

**Co(NO₃)₂/covalent organic framework nanoparticles for
efficient photocatalytic oxidation of thioanisole under mild
conditions**

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1. Materials and Methods

Materials. 1,3,5-Tris(4-aminophenyl)benzene (TAPB) and [2,2'-Bipyridine]-5,5'-dicarboxaldehyde (Bp) were obtained from Jilin Yanshen Technology Co., Ltd., China. $\text{Co}(\text{NO}_3)_2$, acetic acid and polyvinyl pyrrolidone (PVP) were provided by Beijing InnoChem Science & Technology Co., Ltd. Ethanol (A.R. Grade) and acetonitrile (A.R. Grade) were purchased from Beijing Chemical Works. Purified water was purchased from Beijing Analysis Instrument Factory. Nafion D-521 dispersion (5% w/w in water and 1-propanol, ≥ 0.92 meq/g exchange capacity) was purchased from Alfa Aesar China Co., Ltd. All commercially purchased reagents were used without further purification.

Synthesis of COF. TAPB, Bp and PVP were added into 100 mL of acetonitrile. The mixture was stirred at room temperature for 5 min, and then 5 mL of acetic acid was added thereto and stirred at room temperature. After 12 h, the solid was collected by centrifugation and washed three times with acetonitrile and ethanol. Finally, the product was obtained after drying in a vacuum oven at 80 °C for 12 h.

Synthesis of $\text{Co}(\text{NO}_3)_2/\text{COF}$. COF (20 mg) was dispersed in ethanol (10 mL), followed by the addition of a certain amount of ethanol solution containing $\text{Co}(\text{NO}_3)_2$ (1 mg/mL). After stirring the mixture at 60 °C for 6 h, the solid product was filtered, washed twice with acetonitrile and ethanol. The obtained solid products were named as $\text{Co}(\text{NO}_3)_2/\text{COF-x}$, $x=0.5, 1, 2, 3, 4$ and 5, where x represents the weight percentage of $\text{Co}(\text{NO}_3)_2$ to COF. The $\text{Co}(\text{NO}_3)_2/\text{COF}$ mentioned in the manuscript refers to $\text{Co}(\text{NO}_3)_2/\text{COF-1}$.

Characterizations. X-ray diffraction (XRD) patterns were determined by a Rigaku D/max-2500 diffractometer equipped with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 200 mA. Transmission electron microscopy (TEM, JEOL JEM-1011) and high-resolution TEM (HRTEM, JEOL-2100F) were operated at 200 kV. X-ray photoelectron spectra (XPS) were carried out with a multipurpose X-ray photoemission spectroscope (Thermo Scientific ESCALAB 250Xi). Fourier transform infrared (FT-IR) spectra were determined by a Bruker Tensor 27 spectrometer. The KBr pellet method was applied to prepare the solid samples. The optical absorption properties were characterized by ultraviolet-visible diffused reflectance spectra (UV-Vis DRS, V-2600, SHIMADZU)

using BaSO₄ as a reference for diffuse experiments. Photoluminescence (PL) spectra were recorded in the air and at room temperature with a Hitachi F-4600 fluorescence spectrophotometer with the excitation wavelength of 410 nm. The Co, C and N contents of sample were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, VISTA-MPX, Varian). Electron spin resonance (ESR) spectra were collected on a Bruker ESP-300 spectrometer.

Photocatalytic oxidation of thioanisole. In a typical experiment, 10 mg photocatalyst and 0.30 mmol of substrate were dispersed in 5 mL of acetonitrile in a 100 mL round-bottom flask and then vigorously stirred in air for 30 min to obtain a suspension. Then the flask was plugged with a rubber stopper and irradiated by a 300 W Xe lamp ($350 < \lambda < 780$ nm, Aulight CEL-HX, Beijing). Xenon lamps are the most commonly used solar simulators in accordance with international standards and are used in a wide range of research areas, including photobiology¹, photo-oxidation², photodegradation³, and photocatalysis⁴. The reaction system was kept at 25 °C by a circulating water device. After the desired irradiation time, the liquid product was analyzed by ¹H nuclear magnetic resonance (¹H NMR, Bruker Avance III 400 HD). The conversion of thioanisole and selectivity to sulfone were calculated from the integration of ¹H NMR peaks. For the reusability study, the Co(NO₃)₂/COF catalyst after 5 h of reaction was recovered by centrifugation, washed with ethanol and dried under vacuum. Then the catalyst was added into 5 mL acetonitrile containing 0.30 mmol of thioanisole for a consecutive run.

