Green Chemistry

Cite this: *Green Chem.*, 2012, **14**, 1904

www.rsc.org/greenchem

PAPER

Metal-free oxidation of sulfides by carbon nitride with visible light illumination at room temperature†

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Received 31st January 2012, Accepted 30th March 2012
DOI: 10.1039/c2gc35148j

Mesoporous graphitic carbon nitride (mpg-C_3N_4) has been developed as a non-metal, heterogeneous photocatalyst for the selective oxidation of sulfides to sulfoxides with O_2 at room temperature. Especially, the combination of mpg-C_3N_4 and aldehydes was a highly active system under visible-light irradiation. For example, mpg-C_3N_4/isobutyraldehyde catalytic oxidation of methyl phenyl sulfide afforded 97% conversion with 98% selectivity for the methyl phenyl sulfoxide in 4 h. Moreover, the mpg-C_3N_4 can be easily recovered by filtration and then reused at least four times without losing activity. By exploring the electron spin resonance and some comparative experiments, a catalytic mechanism of this oxidation was provided. Finally, the system also works well in the oxidation of a number of sulfides, including sulfides bearing various groups, and phenyl disulfide. The use of a metal-free heterogeneous catalyst and visible light energy, along with the mild reaction conditions makes this oxidation reaction an environmentally benign and energy-saving chemical process.

1. Introduction

Historically, sulfoxides have comprised an important niche in the organic chemistry,[1–3] owing to their versatile usage as intermediates or products in the synthesis of pharmaceuticals, agrochemicals, and other fine chemicals.[4–6] The most frequently used method for the preparation of sulfoxides is the oxidation of the sulfides, as a result wide variety of reagents have been developed for this purpose. Traditionally, some inorganic oxidants such as trifluoroperacetic acid,[7] HNO_3–H_2SO_4 solution in nitromethane,[8] iodic acid,[9] and other hypervalent iodides[10–12] are available for the oxidation of sulfides. However, these processes are accompanied by the use of a great excess of oxidant and are abundant with noxious byproducts, which also bear low selectivity due to the uncontrolled over-oxidation to sulfone. In recent years, the use of catalytic amounts of effective catalysts (metal catalysts,[13–20] inorganic catalysts,[21–24] organocatalysts[25] or enzymes[26]) in combination with *t*-butyl hydroperoxide or hydrogen peroxide was also developed. Nonetheless, compared with molecular oxygen, which is the most ubiquitous and available oxidizing agent,[27,28] these catalytic systems are too expensive, especially for large-scale industrial application.

Molecular oxygen is an ideal 'green' oxidant for the oxidation of sulfides. However, due to its triplet ground state structure, molecular oxygen is an inactive molecule. As a result, some metal-containing catalysts (Fe,[29] Ti,[30] Mo,[31] Ru,[32] Co,[33], *etc.*) have been explored to catalyze molecular oxygen for the sulfide oxidations. From the standpoint of so-called green and sustainable chemistry, the development of metal-free catalytic systems for sulfide oxidations is needed. As solid heterogeneous catalysts are convenient for recovering and recycling catalysts from reaction environments and readily used in flow reactors,[34,35] discovery of a stable and efficient heterogeneous catalyst, without any metal, based on earth-abundant elements for the oxidations of sulfides would be highly attractive.

Recently, mesoporous graphite-like carbon nitride (mpg-C_3N_4) has drawn more and more attention,[36] partly due to its application as a catalyst[37] or catalyst support.[38] The most active system in mpg-C_3N_4 is in fact presumably a defectuous, N-bridged "poly(tri-s-triazine)", which forms π-conjugated planar layers. Though the solid-state material has many defects, it is relatively chemically inert and is stable up to 600 °C. With a semiconductor band gap of 2.7 eV (conduction band (CB) at -1.3 V ($pH = 7$) *vs.* the normal hydrogen electrode (NHE) ($E°$); valence band (VB) at 1.4 V), mpg-C_3N_4 in principle can reduce O_2 to $^{\cdot}O_2^-$ ($E°(O_2/^{\cdot}O_2^-) = -0.16$ V) by the light-excited electron under visible light illumination, then trigger the aerobic oxidation.[39–43] Actually, recent works were achieved by the use of this material as an efficient photocatalyst for the oxidation of alcohols under visible light irradiation.[44] By combination of the characteristic feature of mesoporous materials (large surface area, surface active site, high stability) and the unique properties of semiconductor (redox potential), mpg-C_3N_4 contains all the prerequisites required for a "golden" heterogeneous catalyst, to realize the non-metal oxidation of sulfides by O_2.

