

Supporting Information

Fabrication of water-floating litchi-like polystyrene-sphere-supported TiO₂/Bi₂O₃ S-scheme heterojunction for efficient photocatalytic degradation of tetracycline

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Experimental Procedures

Chemicals and Materials

The styrene, hexadecylamine (HDA) and tartaric acid (TA, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$) were bought from Sigma-Aldrich Chemical Co. Ltd. The ammonium persulfate (APS), 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and polyvinylpyrrolidone (PVP, $M_w \approx 58$ kDa) were purchased from Aladdin Biochemical Technology Co. Ltd. The tetracycline hydrochloride (TC) and titanium isopropoxide ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$) were bought from Macklin Reagents Co. Ltd. The bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), sodium hypophosphite (NaH_2PO_2), sodium hydroxide (NaOH), sodium oleate (SOA), isopropyl alcohol (IPA), Triethanolamine (TEOA) were from Beijing InnoChem Technology Co. Ltd. The entire reagents were analytically pure (AR), allowing for use without additional purification.

Apparatus

Transmission electron microscopy (TEM, JEOL 2100F) and scanning electron microscopy (SEM, JEOL JSM-7001F) were used to examine the morphology and structure of the as-prepared catalysts. A 300 W Xe lamp and the photochemical reactor were mounted on a CEL-GPPCL system (Beijing China Education Au-light Company). In situ irradiated X-ray photoelectron spectrometer (XPS, Thermo ESCALAB250Xi) was adopted to investigate the charge transfer mechanism of photocatalyst. Mott-Schottky plots were recorded using an electrochemical workstation (CHI Instruments CHI760-1). Diffuse reflection spectroscopy (DRS, HITACHI UV-3900) was used to obtain the absorption spectra. Ultraviolet-visible spectrum of TC was measured through a UV-2550 spectrophotometer (Shimadzu UV-18700). Electrochemical impedance spectroscopy (EIS) was tested via a CHI1030B electrochemical workstation. The degradation intermediate products of TC were determined using liquid

chromatography-mass spectrometry (LC-MS, Agilent 1260-6460) with electrospray positive ion mode.

Preparation of polystyrene spheres

The polystyrene spheres (PS) were prepared according to the previous reference with minor improvement.^{S1} Polymerization took place in a 100 mL round-bottom flask with magnetic stirring. The round-bottom flask was initially filled with preweighed PVP and initiator. In a typical polymerization, the mass of PVP was 0.01 g as well as the APS concentration was 15 mM. Afterward, 6.0 mL of deionized water and 50 mL of ethanol were poured into the flask. Then, a magnetic bar was used to thoroughly agitate the liquid for 10 min at room temperature. Finally, 4.4 mL of styrene monomer was added and the polymerization temperature was kept at 70°C under the condition of full agitation in the oil bath for 6 h. After polymerization is complete, any further reaction is terminated by placing round-bottom flask in ice water for 30 min. The round-bottom flask was submerged in ice water for 30 min after the polymerization process was finished to stop any potential additional reactions. After centrifuging the vial at 12,000 rpm, the resulting products were collected and repeatedly rinsed with deionized water to get rid of any remaining PVP and styrene. The final products were dried at 60°C and stored in a glass bottle for further use.

Synthesis of PS@TiO₂ composites

550 mg of PS was ultrasonically dispersed in 175 mL ethanol for 1 h. Then, 1.6 g of HDA and 4.0 mL of NH₃·H₂O were added into the above solution and magnetically stirred for 30 min to form a uniform suspension. Then, 1.0 mL of titanium isopropoxide was quickly dropped into the suspension to avoid hydrolysis in air. After reaction for 1

h, the products were collected, rinsed with ethanol and deionized water alternately for several times, and then dried at 60°C for later use.

Synthesis of PS@TiO₂/Bi₂O₃ photocatalyst

The PS@TiO₂/Bi₂O₃ photocatalyst was synthesized according to the previous reports with some modification.^{S2,S3} Typically, 0.5 g of PS@TiO₂, 0.6 g of tartaric acid, 5 mL of Bi(NO₃)₃·5H₂O solution (containing 0.01 mol HNO₃) with different molar mass (0.2, 0.4, 0.6 and 0.8 M, respectively) and 15 mL deionized water were mixed together, and stirred vigorously for 30 min. Next, 2.4 g of NaOH was dissolved in 35 mL deionized water, further added into the above mixture, and continued to stir at room temperature for 10 min. Then, the solution was transferred to a three-necked flask at 90°C, into which 0.015g sodium oleate was added and stirred for 10 min. Also 40 mL of 5 M NaH₂PO₂ was added into the solution, and stirring constantly continued for 5 h. After the reaction was completed, the resulting products were collected by washing with deionized water and ethanol for several times to obtain PS@TiO₂/Bi hybrids. Finally, continuous drying at 80°C for 12 h induces PS@TiO₂/Bi to be gradually oxidized into PS@TiO₂/Bi₂O₃ composites. The PS@TiO₂ loaded with Bi₂O₃ in varying proportions were denoted as PS@TiO₂/Bi₂O₃-0.2, PS@TiO₂/Bi₂O₃-0.4, PS@TiO₂/Bi₂O₃-0.6 and PS@TiO₂/Bi₂O₃-0.8, respectively. In addition, the single Bi₂O₃ sample served as contrast photocatalyst was also prepared using a similar method without the addition of PS@TiO₂. To facilitate the comparison, the pure TiO₂/Bi₂O₃-0.4 composite was also fabricated using a similar procedure of “Synthesis of PS@TiO₂/Bi₂O₃” without adding PS microspheres.

