Supporting Information

Visible-Light-Driven Organic Oxidation over CdS Doped Metal-Organic Frameworks

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1. Experimental Section.

Materials and methods

Materials and Methods. All chemical reagents and solvents were purchased from commercial companies and without further purification. Zirconium chloride (ZrCl₄, purity>98%) and 2,6-Naphthalenedicarboxylic acid [H₂(2,6-NDC), purity>98%], Thioacetamide (purity>99%) acetic acid (99.5%) Cadmium acetate dihydrate [Cd(CH₃COO)₂·2H₂O, purity>98%] were purchased from Energy Chemical. N,N-Dimethylformamide (DMF), Ethanol were bought from Tianjin Kemiou Chemical Reagent Co., Ltd.

Powder X-ray diffraction (PXRD) using a Bruker D8 Advance X-ray diffractometer (Cu K α radiation, $\lambda = 1.5418$ Å) in the range of 5-60°(2 θ). Solid UV–vis spectra were obtained using a Hitachi U-4100 UV–vis–NIR spectrophotometer and a white standard of BaSO4 was used as a reference. Scanning electron microscope (SEM) experiments used JSM-7610F Plus record. Transmission electron microscopy (TEM) were performed on Tecnai F30. GC analyses were carried out an Agilent Technologies 6890 N GC system, equipped with the FID detector and the chromatographic column of HP-50+, with N₂ used as the carrier gas. Electrochemical experiments were carried out on CHI760E workstation with three-electrode system. Electron paramagnetic resonance (EPR) measurements were carried out on a Bruker E500 instrument. The spectra of the Advanced Fourier Transform Infrared Spectrometer were measured with a ThermoFisher 6700 instrument (KBr pellets). N₂ sorption isotherm at 77 K were carried out on Micromeritics 3Flex Surface Characterization Analyzer.

Photoelectrochemical Characterization. Photocurrent curves, Electrochemical impedance spectra, Mott-Schottky plots for CdS@DUT-52 were carried out on a three-electrode system with the photocatalyst-coated FTO, a Pt plate and Ag/AgCl as the working electrode, counter electrode, reference electrode, respectively. All measurements were made in a solution of 1.0 M potassium chloride at room temperature. A 425 nm LED was used as light source. A mixture solution containing 20.0 μ L Nafion, 500 μ L of ethanol and 500 μ L H₂O was added to the catalyst (5.0 mg). The working electrode is prepared by dripping the mixture onto the surface of the FTO glass about one square centimeter and drying it naturally.

General Procedure for the Reaction. For oxidation of benzylamines: Under the standard conditions, the mixture of catalyst(10.0 mg),CH₃CN(2.0 mL),substrates(0.2 mmol) was added into the quartz tube(15 mL) equipped with circulating water to ensure reacted at room temperature. The reaction mixture was stirred with irridation of 425 nm LED for 1 h. After reation, the yield was determined by GC-MS. For oxidation of sulfides, the conditions were the same as oxidation of benzylamines except that the substrate (0.1 mmol) and the solvent was 2.0 ml CH₃OH reacted in an oxygen atmosphere for 12 h. For oxidation of alchohols, were the same as oxidation of sulfides except that the solvent was CH₃CN (2.0 ml).

EPR detection of superoxide radical. The EPR spectra were obtained in the presence of DMPO. Typically, 10 μL DMPO was mixed with 1mL of CdS-3@DUT-52/CH₃OH (2.0 mg/1.0 ml). The mixture were then added to EPR tube. EPR measurements were carried out under 425 nm illumination for 2 or 5 minutes.

DUT-52 is prepared by reported method^{S1}. Preparation of CdS@DUT52 with different CdS contents using Cd(CH₃COO)₂·2H₂O and thioacetamide as the cadmium and sulfur sources^{S2}, respectively.

Synthesis of DUT-52. ZrCl₄ (230 mg, 1.03 mmol) and 2,6-naphthalenedicarboxylic acid [H₂(2,6-ndc) (216 mg, 1 mmol)] was dissolved in DMF by sonication for 30 minutes. 3ml (47.6 mmol) of acetic acid were added and the mixture was sonicated for additional 30 minutes. The solution was transferred to a Teflon-lined stainless steel autoclave (100 ml) heated at 120°C for 24h. The white precipitates obtained were purified and washed three times with DMF and ethanol, respectively.

Synthesis of CdS. 92 mg of Cd(CH₃COO)₂·2H₂O was dissolved in 10ml of ethanol. Thereafter, the mixture was heated for 10 mins at 80 °C, then 10 ml of aqueous solution (thioacetamide, 26 mg) was injected into the flask dropwise, stirred and heated vigorously at 80 °C, and heated for 30 mins. The sediment was filtered several times and flushed with H₂O and ethanol. Finally, dry at 60 °C in a vacuum for 12 h

Synthesis of CdS-1@DUT-52. 8 mg of Cd(CH₃COO)₂·2H₂O was dissolved in 10 mL of ethanol. Next, 40 mg of DUT-52 was mixed with the solution and then ultrasound was performed for 30 mins. Thereafter, the mixture was heated for 10 mins at 80°C, then 10ml of aqueous solution [thioacetamide (TAA), 2.3 mg] was injected into the flask dropwise, stirred and heated vigorously at 80 °C, and heated for 30 mins.

Synthesis of CdS-2@DUT-52. The synthesis process is almost identical to that of CdS-1@DUT-52, except for using12 mg of Cd(CH₃COO) ₂.2H₂O and 3.6 mg of TAA.

