

Two-Dimensional Crystalline Covalent Triazine Frameworks via Dual Modulator Control for Efficient Photocatalytic Oxidation of Sulfides

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1. Materials and Characterization

p-phthalaldehyde, cesium carbonate (Cs_2CO_3), *p*-phthalaldehyde, 4-(hydroxymethyl)benzaldehyde, 2,5-dimethoxyterephthal-aldehyde, terephthalamidine, aniline, *p*-toluidine, 2,4,6-trimethylaniline, 4-bromoaniline, toluene, mesitylene, *n*-Hexadecane, *o*-dichlorobenzene(*o*-DCB), benzene-1,4-dicarbonitrile, lithium bis(trimethylsilyl)amide, *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) were purchased from Aladdin reagent (Shanghai) Co., Ltd. And terephthalamidine dihydrochloride was synthesized following the reported method.^[1] All these chemicals were directly used without further purification. The characterization of materials are referred to the literature previously reported by our group.^[1]

2. Synthesis of CTF materials

The general synthesis procedure: a mixture of aldehyde monomer (0.5 mmol), terephthalamidine (1.0 mmol), Cs_2CO_3 (2.2 mmol), aniline derivatives (according to actual experiments required) and DMSO or other mixed solvents (10 mL) were added into a flask. Then the reaction was heated at 100 °C for 24 h, 120 °C for 24 h and 160 °C for 48 h. After cooling to the room temperature, the mixture was washed with DMF and water. The detailed process is as follows.

2.1 Synthesis of the CTFs under different optimization conditions

2.1.1 Optimization of aniline modulators

CTF-HUST-D1: The mixture of *p*-phthalaldehyde (0.5 mmol), terephthalamidine (1.0 mmol), Cs_2CO_3 (2.2 mmol), aniline modulators (3.0 mmol: aniline, *p*-toluidine, 2,4,6-trimethylaniline, or 4-bromoaniline) and DMSO (10 mL) were added into a single neck flask (25 mL). Then the reaction was heated at 100 °C for 24 h, 120 °C for 24 h and 160 °C for 48 h. After cooling to the room temperature, the mixture was poured into 150 mL 0.1 M HCl aqueous, washed with DMF twice, then with water once (at least 10 h each time) and finally the sample was freeze-dried. The products are gray-yellow powders (aniline: 0.149 g, yield: 71%; *p*-toluidine: 0.141 g, yield: 67%; 2,4,6-trimethylaniline: 0.112 g, yield: 53%; 4-bromoaniline: 0.101 g, yield: 49%). The synthesis process of the CTF-HUST-d1 was the same condition in the absence of aniline modulators (0.145 g, 69%).

2.1.2 Optimization of *p*-toluidine ratio

CTF-HUST-D1: The mixture of *p*-phthalaldehyde (0.5 mmol), terephthalamidine (1.0 mmol), Cs_2CO_3 (2.2 mmol), *p*-toluidine (1.0 mmol, 3.0 mmol, 6.0 mmol and 9.0 mmol) and DMSO (10 mL) were added into a single neck flask (25 mL). Then the reaction was heated at 100 °C for 24 h, 120 °C for 24 h and 160 °C for 48 h. After cooling the room temperature, the mixture was poured into 150 mL 0.1M HCl aqueous, washed with DMF twice, then with water once (at least 10 h each time) and finally the sample was freeze-dried. The products are gray-yellow powders (0.165 g, 79%; 0.141 g, 67%; 0.109 g, 52%; 0.092 g, 44%).

CTF-HUST-E1: The mixture of 4-(hydroxymethyl)benzaldehyde (0.5 mmol), terephthalamidine (1.0 mmol), Cs₂CO₃ (2.2 mmol), *p*-toluidine (0.5 mmol, 1.0 mmol, or 1.5 mmol) and DMSO (10 mL) were added into a single neck flask (25 mL). Then the reaction was heated at 100 °C for 24 h, 120 °C for 24 h and 160 °C for 48 h. After cooling to the room temperature, the mixture was poured into 150 mL 0.1 M HCl aqueous, washed with DMF twice, then with water once (at least 10 h each time) and finally the sample was freeze-dried. The products are gray-yellow powders (0.167 g, 80%; 0.146 g, 70%; 0.121 g, 58%). The synthesis process of the CTF-HUST-e1 was the same condition in the absence of *p*-toluidine (0.167 g, 80%).

2.1.3 Optimization of mixed solvents

CTF-HUST-D1: The mixture of *p*-phthalaldehyde (0.5 mmol), terephthalamidine (1.0 mmol), Cs₂CO₃ (2.2 mmol), *p*-toluidine (3.0 mmol), DMSO (5.0 mL) and another solvent (5.0 mL, toluene, *n*-hexadecane, *o*-DCB or mesitylene) were added into a single neck flask (25 mL). Then the reaction was heated at 100 °C for 24 h, 120 °C for 24 h and 160 °C for 48 h. After cooling to the room temperature, the mixture was poured into 150 mL 0.1 M HCl aqueous, washed with DMF twice, then with water once (at least 10 h each time) and finally the sample was freeze-dried. The products were gray-yellow powder (toluene: 0.115 g, yield: 55%, *n*-hexadecane: 0.129 g, yield: 62%, *o*-DCB: 0.148 g, yield: 71%, mesitylene: 0.152 g, yield: 73%).

