

Supplementary Material

Simultaneous photocatalytic tetracycline oxidation and chromate reduction via a jointed synchronous pathway upon Z-scheme Bi₁₂O₁₇Cl₂/AgBr: Insight into intermediates and mechanism

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Determination of degradation intermediates:

The degradation products of TC were identified by the liquid chromatography-mass spectrometry (LC-MS) system. LC-MS was performed with an Agilent Technologies 6470 Triple Quad LC/MS system. The detection conditions were as follows: the capillary potential of 3.5 kV, cone voltage of 30 V. Nitrogen was used as the nebulizer gas. The column temperature was thermostated at 30°C. The mobile phase comprised buffer A (HPLC grade water + 0.1% (v/v) formic acid) and buffer B (HPLC grade acetonitrile). The flow rate was 0.2 mL/min. The eluent gradient started with 10% of eluent B gradually increasing to 90% in 10 min, and the system was then kept for 4 min, returning to 10% in 1 min and equilibrating for 1 min (returning to initial condition and re-equilibrating the column). Mass spectrometry (MS) analysis was performed in a positive mode. The mass range was 70-800 (m/z)

Table S1. Comparison of relative researches of simultaneous Cr (VI) reduction (a) and organics oxidation results with our work.

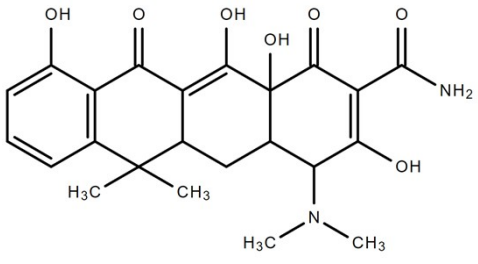
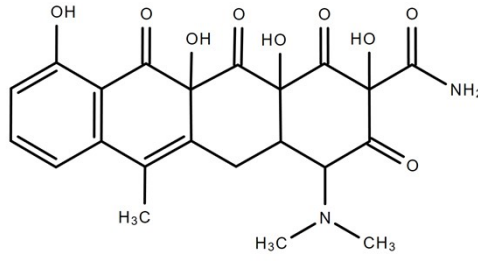
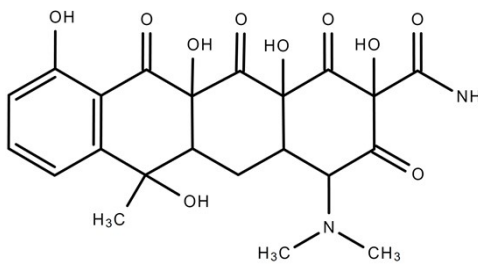
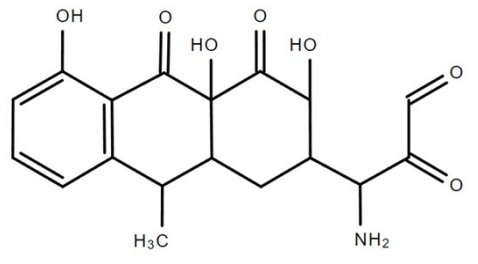
(a):

Photocatalyst	Concentration (Cr (VI), mg/L ⁻¹)	Dosage (g/L ⁻¹)	Time (min)	Removal (%)	Rate (min ⁻¹)	Light Source	Ref.
TiO ₂ /BiOCl 45%	15	1	180	98	0.0189	300 W XL (λ ≥ 400 nm)	1
BiVO ₄ -4	10	1	90	83.42	—	300 W XL (λ ≥ 420 nm)	2
0.3-AgI/BiVO ₄	15	0.4	100	~70	—	500W XL (λ ≥ 420nm)	3
1.5 ZnO/rGO	20	0.5	120	—	0.0159	two non- halogen lamps (24 V, 250 W)	4
MP9% (pH = 2.0)	10	0.25	120	100	—	300 W XL	5
B₁₂/AB 1:1	10	0.5	60	92.6	0.0442	300W XL (λ ≥ 420 nm)	Our work

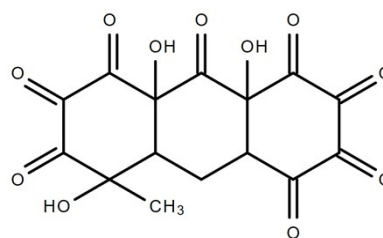
(b):

Photocatalyst	Concentration (mg/L ⁻¹)	Dosage (g/L ⁻¹)	Time (min)	Removal (%)	Rate (min ⁻¹)	Light Source	Ref
TiO ₂ /BiOCl 45%	30	1	240	97	0.0115	300W XL (λ ≥ 400 nm)	1
BiVO ₄ -4	20	1	90	81.22	—	300W XL (λ ≥ 420 nm)	2
0.3-AgI/BiVO ₄	20	0.4	100	~88	—	500W XL (λ ≥ 420nm)	3
1.5 ZnO/rGO	20	0.5	120	—	0.0096	two non- halogen lamps (24 V, 250 W)	4
MP9% (pH = 2.0)	10	0.25	120	84	—	300W XL	5
B₁₂/AB 1:1	50	0.5	60	74.83	0.0275	300W XL (λ ≥ 420nm)	Our work

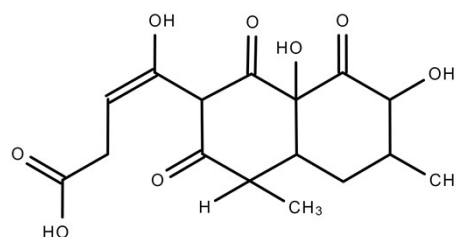
Table S2 Possible degradation intermediates identified by LC-MS.

