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High efficiency photo-oxidation of thioethers over C₆₀@PCN-222 under air

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Selective oxidation of primary thioethers to sulfoxides is an important reaction in the production of pharmaceuticals, agrochemicals, and other valuable fine chemicals. However, the high conversion and selectivity toward sulfoxide in the thioether oxidation under mild conditions still remain a great challenge. In this work, we found a new method to rise to the challenge by applying C_{60} @PCN-222 composite as the catalyst in the photo-oxidation of thioethers. The C_{60} @PCN-222 composite is the integration of guest C_{60} molecules and a porous porphyrin-based metal-organic framework (MOF), PCN-222. We propose that the photogenerated electron–hole separation of PCN-222 could be greatly enhanced through encapsulation of C_{60} molecules with highly delocalized large π conjugation, which makes great contribution to the high conversion and selectivity of this type of reaction. Under air and low optical power (50 mW/cm²) at room-temperature, the composite exhibited excellent catalytic performance. We further explored the underlying mechanism for this photocatalyst by recognizing reactive oxygen species via ESR spectra analysis and experimental conditions adjustment. It has been revealed that the superoxide radicals, generated by electron transfer from a photoexcited MOF to C_{60} molecules, are served as the main active species for the oxidations.

Introduction

Sulfoxides are valuable synthetic reagents for the production of a variety of significantly chemical and biological molecules.¹ Thioethers oxidation is a common method to prepare the corresponding series of sulfoxides. This process is widely used in the industry of medicine, precombustion desulfurization of fuels, innocent treatment of wastewater and chemical warfare agents, etc.² Traditionally, the reaction can be achieved through thermal oxidation process by the use of several kinds of oxidants, such as trifluoro peracetic acid, hydrogen peroxide, tert-butyl hydroperoxide, and iodobenzene diacetate.³ Extensive efforts have been devoted to developing new catalytic systems using environmentally benign reagents such as O₂ even air. photocatalysis is one of the most energy-efficient method for organic transformation under mild conditions.⁴ In this regard, photocatalysts including Pt, Ru, Au, and other noble metal-based nanoparticles under O2 atmosphere have been developed as effective catalysts,⁵ however, low selectivity and catalytic activity still restrict their potential application in industry. Therefore, the design and preparation of new type of photocatalyst that combines the broad range of light absorption with efficient electron (e-)-hole (h+) separation and high reactive oxygen species (ROS) generation would be highly

desired for the photocatalytic sulfoxides production. Fullerene (C_{60}) with precisely controllable size (0.7 nm) and structure has unique properties owing to its special delocalized conjugated structure which consists of 30 bonding molecular orbitals with 60 π electrons and is a potent generator of reactive oxygen species.⁶ It is also well-known for its excellent electron affinities, which could efficiently cause rapid photoinduced charge separation and relatively slow charge recombination.⁷ It can be expected that C_{60} is a potential excellent visible light photocatalyst for thioethers oxidation while making up its weak absorption. We believe that combining C_{60} with a suitable semiconductor will improve the photoinduced charge separation and transfer, which will overcome the disadvantage of different single components and highly enhance the photocatalytic activity.

Serving as a very promising catalytic platform, Metal-organic frameworks (MOFs) are able to organize different components to achieve photoresponse, which have attracted increasing research interest in the application of artificial photosynthesis.⁸ Particularly, the most important advantage of MOFs with respect to other catalysts is their diversified and tailorable structures, which means that it is possible to tune the performance of MOF photocatalysts by the selection of appropriate building blocks and/or particular functional groups for target structures. Recently, porphyrin-based MOFs are very active in the research field of optoelectronic functional materials due to the special photoelectric properties of porphyrin molecules.⁹ Some porphyrin-based MOFs have been reported to be effective photosensitizers for strong absorption in the region of 200–800 nm and be consistent with the typical n-type semiconductors.¹⁰ Several porphyrin-based MOFs have

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 $\mbox{Scheme 1}$ Schematic illustration of the assembly of C_{60}@PCN-222 for photocatalytic oxidation of thioethers.

shown promise as photocatalytic agents facilitating the oxidation of organics.¹⁰ Besides, it has been known that strong π - π interactions between the curved π -surfaces of fullerenes and the flat π -planes of porphyrins exist in both solution and crystalline state.^{11, 12} Based on the above analysis, the combination of porphyrins (electron donor) and C_{60} molecules (electron acceptor) should be a good candidate for efficient photoinduced charge separation because of the small reorganization energy in electron transfer reactions.13, 14 Therefore, the integration of C₆₀ molecules with semiconductor-like porphyrin-based MOFs as ROS generator may achieve efficient catalysis for thioether oxidation while the synergistic effect occurs.