Electrochemical Tests

The electrochemical test was completed via a CHI760-1 electro-chemistry workstation (Shanghai Chenhua, China) with a three-electrode cell. The glass-carbon electrode loaded catalyzer was the work electrode, and the saturated Ag/AgCl electrode and platinum foil were the reference electrode and anti-electrode, separately. The transient photocurrent response curves were harvested during the illumination (on/off) every 20 s at an applied potential of 0 V (vs Ag/AgCl) in 0.1 M Na₂SO₄ solution from the back side of the work electrode. The electrochemical impedance spectroscopy (EIS) measurements were completed by using an AC voltage amplitude of 5 mV in the frequency range between 105 and 0.01 Hz in Na₂SO₄ electrolyte under open circuit potential (OCP) conditions and 300 W xenon light irradiation. The Mott–Schottky (M–S) plots were implemented with the electrochemical window ranging between -1.0 to +1.5 V, using 800 or 1000 Hz as well as an AC amplitude of 10 mV at each of the potentials.

Electron paramagnetic resonance (EPR) measurement

The EPR technology was used to detect free radical species such as hydroxyl radical ($\cdot\text{OH}$) and superoxide radical ($\cdot\text{O}_2^-$) with the assistance of 5,5-dimethyl-1-pyrroline N-oxide (DMPO). Briefly, for the detection of hydroxyl radical ($\cdot\text{OH}$), the as-prepared sample was dispersed into deionized water to form a 2.5 mg mL⁻¹ suspension under ultrasonic conditions. Subsequently, 50 μL DMPO was added into the above suspension under rapid stirring. Then, this mixture was irradiated for 5 min using a 300 W Xe lamp under the rapid agitation. After that, the supernatant of above mixture was quickly sampled and tested in the EPR equipment. Additionally, the detection procedure of superoxide radical ($\cdot\text{O}_2^-$) was the same as that of hydroxyl radical ($\cdot\text{OH}$), except that the deionized water was replaced by methanol.

Measurement of photocatalytic performances

The photocatalytic activity of the as-prepared photocatalysts was assessed by degrading TC in water. In brief, 20 mg of photocatalyst was placed in 100 mL of TC solution (50 mg L⁻¹). The above mixture was continually stirred in the dark for 30 min until it reaches equilibrium. Next, the photocatalytic process is conducted utilizing 300 W xenon lamp (full-pectrum) illumination while being mechanically agitated. Then, the surplus photocatalyst was removed using filter paper after a tiny amount of the reaction solution was taken out at varied irradiation intervals. The upper transparent layer was determined by recording the maximum absorbance of TC at 357 nm with a UV-visible spectrophotometer. Finally, the removal rate of TC was calculated using the following formula:

$$\eta_{\text{TC removal rate}} (\%) = (1 - C_t/C_0) \times 100\%$$

Where C_t is the TC concentration recorded during interval sampling as well as C_0 is the initial TC concentration.

Density functional theory (DFT) calculation analysis

Fukui function based on the density functional theory (DFT) was used to predict the regioselectivity of ROS ($\cdot\text{OH}$ and $\cdot\text{O}_2^-$) towards the TC molecules. All of the calculations were performed using the Gaussian 16 (Revision C.01) software.^{S4} The geometry optimization and single-point energy calculations were executed using the B3LYP method with the 6-31+G(d,p) basis set. The orbital energy level analysis, electrostatic potential (ESP) analysis and Fukui function analysis were performed by Multiwfn package. Fukui function is an important concept in the conceptual density functional theory (CDFT), and it has been widely used in prediction of reactive sites of

electrophilic, nucleophilic and general radical attacks.^{S5} Specifically, Fukui function is defined as:

$$f(r) = \left[\frac{\partial \rho(r)}{\partial N} \right]_v \quad (1)$$

where $\rho(r)$ is the electron density at a point r in space, N is the electron number in the present system, and the constant term v in the partial derivative is the external potential. In the condensed version of Fukui function, the atomic population number is used to represent the electron density distribution around an atom. The condensed Fukui function can be calculated as:

$$\text{Electrophilic attack: } f_A^- = q_{N-1}^A - q_N^A \quad (2)$$

$$\text{Nucleophilic attack: } f_A^+ = q_N^A - q_{N+1}^A \quad (3)$$

$$\text{Radical attack: } f_A^0 = (q_{N-1}^A - q_{N+1}^A)/2 \quad (4)$$

where q^A is the atom charge of atom A at the corresponding state. The Fukui function contains relative information about different sites of one molecule, and the reactive sites of the exact molecule usually have larger value of condensed Fukui function (CFF) than other regions. Hydroxyl radical ($\cdot\text{OH}$) and superoxide radical ($\cdot\text{O}_2^-$) were the primary attack reactive oxygen species (ROS), which are classified as a kind of electrophile, which is more likely to attack the sites that can readily lose electrons.^{S6} Thus, we calculated the Fukui index (f^+ and f^0) of TC for nucleophilic and radical attacks. In this study, the natural population analysis (NPA) charge is used to study the reactive sites, as it is considered to be one of the most suitable methods to calculate Fukui index.^{S7}