Number	Formula	RT (min)	m/z	Proposed structure
TC	$C_{22}H_{24}N_2O_8$	5.10	445.02	
P1	$C_{22}H_{24}N_2O_9$	5.30	459.13	
P2	$C_{22}H_{24}N_2O_{10}$	4.09	476.16	
P3	$C_{18}H_{18}NO_7$	3.66	362.13	

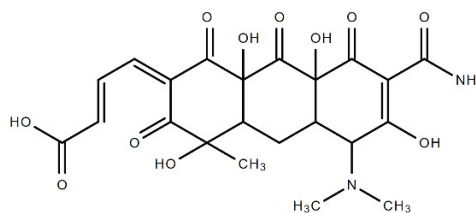
P4 $C_{15}H_9O_{11}$ 2.09 373.06



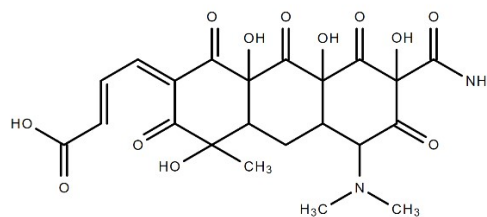
P5 $C_{16}H_{20}O_8$ 4.56 340.18



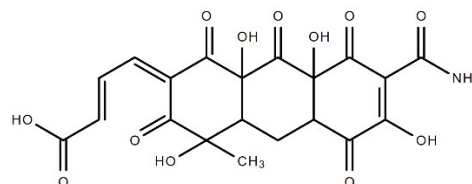
P6 $C_{23}H_{24}N_2O_{11}$ 8.61 516.11



P7 $C_{23}H_{24}N_2O_{12}$ 7.97 521.21



P8 $C_{21}H_{17}NO_{12}$ 6.39 488.94



P9	$C_{10}H_4O_8$	5.47	262.17	
P10	$C_8H_6O_8$	3.21	240.12	
P11	$C_{10}H_{12}O$	8.61	218.18	
P12	$C_3H_2O_5$	9.70	114.63	
P13	$C_2H_2O_4$	9.33	90.82	

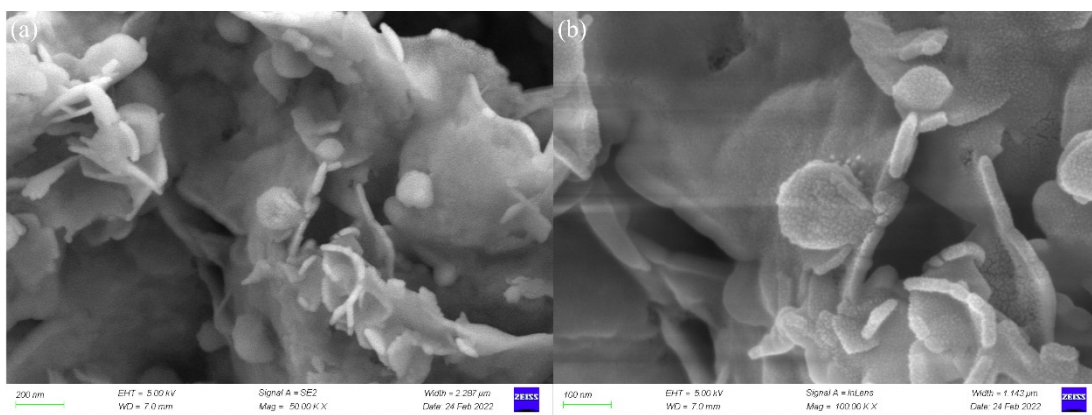


Fig. S1. SEM images of B₁₂/AB 1:1.