CTF-HUST-E1: The mixture of 4-(hydroxymethyl)benzaldehyde (0.5 mmol), terephthalamidine (1.0 mmol), Cs₂CO₃ (2.2 mmol), *p*-toluidine (1.0 mmol), DMSO (5.0 mL) and another solvent (5.0 mL, toluene, *n*-hexadecane, *o*-DCB or mesitylene) were added into a single neck flask (25 mL). Then the reaction was heated at 100 °C for 24 h, 120 °C for 24 h and 160 °C for 48 h. After cooling to the room temperature, the mixture was poured into 150 mL 0.1 M HCl aqueous, washed with DMF twice, then with water once (at least 10 h each time) and finally the sample was freeze-dried. The products are gray-yellow powders (toluene: 0.109 g, yield: 52%, *n*-hexadecane: 0.128 g, yield: 61%, *o*-DCB: 0.139 g, yield: 66%, mesitylene: 0.132 g, yield: 62%).

2.1.4 Optimization of mixed solvents ratio

CTF-HUST-D1: The mixture of *p*-phthalaldehyde (0.5 mmol), terephthalamidine (1.0 mmol), Cs₂CO₃ (2.2 mmol), *p*-toluidine (3.0 mmol), DMSO/*o*-DCB (10 mL, V_{DMSO}/V_{*o*-DCB} = 3/1, 1/1, 1/3, 1/6) were added into a single neck flask (25 mL). Then the reaction was heated at 100 °C for 24 h, 120 °C for 24 h and 160 °C for 48 h. After cooling the room temperature, the mixture was poured into 150 mL 0.1M HCl aqueous, washed with DMF twice, then with water once (at least 10 h each time) and finally the sample was freeze-dried. The products were gray-yellow powder (0.151 g, 72%; 0.148 g, 71%; 0.137 g, 65%; 0.117 g, 56%).

CTF-HUST-E1: The mixture of 4-(hydroxymethyl)benzaldehyde (0.5 mmol), terephthalamidine (1.0 mmol), Cs₂CO₃ (2.2 mmol), *p*-toluidine (1.0 mmol), DMSO/*o*-DCB (10 mL, V_{DMSO}/V_{*o*-DCB} = 3/1, 1/1, 1/3) were added into a single neck flask (25 mL). Then the reaction was heated at 100 °C for 24 h, 120 °C for 24 h and 160 °C for 48 h. After

cooling to the room temperature, the mixture was poured into 150 mL 0.1 M HCl aqueous, washed with DMF twice, then with water once (at least 10 h each time) and finally the sample was freeze-dried. The products are gray-yellow powders (0.143 g, 68%; 0.139 g, 66%; 0.135 g, 63%).

2.1.5 Synthesis of CTF-HUST-D2

The mixture of 2,5-dimethoxyterephthalaldehyde (0.5 mmol), terephthalamidine (1.0 mmol), Cs₂CO₃, (2.2 mmol), *p*-toluidine (1.0 mmol), DMSO/*o*-DCB (by volume, 2.5 mL/7.5 mL) were added into a single neck flask (25 mL). Then the reaction was heated at 100 °C for 24 h, 120 °C for 24 h and 160 °C for 48 h. After cooling to the room temperature, the mixture was poured into 150 mL 0.1 M HCl aqueous, washed with DMF twice, then with water once (at least 10 h each time) and finally the sample was freeze-dried. The product are yellow powder (0.162 g, 70%).

2.1.6 Synthesis of CTF-HUST-d1, CTF-HUST-e1 and CTF-HUST-d2

CTF-HUST-d1, CTF-HUST-e1 and CTF-HUST-d2 were obtained using a similar synthesis process as CTF-HUST-D1, CTF-HUST-E1 and CTF-HUST-D2, except that *p*-toluidine was not added and DMSO (10 mL) was substituted by the mixed solvents (CTF-HUST-d1: 145 mg, 69% , CTF-HUST-e1: 167 mg, 80%, CTF-HUST-d2: 141 mg, 61%).

3. Photocatalytic oxidation of sulfides.

In a typical reaction, sulfide (0.5 mmol), CTF photocatalyst (0.01 mmol calculated based on repeating unit) were added to 5 mL of CH₃OH in a Pyrex vessel. After the reaction mixture was stirred for 30 min in dark to reach adsorption equilibrium, O₂ was purged into the Pyrex vessel to raise the initial pressure to 0.1 MPa. The reaction mixture illuminated with blue LED irradiation at room temperature, and the products were quantitatively analysed by gas chromatography (GC) equipped with a flame ionization detector (FID) using chlorobenzene as the internal standard.

Conversions for oxidation of substrates, yields, and selectivities to the desired products were defined as follows:

$$\text{Conv. [\%]} = [(C_0 - C_s) / C_0] \times 100$$

$$\text{Yield [\%]} = C_p / C_0 \times 100$$

$$\text{Sel. [\%]} = [C_p / (C_0 - C_s)] \times 100$$

where C₀ is the initial concentration of substrates, and C_s and C_p are the concentrations of substrates and products at a certain time during the photocatalytic reaction.

