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Supporting Information

Structure induced activity enhancement of tungsten oxide for tetrabromobisphenol A photodegradation under visible light illumination

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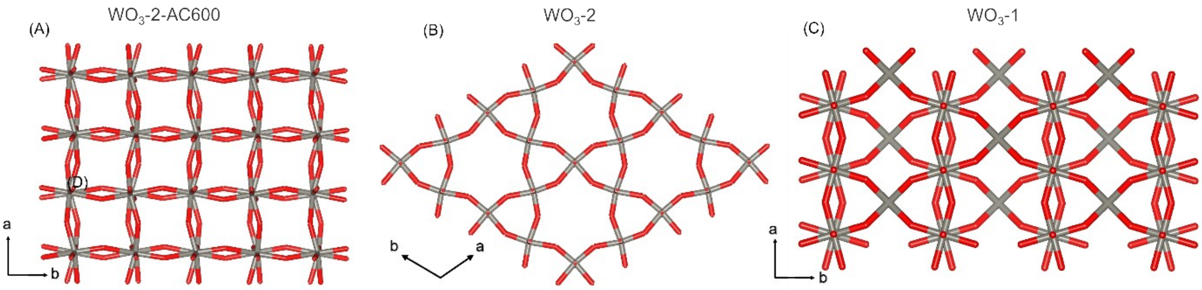


Fig. S1 WO_3 with different crystalline phases, (A) monoclinic, (B) hexagonal, and (C) orthorhombic, W (gray), O (red).

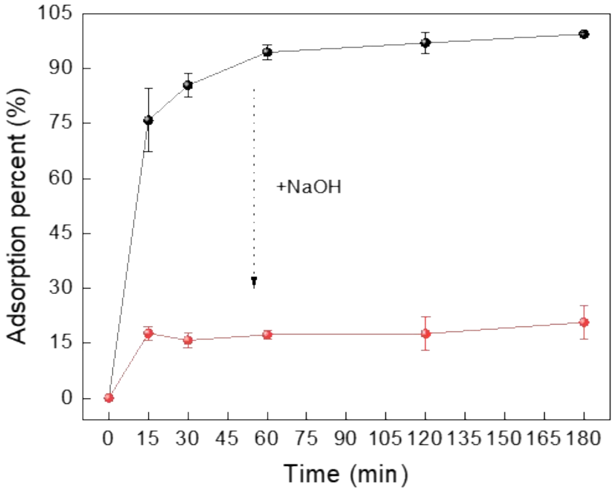


Fig. S2 (black) Adsorption of TBBPA on WO_3-2-AC600 under dark at room temperature and (red) after adding NaOH solution. Adsorption conditions: $[TBBPA]_0$ = 50.0 μmol/L, $[WO_3]_0$ = 0.5 g/L, [NaOH]=10.0 mmol/L and 0.02 mol/L buffer (Na_2HPO_4-NaH_2PO_4 at pH 8.2).