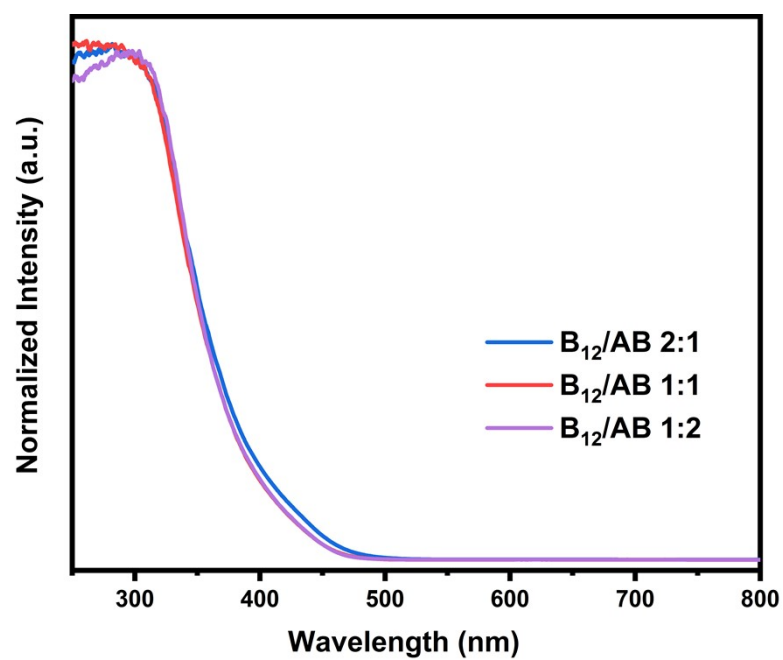


Fig. S2. Normalized UV Diffuse Reflectance Spectra of B₁₂/AB x.

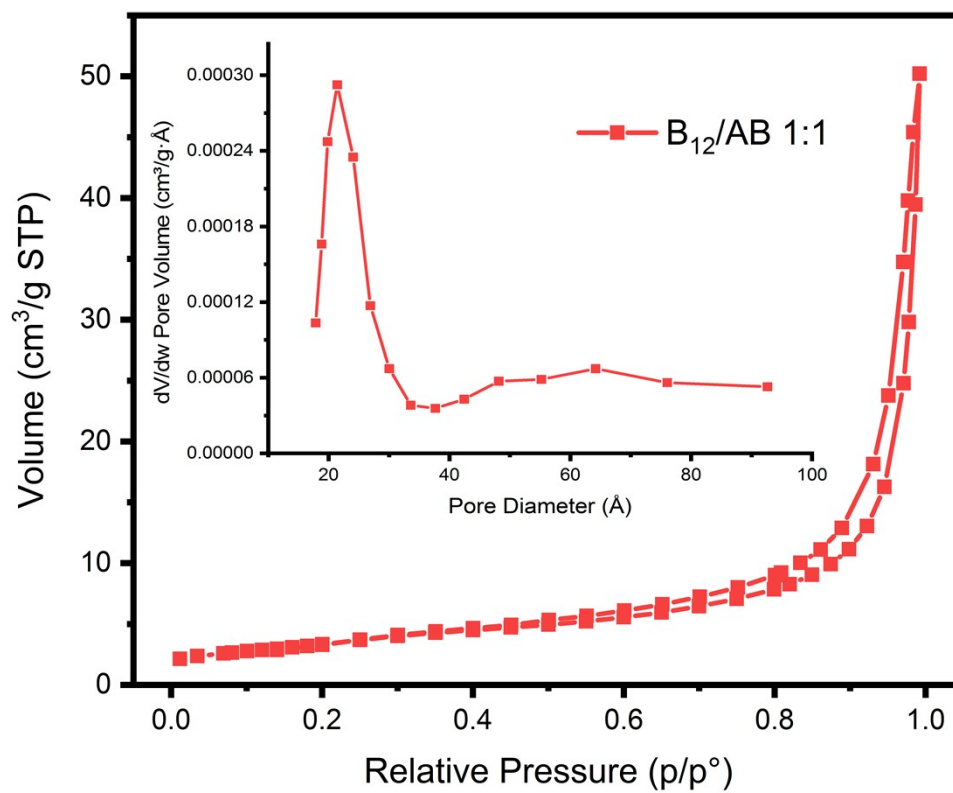


Fig. S3. N₂ adsorption-desorption isotherm of B₁₂/AB 1:1.