Experimental Figures

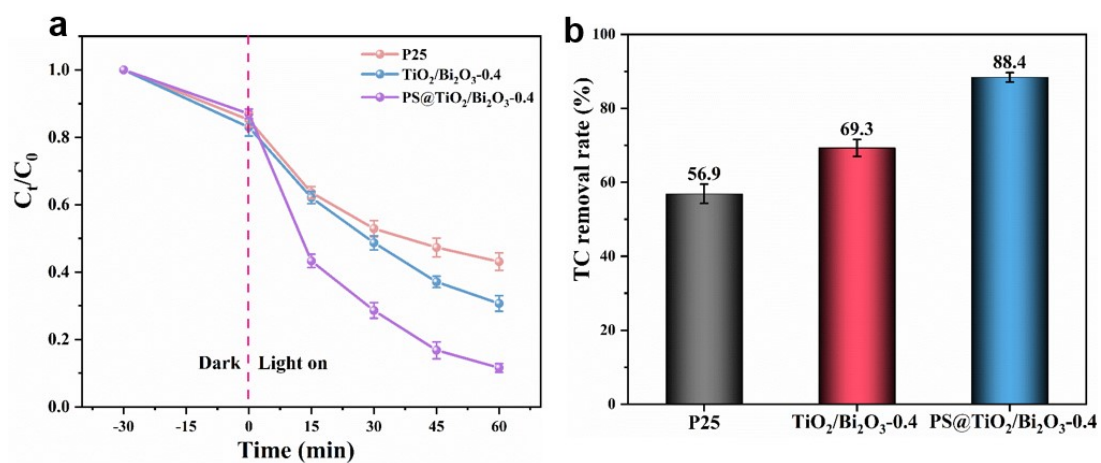


Fig. S1. Photodegradation of TC (a) and the TC removal rate over different photocatalysts. (New supplemented data)

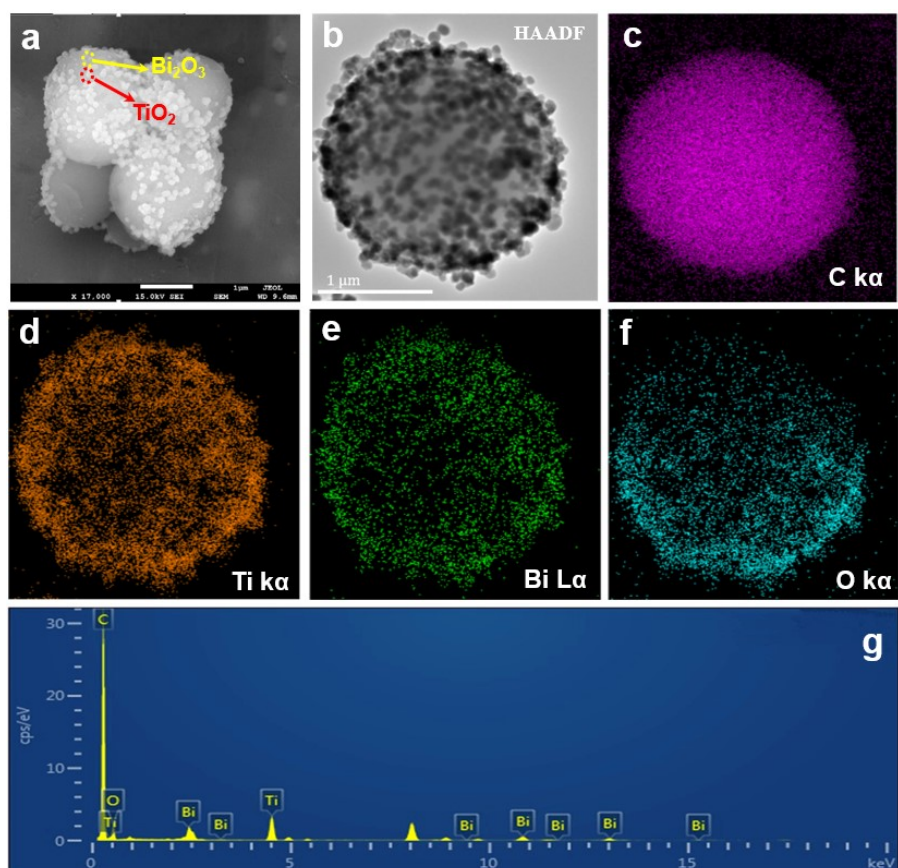


Fig. S2 SEM (a) and STEM-EDS elemental mapping (b-f) of the PS@TiO₂/Bi₂O₃-0.4 after 5 cycling test; EDS (g) of PS@TiO₂/Bi₂O₃-0.4 after 5 cycle experiments of photocatalytic degradation of TC.
(New supplemented data)

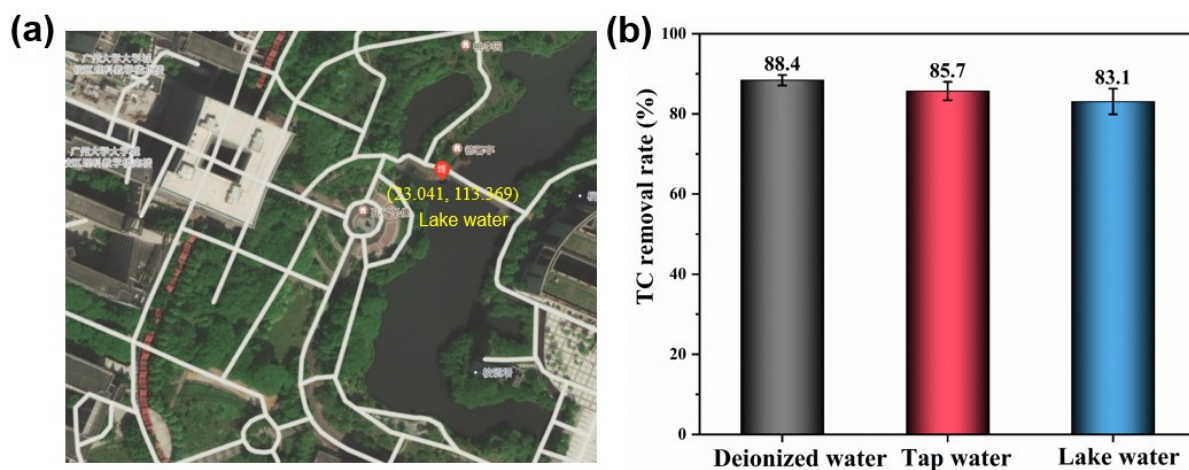


Fig. S3. (a) Natural water intake point (e.g. lake water); (b) Photocatalytic degradation of TC by PS@TiO₂/Bi₂O₃-0.4 in different water quality.

