A Visible-Light-Driven Photocatalyst of a stable Metal−Organic Framework based on Cu_4Cl Clusters and TIPE spacers†

He Chen, Ping-Xiao Liu, Ning Xu, Xing Meng, Hai-Ning Wang* and Zi-Yan Zhou*

College of Chemical Engineering, Shandong University of Technology, Zibo, Shandong, 255049, People's Republic of China

Supplementary captions:

S1. The 4-factor and 3-level orthogonal test for degradation of RhB, MB, MO

Table S1 Design of 4-factor and 3-level orthogonal test of MO

Levels	Factors			
	pH (A)	30% H_2O_2/(mol/L) (B)	MOFs/mg (C)	Initial MO/10^{-5}(mol/L) (D)
1	5	0.04	15	1

2	7	0.08	25	2
3	11	0.16	35	5

Table S2 Orthogonal experimental results of MO

Entry	pH (A)	30%H_2O_2/(mol/L) (B)	MOFs/mg (C)	Initial MO/10^{-5}(mol/L) (D)	5h Degradation rate/%
1	1(5)	1(0.04)	1(15)	3(5)	23.13
2	1(5)	2(0.08)	2(25)	1(1)	86.99
3	1(5)	3(0.16)	3(40)	2(2)	47.02
4	2(7)	1(0.04)	2(25)	2(2)	68.36
5	2(7)	2(0.08)	3(40)	3(5)	81.02
6	2(7)	3(0.16)	1(15)	1(1)	72.44
7	3(11)	1(0.04)	3(40)	1(1)	55.52
8	3(11)	2(0.08)	1(15)	2(2)	87.83
9	3(11)	3(0.16)	2(25)	3(5)	77.62

Table S3 Optimization results of MO

Entry	pH (A)	30% H_2O_2 /(mol/L) (B)	MOFs/mg (C)	Initial MO/10^{-5}(mol/L) (D)
K1	154.14	147.01	183.40	214.95
K2	221.82	255.84	232.97	203.21
K3	220.97	197.08	183.56	181.77
$\overline{K_1}$	52.38	49.00	63.13	71.65
$\overline{K_2}$	73.94	85.28	77.66	67.74
$\overline{K_3}$	73.66	65.69	61.19	60.59
R	21.56	36.28	16.52	11.06

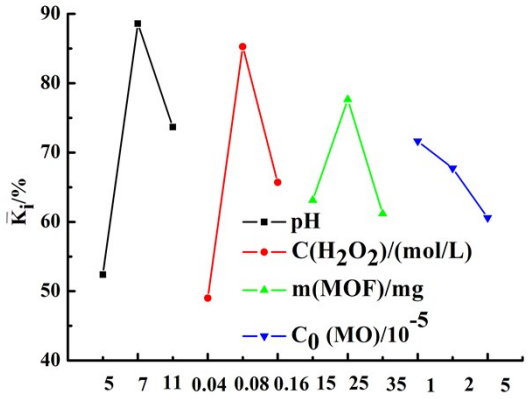

Fig. S1 $\bar{K}_i$ vs the levels of the factors for MO

Table S4 Design of 4-factor and 3-level orthogonal test of RhB

Levels	Factors			
	pH (A)	30% H_2O_2/(mol/L) (B)	MOFs/mg (C)	Initial RhB /10^{-5}(mol/L) (D)
1	5	0.04	10	1
2	7	0.08	20	2
3	11	0.16	30	5

Table S5 Orthogonal experimental results of RhB

Entry	pH (A)	30% H_2O_2/(mol/L) (B)	MOFs/mg (C)	Initial RhB/10^{-5} (D)	4h Degradation rate/%
1	1(5)	1(0.04)	1(10)	3(5)	71.18
2	1(5)	2(0.08)	2(20)	1(1)	87.73
3	1(5)	3(0.16)	3(30)	2(2)	62.89
4	2(7)	1(0.04)	2(20)	2(2)	19.59
5	2(7)	2(0.08)	3(30)	3(5)	97.84
6	2(7)	3(0.16)	1(10)	1(1)	65.33
7	3(11)	1(0.04)	3(30)	1(1)	80.65
8	3(11)	2(0.08)	1(10)	2(2)	35.28
9	3(11)	3(0.16)	2(20)	3(5)	91.12

Table S6 Optimization results of RhB

Entry	pH (A)	30% H_2O_2 /(mol/L) (B)	MOFs/mg (C)	Initial RhB /10^{-5}(mol/L) (D)

K1	221.80	171.42	171.79	260.13
K2	182.75	220.84	198.43	233.71
K3	207.05	219.34	241.38	117.76
$\overline{K_1}$	73.93	57.14	57.26	86.71
$\overline{K_2}$	60.92	73.16	66.14	77.90
$\overline{K_3}$	69.02	73.11	80.46	39.25
R	13.02	16.47	23.20	47.46