Herein, we rationally designed and prepared a new type of photocatalyst, a composite C₆₀@PCN-222 in which C₆₀ molecules were stabilized by porphyrin-based MOF PCN-222.15 The optimized 3%-C₆₀@PCN-222 exhibit excellent catalytic activity and selectivity in the oxidation of primary thioethers to sulfoxides in air by using visible-light irradiation (Scheme 1) while integrating the advantages of both C₆₀ molecules and PCN-222, lying in their optical properties and ROS production ability. To the best of our knowledge, this is the first catalyst to present high conversion and selectivity for visible-light photocatalytic oxidation of thioethers in air.

Experimental

Materials

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Zirconium (IV) chloride (ZrCl₄, Inochem, 98%), benzoic acid (Aladdin, 99%), N,N-diethylformamide (DEF, Aladdin, 98%), N, N-dimethylformamide (DMF, Xilong, > 99.9%), toluene (Xilong, > 99.5%), fullerene (C₆₀, Tanfeng Tech. Inc., 99.9%), methanol (Aladdin, 99%), β -carotene (Alfa Aesar, 99%), *p*-benzoquinone (Aladdin, 97%), 5,5-dimethyl-1-pyrroline N-Oxide (DMPO, Sigma, 97%), 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, Tci, 99%). All materials were used as received without further purification.

Instrumentation

Powdered X-ray diffraction (PXRD) patterns of all samples were recorded using Rigaku Ultima-IV X-ray diffractometer equipped with graphite-monochromatic Cu K α radiation (λ = 1.54178 Å), tube voltage 40 kV and current 40 mA. N₂ adsorptiondesorption isotherms were measured by Micromeritics ASAP 2020 surface and porosity analyzer at 77 K. Specific surface area

was measured by BET method. High resolution transmission electron microscope (HRTEM) images wହିନ୍ୟ ଡିbtaନନ୍ଦ୍ରେମିନ୍ତନିକ୍ୟି Tecnai F20 electron microscope operated at 200 kV. UV-vis absorption spectra were recorded on a Lambda 950 spectrophotometer in the wavelength range of 200-800 nm. Photocurrent measurements and electrochemical impedance spectroscopy (EIS) measurements were performed on a CHI660E electrochemical workstation (Shanghai Chenhua Apparatus, China) in a conventional three-electrode cell, while saturated calomel electrode (SCE) was used as the reference electrode and a Pt plate was used as the counter electrode. Electron spin resonance spectra (ESR) were recorded on JES-FA300 electron paramagnetic resonance spectrometer under visible-light irradiation (λ > 400 nm). Scanning electron

microscopy (SEM) measurements were taken on a Gemini 300 with an acceleration voltage of 5 kV. The photoluminescence (PL) spectra were measured on PTI QM-TM fluorescence spectrometers. After the reaction, products were analyzed by gas chromatography (GC, Agilent 7980B) with flame ionization detector using HP-5 capillary column (30 m length, 0.32 ID and 0.25 μ m film thickness) and confirmed by gas chromatographymass spectrometer (GC-MS, Shimadzu QP-2010 Ultra System). Preparation of the porphyrin ligand (H₂TCPP). The tetrakis(4carboxyphenyl)porphyrin (H₂TCPP) ligand was synthesized

Synthesis of PCN-222, $Zr_6(\mu_3-OH)_8(OH)_8(TCPP)_2$

according to the previous reports.¹⁶

The MOF was synthesized based on the previous report with minor modifications.¹⁵ Zirconium (IV) chloride (ZrCl₄, 0.15 g), H₂TCPP (0.1 g) and benzoic acid (5.4 g) in 20 mL of N, Ndiethylformamide (DEF) were ultrasonically mixed in a 48 mL thick wall pressure bottle. The bottle was heated in oil bath at 120 °C under stirring with a stir bar inside for 24 h. After cooling down to room temperature, purple needle shaped crystals were harvested by filtration and washed with N, Ndimethylformamide (DMF). Prior to use, the solid was soaked in 200 mL acetone for 24 h to exchange DMF, and then filtered and dried under vacuum.

