

Supplementary Materials

Constructing Z-Scheme 0D/2D TiO₂ Nanoparticles/Bi₂O₃ Nanosheet Heterojunctions with Enhanced Visible Light Induced Photocatalytic Antibiotics Degradation and Hydrogen Evolution

Lijia Xie¹, Piaopiao Wu¹, Qiong Lei², Chong Xu¹, Weiya Huang^{1,*}, Xunjun Chen¹, Kai Yang¹, Hua He³

¹ Faculty of Materials, Metallurgical and Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, China;

² Ganzhou center for disease control and prevention, Ganzhou 341000, China.

³ Department of Laboratory Medicine, First Affiliated Hospital of Gannan Medical University, Ganzhou, 341000, China

S1. Materials

Titanate isopropyl ((CH₃CH₂CHO)₄Ti), acetic acid, anhydrous ethanol, bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), tetracycline hydrochloride (TC), and tert-butanol (TBA) were purchased from Shanghai Aladdin Reagent Co. Ltd. (Shanghai, China). Hydrochloric acid and ethanol were provided by Xilong Scientific Co. Ltd. (Guangzhou, China). P-benzoquinone (p-BQ) was purchased from Shanghai Macklin Biochemical Co. Ltd. (Shanghai, China). All of the chemical reagents were of analytical grade and used without further purification.

S2. Characterization

The X-ray diffraction (XRD) patterns were recorded using a Bruker D8-Advance X-ray powder diffraction instrument with Cu K α radiation (λ = 0.15418 nm). The morphology and surface composition structure were characterized by a scanning electron microscope (SEM, FEI Quanta 250, Portland, OR, USA) and a transmission electron microscope (TEM, FEI Tecnai G² 20). The chemical compositions of the obtained samples were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, Waltham, MA, USA). The specific surface areas of samples were measured by a nitrogen adsorption analyzer (Micromeritics ASAP 2020, Norcross, GA, USA). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 5700 FT-IR spectrometer (Thermo Electron Corporation, Waltham, MA, USA). The UV-Vis diffuse reflectance spectra (DRS) were recorded with a UV-Vis spectrophotometer (Shimadzu UV-2600, Kyoto, Tapan) in the range of 200–800 nm. The electron spin resonance (ESR) spectra were recorded on an electron spin resonance spectrometer (Bruker A300, Billerica, MA, USA) with 5,5-dimethyl-1-pyrroline N-oxide (DMPO: 50 mM, 0.2 mL). The electrochemical measurements of the samples were performed on an electrochemical workstation with a standard three-electrode system (Shanghai Chenhua, CHI 660D, Shanghai, China) and a 300 W Xe lamp (PLS-SXE300, Perfect Light Company, Beijing, China) as the light source.

S3. Evaluation of Adsorption Performance

The adsorption data in the dark reaction were fitted to the pseudo-first-order and pseudo-second-order kinetic models.

Pseudo-first-order kinetic model equation, as shown in Equation (1):

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (1)$$

Pseudo-second-order kinetic model equation, as shown in Equation (2):

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (2)$$

where q_t and q_e (mg/g) are the amount of pollutants adsorbed over a given period of time t and at equilibrium time, respectively; t is the adsorption time (min); k_1 (1/min) and k_2 (g/mg min) are the adsorption rate constant of the pseudo-first-order and the pseudo-second-order kinetic models, respectively.

Figures

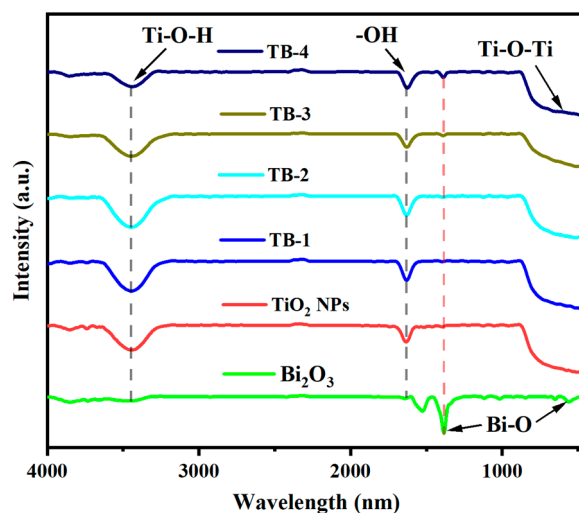


Figure S1. FT-IR spectra of TiO_2 NPs, Bi_2O_3 , and TiO_2 NPs/ Bi_2O_3 composites.