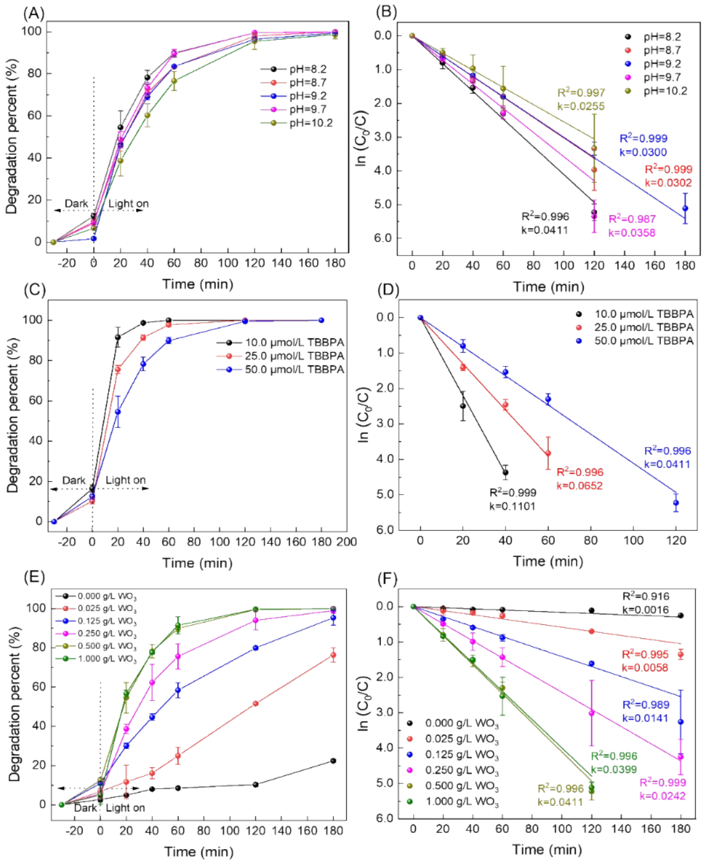


Fig. S3 (A) Effect of initial pH on the TBBPA photodegradation and (B) pseudo-first order kinetic curves, reaction conditions: $[TBBPA]_0 = 50.0$ μmol/L, $[H_2O_2]_0 = 1.25$ mmol/L, $[WO_3]_0 = 0.500$ g/L, and 0.02 mol/L buffer (Na_2HPO_4-NaH_2PO_4 at pH 8.2-8.7, Na_2CO_3-$NaHCO_3$ at pH 9.2-10.2). (C) Effect of TBBPA concentration on the TBBPA photodegradation and (D) pseudo-first order kinetic curves, reaction conditions: $[TBBPA]_0 = 10.0$-50.0 μmol/L, $[H_2O_2]_0 = 1.25$ mmol/L, $[WO_3]_0 = 0.500$ g/L, and 0.02 mol/L buffer (Na_2HPO_4-NaH_2PO_4 at pH 8.2). (E) Effect of the amount of WO_3-2-AC600 on the TBBPA photodegradation and (F) pseudo-first order kinetic curves, reaction conditions: $[TBBPA]_0 = 50.0$ μmol/L, $[H_2O_2]_0 = 1.25$ mmol/L, $[WO_3]_0 = 0.000$-1.000 g/L, and 0.02 mol/L buffer (Na_2HPO_4-NaH_2PO_4 at pH 8.2).