4. PXRD patterns of CTF-HUST-D1 and CTF-HUST-E1 synthesized under different conditions.

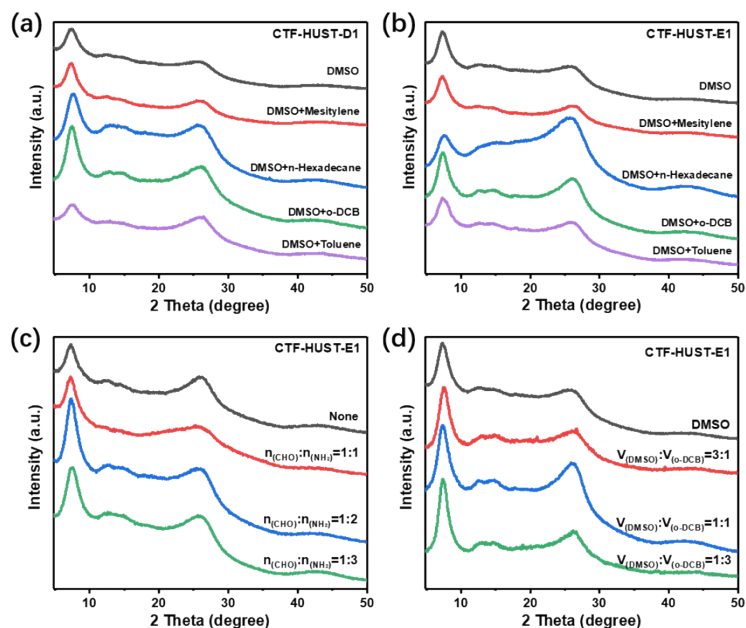


Figure S1. Experimental powder X-ray diffraction patterns of the crystalline CTFs, (a, b) the comparison of different mixed solvents for CTF-HUST-D1 and CTF-HUST-E1, (c) the optimization of p-toluidine addition, (d) the ratio of mixed solvent DMSO and o-dichlorobenzene.

5. SEM images and Brunauer-Emmett-Teller (BET) surface areas of CTF-HUST-D1 and CTF-HUST-E1.

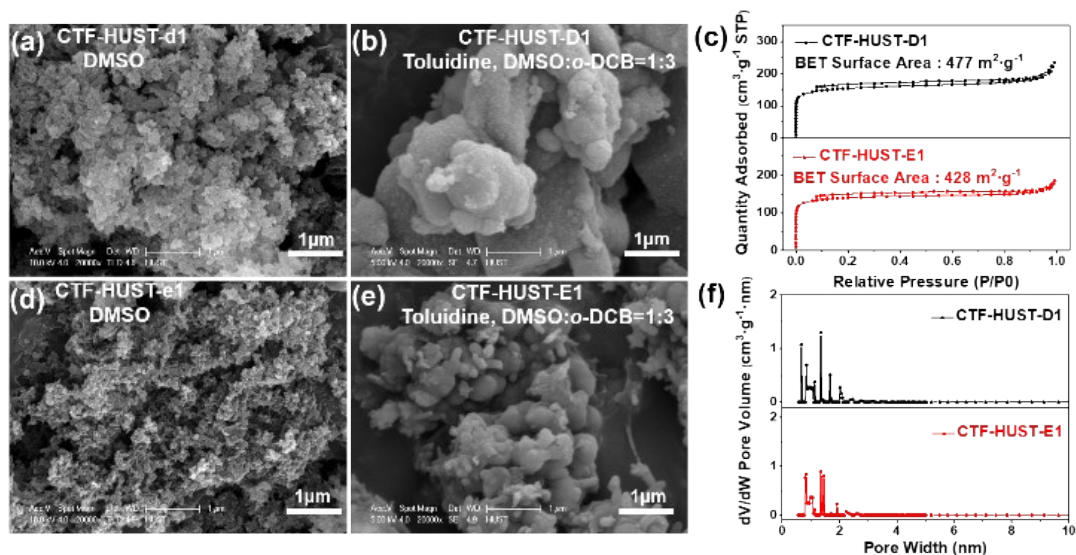


Figure S2. SEM images of CTF-HUST-d1 (a), CTF-HUST-D1 (b), CTF-HUST-e1 (d) and CTF-HUST-E1 (e), (c) N₂ adsorption and desorption isotherms (77 K) of CTF-HUST-D1 (black) and CTF-HUST-E1 (red), (f) The pore size distributions of CTF-HUST-D1 (black) and CTF-HUST-E1 (red).