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† Electronic supplementary information (ESI) available: additional analytical and experimental data. See DOI: 10.1039/c2gc35148j

Here, we wish to report our efforts to search for a novel and green method for the preparation of sulfoxides using mpg-C_3N_4 as the catalyst and molecular oxygen as the ultimate oxidant. By coupling with aldehyde, mpg-C_3N_4 showed excellent performance in the oxidation of methyl phenyl sulfide and other substituted aromatics sulfides with good conversion and high sulfoxide selectivity.

2. Experimental

2.1 Materials and methods

Unless otherwise stated, all solvents and chemicals were of analytical grade. They were commercially purchased and used without further treatment. The mpg-C_3N_4 was synthesized using our previously reported method.[45] A mercury lamp (150 W) together with a 420 nm cut-off filter was used as a visible light source for the irradiation of reaction system. All GC experiments were carried out and recorded using a SHIMADZU GC-2010 with FID detector. The structure of products and by-products was identified using HP6890 GC/MS spectrometer by comparing retention times and fragmentation patterns with authentic samples.

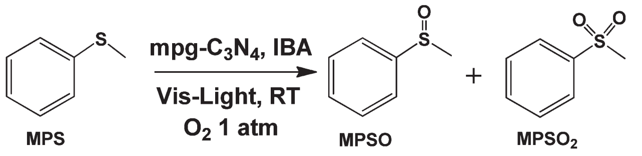
2.2 Typical procedure for the catalytic oxidation of methyl phenyl sulfide and other sulfides

As seen in Fig. S1,† the typical oxidation of sulfides was performed in a self-assembly photo-reactor. In a typical oxidation, 1 mmol substrate, catalysts used as described in the manuscript and 3 mL solvent were added into a 10 mL round bottom glass-reactor, which was fitted with a magnetic stirrer and an O_2 inlet tube. The reaction was performed at 25 °C in a water bath with magnetic stirring. A stream of dioxygen was conducted into the reaction mixture and controlled by a flowmeter at a constant flow rate (10 mL min^{-1}). A mercury lamp (150 W) together with a 420 nm cut-off filter was placed at a distance of ~10 cm from the reactor as a visible light source for the irradiation of this reaction system. To carry out the reaction in the dark, the glass-reactor was covered with aluminium foil. After completion of the reaction, methyl benzoate was added to the mixture as the internal standard. Selectivities and conversions were calculated from the equations: selectivity (%) = [sulfoxides]/[consumed sulfides] × 100; conversion (%) = [consumed sulfides]/[initial sulfides] × 100, respectively.

3. Results and discussion

Initial attempts to optimize the reaction conditions for the oxidation of sulfides were performed with methyl phenyl sulfide (MPS) as a model substrate in the presence of mpg-C_3N_4, different aldehydes, and solvents (Table 1). Catalyzed by mpg-C_3N_4, the oxidation of MPS occurred at room temperature (RT) under visible-light irradiation with a remarkable selectivity (99%) for methyl phenyl sulfoxide (MPSO), though the conversion (8%) was only moderate (Table 1, entry 1). The conversion of MPS was doubled as the temperature increased from 25 °C to 60 °C (Table 1, entry 2). However, there was still the room for improvement. Then, we tested this process at 100 °C with 10 atm O_2 and the conversion of MPS was further improved to 27%, while still keeping good selectivity for MPSO (Table 1, entry 3). As a metal-free heterogeneous organocatalyst, mpg-C_3N_4 drives the oxidation of sulfides with O_2, but these results seem unsatisfactory for the preparation of sulfoxides. Moreover, considering the energy issue, we focussed on carrying out this oxidation under mild conditions (RT, O_2 1 atm).