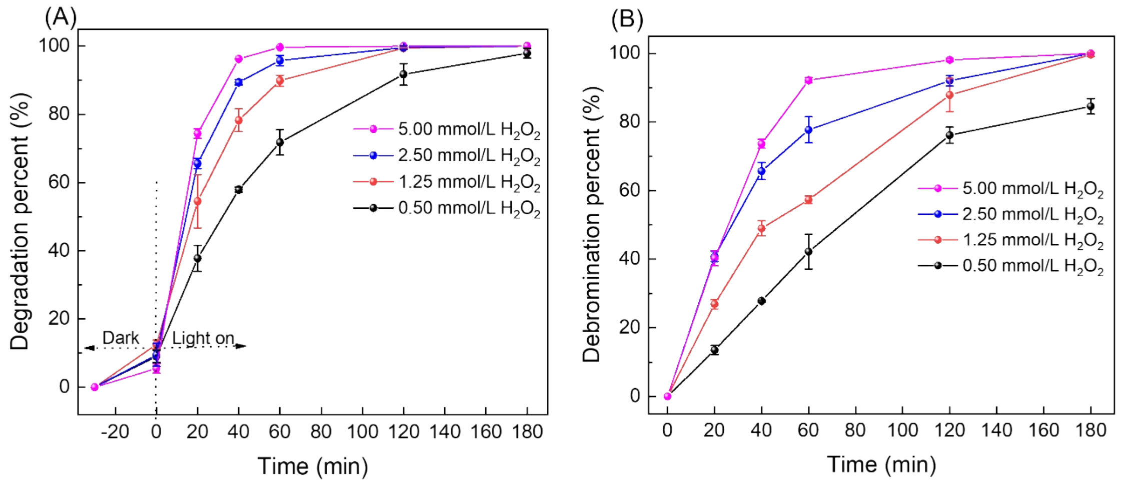


Fig. S4 (A) Degradation percent and (B) debromination percent of TBBPA in different concentrations of H_2O_2, reaction conditions: $[TBBPA]_0$ = 50.0 μmol/L, $[WO_3]_0$ = 0.500 g/L, and 0.02 mol/L buffer (Na_2HPO_4-NaH_2PO_4 at pH 8.2).

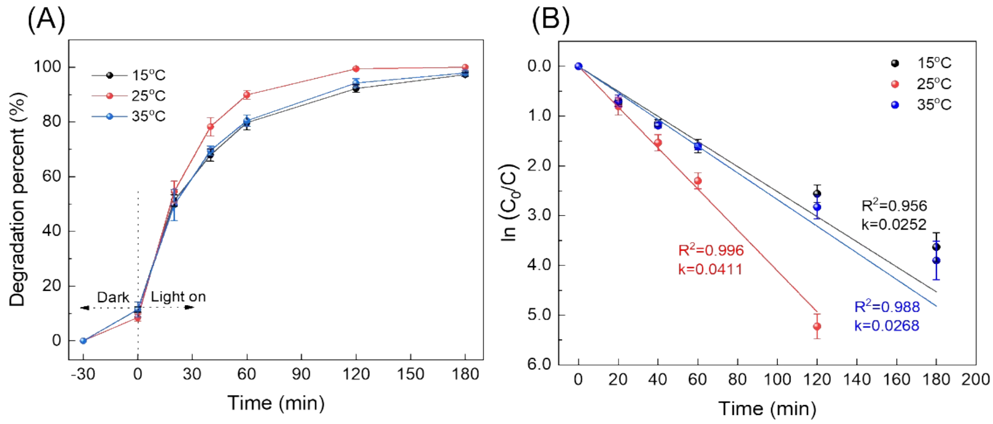


Fig. S5 Degradation percent of TBBPPA at different temperatures, reaction conditions: $[TBBPA]_0$ = 50.0 μmol/L, $[H_2O_2]_0$ = 1.25 mmol/L, $[WO_3]_0$ = 0.5 g/L, and 0.02 mol/L buffer (Na_2HPO_4-NaH_2PO_4 at pH 8.2).

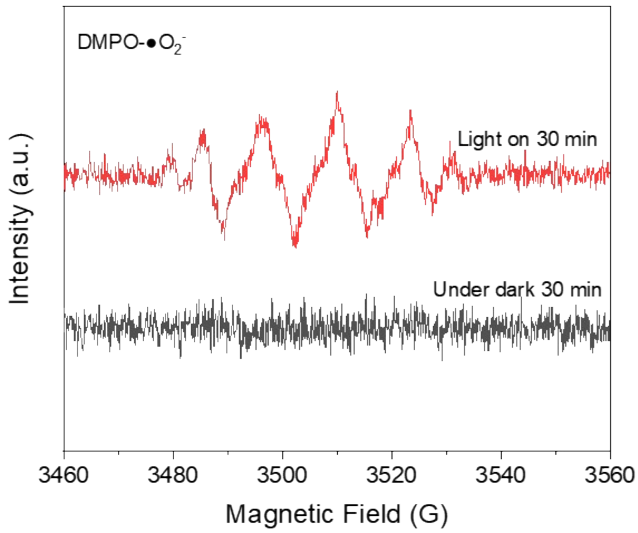


Fig. S6 ESR profiles of TBBPA degradation using only O_2 without peroxides using DMPO as radical capturer •O_2^-- in methanol.