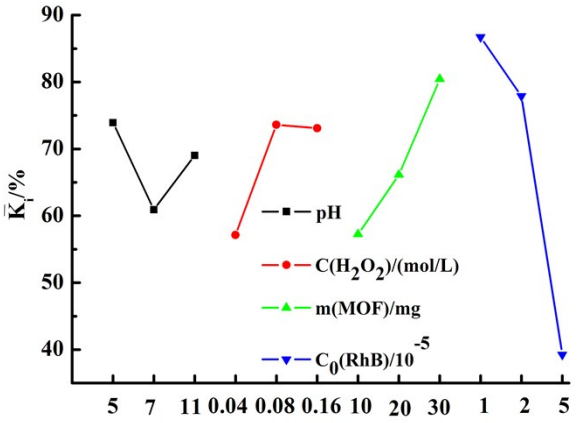

Fig. S2 $\overline{K_i}$ vs the levels of the factors for RhB

Table S7 Design of 4-factor and 3-level orthogonal test of MB

Levels	Factors			
	pH (A)	**30% H_2O_2/(mol/L) (B)**	**MOFs/mg (C)**	**Initial MB /10^{-5}(mol/L) (D)**
1	5	0.02	10	1
2	7	0.04	15	2
3	11	0.06	20	5

Table S8 Orthogonal experimental results of MB

Entry	pH (A)	30% H_2O_2/(mol/L) (B)	MOFs/mg (C)	Initial MB /10^{-5} (D)	2h Degradation rate/ %
1	1(5)	1(0.02)	1(10)	3(5)	69.48
2	1(5)	2(0.04)	2(15)	1(1)	80.40

3	1(5)	3(0.06)	3(20)	2(2)	68.15
4	2(7)	1(0.02)	2(15)	2(2)	52.13
5	2(7)	2(0.04)	3(20)	3(5)	82.94
6	2(7)	3(0.06)	1(10)	1(1)	81.76
7	3(11)	1(0.02)	3(20)	1(1)	75.72
8	3(11)	2(0.04)	1(10)	2(2)	70.41
9	3(11)	3(0.06)	2(15)	3(5)	82.65

Table S9 Optimization results of MB

Entry	**pH (A)**	**30% H_2O_2 /(mol/L) (B)**	**MOFs/mg (C)**	**Initial MB /10^{-5} (D)**
K1	218.03	197.33	221.65	235.07
K2	216.83	233.75	215.18	237.88
K3	228.79	232.57	226.82	190.69
$\overline{K_1}$	72.68	65.78	73.88	78.36
$\overline{K_2}$	72.28	77.92	71.73	79.29
$\overline{K_3}$	76.26	77.52	75.61	63.56
R	3.99	12.14	1.72	14.79

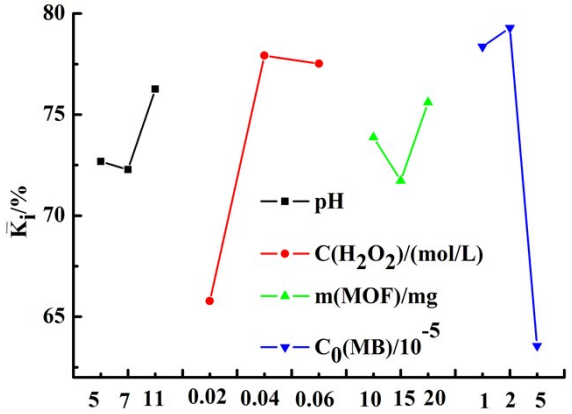

Fig. S3 $\overline{K_i}$ vs the levels of the factors for MB

S2. The reaction rate constants of degrade dyes in different temperature

Table S10 The reaction rate constants of degrade dyes in different temperature

Dye	T/℃	k /min^{-1}	R^2 of k	Ea /(kJ/mol)	R^2 of Ea
RhB	30	0.0151	0.9889	79.71	0.9801
	35	0.0176	0.9954		
	40	0.0426	0.9919		
	45	0.0553	0.9939		
	50	0.0989	0.996		
MB	30	0.0273	0.9981	66.14	0.9965
	35	0.0433	0.9946		
	40	0.0602	0.9915		
	45	0.0988	0.9854		
	50	0.1376	0.9894		
MO	30	0.0039	0.9889	87.26	0.9912
	35	0.0075	0.9926		
	40	0.0125	0.9935		
	45	0.0233	0.9950		
	50	0.0321	0.9960		

S3. The half-life time $t_{1/2}$ (min) for degradation of dyes compared with other materials at room temperature