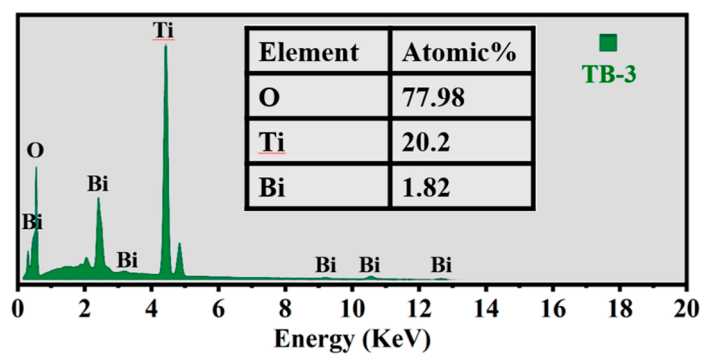


Figure S2. EDS elemental analysis of TB-3 and table of the elemental content (inset).

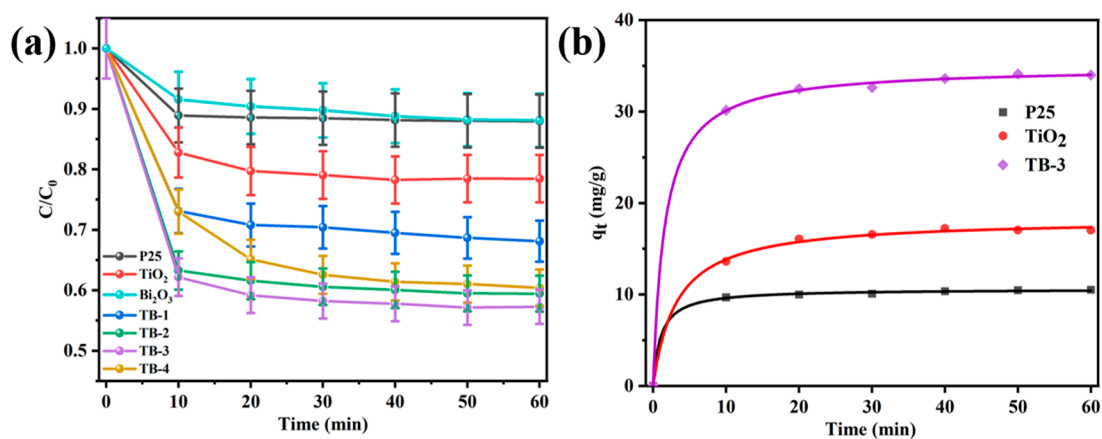


Figure S3. (a) Adsorption of TC in the dark, and (b) pseudo-second-order fitting plots of P25, TiO_2 NPs, and TB-3.