Fabrication of C₆₀@PCN-222 composites via one-pot approach $ZrCl_4$ (0.15 g), H_2TCPP (0.1 g) and benzoic acid (5.4 g) were added into 20 mL of DEF, and then 20 mL toluene solution of C_{60} (0.5 mg/mL) was added to it and stirred for 30 min. The mixture was transferred into a 100 mL thick wall pressure bottle. The bottle was heated in oil bath at 120 °C under stirring with a stir bar inside for 24 h. The product was collected by filtration, washed with DMF until the filtrate became colorless to give 3%-C₆₀@PCN-222. The 5%/8%-C₆₀@PCN-222 (determined by UV-vis analysis, Fig. S1, S2) were obtained through a similar procedure by changing the amount of C_{60} solution to 30 and 40 mL, respectively. Prior to use, the solid was soaked in 200 mL acetone for 24 h to exchange DMF, and then filtered and dried in a vacuum.

Photocurrent measurement

Photocurrent measurements were performed on a CHI660E electrochemical workstation in a standard three-electrode system with the photocatalyst-coated FTO as the working electrode, Pt plate as the counter electrode, and saturated

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calomel electrode (SCE) as the reference electrode. Fibre-optic lights (50 mW/cm²) with a visible-light cut off filter (> 400 nm) was used as the light source. Aqueous solution of Na₂SO₄ (0.2 mol/L) was used as electrolyte. The as-synthesized PCN-222 and C_{60} @PCN-222 composites (5 mg) were added into a mixed solution with 2 μ L of Nafion and 1 mL of ethanol, and the working electrodes were prepared by dropping the suspension (20 μ L) onto the surface of FTO plate. The working electrodes were dried at room temperature, and the photoresponsive signals of the samples were recorded under chopped light at 0.6 V.

Electrochemical impedance spectroscopy (EIS) measurement EIS measurements of photocatalysts were measured on an electrochemical workstation in a standard three-electrode system with the photocatalyst-coated electrode as the working electrode, Pt plate as the counter electrode, and SCE as the reference electrode with a visible-light (50 mW/cm², λ > 400 nm). The preparation procedure of the working electrode is similar to that for the photocurrent measurement described above.

ESR trapping studies

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Photocatalysts (0.5 mg/mL) were mixed with 1 mL of methanol. Then 100 mM DMPO was added into the solution to capture superoxide radicals. In addition, 100 mM TEMPO was added into another sample to capture singlet oxygen. The measurement was conducted at room temperature upon incident light irradiation with a 300 W xenon lamp (λ > 400 nm) under open air conditions in a quartz cube.

Thioether oxidation reactions conducted

In general, a 20 mg portion of dried photocatalyst was dispersed in 8 mL of methanol containing 0.2 mmol of thioether compounds, and the mixture was sonicated to be homogeneous placed in a quartz tube (100 mL). The catalytic oxidation reaction was initiated at ambient temperature (\sim 20 °C) with air flow under visible-light irradiation (fibre-optic lights, 50 mW/cm², λ > 400 nm, FX300, Beijing Perfectlight Technology Co., China). After the reaction, the catalyst was separated by centrifugation, thoroughly washed with methanol, and then reused in subsequent runs. The yield of the product was analyzed by GC with n-dodecane as the internal standard.

Results and discussion

In this work, PCN-222, one of the representative MOFs¹⁵ was employed as a host of composite photocatalyst. PCN-222 possessing a 3D structure with channels larger than 3 nm and high physicochemical stability as well as a large surface area (BET, over 2000 m²g⁻¹), is very suitable for encapsulating functional guest molecules and hosting catalytic reactions.