6. TEM images of CTF-HUST-D1 and CTF-HUST-E1.

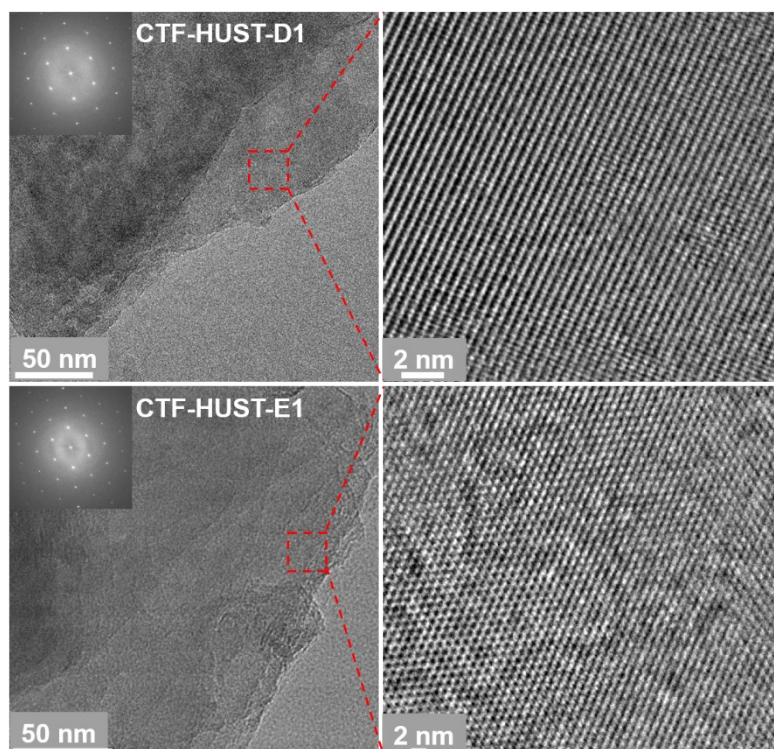


Figure S3. HR-TEM images of CTF-HUST-D1 (a, b) and CTF-HUST-E1 (c, d, insets: FFT images).

7. HAADF-STEM and mapping image of CTF-HUST-D1 and CTF-HUST-E1.

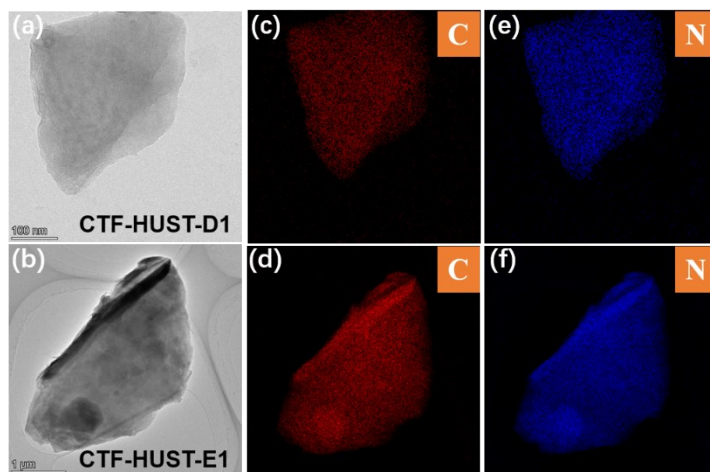


Figure S4. HAADF-STEM image of CTF-HUST-D1 (a) and CTF-HUST-E1 (b). The mapping images for carbon (c, d) and nitrogen (e, f) for CTF-HUST-D1 and CTF-HUST-E1.

8. Thermal stability of CTF-HUST-D1 and CTF-HUST-E1.

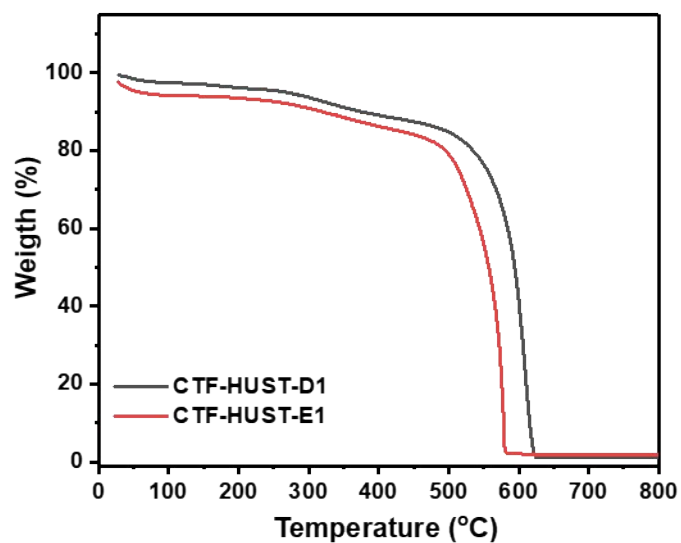


Figure S5. TGA curves of CTF-HUST-D1 and CTF-HUST-E1 under air atmosphere.