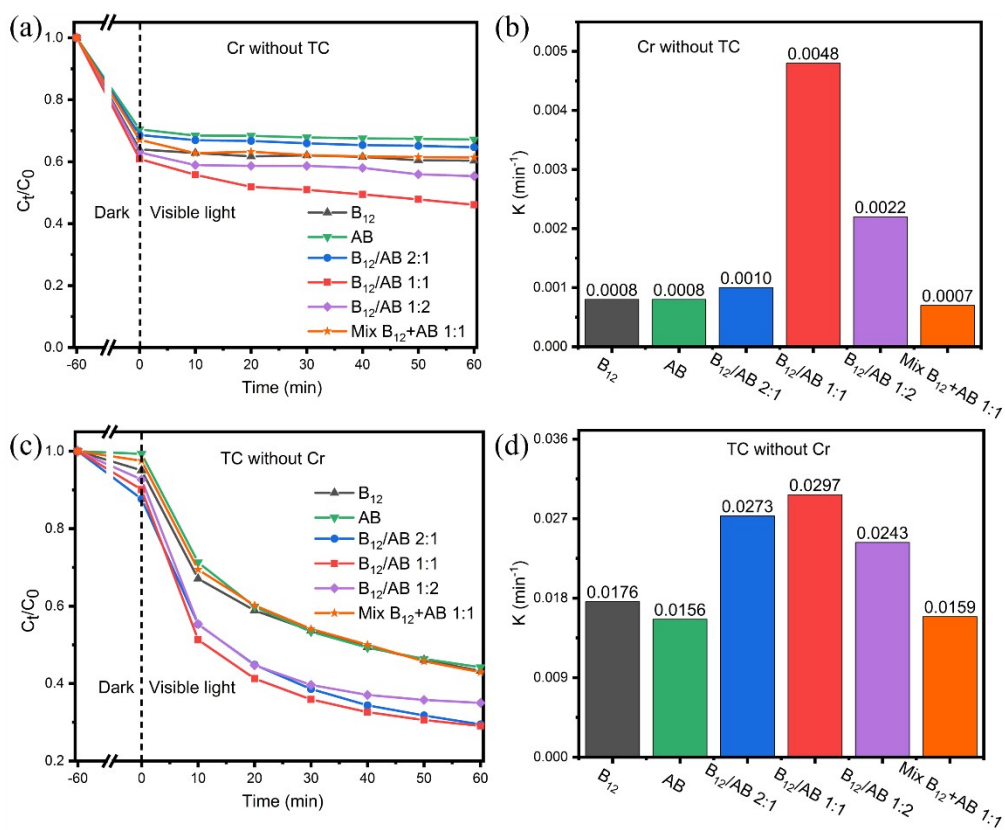


Fig. S4. Dynamic curves and the fitted kinetic constant K (min^{-1}) of photocatalytic reduction of Cr (VI) (a, b), degradation of TC (c, d) in individual Cr (VI), TC solutions.

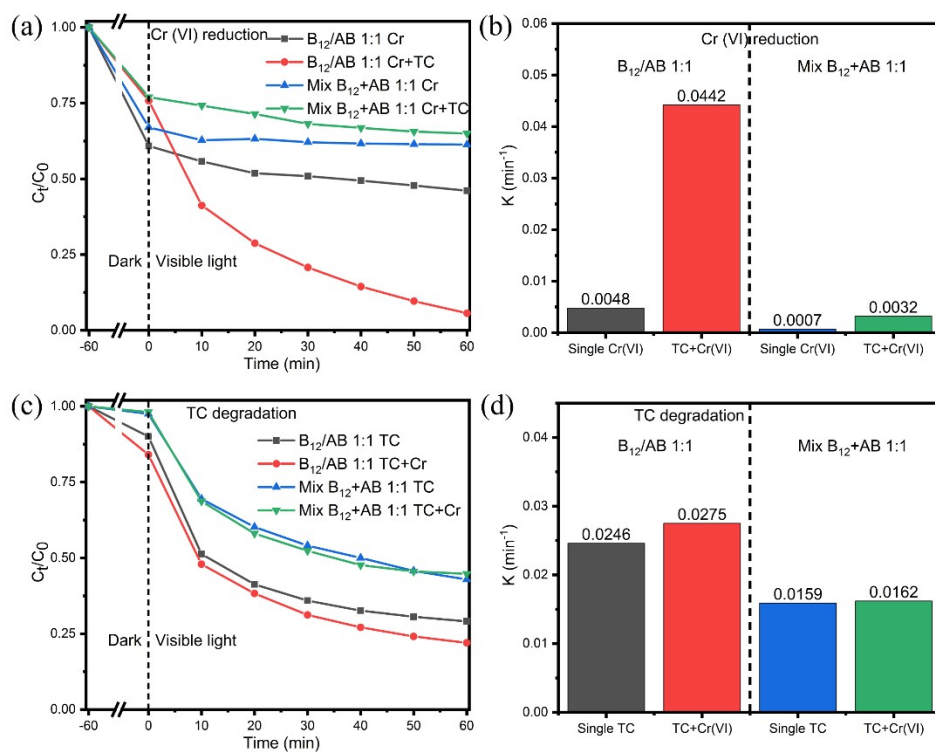


Fig. S5. Simultaneous removal of Cr (VI) (a, b) and TC (c, d) over B_{12}/AB 1:1 and