Table 1 The results of the oxidation of methyl phenyl sulfide under various conditions[a]



Entry	Aldehyde[b] (%)	Solvent	Time (h)	Conv. (%)	Sel. (%) 1b	Sel. (%) 1c
1	—	CH_3CN	8	8	99	—
2[c]	—	CH_3CN	8	16	97	2
3[d]	—	CH_3CN	8	27	98	—
4[e]	IBA 100	CH_3CN	8	3	97	—
5	IBA 100	CH_3CN	8	51	99	—
6	IBA 200	CH_3CN	4	97	98	1
7	IBA 300	CH_3CN	4	100	5	92
8	IBA 200	C_2H_5OH	4	15	98	—
9	IBA 200	CH_2Cl_2	4	39	93	4
10	IBA 200	THF	4	47	97	—
11	IBA 200	Toluene	4	92	57	42
12	BAE 200	CH_3CN	4	35	78	20
13	HCHO 200	CH_3CN	4	32	98	—
14	GOL 100	CH_3CN	4	4	99	—
15[f]	IBA 200	CH_3CN	8	15	69	28

[a] Reaction conditions: MPS 1 mmol, mpg-C_3N_4 50 mg, aldehyde used as described in the table, solvent 3 mL, O_2 1 atm, reaction temperature 25 °C, a mercury lamp (150 W) together with a cut-off filter >420 nm as visible light source. [b] IBA: isobutyraldehyde, BAE: benzaldehyde, GOL: glyoxal. [c] Reaction temperature: 60 °C. [d] Reaction temperature: 100 °C, O_2 10 atm. [e] Without mpg-C_3N_4. [f] In dark.

As radical initiators, aldehydes can undergo autoxidation in the presence of O_2, yielding the acids as the final products. Interestingly, when a mixture of an aldehyde and another organic substrate is submitted to molecular oxygen, the autoxidation of the aldehyde then promotes the oxidation of the less reactive partner.[46,47] The oxidation of sulfides to sulfoxides has been achieved by the aldehyde–O_2 system. However, excessive amounts of aldehyde (~5 equiv) were necessary for these sulfones.[48] Here, only 3% of MPS was oxidized under the influence of isobutyraldehyde (IBA) mainly due to its slow reaction rate of autoxidation, which can be increased by coupling with metal catalysts (Table 1, entry 4).[49–53] Metal catalysts can firstly oxidize aldehydes to the corresponding acyl radical and then accelerate the whole free radical oxidation. More recently, our research group found that mpg-C_3N_4 can promote the splitting of *N*-hydroxyphthalimide to phthalimide *N*-oxyl radical under visible light irradiation, and subsequently induce the radical oxidation process.[41] These findings inspired the examination of the possibility of using the mpg-C_3N_4–aldehyde system in the oxidation of sulfides. To our delight, catalyzed by mpg-C_3N_4–IBA (100 mol%), the MPS oxidation afforded 51% conversion with MPSO as the sole product under the same conditions (Table 1, entry 5). As expected, the mpg-C_3N_4 accelerated the autoxidation rate, possibly contributing to the formation of the corresponding acyl radical. When the quantity of IBA was doubled (200 mol%), MPS was oxidized rapidly, giving a 97% conversion with 98% selectivity to form MPSO in 4 h (Table 1, entry 6). To the best of our knowledge, this is the first successful oxidation of sulfide to sulfoxide by a metal-free heterogeneous catalyst under mild conditions (25 °C, 1 atm O_2). Enhancing the amount of IBA to 300 mol%, 100% conversion of MPS was achieved with 92% selectivity for the over-oxidation product (methyl phenyl sulfone, $MPSO_2$) (Table 1, entry 7). These results indicated that the amount of IBA closely affected the oxidation rate and 200 mol% IBA was adequate, which was selected for further studies.

Optimization of the reaction solvents indicated that acetonitrile was a preferable medium for this process (Table 1, entries 8–11). The influence of the reaction time on the oxygenation of MPS catalyzed by mpg-C_3N_4–IBA system at 25 °C was displayed in Fig. 1. It was observed that MPS was almost linearly oxidized in 4 h until its conversion approach 100%, keeping high selectivity towards MPSO. The results also prove that MPSO was the initial product which could be further converted to $MPSO_2$, yet with lower reaction rate.

