Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Enhancing dye degradation using a novel cobalt metal-organic framework as peroxymonosulfate activator

Tuotuo Li, [ab] *Ahmed Olalekan Omoniyi,* [ab] *Yuliang Wang,* [ab] *Xiaoli Hu* [*ab] *and Zhongmin Su* [*abc]

[a]School of Chemistry and Environmental Engineering, Changchun University of Science and Technology, Changchun, 130022, China.

[b]Jilin Provincial Science and Technology Innovation Center of Optical Materials and Chemistry, Changchun, 130022, China.

[c]Joint Sino-Russian Laboratory of Optical Materials and Chemistry, Changchun 130022, China.

[*] Email: huxiaoli1113@cust.edu.cn; zmsu@nenu.edu.cn

1.Materials

Cobalt nitrate hexahydrate, Peroxymonosulfate ($Co(NO_3)_2•6H_2O$, PMS, Shanghai Aladdin Reagent Co., LTD), 2, 2 '-Bipyridine (BIPY, Adamas-beta), 1,3,5-tri(4-carboxyphenyl) benzene (BTB, Jilin Chinese Academy of Sciences -Yanshen Technology Co., LTD), N,N-dimethylacetamide (DMA, Tianjin Fuyu Fine Chemical Co., LTD), Deionized water (H_2O), Methyl Orange (MO, Tianjin Yongsheng Fine Chemical Co., LTD), Rhodamine B (RhB, Sinopharm Chemical Reagent Co., LTD), Methanol (MeOH, Tianjin Fuyu Fine Chemical Co., LTD), Tert-butanol (TBA, RON), P-benzoquinone, L-histidine (P-BQ, L-His, Shanghai Maclin Biochemical Technology Co., LTD), Sodium hydroxide (NaOH, Fuchen Tianjin Reagent Co., LTD), Hydrochloric acid (HCl, Beijing Chemical Plant), Sodium chloride (NaCl, Tianjin Dingsheng Xin Chemical Co., LTD), Crystalline sodium carbonate ($NaCO_3•10H_2O$, Shenyang Reagent Factory), Sodium dihydrogen phosphate (NaH_2PO_4, Tianjin Damao Chemical Reagent Factory), Anhydrous sodium sulfate (Na_2SO_4, Tianjin Xintong Fine Chemical Co., LTD), Sodium bicarbonate ($NaHCO_3$, Kaiyuan Chemical Reagent Factory). All reagents were used directly as supplied without further purification.

2. Characterization and results

Table S1. Crystal data and structure refinement for **CUST-565**

Identification code	CUST-565
Empirical formula	$C_{74}H_{46}Co_3N_4O_{12}$
Formula weight	1359.94
Temperature/K	294.83
Crystal system	monoclinic
Space group	C2/c
a/Å	27.505(10)
b/Å	17.871(6)
c/Å	16.149(5)
α/°	90
β/°	93.474(13)
γ/°	90
Volume/$Å^3$	7924(5)
Z	4
ρcalcg/cm^3	1.140
μ/mm^{-1}	0.675
F (000)	2780.0
Crystal size/mm^3	0.24 × 0.22 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5 to 50.092
Index ranges	$-32 \le h \le 32$, $-21 \le k \le 21$, $-19 \le l \le 19$

Reflections collected	49227
Independent reflections	6980 [Rint = 0.0520, Rsigma = 0.0279]
Data/restraints/parameters	6980/0/421
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R1 = 0.0381, wR2 = 0.1125
Final R indexes [all data]	R1 = 0.0504, wR2 = 0.1199
Largest diff. peak/hole / e $Å^{-3}$	0.24/-0.38

$wR_1 = \sum||F_0|-|F_c||/\sum|F_0|$. $wR_2=\{\sum[w(F_0^2-F_c^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$

Table S2. Bond Lengths for **CUST-565**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	O1[1]	2.2026(18)	C7	C23	1.382(4)
Co1	O1[2]	2.2026(18)	C7	C26	1.381(4)
Co1	O3	2.0498(18)	C8	C12	1.403(4)
Co1	O3[3]	2.0498(18)	C8	C16	1.490(3)
Co1	O6[4]	2.029(2)	C9	C12	1.382(4)
Co1	O6[5]	2.0293(19)	C10	C13	1.388(4)
Co2	O1[6]	2.1696(18)	C10	C18	1.397(4)
Co2	O2[7]	2.0405(18)	C11	C15	1.490(4)
Co2	O4[6]	2.248(2)	C11	C17	1.384(4)
Co2	O5	2.047(2)	C11	C22	1.393(4)
Co2	N1	2.116(2)	C13	C16	1.396(4)
Co2	N2	2.160(2)	C14	C24	1.489(4)
O1	C15	1.281(3)	C14	C33	1.393(4)
O2	C2	1.260(3)	C16	C28	1.400(4)
O3	C2	1.249(3)	C17	C29	1.386(4)
O4	C15	1.248(3)	C18	C21	1.391(4)
O5	C6	1.261(3)	C19	C26	1.384(4)
O6	C6	1.237(3)	C20	C32	1.372(4)
N1	C20	1.337(3)	C21	C28	1.389(4)
N1	C24	1.351(3)	C21	C30	1.496(4)
N2	C14	1.340(4)	C22	C27	1.391(4)
N2	C31	1.346(4)	C23	C25	1.388(4)
C1	C2	1.507(3)	C24	C36	1.374(4)
C1	C3	1.392(4)	C27	C30	1.387(4)
C1	C9	1.388(4)	C29	C30	1.398(4)
C3	C5	1.382(3)	C31	C34	1.388(5)
C4	C6	1.510(3)	C32	C37	1.365(5)
C4	C19	1.379(4)	C33	C35	1.378(5)
C4	C25	1.376(4)	C34	C35	1.362(5)
C5	C8	1.393(4)	C36	C37	1.379(5)
C7	C10	1.493(4)			

[1]1-X,+Y,1/2-Z;[2]-1/2+X,1/2-Y,-1/2+Z;[3]1/2-X,1/2-Y,-Z;[4]+X,+Y,-1+Z;[5]1/2-X,1/2-Y,1-Z;[6]-1/2+X,1/2-Y,1/2+Z;[7]+X,+Y,1+Z

Table S3. Bond Angles for **CUST-565**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1[1]	Co1	O1[2]	180.00(12)	O5	C6	C4	118.4(2)
O3[3]	Co1	O1[2]	93.10(7)	O6	C6	O5	125.5(2)
O3	Co1	O1[1]	93.10(7)	O6	C6	C4	116.1(2)
O3	Co1	O1[2]	86.90(7)	C23	C7	C10	122.8(3)
O3[3]	Co1	O1[1]	86.90(7)	C26	C7	C10	119.3(3)
O3	Co1	O3[3]	180.0	C26	C7	C23	117.8(3)
O6[4]	Co1	O1[2]	90.86(8)	C5	C8	C12	117.7(2)
O6[5]	Co1	O1[1]	90.86(8)	C5	C8	C16	122.7(2)
O6[4]	Co1	O1[1]	89.14(8)	C12	C8	C16	119.6(2)
O6[5]	Co1	O1[2]	89.14(8)	C12	C9	C1	121.4(3)
O6[5]	Co1	O3	88.16(9)	C13	C10	C7	120.1(2)
O6[4]	Co1	O3[3]	88.16(9)	C13	C10	C18	119.1(2)
O6[5]	Co1	O3[3]	91.84(9)	C18	C10	C7	120.6(2)
O6[4]	Co1	O3	91.84(9)	C17	C11	C15	121.0(2)
O6[5]	Co1	O6[4]	180.00(15)	C17	C11	C22	119.1(2)
O1[6]	Co2	O4[6]	59.36(7)	C22	C11	C15	119.9(2)
O2[7]	Co2	O1[6]	98.87(7)	C9	C12	C8	120.6(3)
O2[7]	Co2	O4[6]	91.07(8)	C10	C13	C16	121.2(2)
O2[7]	Co2	O5	101.03(8)	N2	C14	C24	115.1(2)
O2[7]	Co2	N1	93.69(8)	N2	C14	C33	121.5(3)
O2[7]	Co2	N2	169.66(8)	C33	C14	C24	123.4(3)
O5	Co2	O1[6]	102.05(8)	O1	C15	C11	120.4(2)
O5	Co2	O4[6]	159.50(8)	O4	C15	O1	119.8(2)
O5	Co2	N1	109.29(8)	O4	C15	C11	119.8(2)
O5	Co2	N2	83.96(9)	C13	C16	C8	121.3(2)
N1	Co2	O1[6]	143.20(8)	C13	C16	C28	118.5(2)
N1	Co2	O4[6]	86.10(8)	C28	C16	C8	120.1(2)
N1	Co2	N2	76.06(9)	C11	C17	C29	120.6(3)
N2	Co2	O16	88.82(8)	C21	C18	C10	121.0(2)
N2	Co2	O46	86.89(8)	C4	C19	C26	121.0(3)
Co2[8]	O1	Co1[2]	106.19(8)	N1	C20	C32	123.2(3)
C15	O1	Co1[2]	134.41(16)	C18	C21	C30	120.6(2)
C15	O1	Co2[8]	91.73(15)	C28	C21	C18	119.0(3)
C2	O2	Co2[4]	130.41(16)	C28	C21	C30	120.4(2)
C2	O3	Co1	138.02(17)	C27	C22	C11	120.2(3)
C15	O4	Co2[8]	89.01(15)	C7	C23	C25	120.9(3)
C6	O5	Co2	121.70(17)	N1	C24	C14	114.6(2)
C6	O6	Co17	147.01(19)	N1	C24	C36	121.2(3)
C20	N1	Co2	123.58(18)	C36	C24	C14	124.2(3)
C20	N1	C24	118.0(2)	C4	C25	C23	121.0(3)
C24	N1	Co2	116.55(18)	C7	C26	C19	121.1(3)
C14	N2	Co2	115.83(18)	C30	C27	C22	120.8(3)