Photoelectrochemical test. The photoelectrochemical measurement was implemented in a three-electrode system at electrochemical workstation (CHI660E, Chenhua Instrument, Shanghai, China) with the photocatalyst-coated indium-tin oxide (ITO) as working electrode (Fig. S6), an Ag/AgCl with 3.5 M KCl as a reference electrode and Pt net (1 cm²) as the counter electrode. The illumination source adopted in photocurrent ON/OFF cycles was a 300 W Xe lamp ($350 < \lambda < 780$ nm). A 0.5 M Na₂SO₄ solution (pH = 6.8) was applied as electrolyte. To prepare the catalyst ink, 3 mg of the photocatalyst and 10 μL of 5 % Nafion 117 solution, as conducting binder, were introduced into 200 μL of ethanol and sonicated for 1 h. Then the catalyst ink was

dropped on the surface of an ITO plate (1 cm²) to prepare working electrode. Transient photocurrents, Mott-Schottky measurements and electrochemical impedance spectra (EIS) Nyquist plots were performed in 0.5 M Na₂SO₄ solution. All the potentials were recorded versus Ag/AgCl (vs. Ag/AgCl) electrode.

2. Results

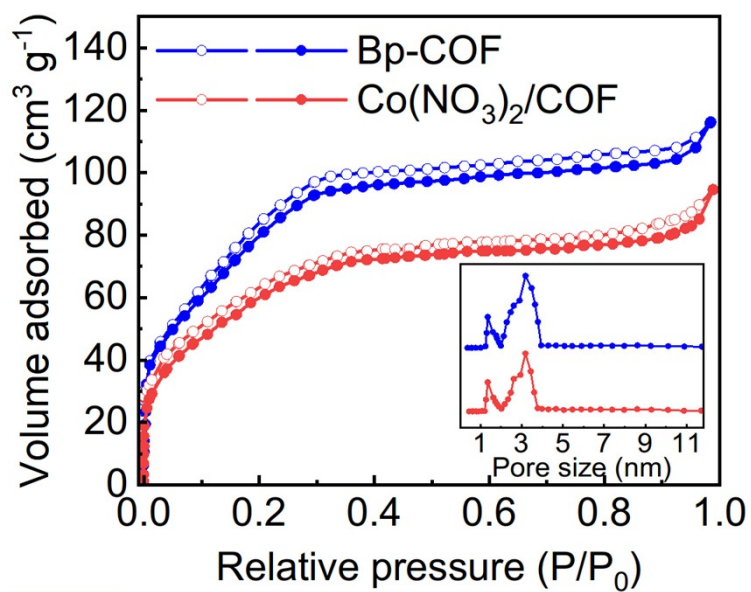


Fig. S1. N₂ adsorption-desorption isotherms and pore size distribution curves of Bp-COF and Co(NO₃)₂/COF.

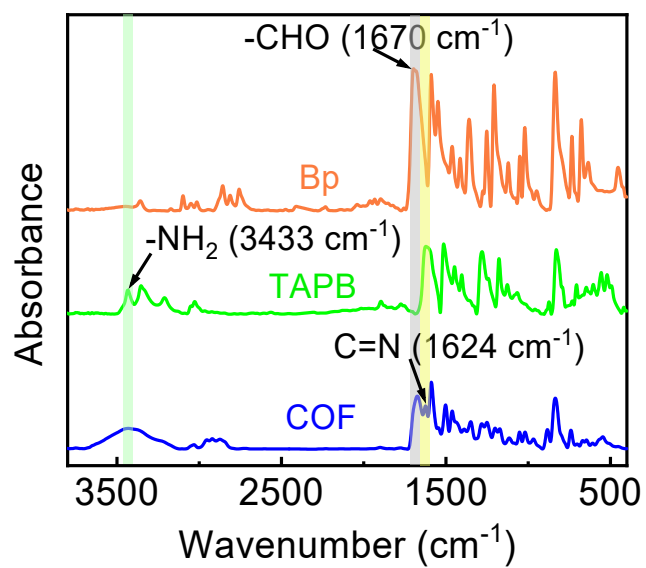


Fig. S2. FT-IR spectra of Bp, TAPB and COF.