The effects of three aldehydes (benzaldehyde, methyl aldehyde, glyoxal) on the mpg-C_3N_4-catalyzed oxidation of MPS under the same conditions were examined and IBA illustrated the best promotional effect among the aldehydes examined (Table 1, entries 12–14).

The oxidation gave a comparably low conversion (15%), when it was carried out in the dark (Table 1, entry 15). It strongly implied that visible light plays an important role in this process. The photooxidation of MPS by mpg-C_3N_4–IBA was also examined using different long pass optical filters. The catalytic activity decreased as the wavelength of used visible light increased, which provides evidence that the transformation was really induced by light (Fig. S2†).

As a heterogeneous catalyst, the mpg-C_3N_4 can easily be separated from the reaction solution by simple filtration, which was then washed with 0.2 M NaOH and dried at 70 °C for subsequent test. The mpg-C_3N_4 can be reused at least four times without losing activity and show no significant difference with the fresh one in FT-IR spectra, which is a prerequisite for practical applications (Fig. 2, S3 and S4†).

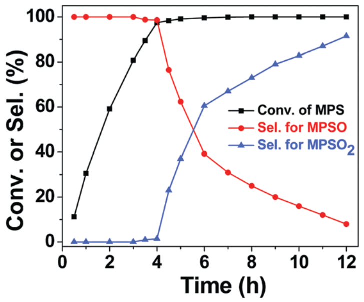


Fig. 1 The conversion of MPS and selectivity for MPSO and $MPSO_2$ *vs.* time plot for the oxidation of MPS by mpg-C_3N_4–IBA system. Reaction conditions: methyl phenyl sulfide 1 mmol, mpg-C_3N_4 50 mg, IBA 2 mmol, CH_3CN 3 mL, 25 °C, 1 atm O_2, visible light irradiation (>420 nm).

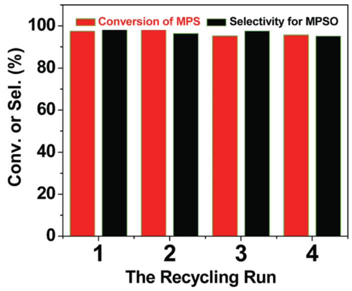
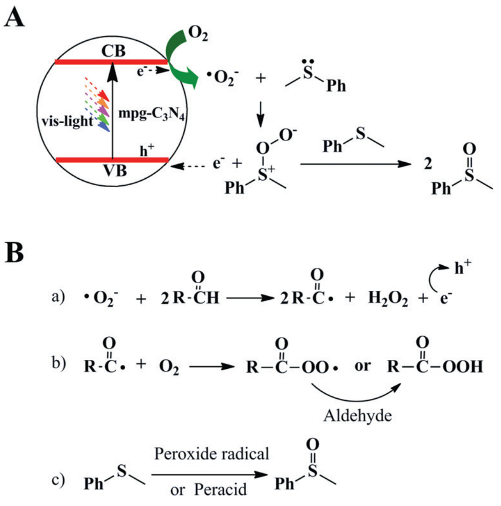


Fig. 2 Four runs to test the reusability of mpg-C_3N_4. MPS: methyl phenyl sulfide; MPSO: methyl phenyl sulfoxide. Reaction conditions: methyl phenyl sulfide 1 mmol, mpg-C_3N_4 50 mg (recovered), IBA 2 mmol, CH_3CN 3 mL, 25 °C, O_2 1 atm, a mercury lamp (150 W) together with a cut-off filter >420 nm as visible light source.



Scheme 1 A possible reaction mechanism for the catalytic cycle of the mpg-C_3N_4 and mpg-C_3N_4–aldehyde system.

