe	6	100	100
2		6	100	100
3	MeO-SMe	6	100	100
4	O ₂ N-SMe	12	88.2	99.6
5	CI-SMe	12	90.6	97.7
6	Cl SMe	16	85.7	96.6
7	✓ SEt	6	81.4	96.7
8	C) ^S C)	20	70.8	98.2
9	C S C	12	99.8	99.6
10	//~S	6	82.9	99.7
11	~~~s~~~	6	85.3	94.9
12	° S∖	6	86.8	98.5
[a] Reaction conditions: substrates (0.2 mmol), 4 wt% C_{60} /g- C_3N_4 (30 mg), CH ₃ OH (5 mL), 25 °C, 1 atm O_2 , visible-light irradiation (>400 nm).				

drance. Based on the above analysis, it can be concluded that the presence of electron-donating groups accelerates the conversion of sulfide into sulfoxide, whereas a large steric hindrance effect is unfavorable for the photocatalytic oxidation of sulfide. More importantly, this method was also effective for aliphatic sulfides and a substrate with a heteroatom ring (Table 3, entries 10–12).

Catalyst recycling experiments

One of the most important merits of heterogeneous catalysts is that they can be recycled and reused. Thus, the recyclability of the 4 wt% C_{60}/g - C_3N_4 catalyst was investigated for the oxidation of **1a**. After the first catalytic run, the catalyst was separated by centrifugation at 8000 rpm, then leached and washed with methanol three times, and dried at 50 °C under vacuum. The spent 4 wt% C_{60}/g - C_3N_4 catalyst was subjected to a second run under the same conditions. As shown in Figure 7, the 4 wt% C_{60}/g - C_3N_4 catalyst demonstrated excellent recyclability. After six consecutive runs, the conversion of **1a** and the selectivity of **1b** were maintained without significant decreases.

Proposed mechanism for the oxidation of sulfides

The conversion of sulfides into sulfoxides was greatly enhanced with the use of C_{60}/g - C_3N_4 . Generally speaking, superoxide radicals (O_2^-), singlet oxygen (1O_2), and hydroxyl radicals ('OH) were reported to be the active species for photocatalytic reactions. Because the photocatalytic reaction was performed

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Figure 7. Recycling experiments of the 4 wt% $C_{60}/g-C_3N_4$ catalyst. Reaction conditions: 1 a (0.2 mmol), 4 wt% $C_{60}/g-C_3N_4$ (30 mg), CH₃OH (5 mL), 25 °C, oxygen balloon, visible-light irradiation (>400 nm).

in methanol, methanol had the ability to quench 'OH.^[38] Therefore, 'OH should not be the oxidative species for the photocatalytic oxidation of sulfides. Furthermore, extra experiments were performed with the use of scavengers to detect oxidative species. *p*-Benzoquinone (BQ), *beta*-carotene, and KI were added as scavengers to capture superoxide radicals ('O₂⁻), singlet oxygen (¹O₂), and photoinduced holes (h⁺) during the photocatalytic reaction process, respectively (Table 4).^[39,40] High conversion of **1a** and high selectivity of **1b** were attained without any additive (Table 4, entry 1). The reaction stopped if KI was added (Table 4, entry 2), which indicated that photoinduced electron–hole separation was crucial for activation.^[41]

Table 4. The effect of scavengers on the oxidation of sulfides. ^[a]				
Entry	Quencher	Quenching group	Conversion [%]	Selectivity [%]
1	_	_	99.5	99
2	KI	h ⁺	< 1	-
3	beta-carotene	¹ O ₂	26.7	99
4	BQ	'O ₂ ⁻	33.68	99
[a] Reaction conditions: 1 a (0.2 mmol), 4 wt % C ₆₀ /g-C ₃ N ₄ (30 mg), methanol (5 mL), oxygen balloon, visible-light irradiation (λ > 400 nm) for 6 h.				

The conversion of **1a** dropped from 100 to 26.7% in the presence of *beta*-carotene without loss in the selectivity of **1b** (Table 4, entry 3), which suggested that ${}^{1}O_{2}$ was present in the reaction system and served as an oxidative species for the photocatalytic oxidation of sulfides.^[5,42] Similarly, the conversion also decreased to 33.7% with BQ as a scavengers to capture 'O₂⁻ (Table 4, entry 4). The results in Table 4 clearly indicated that 'O₂⁻ and ${}^{1}O_{2}$ were the oxidative species for the photocatalytic oxidation of sulfides. The EPR spin-trapping technique was then used to directly to probe ${}^{1}O_{2}$ and 'O₂⁻.