9. Powder X-ray diffraction patterns and FT-IR spectra of CTF-HUST-D2.

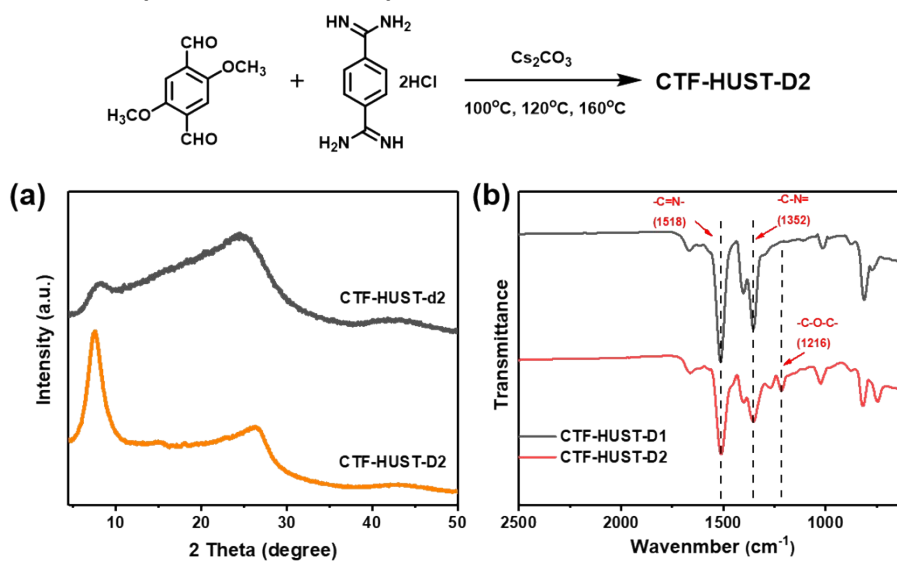


Figure S6. Powder X-ray diffraction patterns (a) and FT-IR spectra (b) of CTF-HUST-D2.

10. Structural characterization of CTF-HUST-D2.

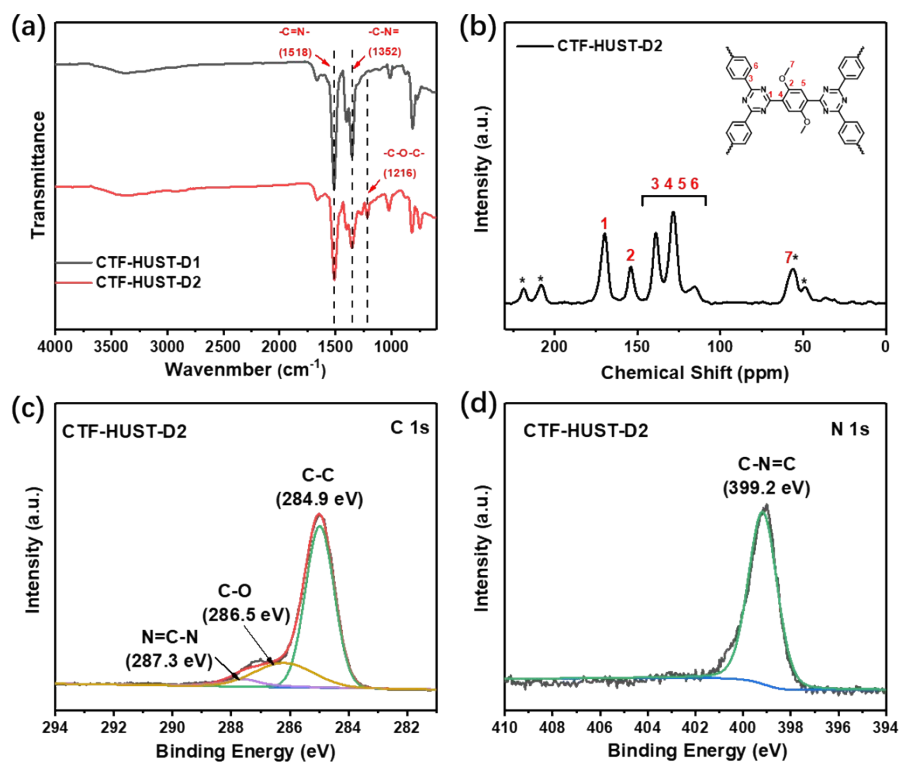


Figure S7. FT-IR spectra (a), solid-state ^{13}C NMR spectra (b) and high-resolution XPS C1s and N1s spectra (c, d) for CTF-HUST-D2.

11. HR-TEM images of CTF-HUST-D2.

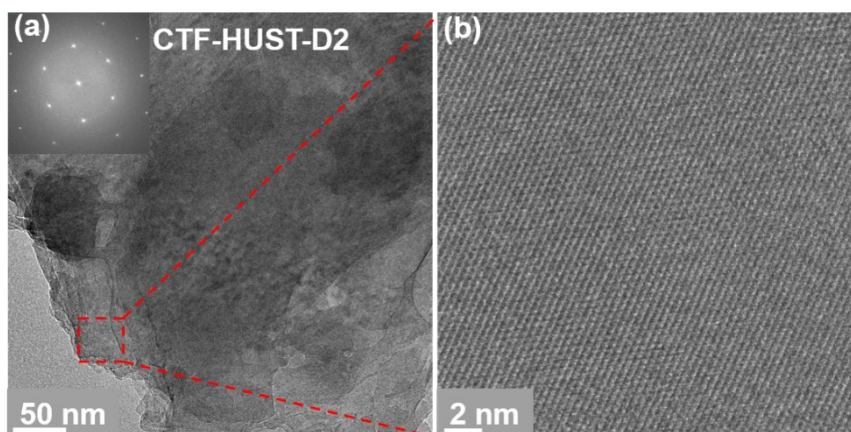


Figure S8. HR-TEM images of CTF-HUST-D2 (a and b, insets: FFT images)