C14	N2	C31	118.8(2)	C21	C28	C16	121.3(2)
C31	N2	Co2	125.1(2)	C17	C29	C30	120.6(3)
C3	C1	C2	122.1(2)	C27	C30	C21	120.4(3)
C9	C1	C2	119.9(2)	C27	C30	C29	118.6(3)
C9	C1	C3	118.0(2)	C29	C30	C21	121.0(3)
O2	C2	C1	117.2(2)	N2	C31	C34	122.0(3)
O3	C2	O2	126.8(2)	C37	C32	C20	118.6(3)
O3	C2	C1	116.0(2)	C35	C33	C14	119.0(3)
C5	C3	C1	120.9(2)	C35	C34	C31	119.1(3)
C19	C4	C6	119.3(2)	C34	C35	C33	119.6(3)
C25	C4	C6	122.5(2)	C24	C36	C37	119.8(3)
C25	C4	C19	118.1(2)	C32	C37	C36	119.0(3)
C3	C5	C8	121.3(2)				

[1]-1/2+X,1/2-Y,-1/2+Z;[2]1-X,+Y,1/2-Z;[3]1/2-X,1/2-Y,-Z;[4]+X,+Y,-1+Z;[5]1/2-X,1/2-Y,1-Z;[6]-1/2+X,1/2-Y,1/2+Z;[7]+X,+Y,1+Z;[8]1/2+X,1/2-Y,-1/2+Z

Table S4. Data on dyes degradation in different systems.

Pollutant	**Different system**	**Catalyst dosage (g/L)**	**PMS dosage (g/L)**	**K (min^{-1})**	**Degradation time (min)**	**Degradation efficiency (%)**
MO	CUST-565 only	0.16	0	0.0002	30	0
	PMS only	0	0.12	0.0674	30	86
	CUST-565+PMS	0.16	0.12	0.1220	30	97
	$Co(NO_3)_2$•$6H_2O$+PMS	0.16	0.12	0.7146	6	99
RhB	CUST-565 only	0.16	0	0.0007	30	0
	PMS only	0	0.12	0.0251	30	53
	CUST-565+PMS	0.16	0.12	0.1312	30	98
	$Co(NO_3)_2$•$6H_2O$+PMS	0.16	0.12	1.1526	6	100

Table S5. Comparison of the effect of molar ratio between **CUST-565**, PMS, and MO on degradation efficiency.

Pollutant	**CUST-565 (Molar amount/mmol)**	**PMS (Molar amount/mmol)**	**CUST-565：PMS (Molar ratio)**	**CUST-565：PMS：MO (Molar ratio)**	**Degradation efficiency(%)**
MO	0.001323	0.009760	0.1356	0.1356：1：0.1956	89.99
0.625mg=	0.001984	0.009760	0.2033	0.2033：1：0.1956	97.42
0.001909	0.002646	0.009760	0.2711	0.2711：1：0.1956	97.64
mmol	0.003307	0.009760	0.3388	0.3388：1：0.1956	96.57
	0.002646	0.006517	0.4060	0.4060：1：0.2929	82.97
	0.002646	0.009760	0.2711	0.2711：1：0.1956	97.42
	0.002646	0.013013	0.2033	0.2033：1：0.1467	97.14
	0.002646	0.016267	0.1627	0.1627：1：0.1174	96.81

Table S6. Comparison of the effect of molar ratio between **CUST-565**, PMS, and RhB on degradation efficiency.

Pollutant	CUST-565 (Molar amount/mmol)	PMS (Molar amount/mmol)	CUST-565：PMS (Molar ratio)	CUST-565：PMS：MO (Molar ratio)	Degradation efficiency(%)
RhB	0.001323	0.009760	0.1356	0.1356：1：0.1337	57.62
0.625mg=	0.001984	0.009760	0.2033	0.2033：1：0.1337	84.83
0.001305	0.002646	0.009760	0.2711	0.2711：1：0.1337	98.07
mmol	0.003307	0.009760	0.3388	0.3388：1：0.1337	97.94
	0.002646	0.006517	0.4060	0.4060：1：0.2002	89.55
	0.002646	0.009760	0.2711	0.2711：1：0.1337	98.07
	0.002646	0.013013	0.2033	0.2033：1：0.1003	99.44
	0.002646	0.016267	0.1627	0.1627：1：0.0802	98.87

Table S7. ComparCison of dyes degradation by **CUST-565** with other catalysts.

Sample	Catalyst dosage (mg)	Dyes	Dyes concentration (mg/L)	Volume (mL)	Time (min)	Removal Efficiency (%)	Ref.
Ag-Ce/ZnO	30	RhB	10	120	30	97	1
[Cd(NiL)(PTA)]DMAC$_3$	-	MO	20	50	240	85	2
{(Cu$_5$Br$_6$)(Cu$_6$Br$_9$)[Cu$_3$Br(TTTMB)$_2$]}	5	MO	10	40	150	~90	3
CC-10/CN	25	MO	40	50	35	97	4
ZnO/gC$_3$N$_4$-ZCN	50	MO	10	50	180	57.7	5
CuO/Cu$_2$O	40	MO	5	50	240	60	6
7wt%Co@ZnSQDs/gC$_3$N$_4$/MWCNT	280	RhB	10	220	75	96	7
SDS-(Zn-SnO$_2$)	100	RhB	-	50	100	90	8
[Co$_3$(BTB)$_2$(BIPY)$_2$]•4.5H$_2$O•DMA	3	MO	20	25	30	98	This work
[Co$_3$(BTB)$_2$(BIPY)$_2$]•4.5H$_2$O•DMA	3	RhB	20	25	30	97	This work

References

1 R. Liu, X. Fu, Y. Guo, J. Zhang and W. Tian, *Vacuum*, 2023, **215**, 112337.

2 L.-Q. Zuo, T.-F. Zhang, Z.-K. Zhang, J.-X. Hou, G.-J. Liu, J.-L. Du and L.-J. Li, *Inorg. Chem. Commun.*, 2019, **99**, 113–118.

3 Z.-Y. Zhang, G.-D. Zhang, X.-X. Sheng, Q.-W. Ding, Y.-Z. Bai, Y. Su, H.-K. Liu

and Z. Su, *Cryst Growth Des*, 2021, **1**, 333–343.
4 R. Xu, J. Li, G. Sui, Y. Zhuang, D. Guo, Z. Luo, S. Liang, H. Yao and C. Wang, *Colloids Surf. Physicochem. Eng. Asp.*, 2023, **659**, 130598.
5 H. An, L. M. Huong, N. M. Dat, N. D. Hai, C. Q. Cong, N. T. H. Nam, L. T. Tai, D. N. M. Thi, H. B. Nghi, N. T. T. Huyen, D. T. Y. Oanh, M. T. Phong and N. H. Hieu, *Diam. Relat. Mater.*, 2023, **131**, 109583.
6 F. Tavakoli Joorabi, M. Kamali and S. Sheibani, *Mater. Sci. Semicond. Process.*, 2022, **139**, 106335.
7 M. Danish and M. Muneer, *Ceram. Int.*, 2021, **47**, 13043–13056.
8 Sp. Keerthana, R. Yuvakkumar, G. Ravi, M. Manimegalai, M. Pannipara, A. G. Al-Sehemi, R. A. Gopal, M. M. Hanafiah and D. Velauthapillai, *Environ. Res.*, 2021, **199**, 111312.