TEMPO and dimethyl pyridine *N*-oxide (DMPO) were employed to probe the reactive oxygen species generated during visible-light irradiation. After irradiation, the characteristic sig-



nals of the DMPO- O_2^- and TEMPO- $1O_2$ adducts were clearly observed (Figure 8). For comparison, these signals were not observed in the dark, which further confirmed that these oxidative species were generated by light irradiation in the presence of the C₆₀/g-C₃N₄ catalyst. To confirm enhanced conversion with a combination of C₆₀ and C₃N₄, the same experiment was conducted with only g-C₃N₄. As shown in Figures S1 and S2 in the Supporting Information, the only active species of O₂ in the reaction is O_2^- ; the improved conversion of sulfide mainly results from oxidative $1O_2$.



Figure 8. Changes in the ESR spectra for systems containing DMPO or TEMPO and 4 wt% $C_{60}/g-C_3N_4$ in methanol under visible-light irradiation for 12 min ($\lambda > 400$ nm). a) DMPO-'O₂ without substrate and b) TEMPO-¹O₂ without substrate.

On the basis of the above results, a plausible mechanism was proposed for the photocatalytic oxidation of sulfides. As shown in Scheme 1, photoinduced holes (h⁺) in the valence band and electrons in the conduction band (e⁻) were generated with g-C₃N₄ under light irradiation. The generated electrons then transferred from g-C₃N₄ to C₆₀ due to the π structure and excellent electron receptivity of C₆₀; this caused the separation of h⁺ and e⁻ on the surface of C₃N₄ more efficiently.^[26] As shown in Figure 9, the intensity of the photoluminescence (PL) signal for the 4 wt% C₆₀/g-C₃N₄ composite is much lower and exhibits a clear blueshift from λ =444 to 439 nm, in comparison with g-C₃N₄. This result indicates that the 4 wt% C₆₀/g-C₃N₄ catalyst has a lower recombination rate of electrons and holes under visible-light irradiation, and verifies that the C₆₀/g-C₃N₄



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Scheme 1. Possible mechanism for the oxidation of sulfides into sulfoxides in methanol. ISC = intersystem crossing.



Figure 9. Room-temperature PL excitation and emission spectra of $g-C_3N_4$ and $C_{60}/g-C_3N_4$ photocatalysts (λ_{ex} =370 nm).

composite could lead to the separation of photogenerated electron-hole pairs.

On one hand, one oxidative species, O_2^- , was generated through the activation of molecular oxygen (O_2) by receiving one electron from C_{60} ; on the other hand, the other oxidative species, ${}^{1}O_2$, could be produced through triplet energy transfer from photoexcited ${}^{3}C_{60}^{*}$ to ground-state oxygen (${}^{3}O_2$).^[10,43,44] The ${}^{1}O_2$ and ${}^{*}O_2^-$ oxidative species then attack the sulfur atom in the sulfides to produce the peroxysulfoxide reactive intermediate with dipolar (A_1) and diradical (A_2) structures (Scheme 1), which were both present in the reaction system.^[10] During this process, one electron was simultaneously released and then transferred to the photoinduced holes (h^+). Methanol could stabilize the persulfoxides through hydrogen-bonding interactions to generate intermediate B.^[44] Finally, the addition of another sulfide molecule to intermediate B afforded two molecules of the sulfoxide product.

Conclusions

We have developed a metal-free heterogeneous catalytic system for the selective photo-oxidation of sulfides to sulfoxides. The 4 wt % C_{60} /g- C_3N_4 catalyst demonstrated high catalyt-



ic activity in the oxidation of sulfides to sulfoxides with O_2 under visible-light illumination due to the synergetic effect between C_{60} and $g-C_3N_4$. The reaction solvent was found to be crucial for the activity of the 4 wt% $C_{60}/g-C_3N_4$ catalyst, as well as product selectivity, and methanol proved to be the best solvent. This catalytic method could smoothly promote the transformation of various structurally diverse sulfides to the corresponding sulfoxides. According to the ESR investigation and some control experiments, a possible mechanism was proposed for the photocatalytic oxidation of sulfides with ' $O_2^$ and ' O_2 as the oxidative species. More importantly, the 4 wt% $C_{60}/g-C_3N_4$ catalyst demonstrates excellent stability without the loss of catalytic activity. This photocatalytic system offers the potential to utilize sunlight for effective and economical production of value-added chemicals through oxidative reactions.