12. Thermal stability of CTF-HUST-D2.

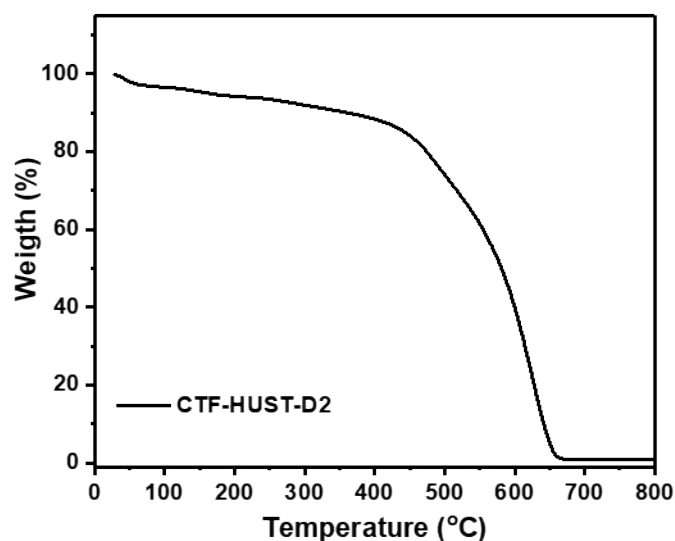


Figure S9. TGA curves of CTF-HUST-D2 under air atmosphere.

13. N₂ adsorption and desorption isotherms and SEM images of CTF-HUST-D2.

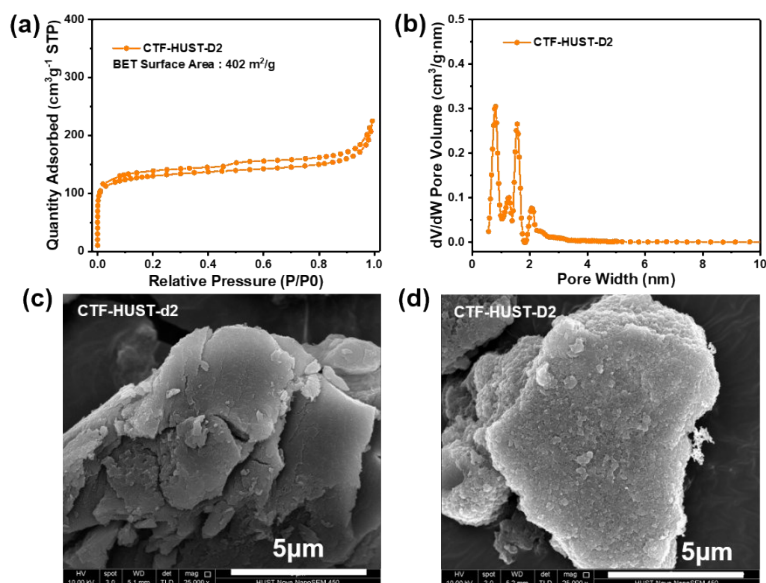


Figure S10. (a, b) N₂ adsorption and desorption isotherms (77 K) and the pore size distributions of CTF-HUST-D2. (c, d) The SEM images of CTF-HUST-d2 and CTF-HUST-D2. The BET surface area is calculated to be 32 m² g⁻¹. The lower surface area is due to the bulky methoxy groups that blocked the pores.

14. In-situ ESR spectra of DMPO- O_2^-

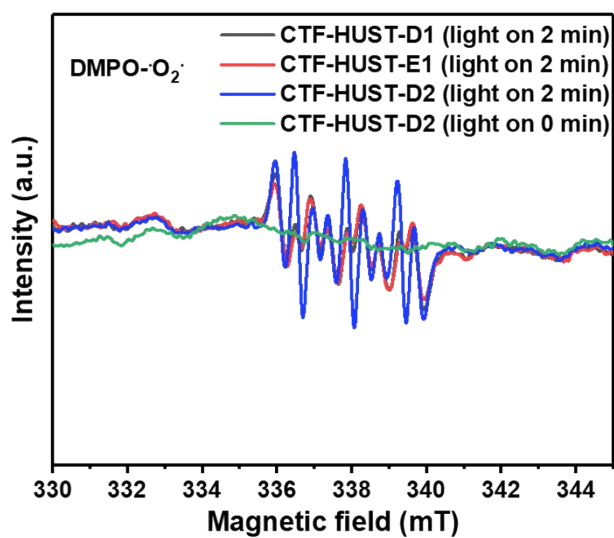


Figure S11. The in-situ ESR spectra for O_2^- detection by DMPO as the trapper under visible-light irradiation.

