

Electronic Supplementary Information

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

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Figure and Table

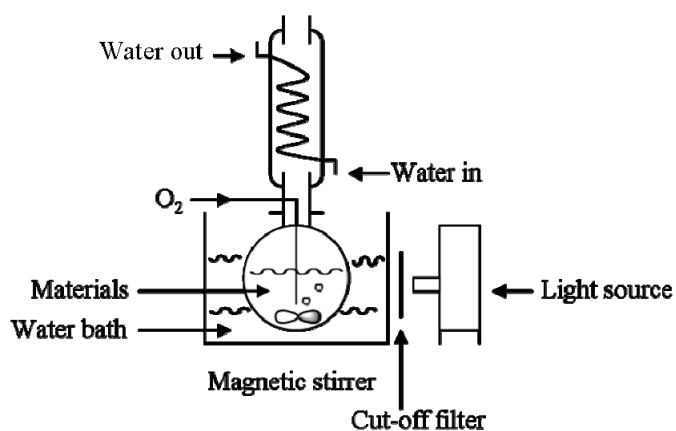


Figure S1. Self-assembly photo-reactor used in this study.

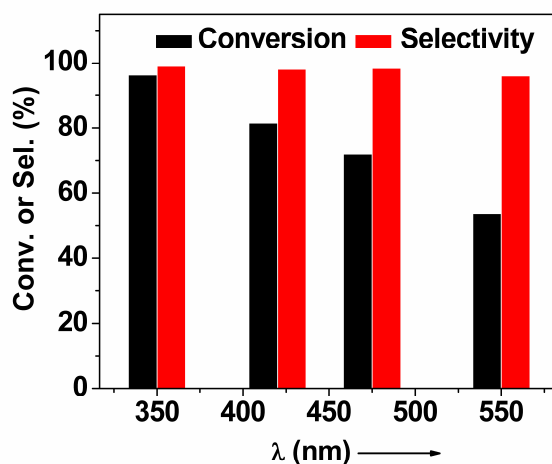


Figure S2. Wavelength dependence of the sulfide oxidation (conversion of methyl phenyl sulfide and selectivity for methyl phenyl sulfoxide) on mpg-C₃N₄/IBA system. Reaction conditions: methyl phenyl sulfide 1 mmol, mpg-C₃N₄ 50 mg, IBA 2 mmol, CH₃CN 3 mL, 25 °C, O₂ 1 atm, 4 h, a mercury lamp (150W) together with a cut-off filter (>350 nm, >420 nm, >475 nm, >550 nm) as visible light source.

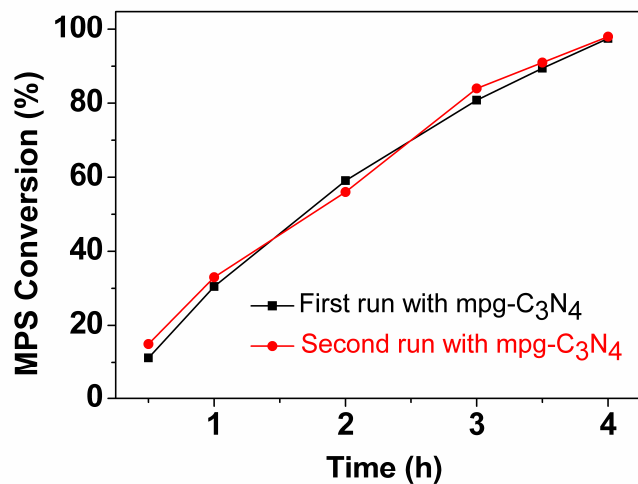


Figure S3. The conversion of MPS vs time plot for the oxidation of MPS by mpg-C₃N₄ (fresh or reused)/IBA system. Reaction conditions: methyl phenyl sulfide 1 mmol, mpg-C₃N₄ (fresh or reused) 50 mg, IBA 2 mmol, CH₃CN 3 mL, 25 °C, 1 atm O₂, visible light irradiation (>420nm).

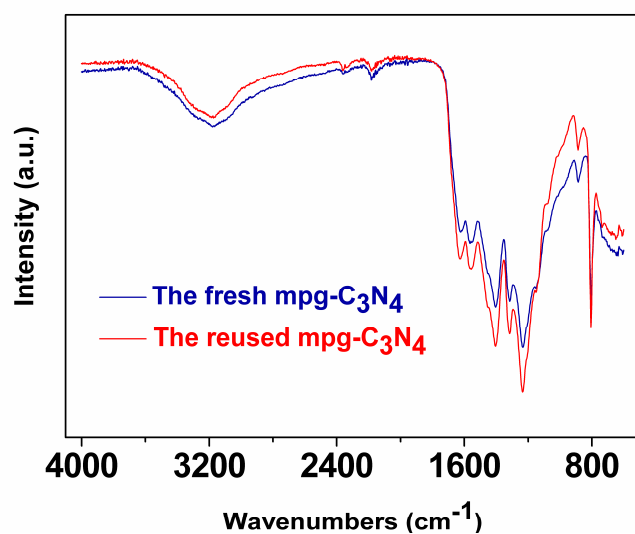


Figure S4. The FT-IR spectra of the fresh mpg-C₃N₄ and reused one.