Synthesis of CdS-3@DUT-52. The synthesis process is almost identical to that of CdS-

1@DUT-52, except for using16.8 mg of Cd (CH₃COO) 2.2H₂O and 4.7 mg of TAA

Synthesis of CdS-4@DUT-52. The synthesis process is almost identical to that of CdS-1@DUT-52, except for using 49 mg of Cd (CH₃COO) ₂.2H₂O and 14 mg of TAA

2. Characterizations of Catalysts.



Figure S1. PXRD pattern of CdS-4@DUT-52 and CdS.



Figure S2. XPS spectra of CdS-3@DUT-52 before and after catalysis: (a) survey spectra and high resolution (b) Zr 3d, (c) Cd 3d, (d) S 2p spectra.



Figure S3. N₂ adsorption–desorption isotherms of DUT-52 and CdS-x(x=1-4)@DUT-

52.



Figure S4. Pore size distributions of DUT-52 and CdS-x(x=1-4)@DUT-52.



Figure S5. PL spectra of CdS and CdS-3@DUT-52 (excitation wavelength: 375nm).



Figure S6. The Tauc/Davis-Mott plots of CdS-3@DUT-52.



Figure S7. Light on-off experiment for the oxidation reaction at 15 min intervals of irradiation and darkness.



Figure S8. PXRD pattern of CdS-3@DUT-52 after catalysis.



Figure S9. IR spectra of CdS-3@DUT-52 before and after catalysis.



Figure S10. SEM image of CdS-3@DUT-52 before catalysis (a) and after catalysis

(b).

3.Catalysis Details



Figure S11. Relationship between the conversion of methylphenyl sulfide and reaction time with (black line) or without CdS-3@DUT-52 (red line) (b)Recycling experiments of oxidation of methylphenyl sulfide.



Figure S12. Relationship between the conversion of benzylic alchohol and reaction time with (black line) or without CdS-3@DUT-52 (red line) (b)Recycling experiments of oxidation of benzylic alchohol.



Figure S13. A plausible mechanism for aerobic oxidation of benzylamine



Figure S14. A plausible mechanism for the aerobic oxidation of phenyl methyl sulfide



Figure S15. A plausible mechanism for the aerobic oxidation of benzyl alcohol

Gas Chromatogram

For the oxidation reaction of amines, the catalyst was separated by centrifugation after the reaction and the residual liquid was taken for GC analysis to calculate the amount of reaction product, using 1,3,5-trimethoxybenzene as an internal standard. For oxidation of sulfides and alcohols, using ethylbenzene as an internal standard.







Figure S16. Gas Chromatograms of the oxidation of the expanded substrates.



The GC-Mass Spectrum of the Oxidation Products









Figure S17. GC-Mass spectrums of the oxidation products.

	CdS contents (wt%)	
CdS-1@DUT-52	4.0	
CdS-2@DUT-52	6.0	
CdS-3@DUT-52	9.4	
CdS-4@DUT-52	18.2	

 Table S1. ICP results of CdS contents for CdS-x(x=1-4)@DUT-52

Table S2. Oxidation of methylphenyl sulfide under different conditions^a

$\bigcup_{i} S_{i} \xrightarrow{\text{Cat. (10mg) 425nm}} \bigcup_{i} S_{i}$			
Entry	deviation from standard conditions	Yield $(\%)^b$	
1	None	80	
2	No catalyst	trace	
3	In dark	trace	
4	Ar instead of air	trace	
5	CdS instead of CdS-3@DUT-52	4	
6	DUT-52	trace	
7	air instead of O ₂	70	
8	CdS-1@DUT-52 instead of CdS-3@DUT-52	67	
9	CdS-2@DUT-52 instead of CdS-3@DUT-52	71	
10	CdS-4@DUT-52 instead of CdS-3@DUT-52	55	

^aStandard conditions: methylphenyl sulfide (0.1 mmol), CdS-3@DUT-52 (catalyst,

10.0 mg) in CH₃OH (2.0 ml) irradiated with 425 nm LED at room temperature under

O₂ atmosphere. ^bDetermined by GC-MS

H Cat. (10mg) 425nm H O			
	O_2 r.t.		
Entry	deviation from standard conditions	Yield $(\%)^b$	
1	None	66	
2	No catalyst	trace	
3	In dark	trace	
4	Ar instead of air	trace	
5	CdS instead of CdS-3@DUT-52	4	
6	DUT-52	trace	
7	air instead of O ₂	55	
8	CdS-1@DUT-52 instead of CdS-3@DUT-52	50	
9	CdS-2@DUT-52 instead of CdS-3@DUT-52	54	
10	CdS-4@DUT-52 instead of CdS-3@DUT-52	44	

Table S3. Oxidation of benzylic alchohol under different conditionsa^{*a*}

^{*a*}Standard conditions: benzylic alchohol (0.1 mmol), CdS-3@DUT-52 (catalyst, 10.0 mg) in CH₃CN (2.0 ml) irradiated with 425nm LED at room temperature under O₂ atmosphere. ^{*b*}Determined by GC-MS

6. References

- S1. V. Bon, I. Senkovska, M. S. Weiss and S. Kaskel, CrystEngComm., 2013, 15, 9572.
- S2. H.-Q. Xu, S. Yang, X. Ma, J. Huang and H.-L. Jiang, ACS Catal., 2018, 8, 11615-11621.