A one-pot synthetic approach was used to introduce C_{60} molecules into PCN-222 pore channels to afford C₆₀@PCN-222 in order to prevent the attachment of functional molecules on the external surface of MOF, thus causing their aggregation. Given the strong π - π interactions between the fullerenes and the porphyrins, the quantitative C₆₀ toluene solution should be



Fig. 1 (a) Powder X-ray diffraction patterns and (b) N₂ adsorption isotherms at 77 K of assynthesized PCN-222 and a series of C60@PCN-222 catalysts before reaction. Filled and open symbols represent adsorption and desorption branches, respectively.

fully incorporated into the MOF pores during the PCN-222 selfassembly process.

PXRD would provide the crystal lattice information and phase purity of crystalline materials. PXRD patterns of PCN-222, C_{60} @PCN-222 were shown in Fig. 1a. There was no apparent loss of crystallinity and structure based on PXRD patterns for PCN-222 after loading C_{60} molecules. Moreover, the PXRD patterns of C_{60} @PCN-222 did not exhibit the identifiable diffraction peaks for C_{60} , implying that there was no C_{60} crystal on the surface of PCN-222.

The BET surface areas of as-synthesized PCN-222, 3%/5%/8%-C₆₀@CN-222 were 2171, 1639, 1261, and 656 m²g⁻¹, respectively (Fig. 1b). Two types of pores with diameters of 1.3 and 3.2 nm were evaluated by density functional theory (DFT) simulation from the N₂ sorption curves (Fig. S3). With the increase of C₆₀ content, the peaks for mesopores of 3.2 nm were weakened. The results implied that the mesopores in the framework could be possibly occupied by C₆₀ molecules.

Fig. 2 were SEM image of as-synthesized PCN-222 and TEM ones of C60@PCN-222 composites. The crystal sizes for the assynthesized MOFs decreased gradually with the increase of C₆₀ content from 10 μ m to 100 nm.

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Fig. 2 SEM images for PCN-222 (a) and TEM images for 3%-C_{60}@PCN-222 (b), 5%-C_{60}@PCN-222 (c) and 8%-C_{60}@PCN-222 (d).

The UV-vis spectrum of PCN-222 showed strong adsorption in the range of 200-800 nm (Fig. S4), representing the photon absorption and electron-hole separation ability upon visiblelight irradiation. According to the UV-vis absorption spectra of C60@PCN-222 composites, the Soret absorption bands of the porphyrin ligand were observed to shift bathochromically, suggesting an electronic interaction of frameworks with C_{60} molecules.¹⁷ In addition, this was further verified by steadystate PL measurement, which provided useful hints for the photoexcited charge transfer and recombination. For the pristine H₂TCPP, the PL spectrum emerges two strong emission peaks at 668 and 723 nm, which were originated from the bandto-band recombination of electrons and holes. The intensity of this emission peak decreased dramatically when the C_{60} molecules were encapsulated, which may mean that the bandto-band recombination of electrons and holes was effectively inhibited (Fig. S5).

Furthermore, the transient photocurrent response of pure PCN-222 and C_{60} @PCN-222 samples were tested to investigate the excitation and transfer of photogenerated charge carriers under visible light irradiation. To unveil the charge-separation efficiency, photocurrent measurements had been carried out and the results showed that the photocurrents of C_{60} -decorated PCN-222 were enhanced when compared to the pristine PCN-222 (Fig. 3a), revealing that the formation of C_{60} -MOF composite facilitate the separation of the photogenerated electron-hole pairs. The 8%- C_{60} @PCN-222 displayed the strongest photocurrent response than that of 5% and 3% samples, suggesting more content of C_{60} molecules, higher efficiency of charge transfer of the composites. This speculation was also supported by the electrochemical impedance spectroscopy (EIS) results (Fig. 3b), in which C_{60} @PCN-222



Fig. 3 (a) Transient photocurrent response and (b) EIS Nyquist plots for PCN-222, 3%/5%/8%-C₆₀@PCN-222 under visible-light (50 mW/cm², λ > 400 nm) irradiation.

samples exhibited a smaller radius, indicative of a lower chargetransfer resistance. Both results suggested that the content of C_{60} played a crucial role in the separation of photogenerated electron-hole pairs of the C_{60} @PCN-222 photocatalysts.