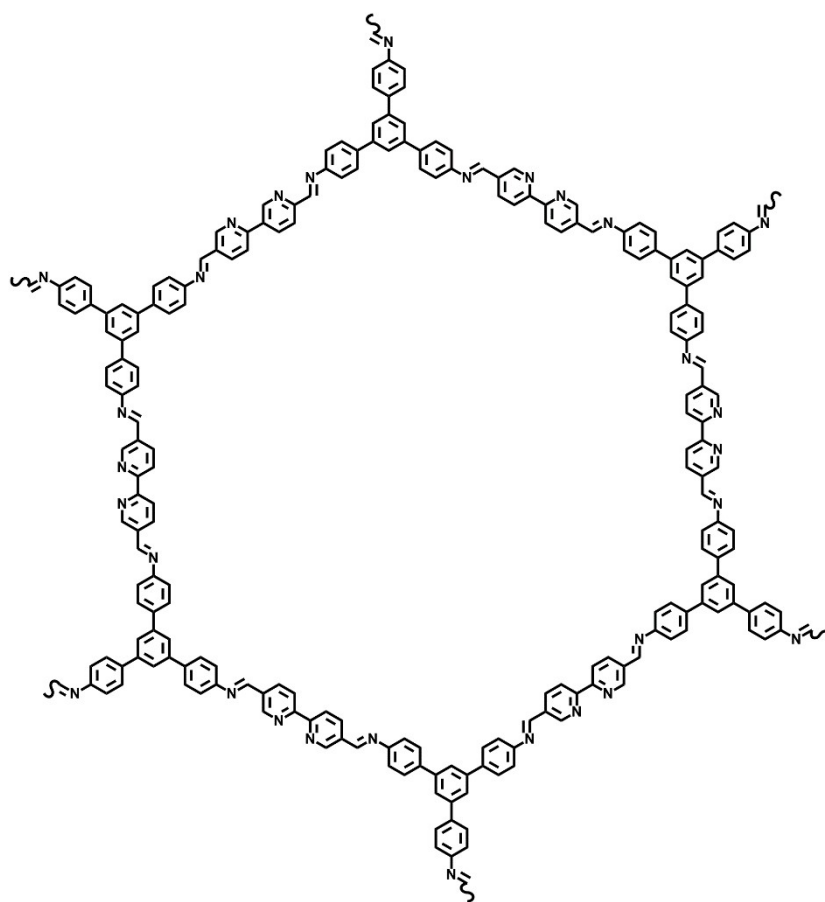


Fig. S3. Molecular structure of COF.

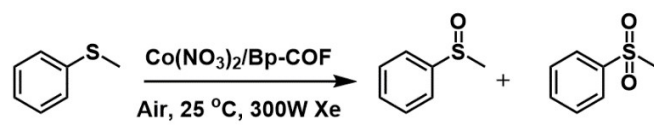


Fig. S4. Photocatalytic reaction of thioanisole to methyl phenyl sulfoxide and sulfone.

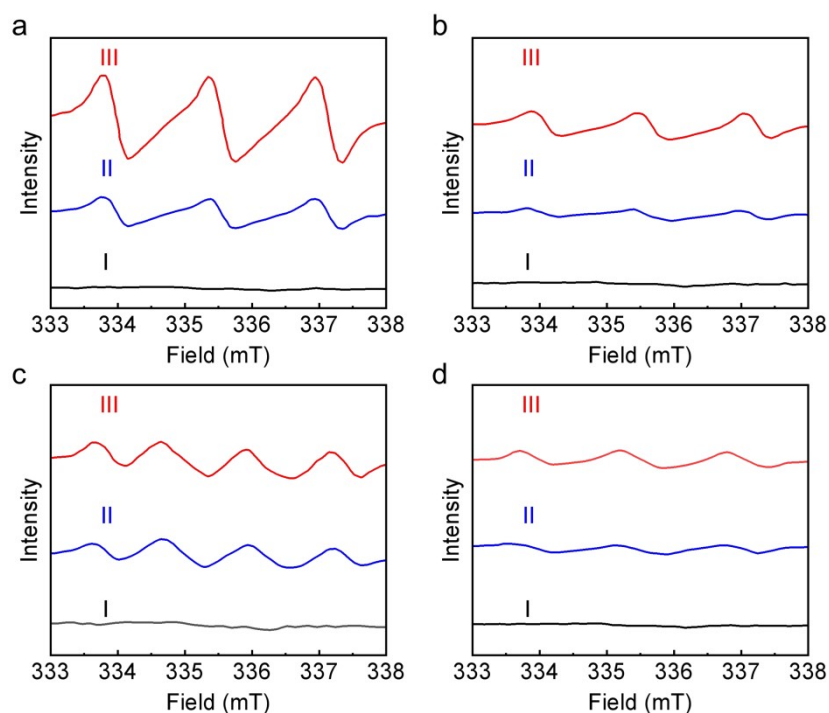


Fig. S5. (a, b) ESR spectra of $\text{Co}(\text{NO}_3)_2/\text{COF}$ (a) and COF (b) in the presence of DMPO. (c, d) ESR spectra of $\text{Co}(\text{NO}_3)_2/\text{COF}$ (c) and COF (d) in the presence of TEMP. Curve I: without thioanisole and in the dark. Curves II and III: without thioanisole and under illumination for 20 s (II) and 40 s (IV), respectively.