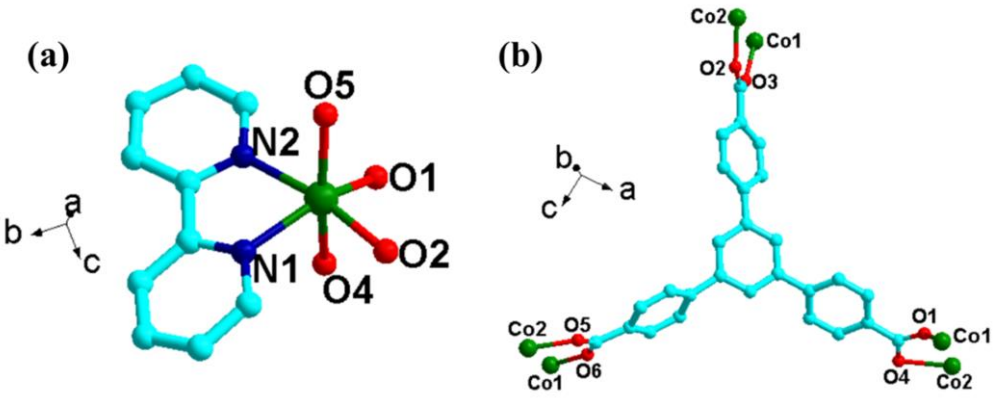

Fig. S1. Coordination environment of BIPY ligand and BTB ligand in **CUST-565.**

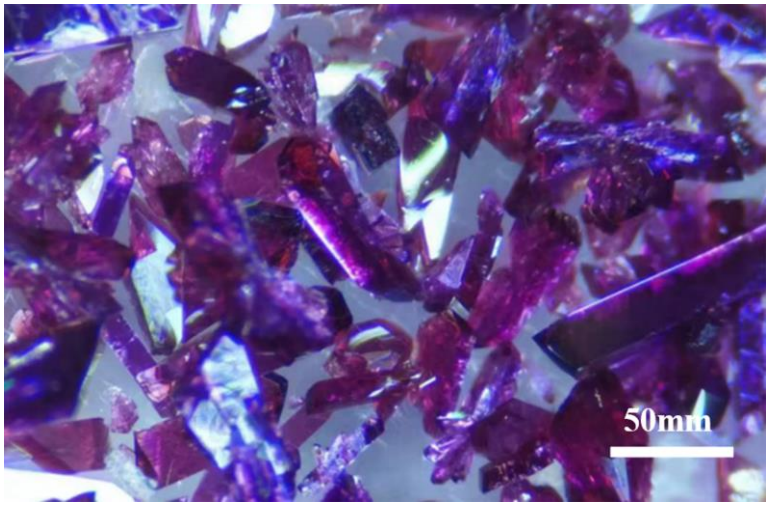

Fig. S2. The morphology of the **CUST-565**.

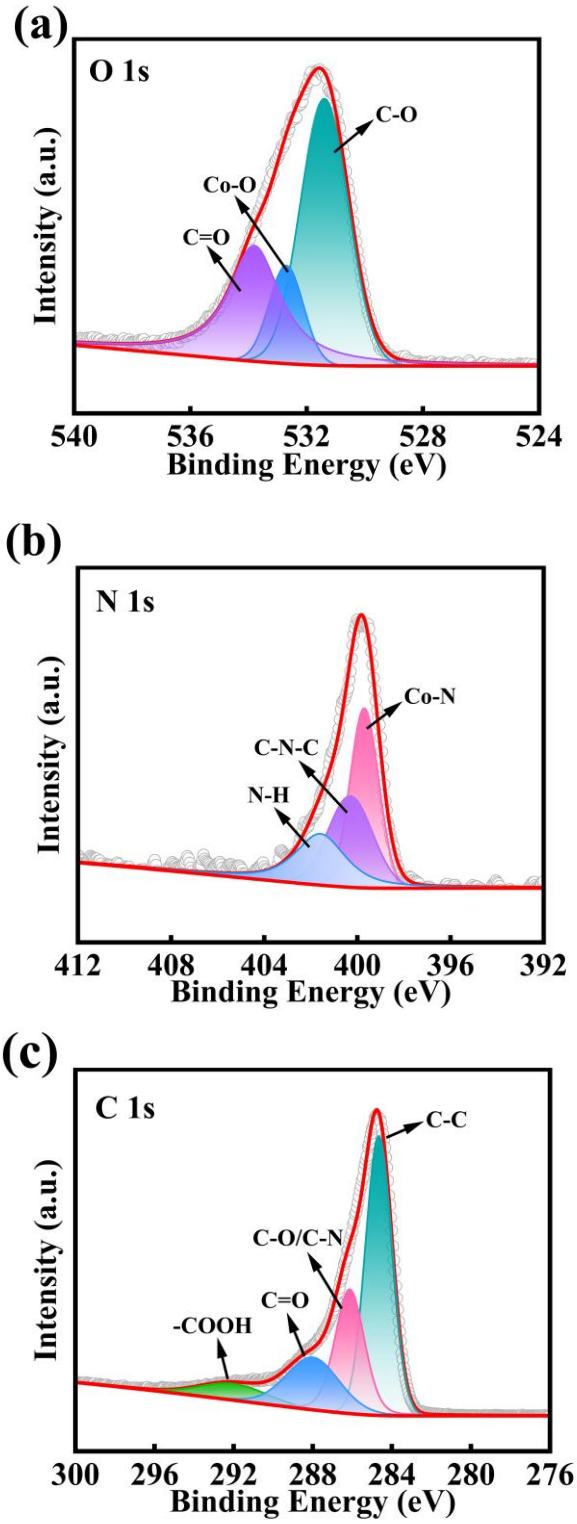

Fig. S3. XPS analysis: high-resolution spectra of (a) O 1s;(b) N 1s and (c) C 1s after use of **CUST-565**.