Encouraged by the remarkable photocatalytic performance, we explored the photo-oxidation of thioethers to produce sulfoxides under air over C_{60} @PCN-222 or related catalysts under visible-light irradiation. Thioanisole was selected as a model substrate in methanol under air at ambient temperature (~ 20 °C). The data for catalytic oxidation of thioanisole in Table 1 demonstrated that all the C_{60} @PCN-222 composites exhibited the highest catalytic activity with 100% conversion and selectivity for sulfoxide production (Table 1). Considering all indexes, the catalysts in this work are undoubtedly the best photocatalyst among all the reported ones including air and pure O₂ as oxidants (Table S1).^{18, 19}

With the increase of C_{60} content (Table 1, entries 1-3), the reaction time decreased from 3 h to 2 h when the conversion and selectivity reached 100%, however, the TOF values based on moles of C_{60} were 80, 71.4 and 45.5 h⁻¹, respectively. These results indicated that C_{60} molecules plays a key role in improving the activity of catalysts, but the increase of C_{60} content may also lead to blockage of pore channels in PCN-222 (Fig. S3) which suppressed the diffusion of substrate molecules, thus reducing

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Table 1 Photocatalytic oxidation of thioanisole (1a)^a

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Entry	Catalytic	Conversion (%)			
		,,,,	1b	1c	
1	3%-C ₆₀ @PCN-222	> 99	100	0	
2 ^b	5%-C ₆₀ @PCN-222	> 99	100	0	
3 ^{<i>b</i>}	8%-C ₆₀ @PCN-222	> 99	100	0	
4	PCN-222	25	100	0	
5 ^{<i>c</i>}	C ₆₀	< 5			
6 ^c	C ₆₀ +PCN-222	22	100	0	
7	No Catalyst	0	0	0	
8 ^{<i>d</i>}	3%-C ₆₀ @PCN-222	0	0	0	
9	3%-C ₆₀ @PCN-222 + <i>p</i> - benzoquinone	3	100	0	
10	3%-C ₆₀ @PCN-222 + β-carotene	89	100	0	

^aReaction conditions: 1a (0.2 mmol), catalyst (20 mg), CH₃OH (5 mL), room temperature, air flow, LED lamp (50 mW/cm², λ > 400 nm) irradiation for 3 h; ^bReaction time: 2 h; ^cThe content of C₆₀ is the same as those in 3%-C₆₀@PCN-222; ^dIn the dark. All products were determined by GC.

the catalytic efficiency. A series of contrasted experiments were designed and carried out under the same reaction conditions. Without C₆₀, PCN-222 only achieved 25% conversion, whereas unique C₆₀ exhibited almost no catalytic activity (Table 1, entry 4-5) because C₆₀ has almost no adsorption in the visible region (Fig. S1). Physical mixing of C_{60} and PCN-222 only gave 22% yield (Table 1, entry 6), which should be ascribed to the absence of interaction between separated C₆₀ molecules and the PCN-222 framework. These results suggested that there existed synergetic effect in the system of as-synthesized composites for photocatalytic oxidation of 1a. Of course, both light and catalyst were necessary (Table 1, entries 7-8). The time course of the product distribution was recorded for the photocatalytic oxidation of 1a in methanol over the 3%-C₆₀@PCN-222 catalyst. During the reaction process, the conversion of 1a gradually

increased (Fig. S6). No intermediates or other byproducts were
observed during the reaction process. After light and a thore for

able 2 Phot	to-oxidation of various ar	omatic thioethe	ers over 3%-C ₆₀ @P	CN-222 ^a
S 31 1-10a	Air flow, hv (50 r	H₃OH, RT mW/cm², λ ≻ 4	→ () 400 nm) R ₁	0 S R ₂ 1-10b
Entry	Substrate	Time	Conversion (%)	Selectivity (%)
1	S 1a	3h	> 99	100
2	Br S	3h	> 99	100
3	CI Sa	3h	> 99	100
4	O ₂ N S 4a	5h	44	100
5	HO Sa	3h	> 99	100
6	H ₂ N 6a	4h	56	100
7		4h	95	100
8	S 8a	6h	> 99	94
9	S 9a	6h	53	100
10	S_S] 6h	90	92

^aReaction conditions: photocatalyst (20 mg), thioethers (0.2 mmol), CH₃OH (5 mL), room temperature, air flow, LED lamp (50 mW/cm², λ > 400 nm) irradiation for 3 h.