Table S11 The half-life time $t_{1/2}$ (min) for degradation of RhB in solution in the presence of oxidant and catalysis

Catalysis	$t_{1/2}$ (min)	Reference
GR/MIL-53(Fe)	12 (UVirradiation)	Ind. Eng. Chem. Res. 2015, 54, 153−163
ZIF-67	18	Journal of the Taiwan Institute of Chemical Engineers. 2015, 53, 40–45
Compound **2**	25	Cryst. Growth Des. 2016, 16, 2277−2288
Compound **1**	30	Cryst. Growth Des. 2016, 16, 2277−2288
Compound **1**	31	Inorg. Chem. 2014, 53, 11584−11588
1	45 (visible-light irradiation)	In this work
Compound **3**	60	Cryst. Growth Des. 2016, 16, 2277−2288
BWO/UiO-66-1	65	RSC Adv., 2014, 4, 64977–64984
PANI/2	217 (UVirradiation)	Z. Anorg. Allg. Chem. 2015, 1125–1129

Table S12 The half-life time $t_{1/2}$ (min) for degradation of MB solution in the presence of oxidant and catalysis

Catalysis	$t_{1/2}$ (min)	Reference
Compound **2**	10	Cryst. Growth Des. 2016, 16, 2277−2288
Compound **1**	15	Cryst. Growth Des. 2016, 16, 2277−2288
Fe_3O_4@MIL-100(Fe)	18 (UV irradiation)	J. Mater. Chem. A, 2013, 1, 14329–14334
1	25 (visible-light irradiation)	In this work
ZIF-6	30 (UV irradiation)	RSC Adv., 2014, 4, 54454–54462
Compound **3**	38	Cryst. Growth Des. 2016, 16, 2277−2288
G-V_2O_5	40 (sunlight irradiation)	Appl. Mater. Interfaces 2015, 7, 14905−14911
compound **1**	120 (UV irradiation)	RSC Adv., 2014, 4, 24755–24761
Fe-TiO_2	300 (UV irradiation)	Ind. Eng. Chem. Res. 2015, 54, 7346−7351

Table S13 The half-life time $t_{1/2}$ (min) for degradation of MO solution in the presence of oxidant and catalysis

Catalysis	$t_{1/2}$ (min)	Reference
$(PSS/TiO_2)_n$	37 (UV irradiation)	Langmuir. 2011, 27, 13590–13597
$[Ni(pytpy)_2Mo_4O_{13}]n$	154 (UV irradiation)	Cryst. Growth Des. 2013, 13, 901−907
1	177 (visible-light irradiation)	in this work
$[Cu(pytpy)_2Mo_4O_{13}]n$	181 (UV irradiation)	Cryst. Growth Des. 2013, 13, 901−907
$(PAH/PW_{12})_n$	231 (UV irradiation)	Langmuir 2011, 27, 13590–13597
TiO_2-200 °C	251 (λ= 420 nm∼800 nm irradiation)	J. Phys. Chem. C 2012, 116, 5764−5772

S4. Reusability of 1 degraded RhB, MB, MO

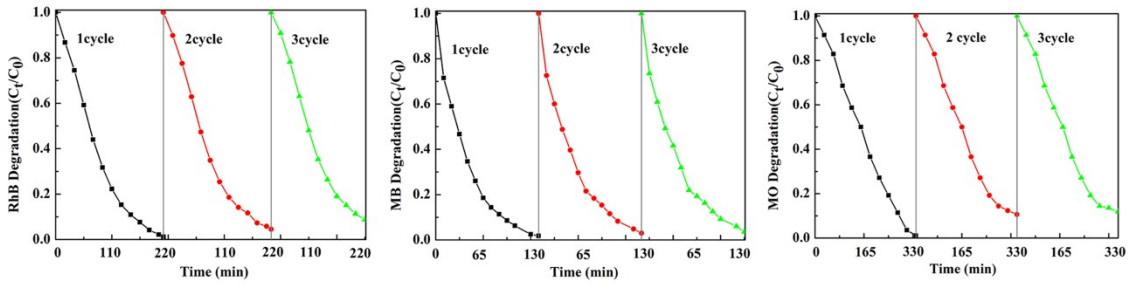

Fig. S4 Cycling runs for the photocatalytic degradation of RhB (a), MB (b), MO (c), over catalyst **1** under LED light irradiation. (Reaction conditions: [RhB] = 1.0×10^{-5} M, pH =5.0, [**1**] = 30 mg, T= 30 °C, [H_2O_2] = 0.08 M; [MB] = 2.0×10^{-5} M, pH =11.0, [**1**] = 20 mg, T= 30 °C, [H_2O_2] = 0.04 M; [MO] = 1.0×10^{-5} M, pH =7.0, [**1**] = 25 mg, T= 30 °C, [H_2O_2] = 0.08 M).