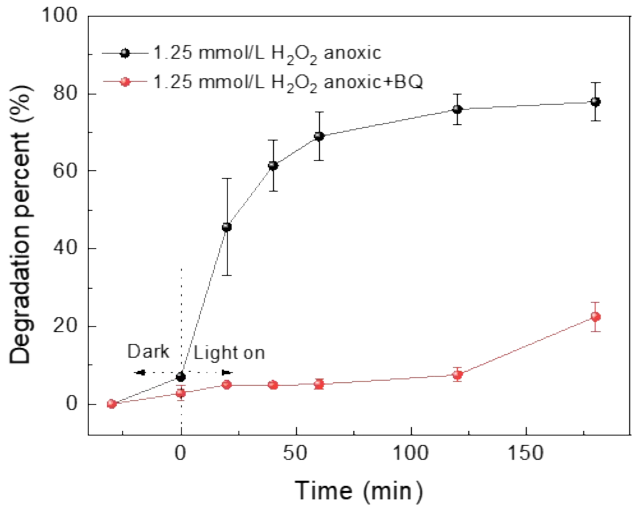


Fig. S7 The degradation percent of TBBPA without air when BQ was added or not, reaction conditions: $[TBBPA]_0 = 50.0$ μmol/L, $[H_2O_2]_0 = 1.25$ mmol/L, $[BQ]_0 = 10.0$ mmol/L, $[WO_3]_0 = 0.500$ g/L, and 0.02 mol/L buffer (Na_2HPO_4-NaH_2PO_4 at pH 8.2).