In the dark, no characteristic ESR signals were detected. After irradiation, there are characteristic signals of the $\text{DMPO-O}_2^{\cdot-}$ and $\text{TEMP-}^1\text{O}_2$ adducts. Notably, the intensities of ESR responses enhance with prolonged illumination time, confirming the formation of $\text{O}_2^{\cdot-}$ and $^1\text{O}_2$ by light irradiation. As shown in Fig. S4a, the signal of DMPO is largely enhanced with the increased illumination time in the presence of $\text{Co}(\text{NO}_3)_2$, indicating more $\text{O}_2^{\cdot-}$ is produced in the photocatalytic oxidation process. In a contrast, the signal of COF is suppressed (Fig. S4b), suggesting much less $\text{O}_2^{\cdot-}$ yield in photocatalytic oxidation process. Moreover, the $\text{Co}(\text{NO}_3)_2/\text{COF}$ system with DMPO shows the ESR spectra with relatively weak signals for $\text{TEMP-}^1\text{O}_2$ (Fig. S4c), corresponding to the little generation of $^1\text{O}_2$. However, the COF system produces considerable $^1\text{O}_2$ in O_2 activation through the charge-transfer process (Fig. S4d), which competes with the energy-transfer process related $\text{O}_2^{\cdot-}$ generation. These results suggest that $\text{O}_2^{\cdot-}$ is key reactive oxygen species for the photocatalytic oxidation of sulfides.

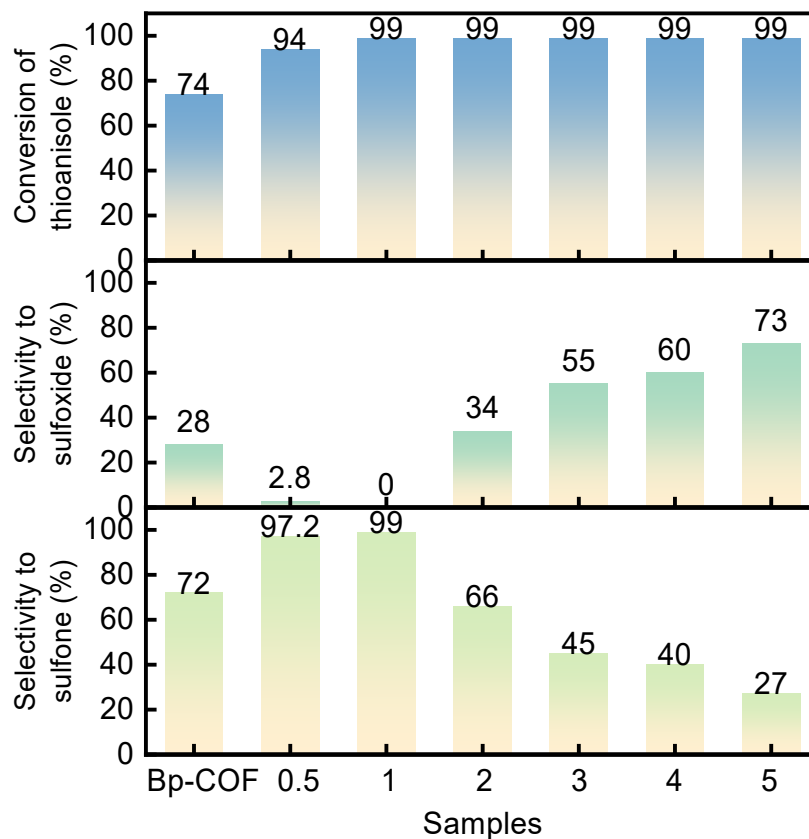


Fig. S6. Conversions and selectivities for the oxidation of thioanisole catalyzed by COF and $\text{Co}(\text{NO}_3)_2/\text{COF}$ -0.5, 1, 2, 3, 4, 5 (The numbers represent the amount of $\text{Co}(\text{NO}_3)_2$ added during the preparation of the composites, respectively.) Reaction conditions: 10 mg catalyst, 5 mL acetonitrile, 0.3 mmol thioanisole, 6 h, 300 W Xe lamp.