15. UV-Visible diffuse reflectance spectra of CTF-HUST-D1, CTF-HUST-E1 and CTF-HUST-D2.

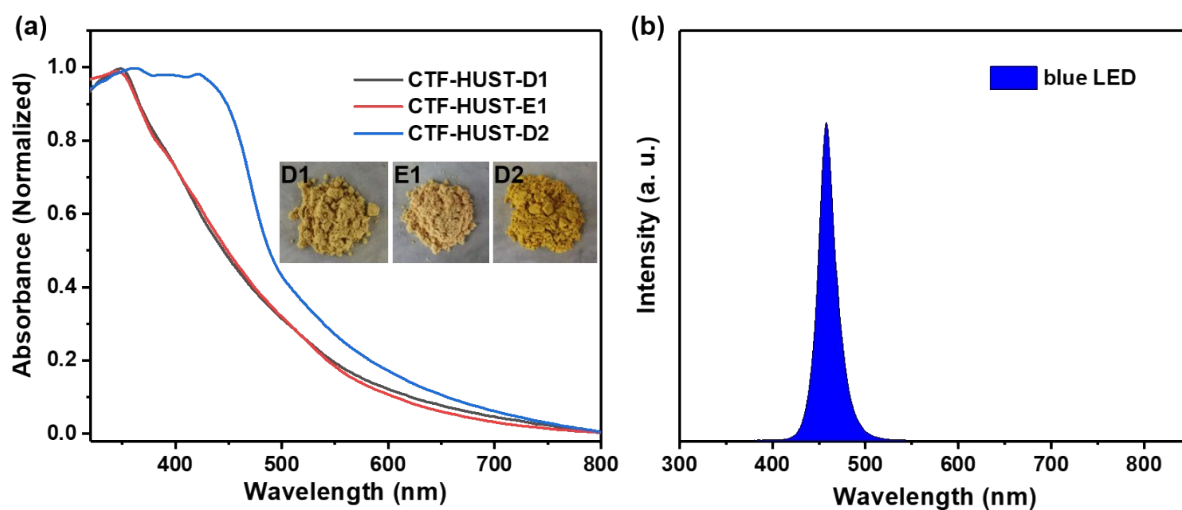


Figure S12. (a) UV-Visible diffuse reflectance spectra of CTF-HUST-D1, CTF-HUST-E1 and CTF-HUST-D2. (b) The light-emitting spectrum of the blue LEDs.

16. Electrochemical impedance of CTFs.

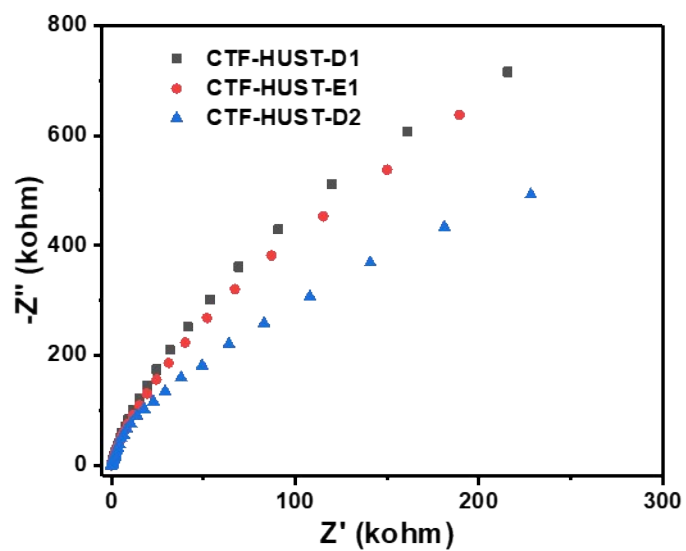


Figure S13. EIS Nyquist plots of CTF-HUST-D1, CTF-HUST-E1 and CTF-HUST-D2.

17. Electrochemical impedance of CTFs.

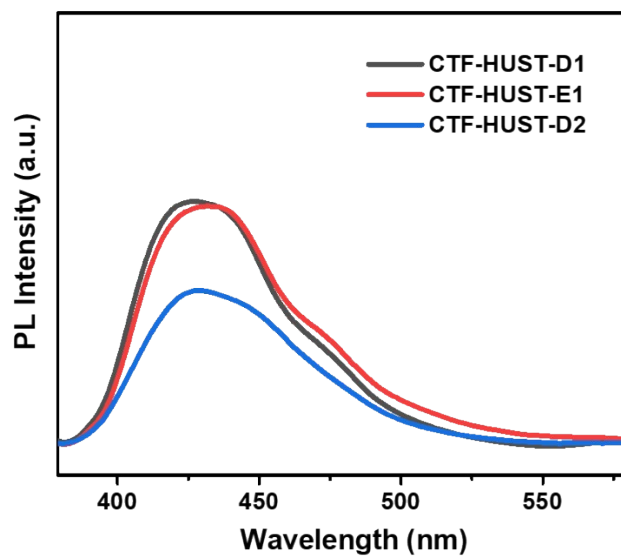


Figure S14. Photoluminescence spectra of CTF-HUST-D1, CTF-HUST-E1 and CTF-HUST-D2.