Experimental Section

Materials

The chemicals used in this study were purchased from Aladdin Chemicals Co. Ltd. (Beijing, P.R. China). The solvents used in this study were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, P.R. China). All chemicals and solvents were used directly without any purification. Preparation of the catalyst was according to the previous report.^[26,45] In a typical process, urea (10 g) was placed in a crucible and heated at 500 °C for 3 h at a heating rate of 5 °Cmin⁻¹ in a Muffle furnace. The resulting yellow powder was ground and collected. The C₆₀/g-C₃N₄ composite was prepared as follows: A mixture of C_{60} and as-prepared $g-C_3N_4$ with a total weight of 500 mg was added to toluene (50 mL) under stirring and ultrasonic treatment for 60 min. After toluene was removed under vacuum, the powder was washed with ethanol at least three times, and dried under vacuum overnight to obtain the gray C60-hybridized g-C₃N₄. A series of C_{60}/g -C₃N₄ hybrids with different weight ratios of C_{60} and g- C_3N_4 from 1 to 5 wt% were prepared.

Catalyst characterization

Powder XRD (Bruker D8 Advance; $Cu_{\kappa\alpha} = 1.5404$ Å) was used to analyze the crystalline phase of the catalysts, operating at a scanning rate of 0.05° s⁻¹ over the 2θ range of 10 to 50° . The chemical state of the product was measured by XPS (VGMultilab 2000 photoelectron spectrometer) by using $Al_{\kappa\alpha}$ radiation as the excitation source under 2×10^{-6} Pa vacuum. UV/Vis diffuse reflectance absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere by using $BaSO_4$ as the reference sample. FTIR spectra of the samples were recorded on a NEXUS 470 spectrometer as conventional KBr pellets. PL spectra were measured at room temperature on an F-7000 fluorescence spectrophotometer with an excitation wavelength of 370 nm.

General procedure for the photocatalytic oxidation of sulfides

In general, catalyst (30 mg) was suspended in methanol (5 mL) containing substrate (0.2 mmol sulfides) in a homemade quartz reactor equipped with cold-water condensation. The suspension was degassed and filled with dioxygen (1 atm) in a balloon. Then the suspension was magnetically stirred and irradiated under visible light (1 W cm⁻² Xe lamp with a λ =400 nm UV cutoff filter). After

the reaction, the content of each compound was identified based on GC-MS analysis and quantified based on the internal standard method with bromobenzene as the internal standard. The conversion of sulfide and the selectivity of sulfoxide were calculated by using Equations (1) and (2), respectively:

Conversion	$[\%] = [(C_0 - C_{\text{sulfide}})/C_0] \times 100$	(1)
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$$Selectivity[(\%] = [C_{sulfoxide} / (C_0 - C_{sulfide})] \times 100$$
(2)

in which C_0 was the initial concentration of sulfide, and $C_{\text{sulfoxide}}$ and $C_{\text{sulfoxide}}$ were the concentrations of substrate sulfides and the corresponding sulfoxides, respectively.

Determining the active oxygen species

To determine the reactive active species involved in the reaction, we performed extra experiments to trap the active oxygen species. Sacrificial agents, BQ, beta-carotene, and KI, were used to capture superoxide radical (O_2^{-}), singlet oxygen (O_2^{-}), and photoinduced holes (h⁺), respectively. Moreover, the active oxygen species were probed by means of EPR analysis. Samples containing catalysts (5 mg) and DMPO (100 mм) or TEMPO(100 mм) were vacuumized and oscillated to suspend the catalyst in methanol evenly, then the mixtures were added to an EPR quartz tube filled with O₂, and irradiated with a 300 W Xe lamp (CERAMAX LX-300) equipped a $\lambda\!=$ 400 nm cutoff filter. The settings of the ESR spectrometer for singlet oxygen were as follows: center field = 337.245 mT, microwave frequency = 9437.606 mGHz, sweep width = 4 G, modulation frequency=100 kHz, and power=0.998 mW; the setting of the ESR spectrometer of superoxide radicals were as follows: center field = frequency = 9054.648 mGHz, 322.767 mT. microwave sweep width = 5 G, modulation frequency = 100 kHz, and power = 0.998 mW.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: fullerenes • heterogeneous catalysis • oxidation • photocatalysts • sulfur

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Metal- and Additive-Free Oxidation of Sulfides into Sulfoxides by Fullerene-Modified Carbon Nitride with Visible-Light Illumination



Unrestricted catalysis: A composite catalyst of C_{60} fullerene and graphitic carbon nitride $(g-C_3N_4)$ exhibits a high photocatalytic activity for the selective oxidation of sulfides into the corresponding sulfoxides, in the presence of other functional groups, under visible-light illumination at room temperature.