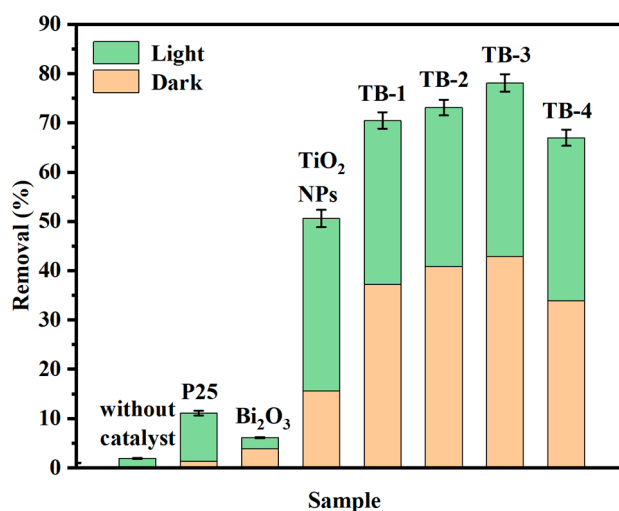
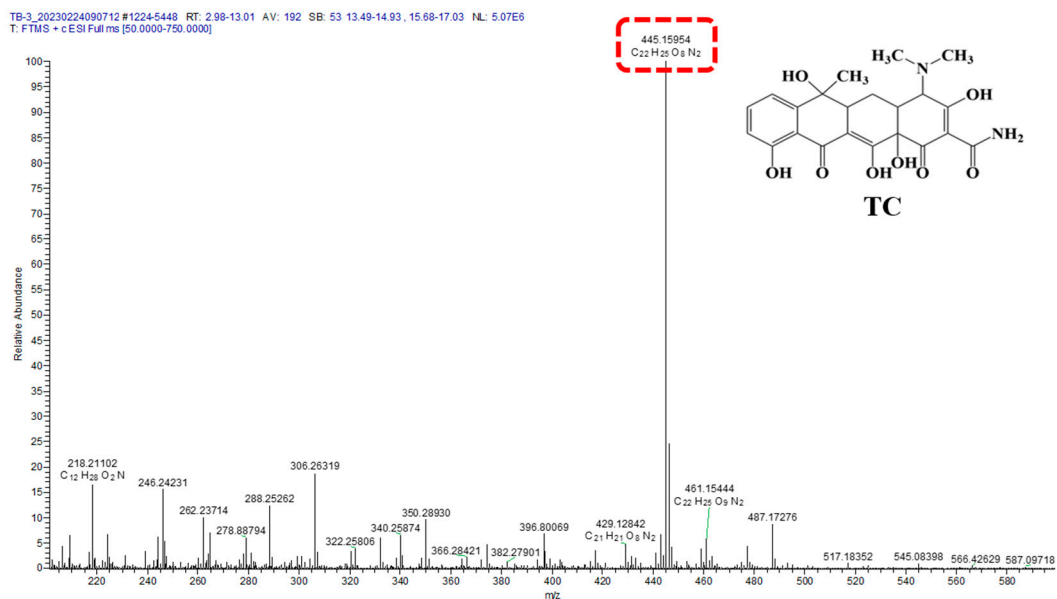
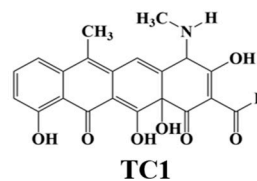


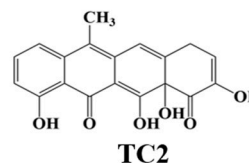
Figure S4. Adsorption in the dark and photocatalytic degradation of TC under visible light irradiation.



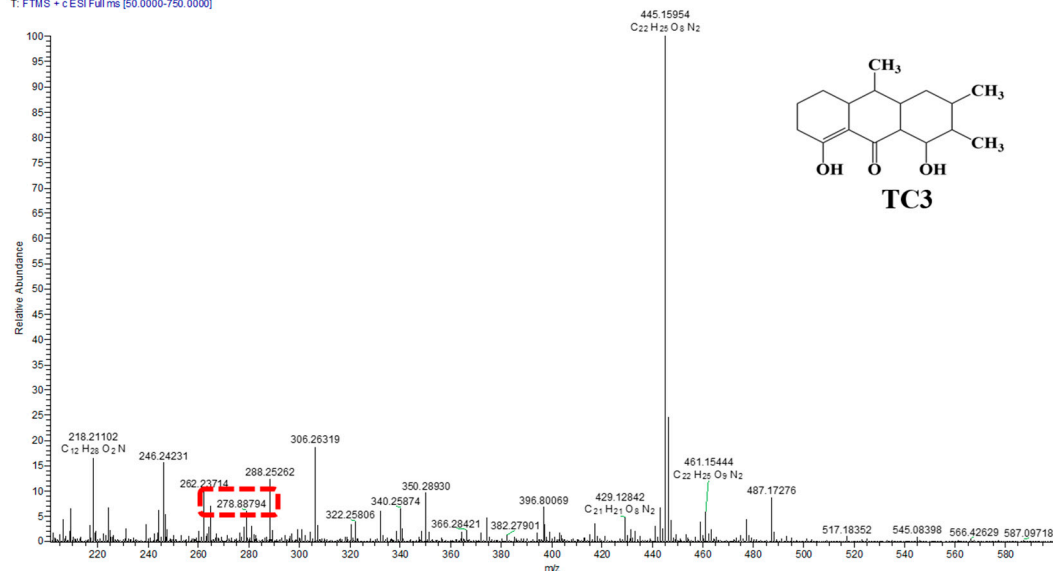
[illegible]

Mass spectrum of TC2 showing relative abundance versus m/z. The base peak is at m/z 445.1594 (C₂₂H₂₅O₈N₂). Other significant peaks are labeled with their m/z values and chemical formulas.