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3 h, **1a** was quantitatively converted into the target product of **1b**.

The recyclability of a heterogeneous catalyst is of great importance for its practical application. Delightedly, the catalytic activity of 3%-C₆₀@PCN-222 was well retained even after five runs of thioanisole oxidation without any treatment or activation (Fig. 4). No significant loss of crystallinity for 3%-C₆₀@PCN-222 was observed from the PXRD patterns (Fig. S7), suggesting excellent recyclability and stability of 3%-C₆₀@PCN-222.

In order to further explore the universality of this new type of photocatalyst, 3%- C_{60} @PCN-222 was chosen to test for the photocatalytic oxidation of a series of thioethers under the previously optimized conditions, and the results were summarized in Table 2. Most of diverse substituted thioethers with different R₁ and R₂ groups were highly efficiently oxidized in different reactions time. According to the previous reports,²⁰, ²¹ thioanisole bearing electron-donating groups as substrate exhibited higher yield than those bearing electron-withdrawing groups under the same reaction condition. However, the reaction time remained unchanged after substitution of the electron-withdrawing group (-Cl and -Br, Table 2, entries 2-3) implying excellent catalytic activity of this catalyst. With

stronger electron-withdrawing group substituted (-NO₂, Table 2, entry 4), the conversion did decrease to 44%. As electrondonating groups -OH and -NH₂ (Table 2, entries 4-5), the conversion of substrates substituted by the latter was only 56% after 4 h oxidation. The reason could be speculated that the basic group -NH₂ on the substrate interacted with the ligand porphyrin resulting in a decrease in catalyst activity. Except for the electronic effect of substituted groups, steric hindrance also affected the reaction efficiency (Table 2, entries 3 vs. 7, para-Cl, 100% conversion in 3 h, ortho-Cl, 95% conversion in 4 h). The size of substrates was another important influence factor as the larger the thioether molecule, the lower the reaction efficiency (Table 2, entries 8-10), due to the slow transport of larger molecules through the channels.

Superoxide radicals (O•-2), singlet oxygen $({}^{1}O_{2})$ and hydroxyl radicals (•OH) were reported to be the active species for photo-oxidation of thioethers. ${}^{19-23}$ Since the photocatalytic reaction



Fig. 5 ESR spectra for systems containing DMPO or TEMPO and C_{60} @PCN-222 samples in methanol upon visible-light irradiation for 10 min (λ > 400 nm). (a) DMPO-0-2 without substrate, (b) DMPO-0-2 with substrate (thioanisole) and (c) TEMPO- $^{1}O_2$ with substrate, (d) TEMPO- $^{1}O_2$ with substrate (thioanisole).

was performed in methanol which would quench ${}^{\circ}OH$,^{18,24} ${}^{1}O_{2}$ and O ${}^{\circ}-2$ were the possible ROS involved in the reaction system as shown in Scheme S1. Then, we explored the underlying mechanism for this new type of photocatalyst by recognizing reactive oxygen species via the ESR investigation and controlled experiments. To recognize reactive oxygen species in photooxidation of thioanisole, a series of ESR measurements were conducted. DMPO and TEMPO were employed to probe the ROS generated upon visible-light irradiation.