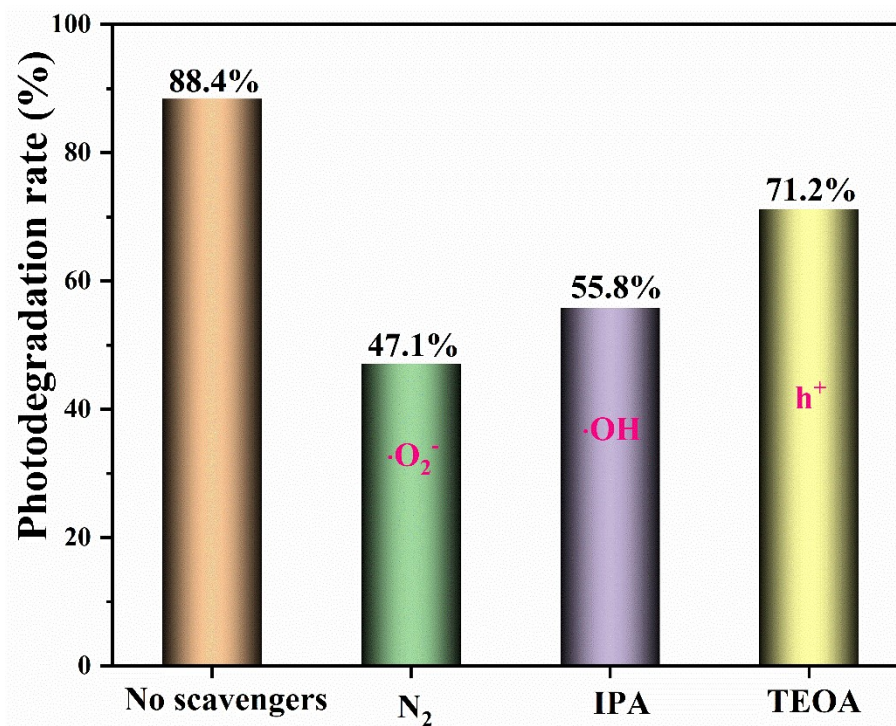


Fig. S4. Photocatalytic activities of TC over PS@TiO₂/Bi₂O₃-0.4 with various scavengers.

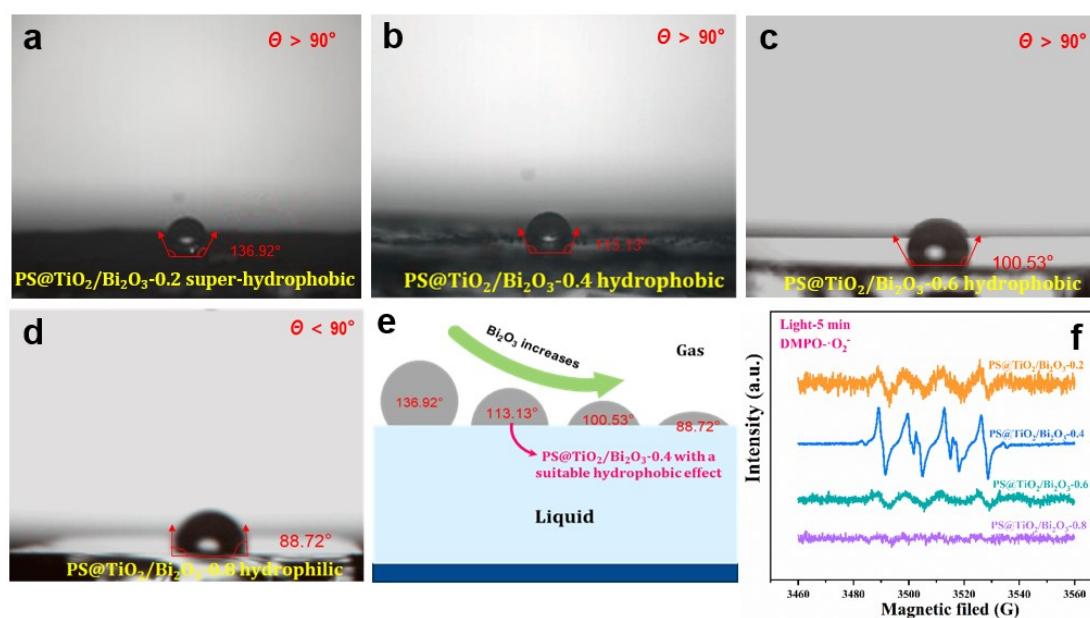


Fig. S5. The contact angle photographs on FTO tablets of PS@TiO₂/Bi₂O₃-0.2 (a), PS@TiO₂/Bi₂O₃-0.4 (b), PS@TiO₂/Bi₂O₃-0.6 (c) and PS@TiO₂/Bi₂O₃-0.8 (d); (e)

Schematic diagram of hydrophilicity and hydrophobicity of PS@TiO₂/Bi₂O₃-x samples (x stands for 0.2, 0.4, 0.6 and 0.8); (f) EPR spectra of DMPO-·O₂⁻ of the as-constructed PS@TiO₂/Bi₂O₃-x samples. **(New supplemented data)**