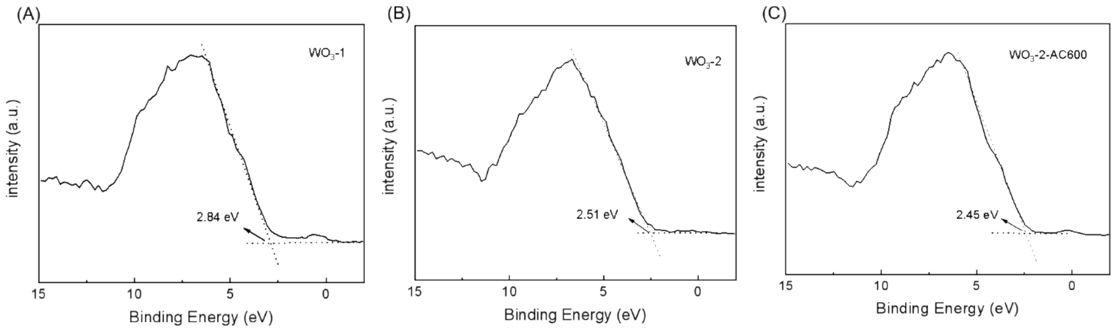


Fig. S8 VB-XPS profiles of (A) WO_3-1, (B) WO_3-2, and (C) WO_3-2-AC600

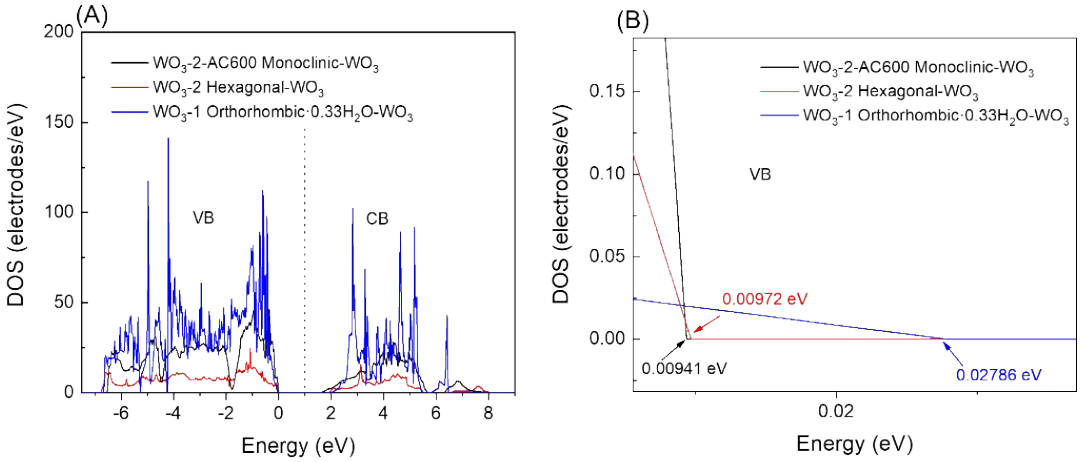


Fig. S9 (A) DOS profiles of WO_3 with different crystalline structures and (B) enlarged DOS profiles.

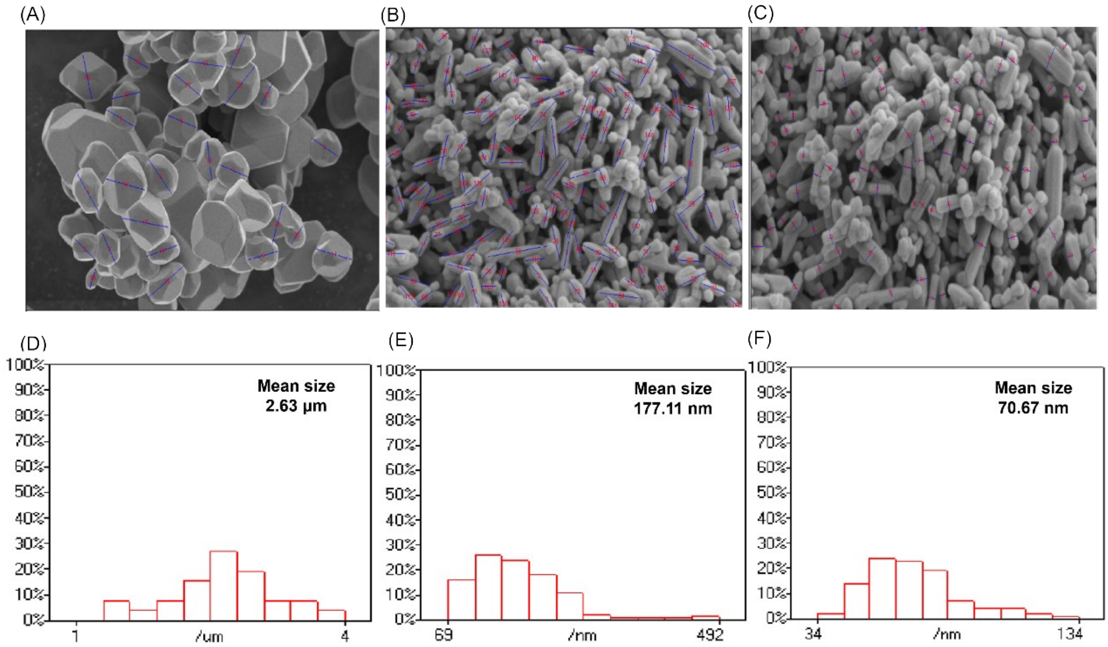


Fig. S10 SEM images of (A) WO_3-2-AC900 with selected diameters, (B) WO_3-2-AC600 with selected length, (C) WO_3-2-AC600 with selected diameter, particle size distribution of (D) WO_3-2-AC900, (E) length distribution of WO_3-2-AC600, and (F) diameter distribution of WO_3-2-AC600.