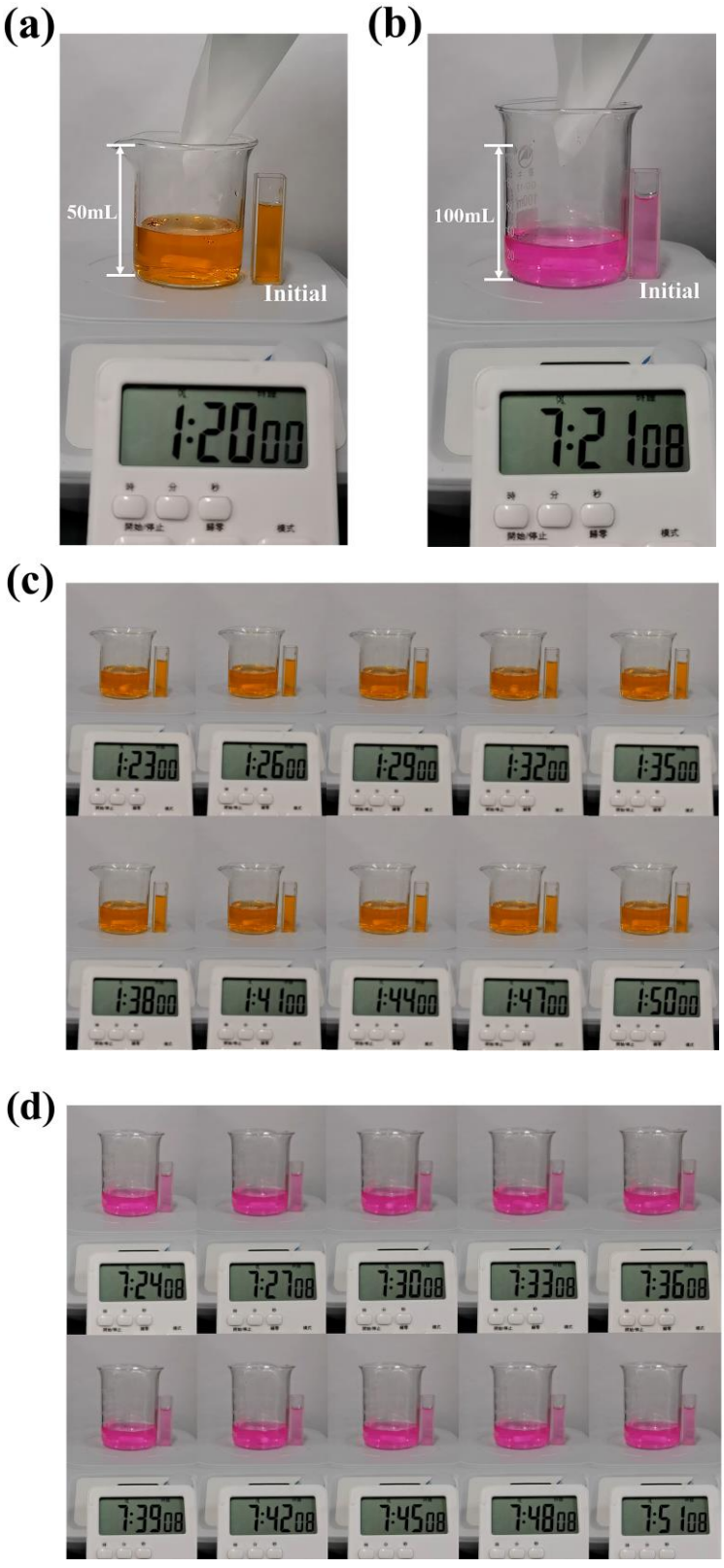

Fig. S4. Adsorption experiment showing (a) initial MO solution;(b) initial RhB solution and (c) MO solutions at three minutes intervals and (d) RhB solutions at three minutes intervals.

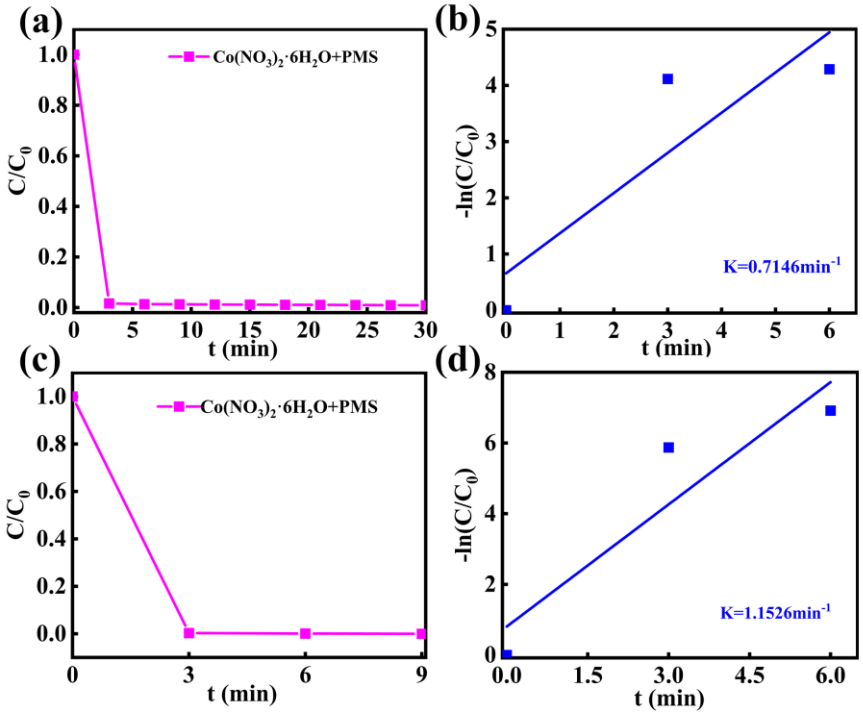

Fig. S5. (a) Degradation efficiency of MO; (b) Kinetic fitting curve of MO; (c) Degradation efficiency of RhB; (d) Kinetic fitting curve of RhB. [MO]=[RhB]=20mg/L, [PMS]=0.12g/L, [$Co(NO_3)_2$•$6H_2O$]=0.16g/L.

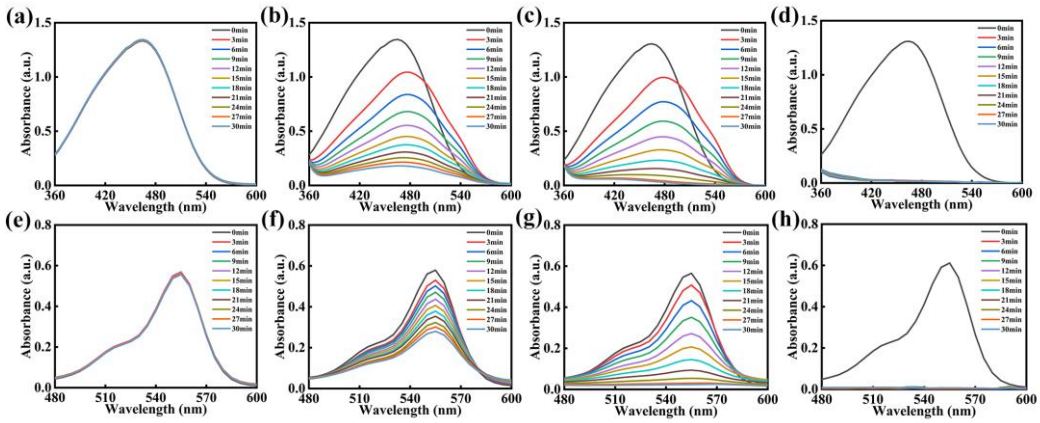

Fig. S6. UV spectrum of MO degradation in different systems (a) **CUST-565** only; (b) PMS only; (c) **CUST-565** and PMS; (d) $Co(NO_3)_2$•$6H_2O$ and PMS. UV spectrum of RhB degradation in different systems (e) **CUST-565** only; (f) PMS only; (g) **CUST-565** and PMS; (h) $Co(NO_3)_2$•$6H_2O$ and PMS.

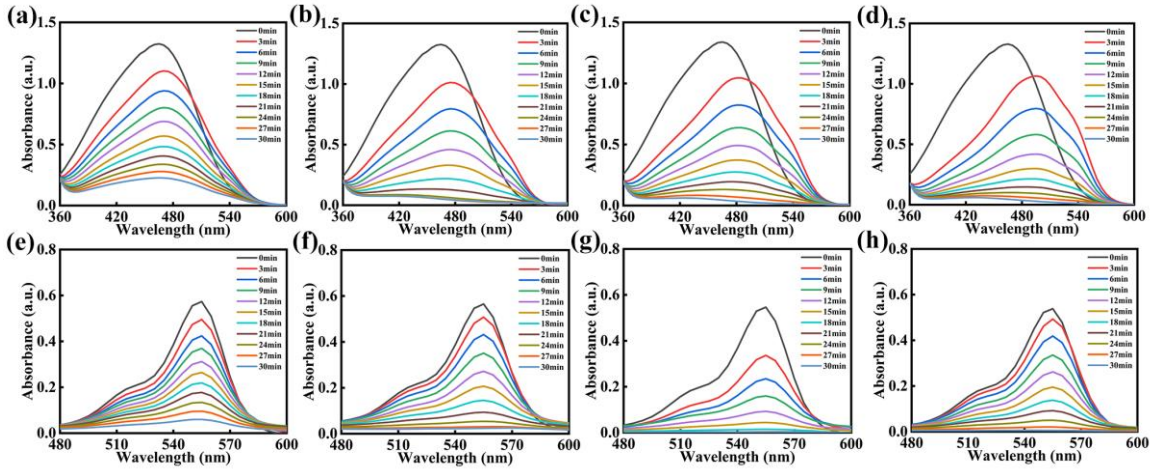

Fig. S7. UV spectrum of effect of catalyst dosage on MO degradation (a) 0.08 g/L; (b) 0.12 g/L; (c) 0.16 g/L; (d) 0.20 g/L. UV spectrum of effect of catalyst dosage on RhB degradation (e) 0.08 g/L; (f) 0.12 g/L; (g) 0.16 g/L; (h) 0.20 g/L.