To obtain more insight into the reaction process, we move toward the mechanism investigation of the mpg-C_3N_4-catalyzed oxidation of sulfides and Scheme 1(A) illustrated a plausible reaction pathway for this oxidation. Visible light can excite electrons (e^-) from the conduction band of the mpg-C_3N_4 nanoparticles, leaving behind a hole (h^+) in the valence band. The active specie (superoxide radical anion, $^{\cdot}O_2^-$), which was formed by the photogenerated electron-induced reduction of O_2 during light irradiation, was detected by electron spin resonance (ESR) (Fig. 3, L1). We purposed that assisted by the oxidation ability of the positively charged hole (h^+), the $^{\cdot}O_2^-$ can attack the sulfur atom, with the formation of the reactive intermediate persulfoxide or thiadioxirane.[54] A careful ESR investigation confirmed that the reaction between $^{\cdot}O_2^-$ and sulfides indeed occurs, as the signals for DMPO-$^{\cdot}O_2^-$ adducts decreased after adding sulfides to the system at the same condition (Fig. 3, L2). Finally, the electrophilic intermediate reacts with starting material to afford two molecules of the sulfoxide product.[55] Though the light-excited mpg-C_3N_4 can realize this process, limited activity was achieved, possibly due to the high energy barrier for $^{\cdot}O_2^-$ attacking the S atom in the sulfides.

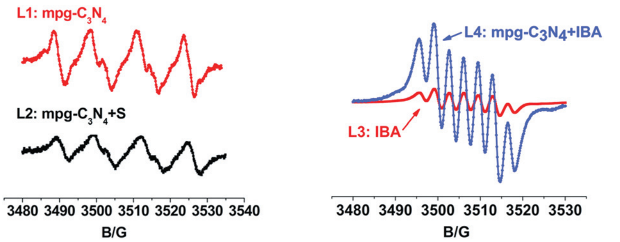


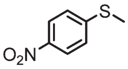
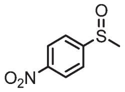
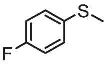
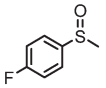
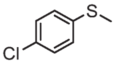
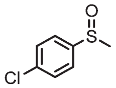
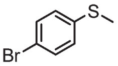
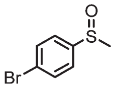
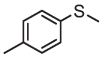
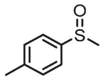
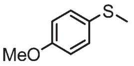
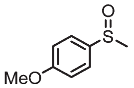
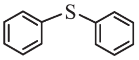
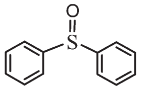
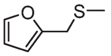
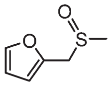
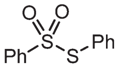
Fig. 3 Changes in the DMPO spin-trapping ESR spectra for mpg-C_3N_4 (4 mg), mpg-C_3N_4 (4 mg)/MPS (10 μL) and mpg-C_3N_4 (4 mg)/IBA (10 μL) in CH_3CN (1 mL). The mixture was stirred with O_2 bubbling and visible light irradiation for 10 min and then put into a quartz tube.

As the combination of mpg-C_3N_4 and IBA had a high catalytic ability, several experiments were then carried out to further understand this system. When hydroquinone (50 mol%), a free radical scavenger, was added into the oxidation of MPS catalyzed by mpg-C_3N_4–IBA, it only gave the conversion of 8%, which was consistent with the result of using mpg-C_3N_4 alone under the same conditions (conv.: 8%) (Table S1,† entry 1). This implied that the oxidation of sulfides proceeded through a radical chain pathway but under the influence of IBA, not mpg-C_3N_4. As shown in Scheme 1(B), firstly, the active $^{\cdot}O_2^-$ radical oxidizes two molecules of aldehydes to the corresponding acyl radicals by injecting a electron into the valence band (VB) of mpg-C_3N_4. The possibility that the $^{\cdot}O_2^-$ radical promoted the oxidation of IBA was studied by comparing the conversion of IBA in the presence and absence of mpg-C_3N_4. After 30 min, the conversion of IBA was 70% in the presence of mpg-C_3N_4 and that was only 14% when mpg-C_3N_4 was absent, showing that mpg-C_3N_4 was catalyzing the oxidation of IBA. (Table S1,† entries 2–3) This process was also confirmed by ESR investigation, in which the signals for DMPO-$^{\cdot}O_2^-$ adducts after adding IBA into the system was replaced by a new seven peak signal (possibly corresponding to the DMPO-$^{\cdot}$CHO adducts as a DMPO–carbon-centered radical) (Fig. 3, L4). IBA alone also afforded a similar but weak seven peak signal, being a straightforward evidence that the $^{\cdot}O_2^-$ can strongly enhance the amount of the $^{\cdot}$CHO radical in the system (Fig. 3, L3).