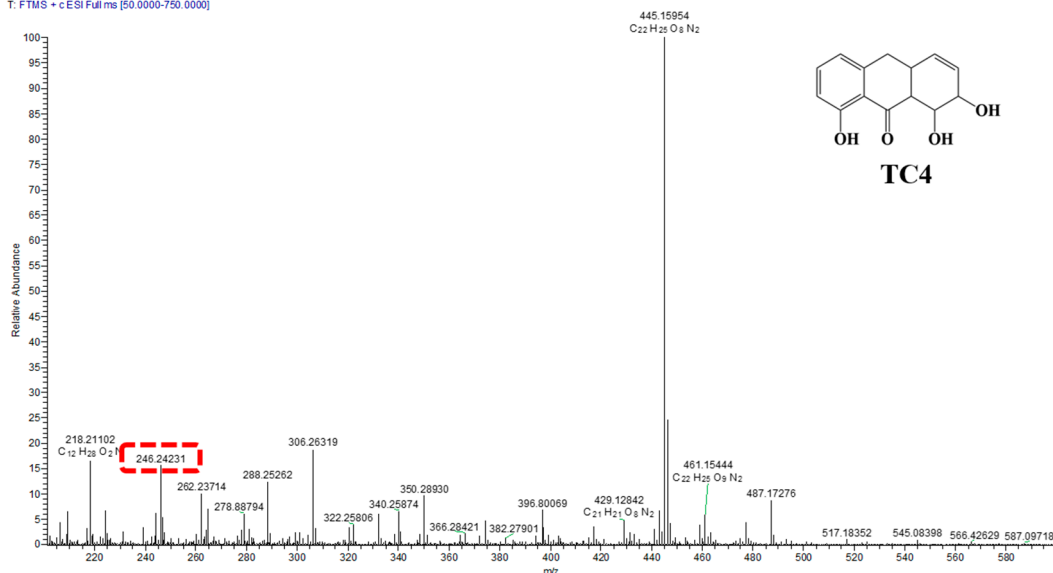
m/z	Chemical Formula
218.21102	C ₁₂ H ₂₁ O ₂ N
246.24231	
262.23714	
278.88794	
288.25262	
306.26319	
322.25366	
340.25874	
366.28421	
382.27901	
396.80069	
429.12842	C ₂₁ H ₂₁ O ₈ N ₂
445.1594	C ₂₂ H ₂₅ O ₈ N ₂
461.15444	C ₂₂ H ₂₅ O ₈ N ₂
487.17276	
517.18352	
545.08398	
566.42629	
587.09718	



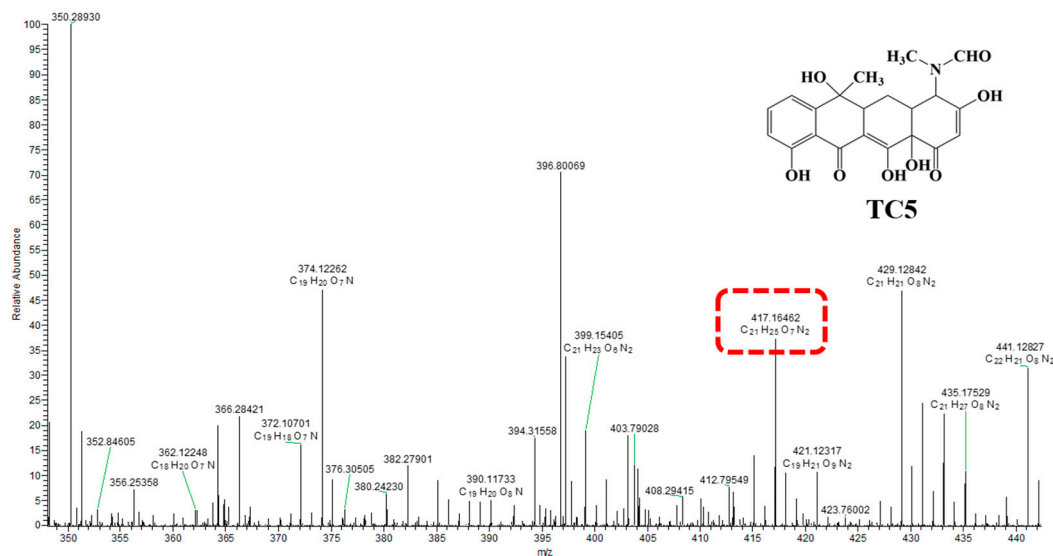
TB-3_20230224090712 #1224-5448 RT: 2.98-13.01 AV: 192 SB: 53 13.49-14.93, 15.68-17.03 NL: 5.07E6
T: FTMS + c ESI Full ms [50.0000-750.0000]