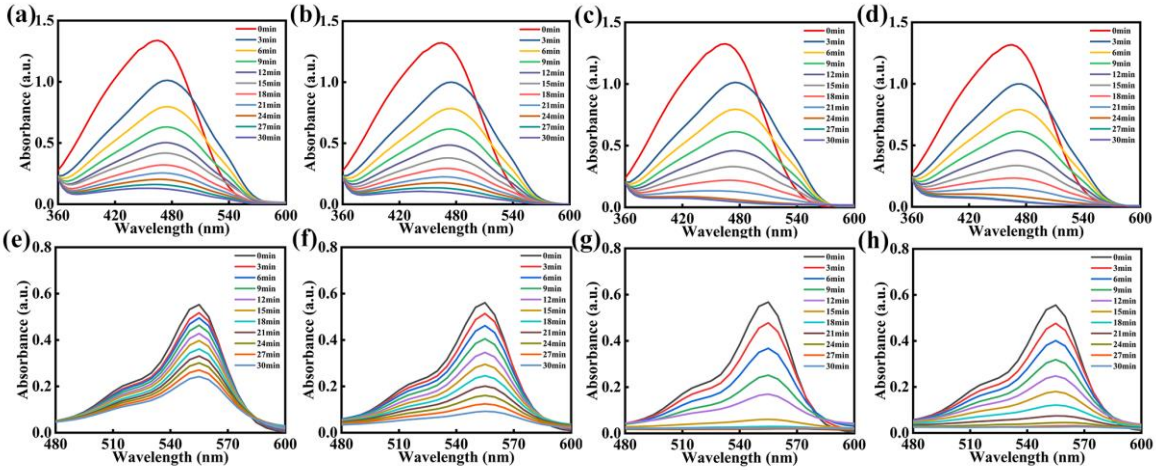

Fig. S8. UV spectrum of effect of PMS dosage on MO degradation (a) 0.08 g/L; (b) 0.12 g/L; (c) 0.16 g/L; (d) 0.20 g/L. UV spectrum of effect of PMS dosage on RhB degradation (e) 0.08 g/L; (f) 0.12 g/L; (g) 0.16 g/L; (h) 0.20 g/L.

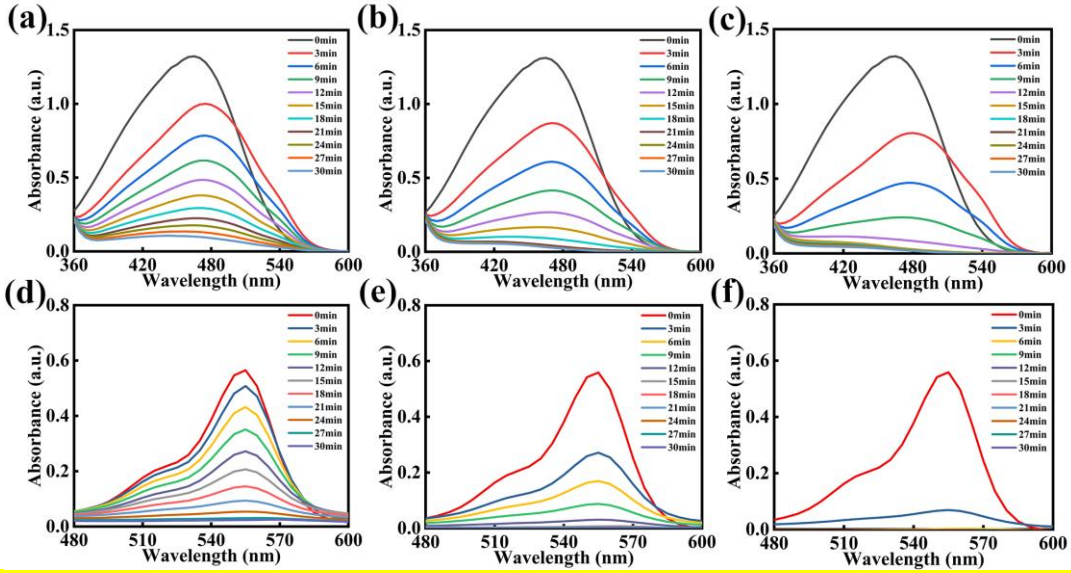

Fig. S9. UV spectrum of effect of temperature on MO degradation (a) 20℃; (b) 40℃; (c) 50℃; Effect of temperature on RhB degradation (d) 20℃; (e) 40℃; (f) 50℃.

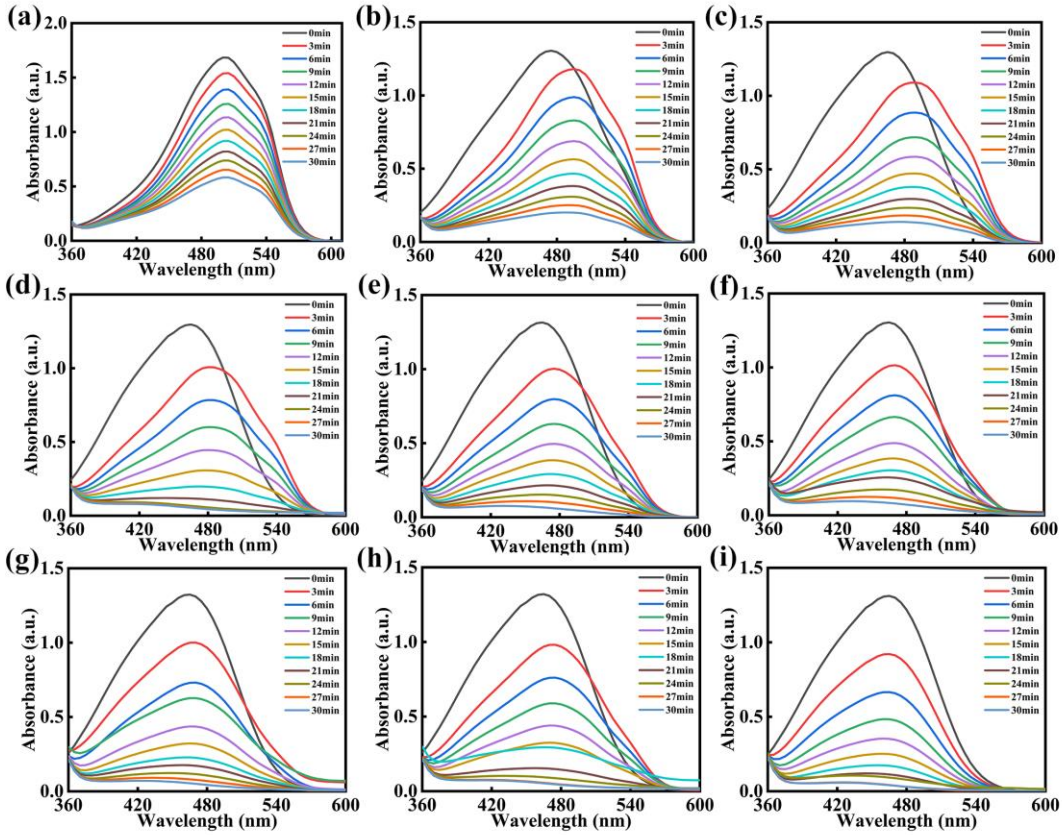

Fig. S10. UV spectrum ofeffect of pH on MO degradation (a) pH3; (b) pH4; (c) pH5; (d) pH6; (e) pH7; (f) pH8; (g) pH9; (h) pH10; (i) pH11.