Then, reacting with O_2, the acyl radical forms a peroxide radical or peracid as intermediates containing active oxygen, which can smoothly oxidize sulfides to the corresponding sulfoxides.[56] We also study the role of mpg-C_3N_4 in the oxidation of MPS by peracids. When peracetic acid (0.25 mmol) was added into the MPS (1 mmol) solution, the reaction was extremely rapid; and all the active oxygen was transferred to MPS in 1 min. The results in the absence (conv.: 24, sel.: >99% for MPSO) and presence of mpg-C_3N_4 (conv.: 24, sel.: >99% for MPSO) gave none difference, indicating that mpg-C_3N_4 mainly contributes to the formation of the peracid and cannot affect the sulfide oxidation after the peracid was present (Table S1,† entries 4–5).

The scope of the reaction was explored under the previously optimized conditions (Table 2). A number of methyl phenyl sulfides bearing electron-withdrawing (Table 2, entries 1–4) or electron-donating substituents (Table 2, entries 5 and 6) on the phenyl ring were efficiently oxidized with both good conversion and selectivity for the corresponding sulfoxides. In particular, the 4-(nitrophenyl) methyl sulfide, an inert molecule, was found to react faster and required shorter reaction time in completion of the reaction, which may be caused by the strong interaction between nitro group and the surface active site of mpg-C_3N_4 (Table 2, entry 1). The oxidation of phenyl sulfide proceeded rapidly, affording 98% conversion in 35 min (Table 2, entry 7). A relatively good result was achieved using methyl furfuryl sulfide as the substrate (Table 2, entry 8). Our catalytic system also has the capability of transforming disulfides to mono sulfone under similar reaction conditions. It is noteworthy that neither sulfoxide nor disulfone was realized in this reaction (Table 2, entry 9).

Table 2 The results of the oxidation of various sulfides by mpg-C_3N_4–IBA system[a]

Entry	Substrate	Product	Time (min)	Conv. (%)	Sel. (%)
1			50	98	98
2			480	76	95
3			330	96	99
4			80	98	99
5			480	92	92
6			300	96	97
7			35	98	97
8			180	89	91
9			240	39	77

[a] Reaction conditions: substrate 1 mmol, mpg-C_3N_4 50 mg, isobutyraldehyde 2 mmol, CH_3CN 3 ml, O_2 1 atm, 25 °C, a mercury lamp (150 W) together with a cut-off filter >420 nm as visible light source.

4. Conclusion

In summary, as a metal-free heterogeneous catalyst, the mpg-C_3N_4 demonstrated some catalytic activity in the oxidation of sulfides to sulfoxides with O_2 under the illumination of visible-light. Particularly, a novel, effective, and environment-friendly catalytic system consisting of mpg-C_3N_4 and IBA has been developed for the oxidation of sulfides at mild conditions (RT, O_2 1 atm). By coupling with IBA, the mpg-C_3N_4 is highly active and selective, is widely applicable to various sulfide substrates, and is capable of facile recycling. According to the ESR investigation and some logic experiments, a possible mechanism of this catalytic system was provided. The attractive non-metal system is expected to illustrate well activity in the oxidation of alcohols, hydrocarbons, and other organic compounds, not limited for the sulfides. We believe that many more organocatalysts and light-sensitive materials can be combined in many ways, thereby opening up several new possibilities for its further use in developing non-metal, light-harvesting, and heterogeneous catalytic methodologies in organic synthesis and the chemical industry.

Acknowledgements

This work was supported by the Joint Petroleum and Petrochemical Funds of the National Natural Science Foundation of China and China National Petroleum Corporation (U1162124), the National Natural Science Foundation of China (no. 20990221), and the Fundamental Research Funds for the Central Universities.

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