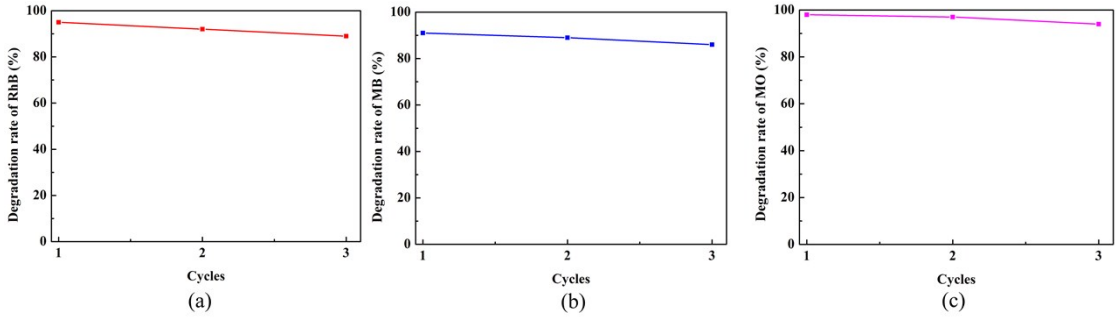

Fig. S5 Cycling runs for the photocatalytic degradation rate of RhB (a), MB (b), MO (c), over catalyst **1** under natural light irradiation at room temperature. (Reaction conditions: [RhB] = 1.0×10^{-5} M, pH =5.0, [**1**] = 30 mg, [H_2O_2] = 0.08 M; [MB] = 2.0×10^{-5} M, pH =11.0, [**1**] = 20 mg, [H_2O_2] = 0.04 M; [MO] = 1.0×10^{-5} M, pH =7.0, [**1**] = 25 mg, [H_2O_2] = 0.08 M).

S5. PXRD and FT-IR spectra

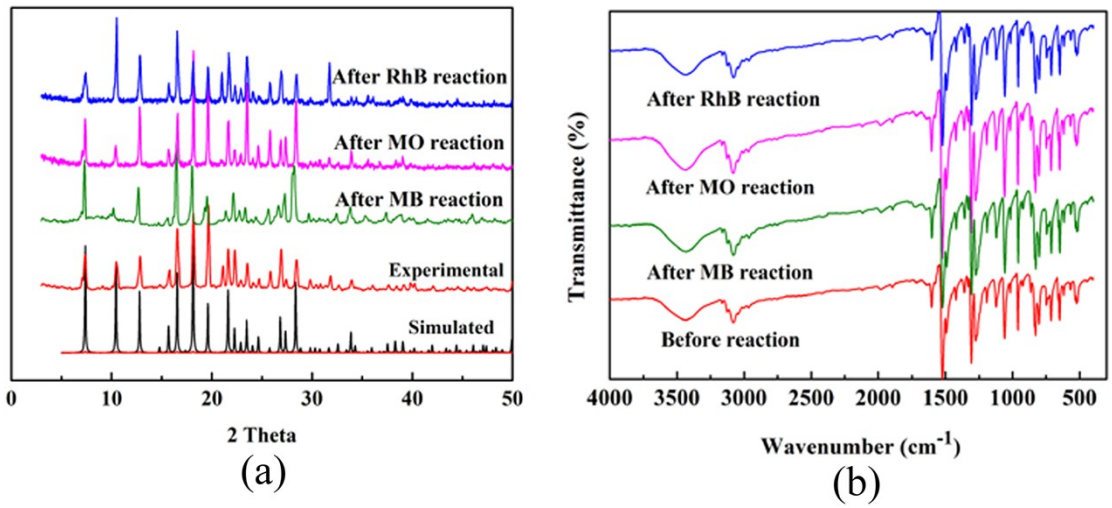

Fig. S6 (a) PXRD and (b) FT-IR spectra of **1** before and after reaction.

S6. Fabrication of the modified carbon paste electrodes

The modified carbon paste electrodes were fabricated as follows: 0.8 g graphite powder was added to the solution of 2 mL acetone containing 65 mg **1**. The mixture was ultrasonically mixed for 3min, followed by evaporation of acetone, which produced rather homogenously covered graphite particles. To the graphite particles 0.66 mL 2-methyl silicon oil was added and stirred with a glass stick. The homogeneous mixture was used to pack a 3 mm inner diameter glass tube to a length of 0.8 cm from one of its

end. In addition, a little extra mixture was retained on the top of the electrode, and the mixture in the tubes was pressed lightly on smooth plastic paper with a copper stick through the back. The electrical contact was established with the copper stick. The surface of the carbon paste electrode was wiped with weighting paper.