The method for estimating surface area of different monoclinic WO_3

According to SEM images, WO_3-2-AC600 was nanorod with different scales in diameter and length and WO_3-2-AC900 was polyhedral with similar scales in each diameter. WO_3-2-AC900 was regarded as a sphere, and the surface area was calculated based on $S1 = 4\pi(r_1)^2/(4/3)\ \pi(r_1)^3\rho$, where S1 was catalyst surface area per unit mass of WO_3-2-AC900 , r_1 was radius, and ρ was density of WO_3-2-AC900. Furthermore, WO_3-2-AC600 was regarded as a cylinder, using the surface area calculation formula $S2 = 2\pi r_2(r_2+h)/(\pi(r_2)^2 h\rho)$ of the cylinder, where S2 was catalyst surface area per unit mass of WO_3-2-AC600, r_2 was the radius of the cylinder, and h was the height of the cylinder. $S2/S1=2r_1(r_2+h)/3r_2h$. When r_1 = 1.315 μm, r_2 = 35.335 nm, and h = 177.11 nm, S1/S2 =29.76. Therefore, the surface area of WO_3-2-AC600 was estimated to be 29.76 times as high as that of WO_3-2-AC900.

Therefore, the dose of WO_3-2-AC900 was 40 times as high as the dose of WO_3-2-AC600 to ensure the surface area of the catalysts to be close for comparison. When the concentration of WO_3-2-AC900 reached 1.000 g/L (Fig. S9), the degradation percent was about 70.3% after 180 min, and the degradation effect was still lower than that of 0.025 g/L WO_3-2-AC600 (76.4%) (Fig. S2E).

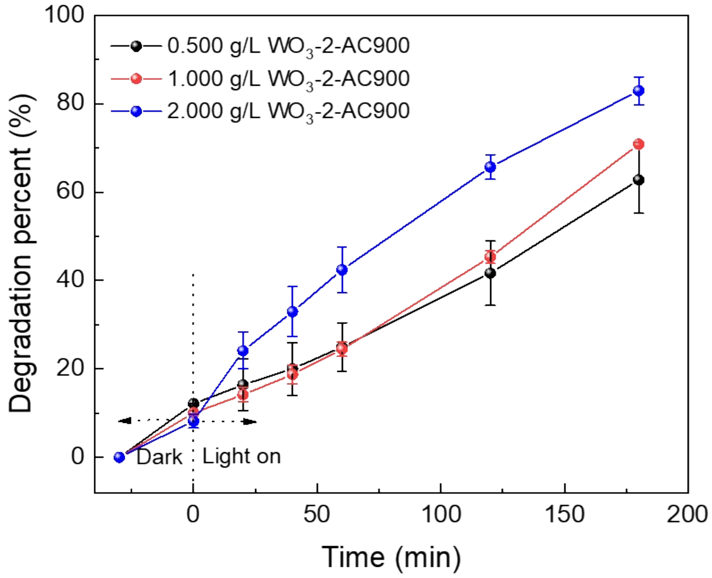


Fig. S11 Effect of the amount of WO_3-2-AC900 on the TBBPA photodegradation, reaction conditions: ($[TBBPA]_0$ = 50.0 μmol/L, $[H_2O_2]_0$ = 1.25 mmol/L, $[WO_3]_0$ = 0.500-2.000 g/L, and 0.02 mol/L buffer (Na_2HPO_4-NaH_2PO_4 at pH 8.2).