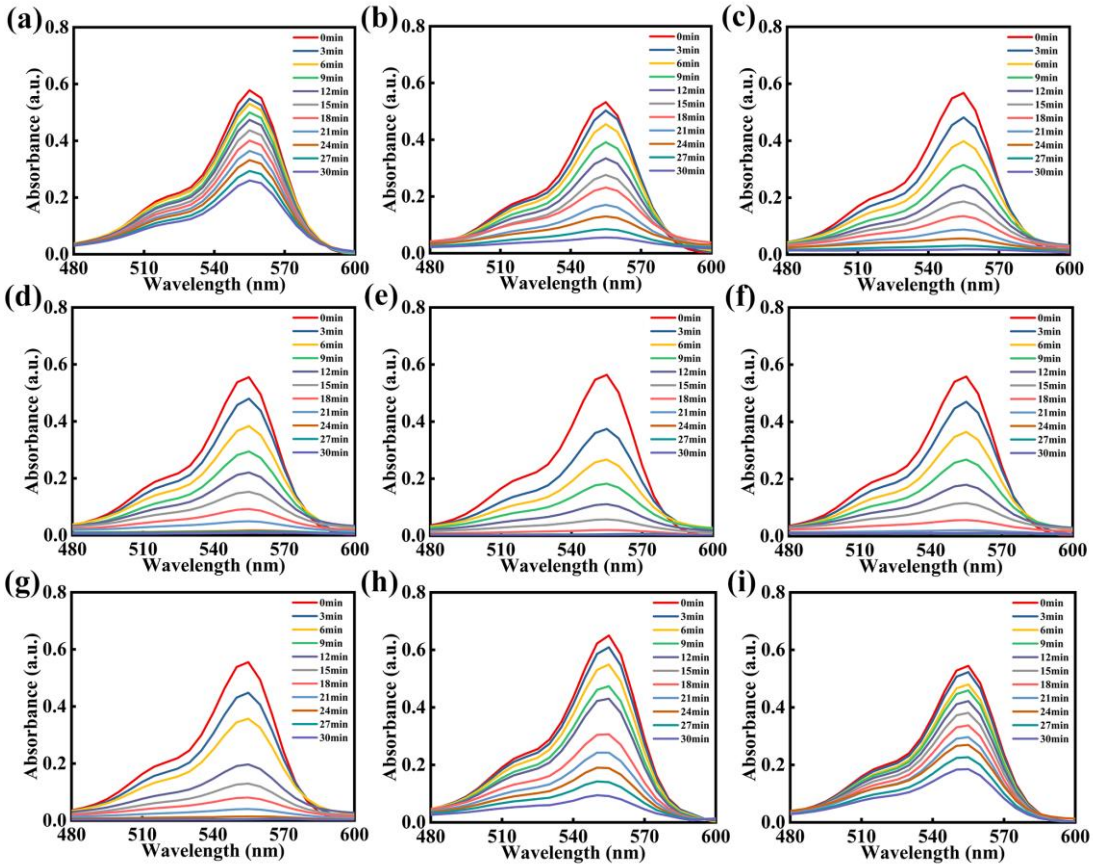

Fig. S11. UV spectrum of effect of pH on RhB degradation (a) pH3; (b) pH4; (c) pH5; (d) pH6; (e) pH7; (f) pH8; (g) pH9; (h) pH10; (i) pH11.

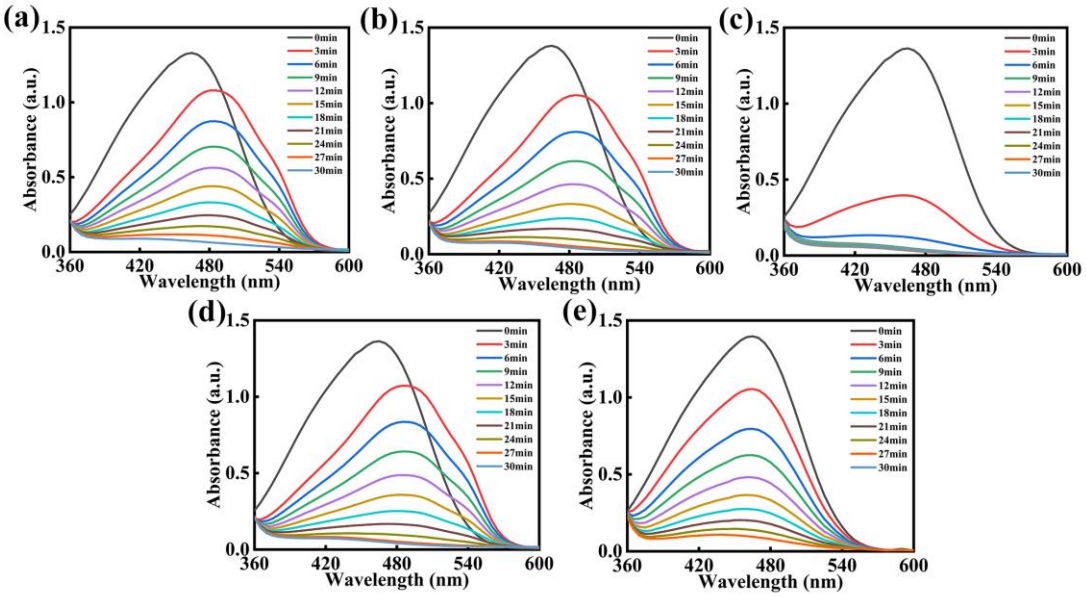

Fig. S12. UV spectrum of effect of different inorganic anions on MO degradation (a) NaCl; (b) NaH_2PO_4; (c) $NaHCO_3$; (d) Na_2SO_4; (e) Na_2CO_3.

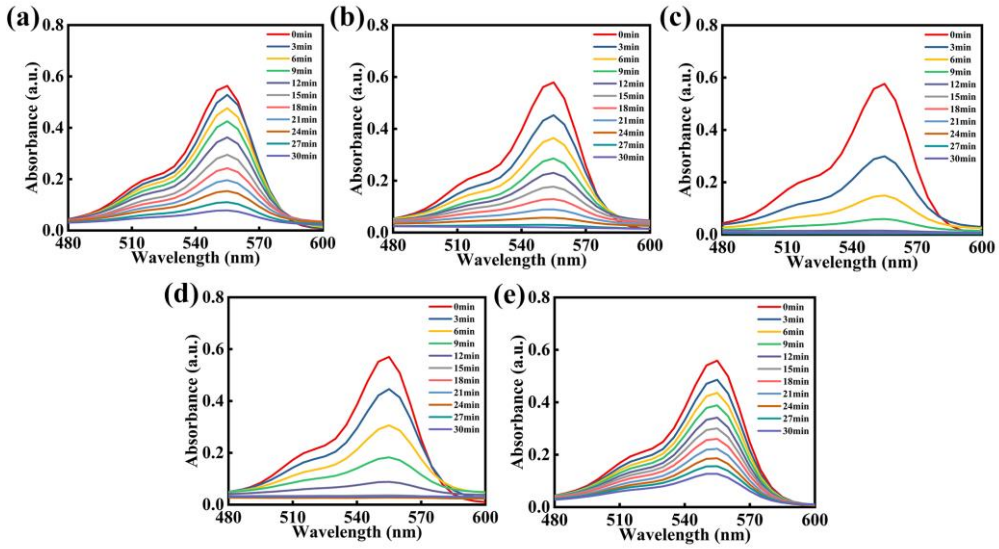

Fig. S13. UV spectrum of effect of different inorganic anions on RhB degradation (a) NaCl; (b) NaH_2PO_4; (c) $NaHCO_3$; (d) Na_2SO_4; (e) Na_2CO_3.

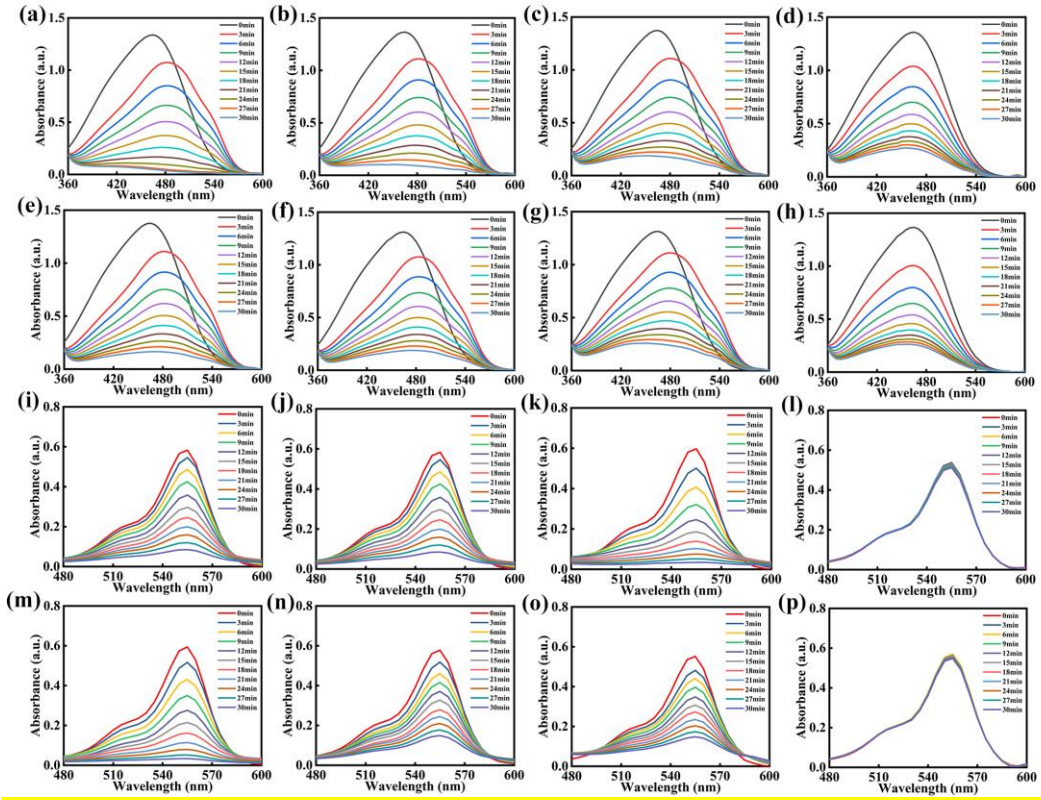

Fig. S14. UV spectrum of effect of different concentrations of quenchers on MO degradation (a) MeOH(100∶1); (b) TBA(100∶1); (c) P-BQ(5∶1); (d) L-His(5∶1); (e) MeOH(500∶1); (f) TBA(500∶1); (g) P-BQ(10∶1); (h) L-His(10∶1). UV spectrum-Effect of different concentrations of quenchers on RhB degradation (i) MeOH(100∶1); (j) TBA(100∶1); (k) P-BQ(5∶1); (l) L-His(5∶1); (m) MeOH(500∶1); (n) TBA(500∶1); (o) P-BQ(10∶1); (p) L-His(10∶1).