Mix $B_{12}+AB$ 1:1

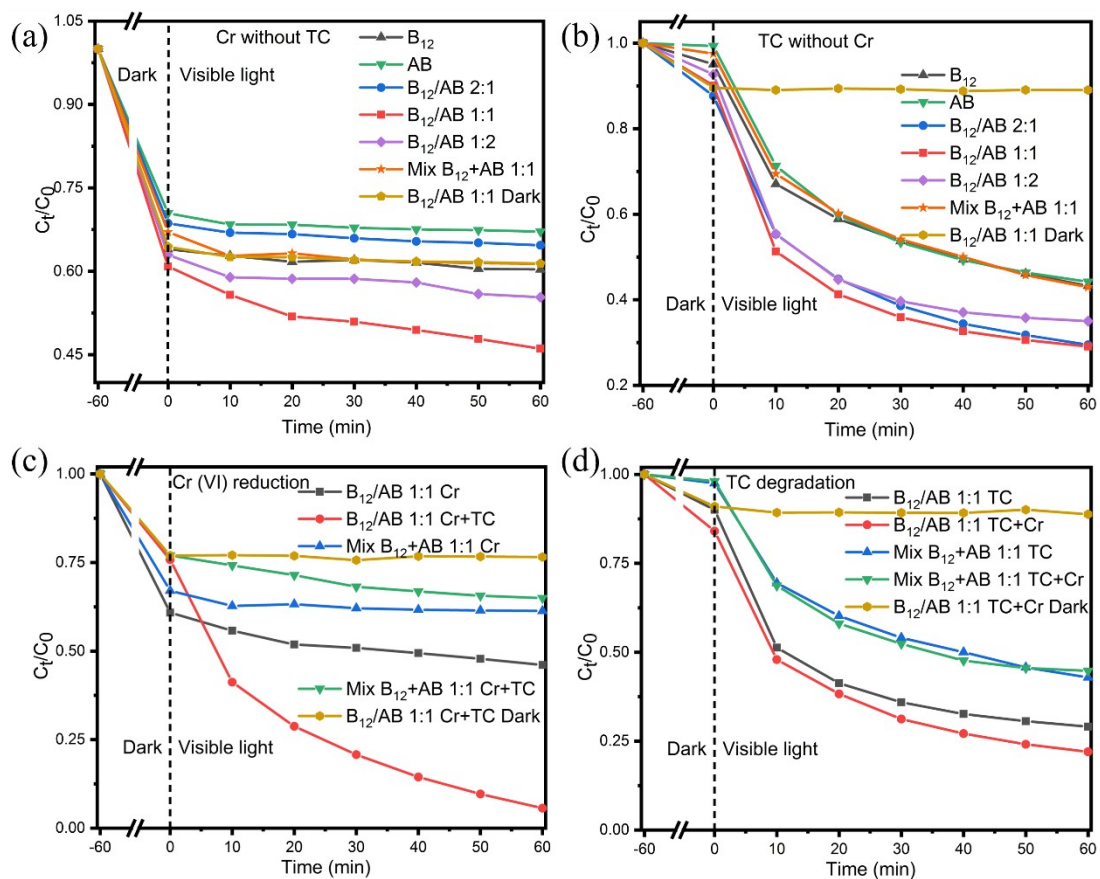


Fig. S6. Dynamic curves of photocatalytic activities with adsorption included.

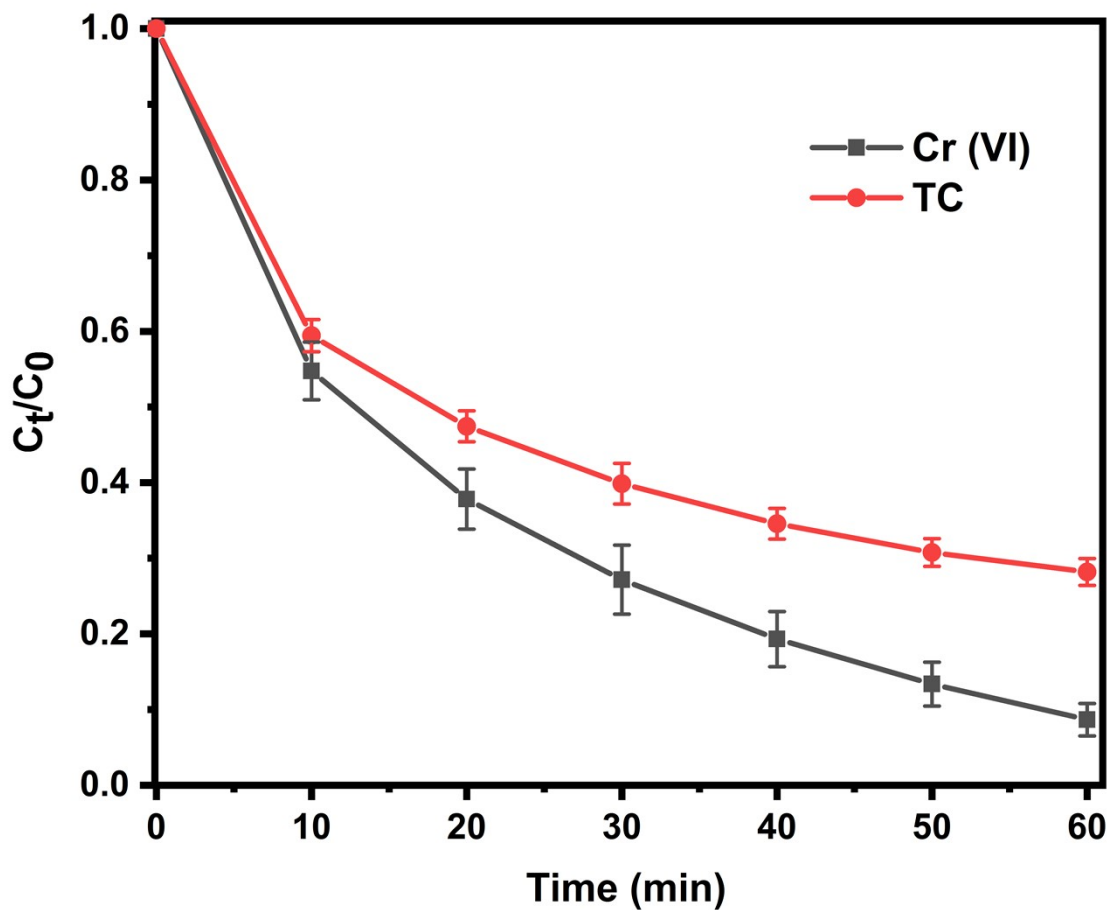


Fig. S7. Error curve of three-times repeated simultaneous Cr (VI) and TC removal over B_{12}/AB 1:1.