Table S1. The summary of these comparable experiments.

Entry	Substrate	Product	Time	Conv. (%)	Sel. (%)
1 ^a	Methyl phenyl sulfide	Methyl phenyl sulfoxide	4 h	8	98
2 ^b	Isobutyraldehyde	Isobutyricacid	0.5 h	14	96
3 ^c	Isobutyraldehyde	Isobutyricacid	0.5 h	70	98
4 ^d	Methyl phenyl sulfide	Methyl phenyl sulfoxide	1 min	24	>99
5 ^e	Methyl phenyl sulfide	Methyl phenyl sulfoxide	1 min	24	>99

^a Reaction conditions: methyl phenyl sulfide 1 mmol, mpg-C₃N₄ 50 mg, IBA 2 mmol, hydroquinone 0.5 mmol, CH₃CN 3 mL, 25 °C, O₂ 1 atm, a mercury lamp (150W) together with a cut-off filter >420 nm as visible light source. ^b Reaction conditions: IBA 2 mmol, CH₃CN 3 mL, 25 °C, O₂ 1 atm, a mercury lamp (150W) together with a cut-off filter >420 nm as visible light source. ^c Reaction conditions: IBA 2 mmol, mpg-C₃N₄ 50 mg, CH₃CN 3 mL, 25 °C, O₂ 1 atm, a mercury lamp (150W) together with a cut-off filter >420 nm as visible light source. ^d Reaction conditions: methyl phenyl sulfide 1 mmol, 18~20% peracetic acid solution 10 μL, CH₃CN 3 mL, 25 °C, O₂ 1 atm, a mercury lamp (150W) together with a cut-off filter >420 nm as visible light source. ^e Reaction conditions: methyl phenyl sulfide 1 mmol, mpg-C₃N₄ 50 mg, 18~20% peracetic acid solution 10 μL, CH₃CN 3 mL, 25 °C, O₂ 1 atm, a mercury lamp (150W) together with a cut-off filter >420 nm as visible light source.

Experimental Section

Materials and general methods

Unless otherwise stated, all solvents and chemicals used were of commercially available analytical grade and used without further treatment. Methyl phenyl sulfide (99%), phenyl sulfide (>99%), methyl furfuryl sulfide (97%), diphenyl disulfide (99%), methyl-4-nitrophenyl sulfide (98%), 4-chlorophenyl methyl sulfide (98%), 4-bromophenyl methyl sulfide (98%), 4-(methylthio)anisole (98%), 4-methyl(thio)anisole (99%), 4-fluorophenyl methyl sulfide (98%), isobutyraldehyde (>99%) and 18~20% peracetic acid solution (AR) were purchased from Aladdin Chemistry Co., Ltd, China. Toluene (99.5%), acetonitrile (>99.5%), THF (>99%), CH₃CH₂OH (>99.5%) and CH₂Cl₂ (>99.5%) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd, China. Benzaldehyde (98.5%), 40% glyoxal solution, 37%-40% formaldehyde solution were purchased from Sinopharm Chemistry Co. Ltd. Hydroquinone (98.5%) was purchased from Nanjing Chemical Reagents Co. Ltd, China. The mpg-C₃N₄ was synthesized as our previous reported method. (F. Goettmann, A. Fischer, M. Antonietti, A. Thomas, *Angew. Chem.*, 2006, 118, 4579; *Angew. Chem. Int. Ed.*, 2006, 45, 4467) The mercury lamp (150W) was provided by LOT-Oriel GmbH & CO. KG. Electron spin resonance (ESR) signals were recorded at room temperature (298 K) with a Bruker ESR A300 spectrometer. 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.

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

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 O₂ 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 (150W) 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 and mpg-C₃N₄ was filtered, then the reaction mixture was injected into the GC for analysis. Selectivities and conversions were calculated from the equations: Selectivity = [Sulfoxides]/[Consumed sulfides] × 100; Conversion = [Consumed sulfides]/[Initial sulfides] × 100, respectively.

Reusing of mpg-C₃N₄

When the first oxidation finished, the reaction mixture was centrifuged for 10 min at 4000 r/min and then the liquid layer was siphoned out. The yellow solid was washed with 0.2 M NaOH, CH₃CN and then centrifuged twice. The catalyst was dried in a vacuum oven at 70°C for 24 h. Finally, the recovered mpg-C₃N₄ was used in the subsequent reaction.