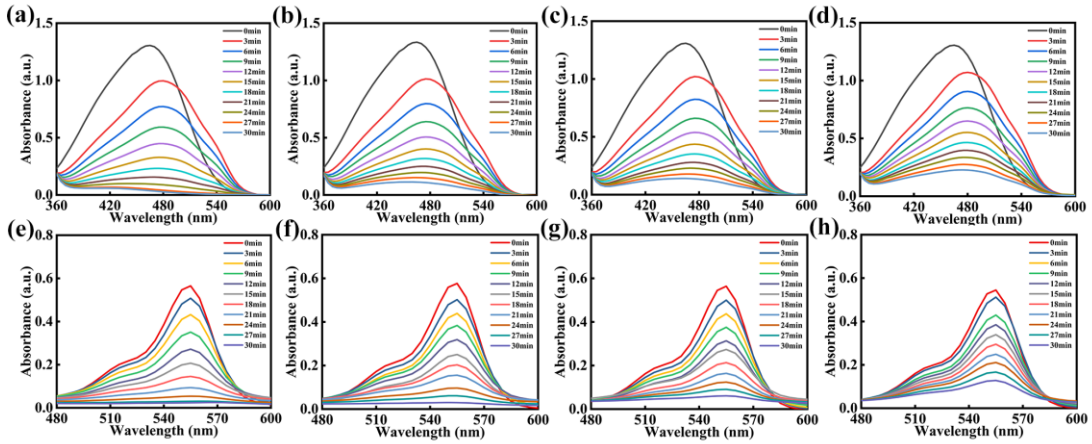

Fig. S15. UV spectrum of the reusability of **CUST-565** in the degradation of MO (a) 1; (b) 2; (c) 3; (d) 4 cycles. UV spectrum of the reusability of **CUST-565** in the degradation of RhB (e) 1; (f) 2; (g) 3; (h) 4 cycles.

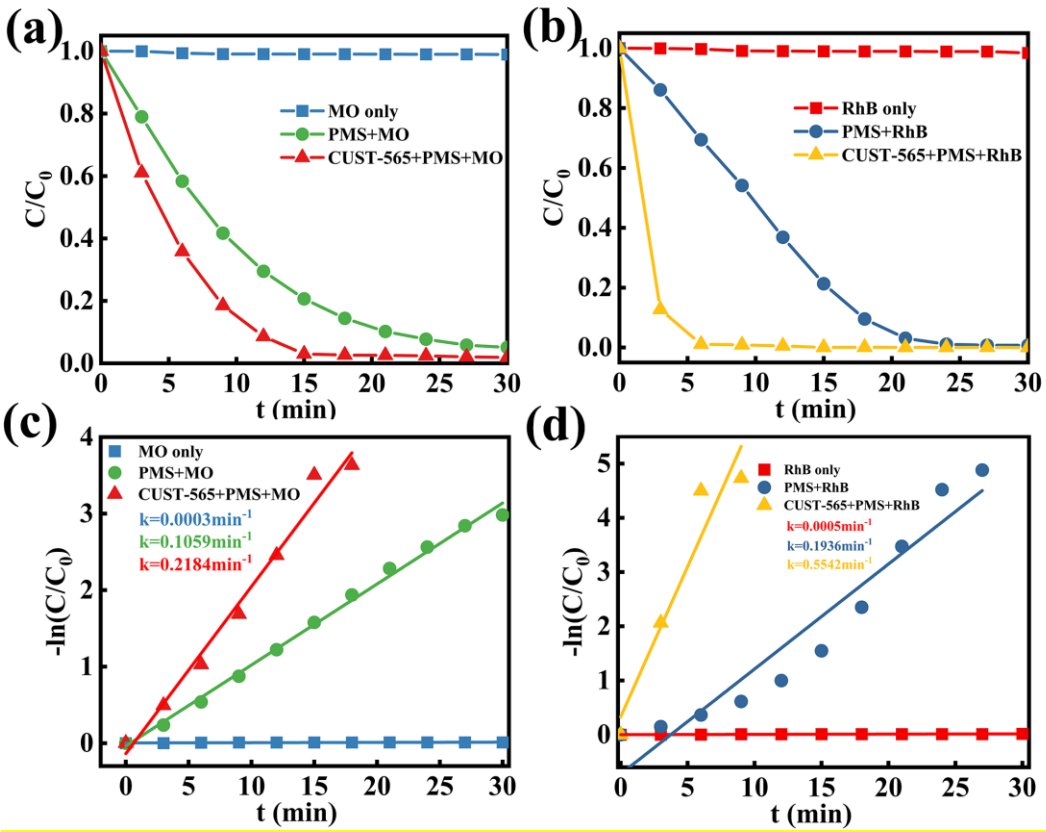

Fig. S16. (a) Degradation efficiency of MO in different systems at 50℃; (b) Kinetic fitting curves of MO; (c) Degradation efficiency of RhB in different systems at 50℃; (d) Kinetic fitting curves of RhB.

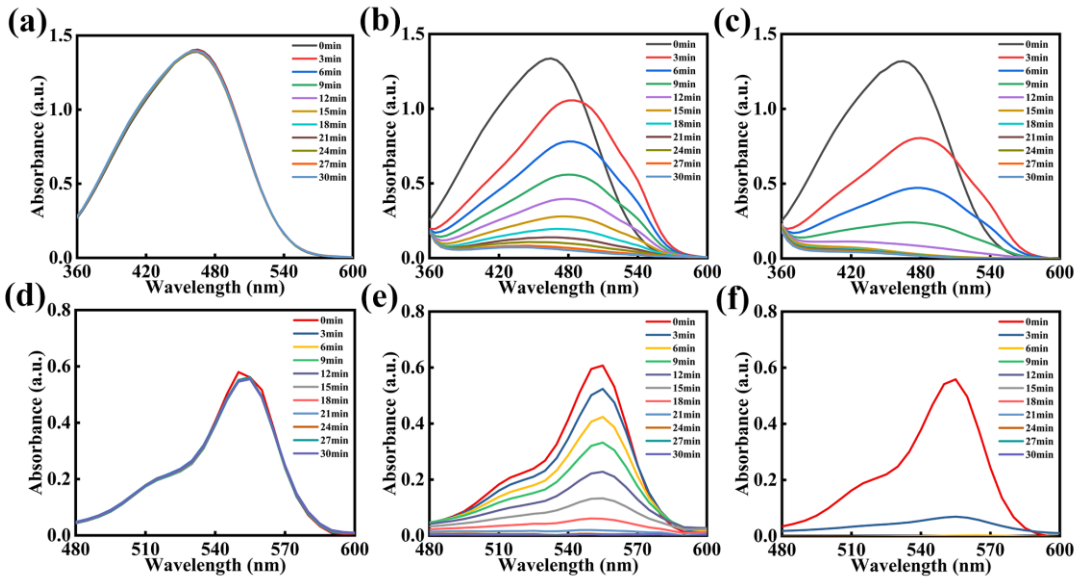

Fig. S17. UV spectrum of degradation efficiency of MO in different systems at 50℃ (a) MO only; (b) PMS and MO; (c) **CUST-565**, PMS, and MO; Degradation efficiency of RhB in different systems at 50℃ (d) RhB only; (e) PMS and RhB; (f) **CUST-565**, PMS, and RhB.