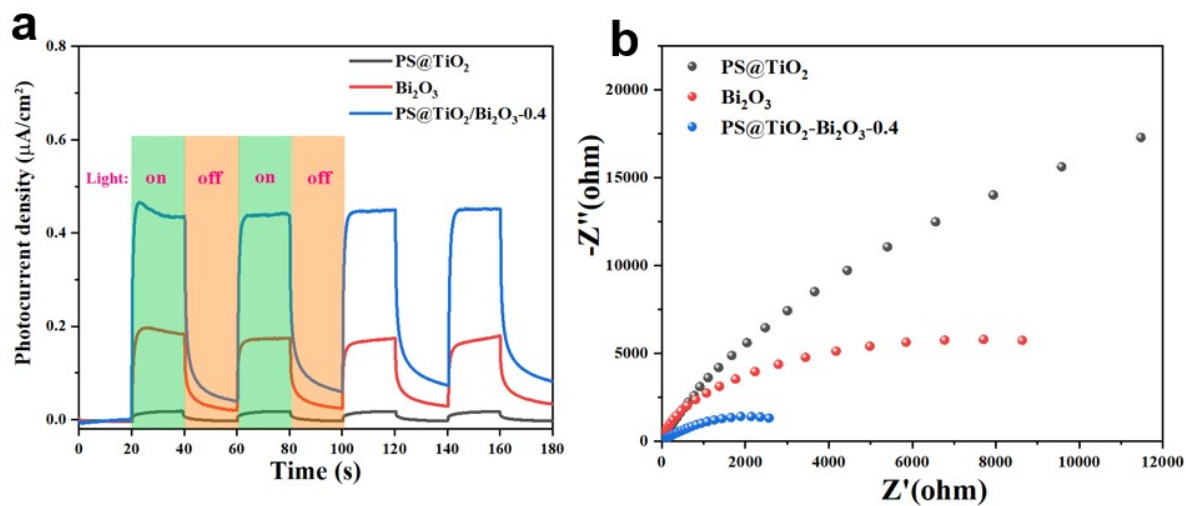


Fig. S6. Transient photocurrent response (a) and electrochemical impedance (b) spectra of PS@TiO₂, Bi₂O₃ and PS@TiO₂-Bi₂O₃-0.4.

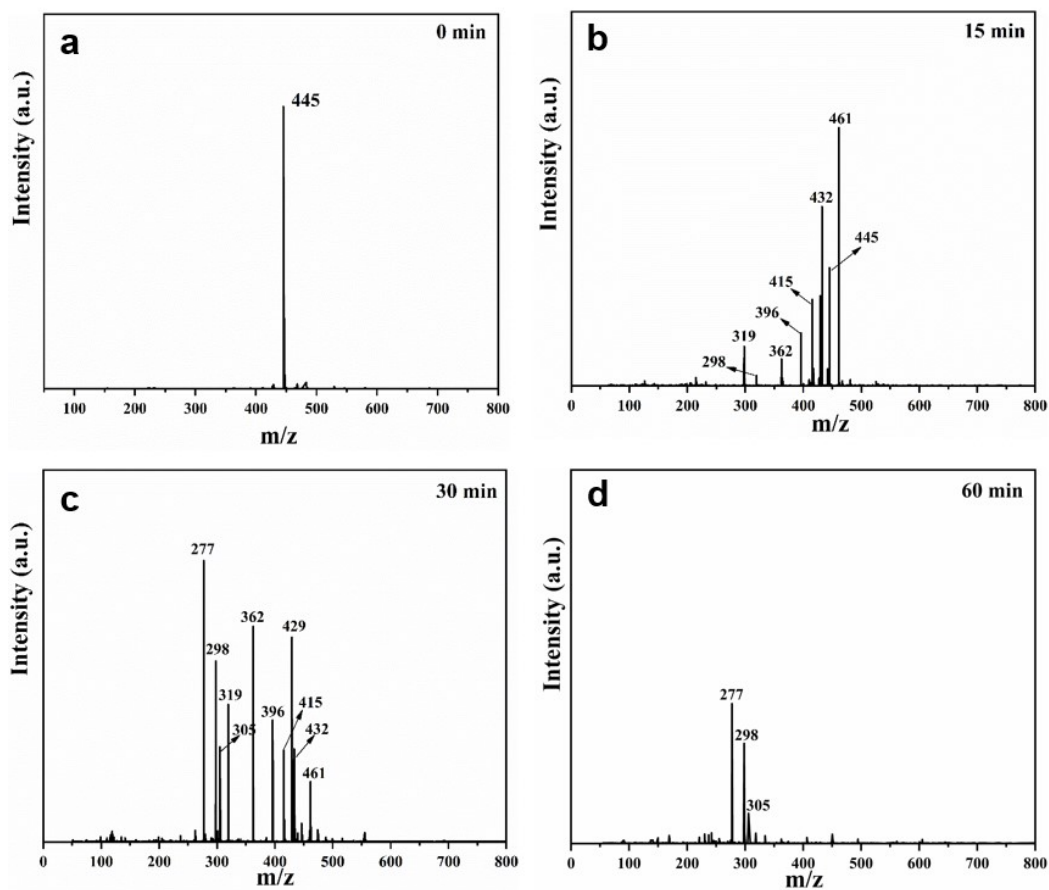


Fig. S7. LC-MS spectra of possible intermediates of TC at different reaction time.