18. Optical band gaps and Mott-Schottky of CTFs

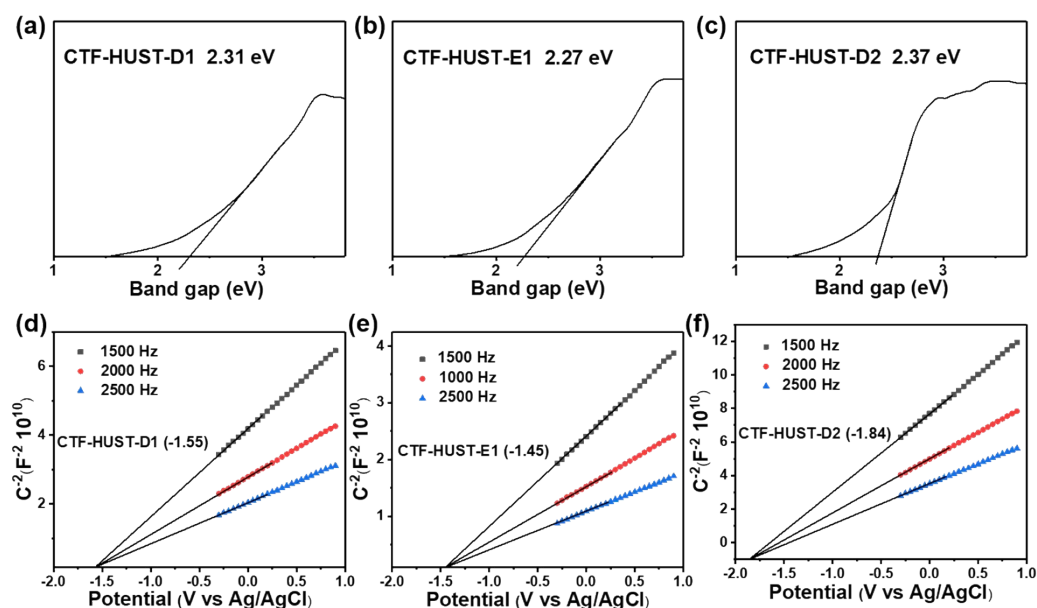


Figure S15. (a, b, c) Band gap of CTFs which was calculated by Kubelka-Munk function based on DRS. (d, e, f) Mott-Schottky test results of CTFs.

19. The FWHM and ordinate intensity of the (100) plane for different CTFs.

Table S1. The FWHM and ordinate intensity of the (100) plane for different CTFs

Entry	W (FWHM) ^a	intensity ^b
CTF-HUST-HC1	1.91	4950
CTF-HUST-C1	1.67	5813
CTF-HUST-D1	1.52	9090
CTF-HUST-E1	1.45	10382

[a] The value is obtained by Gaussian integration. [b] The ordinate intensity of the (100) plane in the XRD pattern.

20. Elemental analysis results of CTF-HUST-D1 and CTF-HUST-E1 and CTF-HUST-D2

Table S2. Elemental analysis results of CTFs

Sample	C (%)		N (%)		H (%)		O (%)	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
CTF-HUST-D1	74.2	67.2	21.6	17.1	4.2	4.4	-	-
CTF-HUST-E1	74.2	68.0	21.6	17.5	4.2	4.4	-	-
CTF-HUST-D2	69.6	64.0	18.7	16.4	4.5	4.5	7.1	8.2

21. Comparison of different CTFs for photocatalytic selective oxidation of thioanisole

Table S3: Comparison of different CTFs for the visible light photocatalytic selective oxidation of thioanisole

Entry	Photocatalyst	Conv. [%]	Sel. [%]
1	CTF-HUST-D1	13	99
2	CTF-HUST-E1	7	99
3	CTF-HUST-D2	55	99

Reaction conditions: Photocatalyst (0.01 mmol calculated based on repeating unit), thioanisole (0.5 mmol), CH₃OH (1 mL), 3 W × 4 blue LEDs, 30 min, air (1atm). The conversion and selectivity were determined by GC-FID using chlorobenzene as the internal standard.

22. Quenching experiments of CTF-HUST-D2

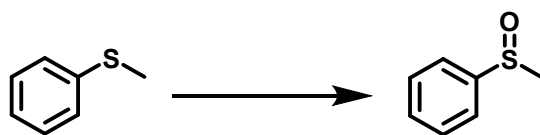
Table S4. Quenching experiments to determine the ROS for the blue light-induced selective oxidation of thioanisole into sulfoxide with air by CTF-HUST-D2 ^[a]

Entry	Quencher (equiv.)	Roles	Conv. (%) ^[b]	Sel. (%) ^[b]
1	--	standard	64	94
2	N ₂ (--)	O ₂ replacement	0	--
3	<i>p</i> -BQ (0.2)	·O ₂ ⁻ scavenger	0	--
4	AgNO ₃ (1)	electron scavenger	3	--
5 ^[c]	CD ₃ OD (--)	singlet oxygen maintainer	66	90

[a] Reaction conditions: sulfide (0.5 mmol), CTF-HUST-D2 (0.01 mmol calculated based on repeating unit), blue LEDs irradiation (3 W × 4), CH₃OH (1 mL), air (1 atm), 45 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of sulfide, selectivity of sulfoxide. [c] CD₃OD (1 mL).

23. Comparison of the photocatalytic performance of CTF-HUST-D2 with reported materials

Table S5. Comparison of the photocatalytic performance with other reported materials under similar conditions.



Catalyst	Condition	Conv.(%)	Sel.(%)	T(h)	Ref.
[Ru(bpy) ₃] ³⁺	500 W halogen lamp, CH ₃ CN/H ₂ O	97	-	4	[2]
TiO ₂	300 W Xelamp, CH ₃ OH	83	92	4	[3]
1,2-DHA-TiO ₂	TEMPO, 520 nm, CH ₃ OH	90	91	1.3	[4]
PPET3-N2	White LED, CH ₃ OH	69	-	8.0	[5]
ARS-TiO ₂	300 W Xelamp, CH ₃ OH	84	90	3.0	[6]
CTF-HUST-D2	3 W blue LED, CH₃OH	90	94	1.0	This work

24. References

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