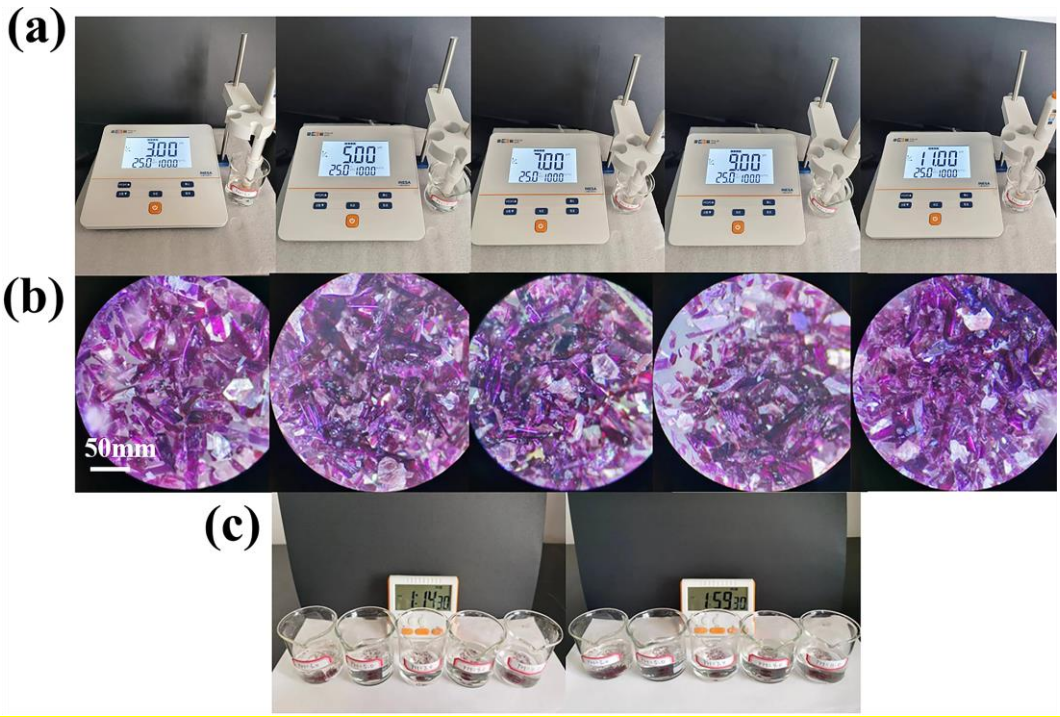

Fig. S18. (a) Different pH aqueous solutions; (b) The morphology of the **CUST-565** after 45 min soaking in different pH aqueous solution; (c) The picture **of CUST-565** soaking time.

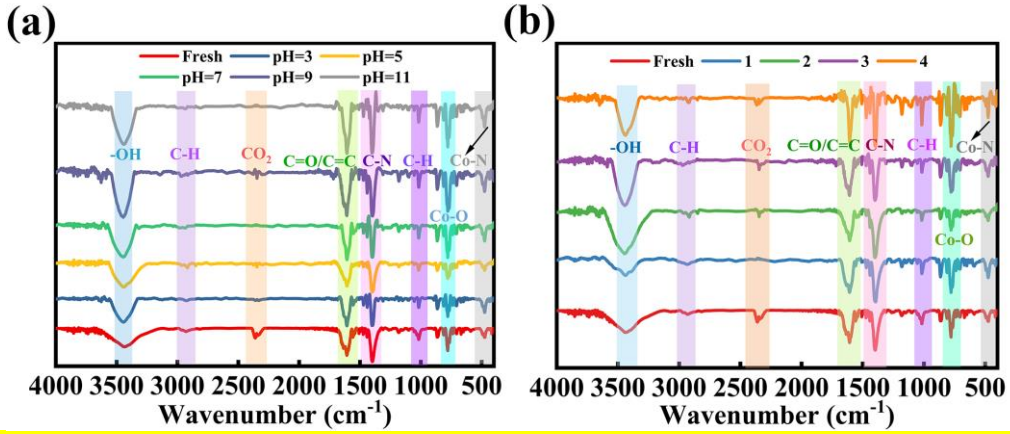

Fig. S19. (a) FTIR spectra of **CUST-565** in different pH aqueous solutions; (b) FTIR spectra of **CUST-565** with different number of usage (cycle).

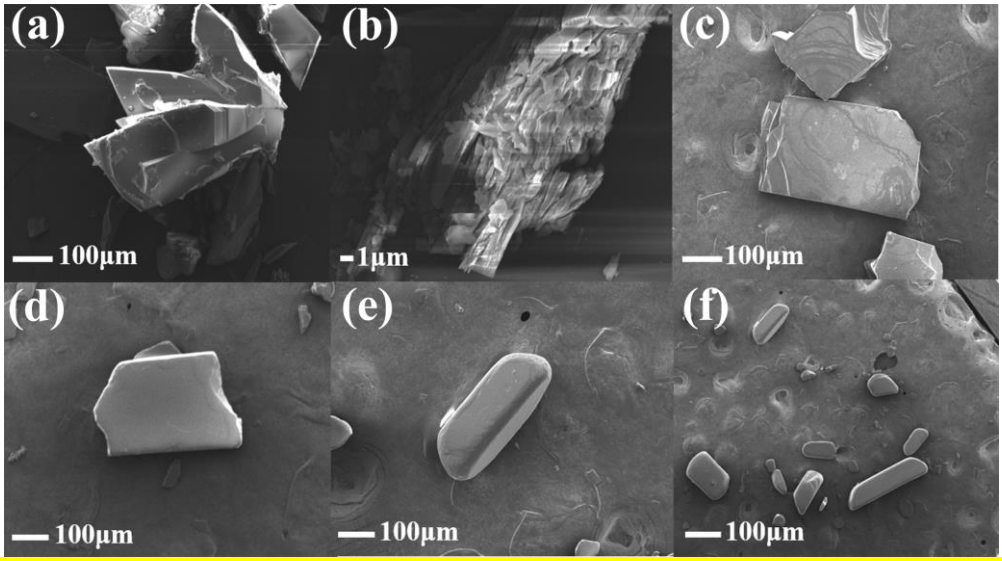

Fig. S20. SEM images of **CUST-565** (a), (b) Fresh; (c) Once usage; (d) Twice usage; (e) Thrice usage; (f) Four times usage.

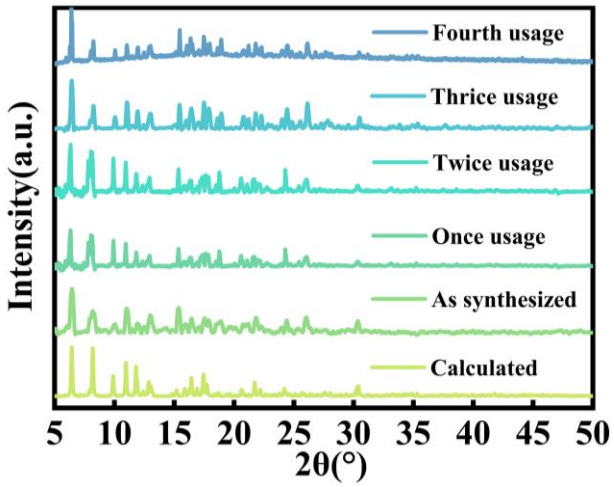

Fig. S21. XRD pattern of **CUST-565** before and after usage.

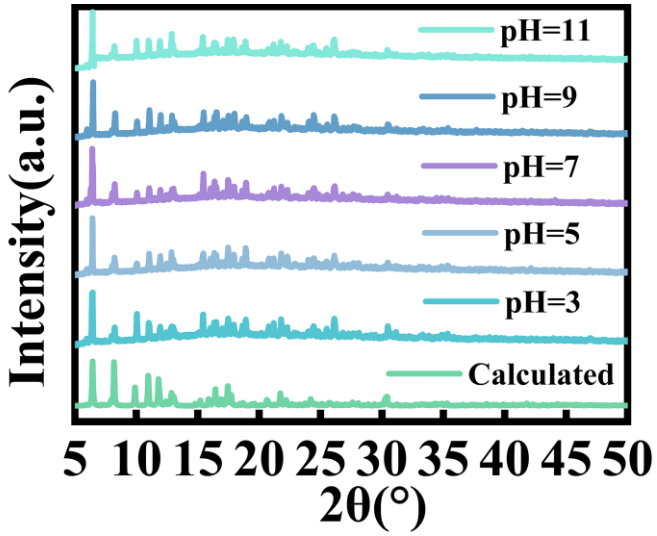

Fig. S22. XRD pattern of **CUST-565** in different pH H_2O.