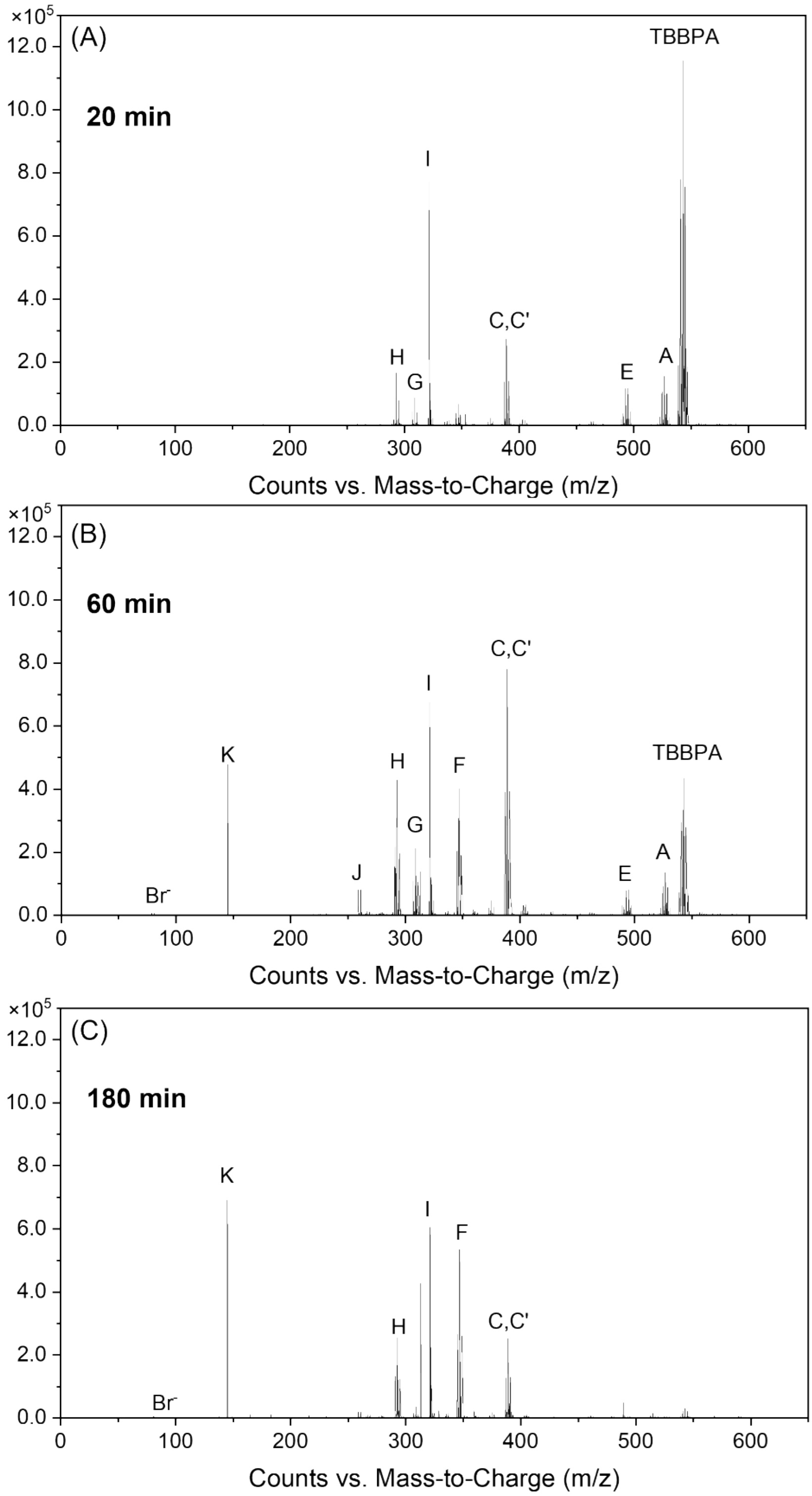


Fig. S12 The HRMS profiles of the TBBPA degradation at (A) 20 min, (B) 60 min, and (C) 180 min.

Table S1. Results of the characterization of various WO_3 obtained by a hydrothermal method.

Catalyst	Crystalline phase	BET Surface area (m^2/g)	Bandgap energy (eV)
WO_3-1	Orthorhombic	6.1	2.73
WO_3-1-AC600	Monoclinic	1.0	2.56
WO_3-2	Hexagonal	46.3	2.66
WO_3-2-AC400	Hexagonal	22.1	2.68
WO_3-2-AC600	Monoclinic	9.8	2.65
WO_3-2-AC900	Monoclinic	<1.0	2.53