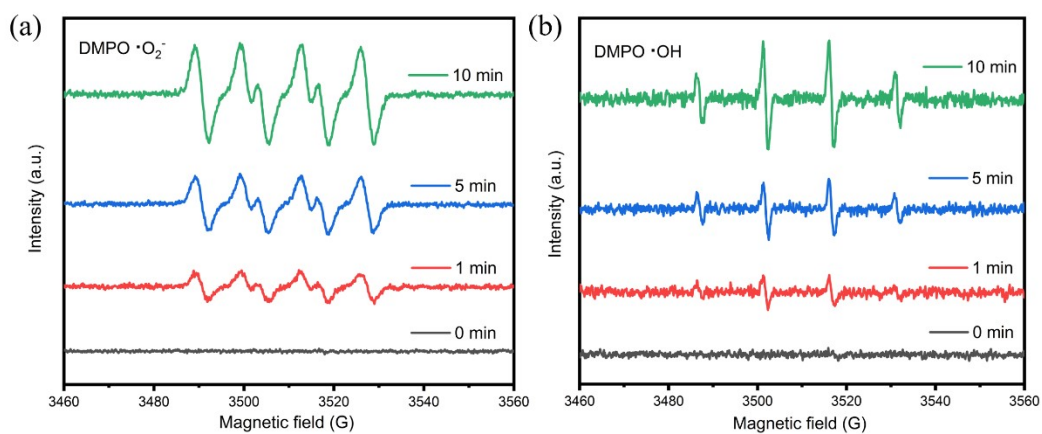


Fig. S8. EPR spectra of B_{12}/AB 1:1 under visible light irradiation ($\lambda \geq 420$ nm)

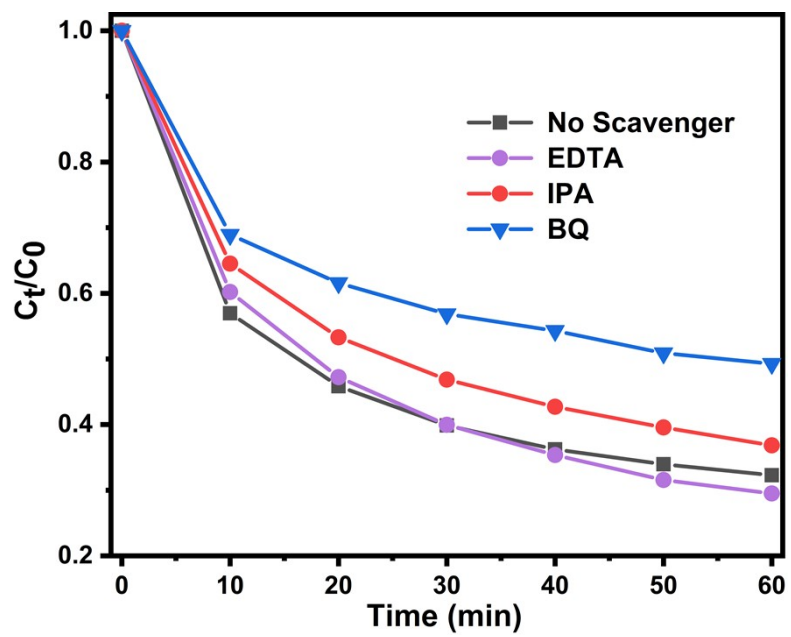


Fig. S9. Active species scavenger experiment of photocatalytic TC degradation over

B_{12}/AB 1:1

20211204-qy-z1 #300-317 RT: 2.42-2.56 AV: 18 SB: 34 0.77-1.04 NL: 7.98E7
T: + c ESI Q1MS [85.000-800.000]