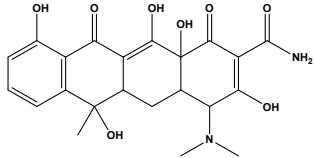
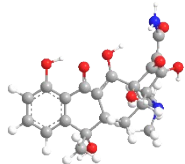
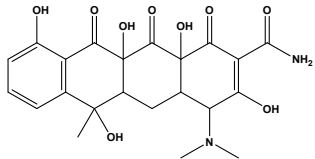
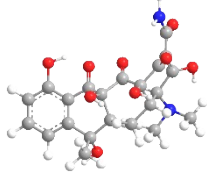
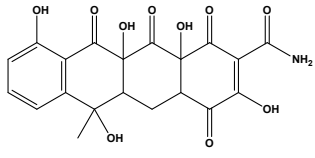
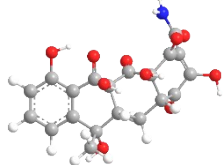
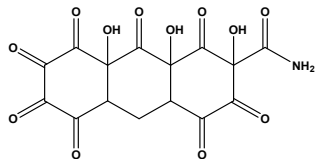
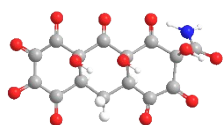
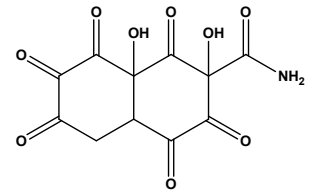
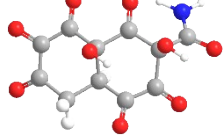
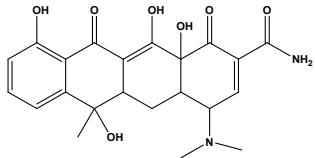
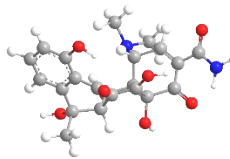
Experimental Tables

Table S1. Comparison of photocatalysts toward the removal of TC.

Pollutants	Catalyst	Operating conditions	Degradation	
			efficiency (k value)	Ref.
TC	PS@TiO ₂ /Bi ₂ O ₃ - 0.4	initial concentration: 50 mg L ⁻¹ Catalyst dosage: 0.2 g L ⁻¹	0.03318 min ⁻¹	This work
TC	TiO ₂ /Bi ₂ O ₃	initial concentration: 15 mg L ⁻¹ Catalyst dosage: 0.4 g L ⁻¹	0.0165 min ⁻¹	[S8]
TC	In ₂ Se ₃ (EDTA- 0.04 M)	initial concentration: 20 mg L ⁻¹ Catalyst dosage: 0.5 g L ⁻¹	0.0175 min ⁻¹	[S9]
TC	Bi ₂ O ₃ QDs/ g-C ₃ N ₄	initial concentration: 10 mg L ⁻¹ Catalyst dosage: 0.1 g L ⁻¹	0.0144 min ⁻¹	[S10]
TC	SZK-0.75	initial concentration: 40 mg L ⁻¹ Catalyst dosage: 0.2 g L ⁻¹	0.0231 min ⁻¹	[S11]
TC	ABO-290	initial concentration: 40 mg L ⁻¹ Catalyst dosage: 0.3 g L ⁻¹	0.013 min ⁻¹	[S12]
TC	α/β - AgAl _{0.4} Ga _{0.6} O ₂	initial concentration: 10 mg L ⁻¹ Catalyst dosage: 0.5 g L ⁻¹	0.0161 min ⁻¹	[S13]
TC	TCN-150	initial concentration: 20 mg L ⁻¹ Catalyst dosage:	0.0206 min ⁻¹	[S14]

0.25 g L⁻¹

Table S2. Possible intermediates in the photocatalytic degradation of TC for PS@TiO₂/Bi₂O₃-0.4 identified by LC-MS.

Compound	[M + H] ⁺ (m/z)	Molecular formula	Possible structure	3D ball & stick model
TC	445	C ₂₂ H ₂₄ N ₂ O ₈		
P1	461	C ₂₂ H ₂₄ N ₂ O ₉		
P2	432	C ₂₀ H ₁₇ NO ₁₀		
P3	396	C ₁₅ H ₉ NO ₁₂		
P4	298	C ₁₁ H ₇ NO ₉		
P5	429	C ₂₂ H ₂₄ N ₂ O ₇		