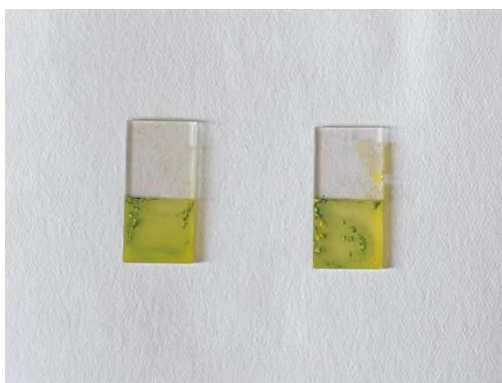


Fig. S7. Photos of $\text{Co}(\text{NO}_3)_2/\text{COF-1}$ (left) and COF (right) on ITO.

Table S1. The Co, N and C contents in the $\text{Co}(\text{NO}_3)_2/\text{COF-1}$ determined by ICP-AES.

Elements	Contents (wt%)
Co	0.88
N	10.61
C	71.91

Table S2. The control experiments for photocatalytic oxidation of thioanisole.

Entry	Reaction time (h)	Conditions	Conversion (%)
1	6	Without photocatalyst	<1
2	6	In dark	<1
3	6	Using Ar to replace air	<1

Normal reaction conditions: 10 mg catalyst, 5 mL acetonitrile, 0.3 mmol thioanisole, 6h, air, 300 W Xe lamp.

Table S3. Comparison of the reaction conditions and performances of different catalysts for photocatalytic oxidation of thioanisole.

Catalysts	Conditions	Time (h)	Conversion (%)	Selectivity (%)	Production rate of Sulfone (mmol g ⁻¹ h ⁻¹)	Ref.
Co(NO ₃) ₂ /COF (10 mg)	Thioanisole (0.3 mmol), acetonitrile (5 mL), air, 25 °C, 300 W Xe lamp.	6	99	99	5.0	This work
mpg-C ₃ N ₄ (50 mg)	Thioanisole (1 mmol), acetonitrile (3 mL), O ₂ (1 atm), 25 °C, Isobutyraldehyde (Initiators) visible light 150 W Hg lamp.	4	100	92	4.6	5
TPP ₄ H ₂ [V ₁₀ O ₂₈] (2 mg)	Thioanisole (0.2 mmol), methyl ethyl ketone (4 mL), air, 30 °C, visible light (λ > 400 nm, 300 W Xe lamp)	24	92	75	2.9	6
CF ₃ SO ₂ Na (40 mg)	Thioanisole (1 mmol); bis(2-butoxyethyl)ether (4 mmol), O ₂ balloon, 25 °C, 385-390 nm LED.	24	99	94	1.0	7
KTaO ₃ (20 mg)	Thioanisole (2 mmol), acetonitrile (10 mL), H ₂ O ₂ (2.0 mmol), 60 °C.	4	55.5	30.7	4.2	8
KTaO ₃ (20 mg)	Thioanisole (2 mmol), acetonitrile (10 mL), H ₂ O ₂ (4.0 mmol), 60 °C.	4	87.4	80.1	17.5	8
KTaO ₃ (20 mg)	Thioanisole (2 mmol), acetonitrile (10 mL), H ₂ O ₂ (4.0 mmol), 20 °C.	4	60.0	60.0	9.0	8
MWCNTs-COOH (20 mg)	Thioanisole (1 mmol), no solvent, H ₂ O ₂ (2.5 mmol), 25 °C.	10	99	99	5.0	9
TBAPWFe	Thioanisole (1 mmol), acetonitrile	0.67	52	40	6.2	10

(50 mg)	(3 mL), H ₂ O ₂ (1.0 mmol), 50 °C.					
P ₂ W ₁₈ Sn ₃ @MIL-101 (50 mg)	Thioanisole (1 mmol), H ₂ O (5 mL), H ₂ O ₂ (5.9 mmol), 25 °C.	2.5	99	98	7.8	11
Pd ₂ LCI ₄ (5 mg)	Thioanisole (1 mmol), acetonitrile (3 mL), H ₂ O ₂ (3.0 mmol), 25 °C.	4	34	53	9.0	12
Pd ₂ LCI ₄ (5 mg)	Thioanisole (1 mmol), acetonitrile (3 mL), H ₂ O ₂ (3.0 mmol), 50 °C.	4	70	99	35.0	12
Pd ₂ LCI ₄ (5 mg)	Thioanisole (1 mmol), acetonitrile (3 mL), H ₂ O ₂ (1.0 mmol), 50 °C.	4	51	80	20.0	12
C ₄ H ₅₈ Mo ₄ Na ₈ Ni						
O ₅₂ P ₄ (25 mg)	Thioanisole (0.5 mmol), acetonitrile (5 mL), H ₂ O ₂ (1.3 mmol), 25 °C.	1	63	78	9.8	13

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