After irradiation, the characteristic signals of the DMPO-O--2 and TEMPO-1O2 adducts were clearly observed by ESR spectra (Fig. 5). 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 C_{60} @PCN-222 photocatalysts. The DMPO solution gave specific DMPO-O•-2 (1:1:1:1 quartet) and TEMPO solution gave specific TEMPO-1O2 (1:1:1 triplet) signals with or without substrate (thioanisole).²⁰⁻ $^{\rm 23}$ Moreover, with the increasing of $C_{\rm 60}$ content in MOF, the signal intensity of O•-2 and ¹O₂ were also increased. However, the addition of substrate would increase the yield of O•-2 (Fig. 5a, b) and decrease the yield of ${}^{1}O_{2}$ (Fig. 5c, d), indicating that the main species of ROS in the reaction is O•-2. According to similar reports,^{6a} upon photoirradiation, C₆₀ was known to form a long-lived triplet state (³C₆₀^{*}), which could react with electron donor (thioanisole), and then ${}^{3}C_{60}^{*}$ was reduced to C•-60 which subsequently reduced O₂ to O•-2

To further prove the role of reactive oxygen species in the reaction system, specific scavengers that would inhibit the generation of ${}^{1}O_{2}$ or O•-2, were introduced into the reaction system. The conversion of **1a** dropped from 100% to 3% in the presence of *p*-benzoquinone (Table 1, entry 9) suggesting that O•-2 was served as a main oxidative species in the reaction process. Differently, the conversion dropped from 100% to 89% with β -carotene as a scavenger to capture ${}^{1}O_{2}$ (Table 1, entry 10). Such results clearly indicated that O•-2 was the major oxidative species for the photocatalytic oxidation of thioethers, which are consistent with the ESR test data.

From the results described above, a possible mechanism was proposed for the photocatalytic oxidation of thioethers. As

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shown in Scheme S1A, photoinduced holes (h⁺) in the valence band (VB) and electrons (e⁻) in the conduction band (CB) were generated from PCN-222 under light irradiation, so PCN-222 was excited to PCN-222*. The generated electrons were then transferred from PCN-222* to $\mathrm{C_{60}}$ due to the π structure and excellent electron acceptability of this molecule which caused the separation of h⁺ and e⁻ more efficiently and the formation of PCN-222⁺. Upon photoexcitation, C_{60} was known to form a long-lived triplet state $({}^{3}C_{60}^{*})$ which could react with electron donors and was reduced to C•-60. This species then subsequently reduced O_2 to $O \bullet -2.6^{a}$ On the other hand, PCN-222⁺ interacted with thioanisole by single-electron transfer to form an S-centered free-radical cation which was also produced by the reaction of thioanisole with ${}^{3}C_{60}{}^{*}$.^{6a} Simultaneously, PCN-222 was regenerated from PCN-222*. The S-centered freeradical cation prefered to react with O•-2 formed at the conduction band of C_{60} , allowing for the evolution of sulfide peroxide. In the protic solvent CH₃OH, the final methyl phenyl sulfoxide is formed. At this stage, this proposed mechanism still lacks direct evidence because of the elusive transition states in the photoinduced radical. Further experimental and theoretical work will be done in the future to present a clearer mechanistic insight.

Conclusion

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We have developed a novel heterogeneous catalytic system can photochemically generate O•-2 as a mild oxidant for the selective photo-oxidation of thioethers to sulfoxides. The reactions could proceed with excellent selectivity and yield within short reaction time under ambient conditions involving visible-light irradiation. Neither strong oxidants were needed, nor obvious loss of catalytic activity was observed after catalysts were recycled and reused. This catalytic method could extend to the transformation from various thioethers to the corresponding sulfoxides. According to the ESR investigation and control experiments, a possible mechanism was proposed for the photocatalytic oxidation of thioethers with O•-2 as the main oxidative species, suggests that O•-2 can improve the conversion and selectivity of thioethers oxidation. This work represents loading $C_{\rm 60}$ molecules can enhance the photogenerated electron-hole separation of MOFs, achieving the acceleration of catalytic organic oxidations under very mild conditions. This also opens up a new pathway to the development of efficiently utilizing O•-2 for photocatalytic organic reactions.

Conflicts of interest

The authors declare no conflict of interest.

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For the first time, fullerene (C_{60}) was used to enhance photogenerated electron-hole separation of MOFs as for catalyst and showed high catalytic activity in the photocatalytical oxidation of thioether in air.

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