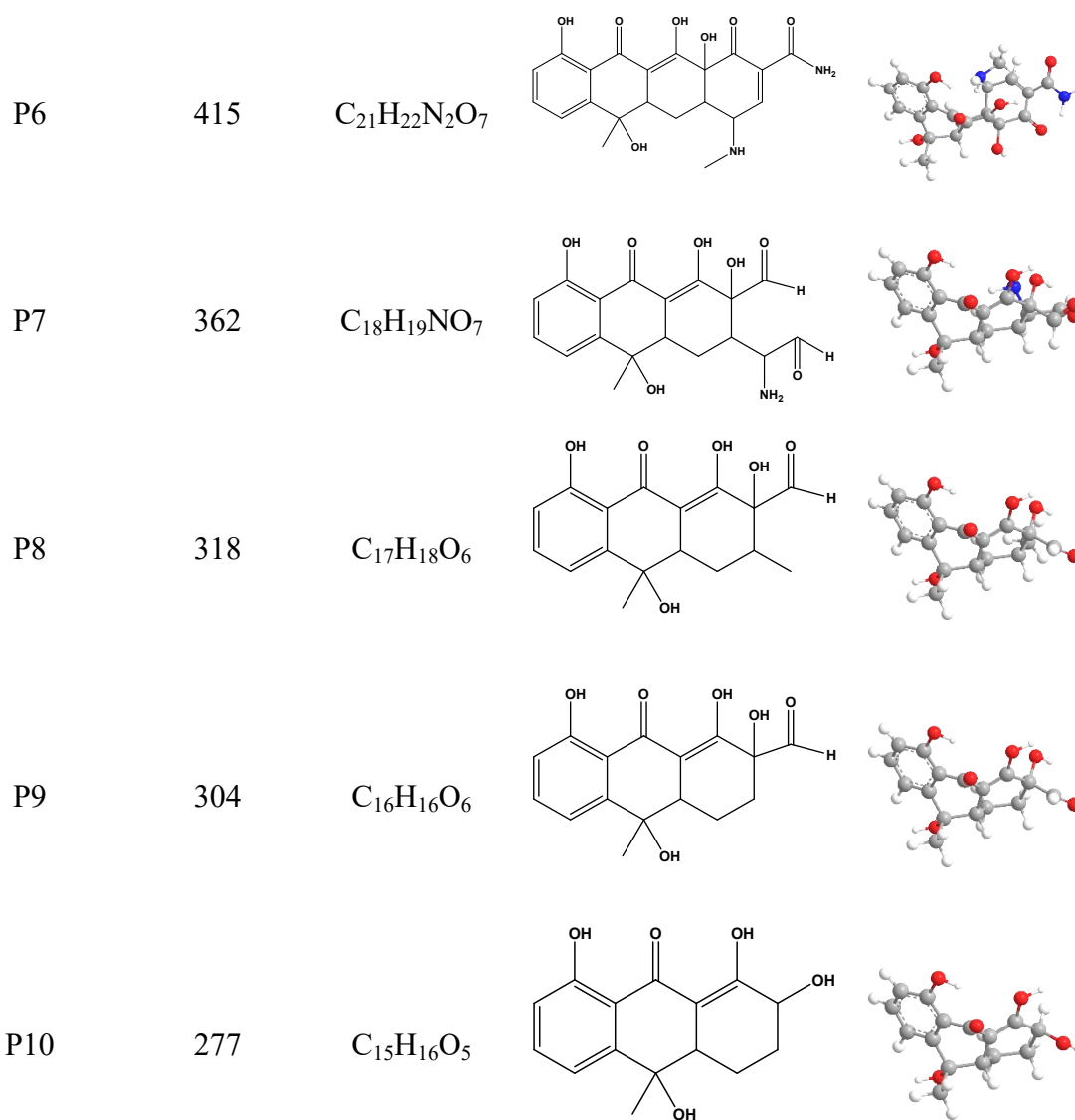


Table S3. Natural population analysis (NPA) charges and calculated Fukui index (f^+ and f^0) of TC for PS@TiO₂/Bi₂O₃-0.4; The isosurface value is 0.004 e/Å³.

Atom	q (N)	q (N+1)	q (N-1)	f^+	f^0
1 (C)	-0.0244	-0.0884	-0.0211	0.064	0.0336
2 (C)	-0.066	-0.0992	-0.063	0.0332	0.0181
3 (C)	0.08	0.0363	0.0838	0.0437	0.0237
4 (C)	-0.0389	-0.0641	-0.0363	0.0252	0.0139
5 (C)	0.0078	-0.0284	0.0088	0.0362	0.0186
6 (C)	-0.0631	-0.0915	-0.0591	0.0284	0.0162
7 (C)	0.2864	0.4983	0.5382	0.0399	-0.1059
8 (C)	-0.1100	-0.2791	-0.1876	0.0915	0.0845
9 (C)	-0.0229	-0.0289	-0.0193	0.006	0.0048
10 (C)	0.0923	0.0877	0.0936	0.0046	0.0029
11 (C)	0.0876	0.0422	0.0985	0.0455	0.0282
12 (C)	0.0741	0.0636	0.0797	0.0106	0.008
13 (C)	-0.0176	-0.0215	-0.0063	0.0038	0.0076
14 (C)	-0.0543	-0.0593	-0.0464	0.0049	0.0064
15 (C)	0.1442	0.0817	0.1525	0.0625	0.0354
16 (C)	-0.0589	-0.062	-0.0351	0.0031	0.0134
17 (C)	0.1299	0.0769	0.1345	0.0531	0.0288
18 (C)	0.0278	0.0268	0.0525	0.001	0.0129
19 (O)	-0.2294	-0.2673	-0.2244	0.0379	0.0214
20 (O)	-0.3177	-0.6379	-0.5960	0.0419	0.1601
21 (O)	-0.1674	-0.2252	-0.1593	0.0578	0.033
22 (O)	-0.1349	-0.1391	-0.117	0.0041	0.011
23 (O)	-0.2961	-0.7091	-0.5706	0.1385	0.2065
24 (C)	0.1551	0.1533	0.1622	0.0018	0.0045
25 (N)	-0.103	-0.1047	-0.0966	0.0017	0.004
26 (O)	-0.4033	-0.4063	-0.3903	0.003	0.008
27 (N)	-0.0789	-0.0805	0.1617	0.0016	0.1211
28 (C)	-0.0567	-0.0609	-0.0289	0.0041	0.016
29 (C)	-0.2571	-0.3294	-0.2401	0.0723	0.0447
30 (C)	-0.0896	-0.098	-0.0882	0.0084	0.0049
31 (O)	-0.2281	-0.2371	-0.2259	0.009	0.0056
32 (O)	-0.23	-0.2506	-0.2192	0.0205	0.0157

Table S4. The acute toxic and chronic toxicity values of TC and degradable intermediate products obtained from ECOSAR program.