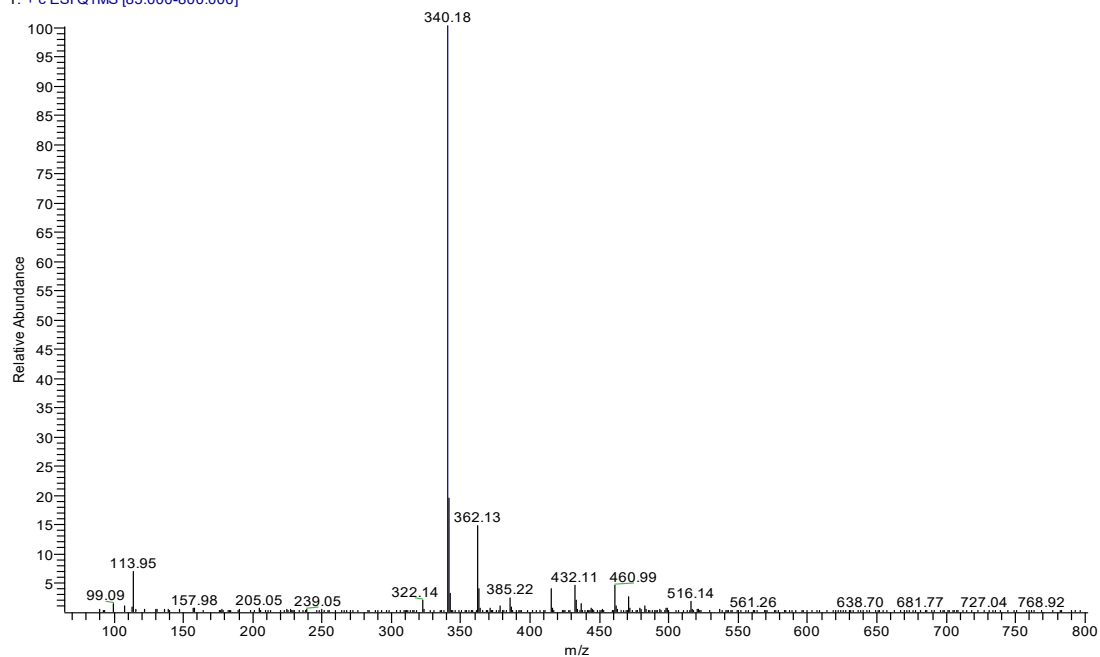


Fig. S10. Mass spectra of degradation intermediates of TC after 20 min degradation at 2.42-2.56 min retention time.

20211204-qy-z1 #330-359 RT: 2.66-2.90 AV: 30 SB: 34 0.77-1.04 NL: 1.48E7
T: + c ESI Q1MS [85.000-800.000]

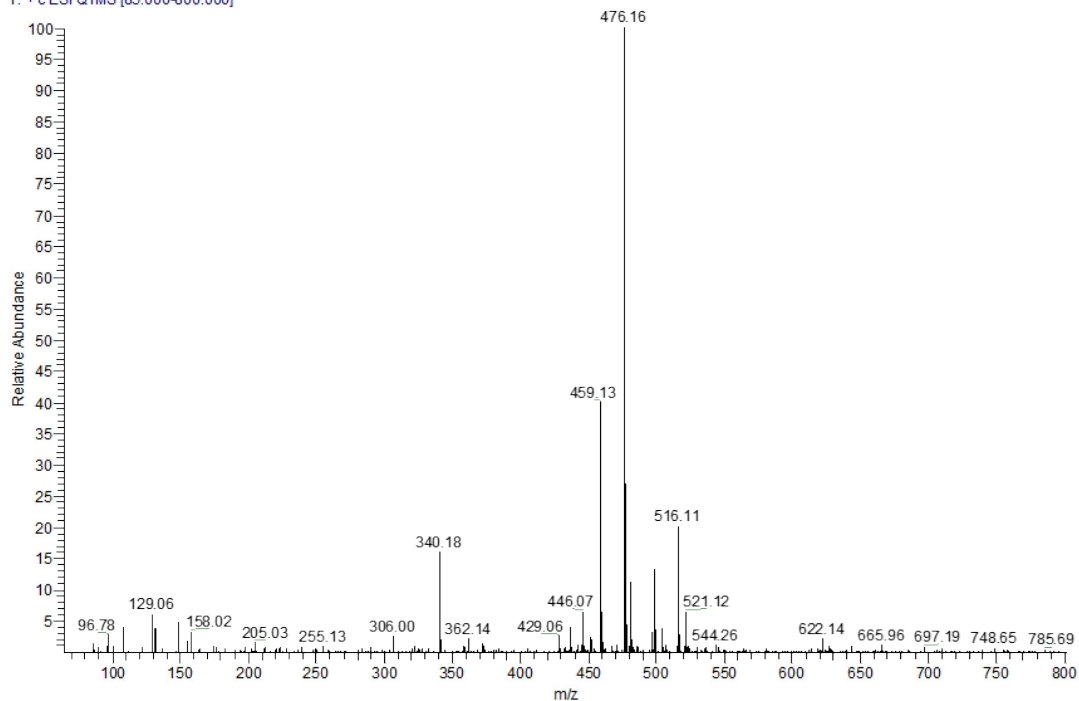


Fig. S11. Mass spectra of degradation intermediates of TC after 20 min degradation at 2.66-2.90 min retention time.