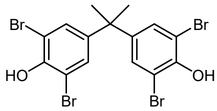
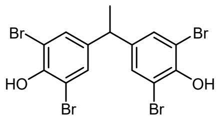
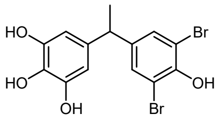
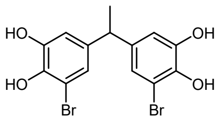
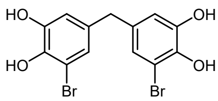
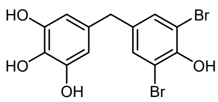
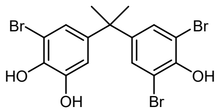
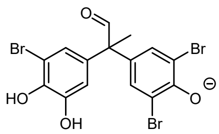
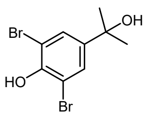
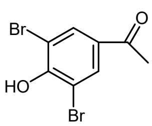
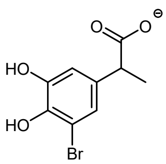
Table S2. Comparisons of TBBPA degradation between the prepared composite and some previously reported catalysts.

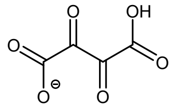
Catalyst	Dosage (g/L)	Light source	TBBPA concentration (μmol/L)	Time	Efficiency (%)	Debromination percent (%)	Peroxide (mmol/L)	References
WO_3-1-AC600	0.5	300 W xenon lamp	50.0	180 min	100.0	100.0	H_2O_2 (1.25)	This work
Fe_3−xTi_xO_4	0.125	6 W UV-light tube	36.8	180 min	92.1	-	H_2O_2 (10.0)	[1]
TiO_2	0.2	100 W high-pressure mercury lamp	91.9	120 min	98.8	-	KPS (2.0)	[2]
Alkaline TiO_2	0.25	75 W high-pressure Hg lamp (UV)	41.7	120 min	100.0	100.0	-	[3]
$MoS_2/SnIn_4S_8$	0.5	300 W xenon lamp	18.4	180 min	89.1	50.0	-	[4]
ZnTMPyP	5.0 μmol/L	16 W LED lamps	50.0	180 min	84.0	32.0	-	[5]
Graphene–TiO_2	0.25	230 W Hg lamp	18.4	60 min	95.5	-	-	[6]
CuO/Ce_2O_3	0.5	500 W Xenon lamp	9.2	120 min	80.46	-	-	[7]
F-TiO_2-g-C_3N_4	0.5	300 W Xenon lamp	18.4	120 min	95.0	-	-	[8]
BiOBr	0.5	800 W xenon lamp	1.84	60 min	100.0	-	-	[9]
tourmaline–TiO_2	1.0	500W medium pressure mercury lamp	18.4	60 min	100.0	-	-	[10]
MIP@C-Fe-Nx	0.5	-	18.4	90 min	100.0	-	PS (1.26)	[11]
$CuFe_2O_4$	0.1	-	18.4	180 min	100.0	67.0	PMS (1.5)	[12]
nZVI	3.0	-	9.2	12 h	78.32	-	PS (25.0)	[13]

FeTPPS	5.0 μmol/L	-	50.0	30 min	95.0	0	PMS (0.125)	[14]
Fe_3O_4/MWCNT	0.5	-	18.4	180 min	90.2	-	H_2O_2 (0.1)	[15]
$Fe^{3+}/S_2O_4^{2-}$	200.0 μmol/L	-	1.0	60 min	93.8	83.9	PS (0.2)	[16]

KPS: $K_2S_2O_8$; PMS: $KHSO_5$; PS: $S_2O_4^{2-}$

Table S3. Toxicity evaluation of Intermediate to Fathead minnow.

Intermediate	Chemical structure	LC50 (mg/L) For Fathead minnow
TBBPA		0.045
A		0.0452
B		0.18
B’		0.18
C		0.13
C’		0.19
D		0.10
E		0.13
G		3.5
H		1.61
J		N/A

K		N/A

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