Com poun ds	Acute toxicity (mg/L)			Chronic toxicity (mg/L)			Chemical Class
	Fish (96 h, LC50)	Daphnid (48 h, LC50)	Green Algae (96 h, EC50)	Fish (Chv)	Daphnid (Chv)	Green Algae (Chv)	
TC	13100	1060	1890	2490	59.9	474	Aliphatic Amines
	11800	1130	914	831	69.5	879	Phenols
	156000	293000	89200	192000	22100	7040	Vinyl/Allyl/Propargyl Ketones
	115000	70500	8560	5010	5060	1780	Benzyl Alcohols
	784	1910	3.3	43.2	7.35	0.789	Acrylamides
	78.5	302	14.5	362	72.5	130	Vinyl/Allyl/Propargyl Alcohols-Unhindered
	4400	1690	315	381	143	1260	Ketone Alcohols
	226	5.30	23.8	1.29	1.25	3.28	Phenol Amines
P1	1300	126	157	142	8.48	44.9	Aliphatic Amines
	1050	203	86.2	86.6	16.3	120	Phenols
	10600	12300	5100	6770	1290	774	Vinyl/Allyl/Propargyl Ketones
	5150	3550	783	311	377	246	Benzyl Alcohols
	115	294	1.46	5.99	1.62	0.394	Acrylamides
	28.8	92.6	3.44	36.1	10.9	27.2	Vinyl/Allyl/Propargyl Alcohols-Unhindered
	369	186	42.3	37.8	19.3	182	Ketone Alcohols
	49.4	2.72	7.01	0.393	0.589	1.11	Phenol Amines
P2	187	58.2	16.0	17.2	5.61	28.5	Phenols
	1580	1320	674	646	173	159	Vinyl/Allyl/Propargyl Ketones
	575	431	142	43.6	59.7	59.2	Benzyl Alcohols
	28.6	75.7	0.771	1.44	0.535	0.225	Acrylamides
	13.4	38.1	1.19	6.97	2.79	8.64	Vinyl/Allyl/Propargyl Alcohols-Unhindered
	63.3	38.3	9.97	7.25	4.57	46.1	Ketone Alcohols

P3	152000	3300000	26700	1940	77600	1640	Amides
	0						
	95900	26300	3780	6740	1710	13600	Ketone Alcohols
P4	522000	15600000	422000	2610	168000	10101	Amides
	00	0		0	0		
	226000	428000	46800	1270	21100	150000	Ketone Alcohols
	0			00			
P5	3320	297	431	459	18.5	116	Aliphatic Amines
	2800	402	224	216	28.7	266	Phenols
	31800	45300	16400	2690	4120	1890	Vinyl/Allyl/Propargyl Ketones
	18500	12100	2060	968	1080	544	Benzyl Alcohols
	247	620	1.96	1.32	2.93	0.501	Acrylamides
	41.8	145	6.02	91.7	23.3	50.3	Vinyl/Allyl/Propargyl Alcohols-Unhindered
	1010	454	94.6	96.2	43.2	398	Ketone Alcohols
	89.5	3.42	11.2	0.618	0.77	1.67	Phenol Amines
P6	4410	386	587	658	23.5	156	Aliphatic Amines
	3780	493	301	285	34	339	Phenols
	44600	67800	23600	4120	5900	2480	Vinyl/Allyl/Propargyl Ketones
	27400	17600	2780	1370	1500	692	Benzyl Alcohols
	312	777	2.13	16.8	3.5	0.535	Acrylamides
	46.6	166	7.12	122	29.3	60.5	Vinyl/Allyl/Propargyl Alcohols-Unhindered
	1370	596	121	128	55.1	503	Ketone Alcohols
	107	3.64	12.8	0.705	0.829	1.88	Phenol Amines
P7	20900	1610	3160	4630	86.1	764	Aliphatic Amines
	19400	1520	1480	1300	86.4	1280	Phenols
	277000	597000	166000	412000	41000	10900	Vinyl/Allyl/Propargyl Ketones
	231000	136000	13900	9110	8740	2580	Benzyl Alcohols
	85.9	348	18	574	102	167	Vinyl/Allyl/Propargyl Alcohols-Unhindered
	148	265	40	27.2	74.4	10.2	Aldehydes (Poly)
	122	249000	35100	0.317	7840	1440	Vinyl/Allyl/Propargyl Aldehydes

	286	5.27	27.7	1.48	1.28	3.67	Phenol Amines
	304	75.6	25.5	26.6	6.67	40.5	Phenols
	2810	2740	1260	1420	322	242	Vinyl/Allyl/Propargyl Ketones
	1170	842	229	79.6	103	83.5	Benzyl Alcohols
P8	13.8	41.6	1.41	10.9	3.83	10.7	Vinyl/Allyl/Propargyl Alcohols-Unhindered
	0.612	1850	637	0.041	103	64.2	Vinyl/Allyl/Propargyl Aldehydes
	563	116	46.6	47.1	9.51	66.8	Phenols
	5590	6210	2640	3360	669	424	Vinyl/Allyl/Propargyl Ketones
	2610	1820	421	162	200	137	Benzyl Alcohols
P9	17.4	55.2	2.01	19.6	6.15	15.7	Vinyl/Allyl/Propargyl Alcohols-Unhindered
	0.642	3870	1150	0.053	196	100	Vinyl/Allyl/Propargyl Aldehydes
	99.1	32.6	8.53	9.22	3.2	15.6	Phenols
	822	661	345	319	88.8	85.9	Vinyl/Allyl/Propargyl Ketones
P10	289	219	75.6	22.5	31.2	32.5	Benzyl Alcohols
	7.91	22.2	0.679	3.73	1.54	4.89	Vinyl/Allyl/Propargyl Alcohols-Unhindered

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