20211204-qy-z1 #484-502 RT: 3.91-4.06 AV: 19 SB: 34 0.77-1.04 NL: 6.03E7
T: + c ESI Q1MS [85.000-800.000]

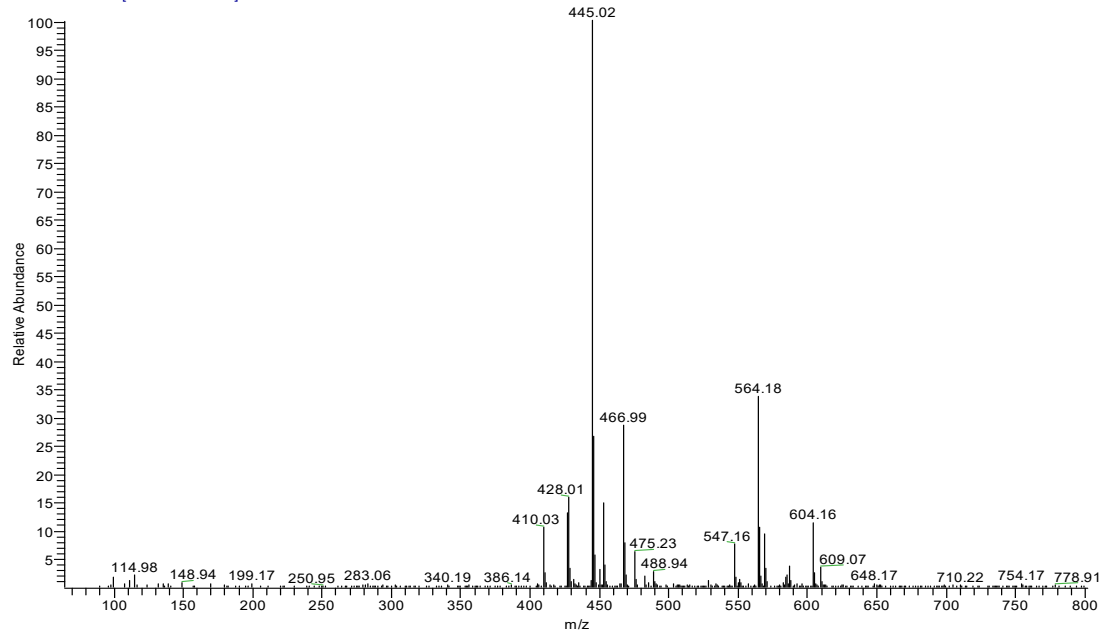


Fig. S12. Mass spectra of degradation intermediates of TC after 20 min degradation at 3.91-4.06 min retention time.

20211204-qy-z2 #655-676 RT: 5.30-5.47 AV: 22 SB: 40 4.68-5.00 NL: 7.45E7
T: + c ESI Q1MS [85.000-800.000]

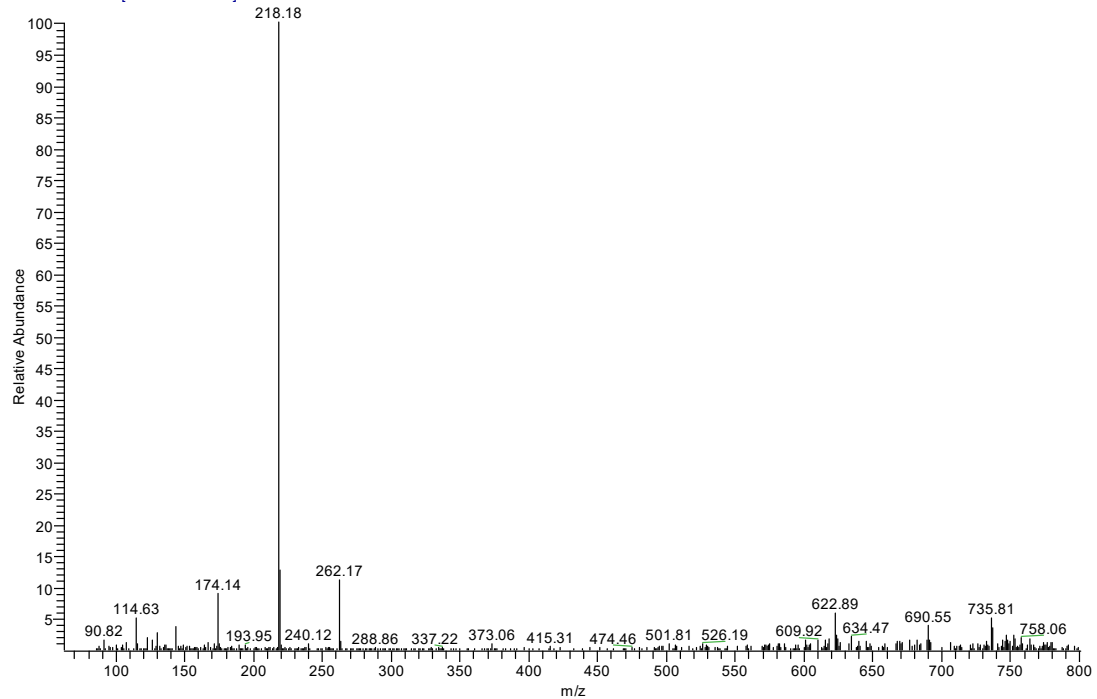


Fig. S13. Mass spectra of degradation intermediates of TC after 60 min degradation at 5.30-5.47 min retention time.

REFERENCES

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