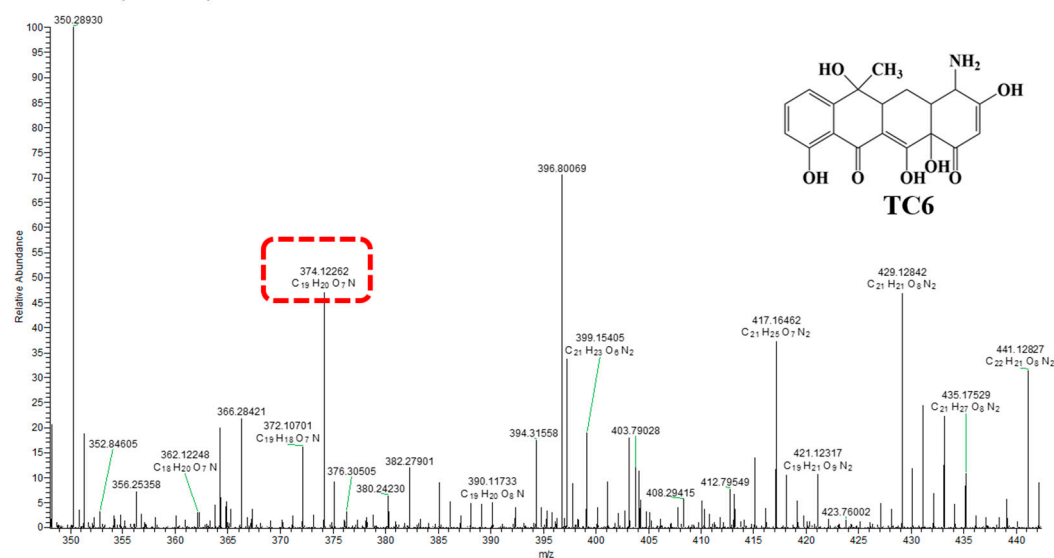
TB-3_20230224090712 #1224-5448 RT: 2.98-13.01 AV: 192 SB: 53 13.49-14.93, 15.68-17.03 NL: 5.07E6
T: FTMS + c ESI Full ms [50.0000-750.0000]



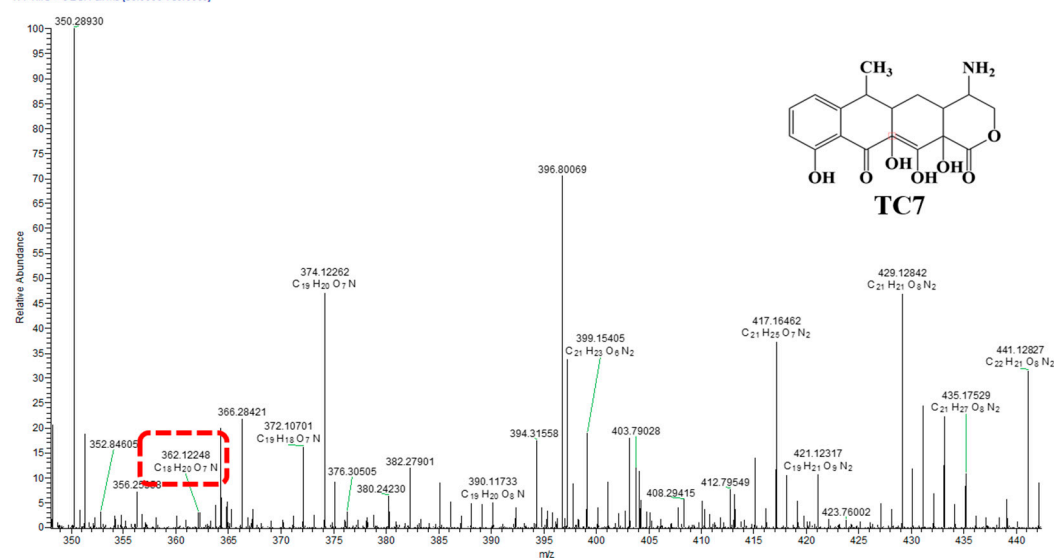
TB-3_20230224090712 #1224-5448 RT: 2.98-13.01 AV: 192 SB: 53 13.49-14.93, 15.68-17.03 NL: 4.88E5
T: FTMS + c ESI Full ms [50.0000-750.0000]



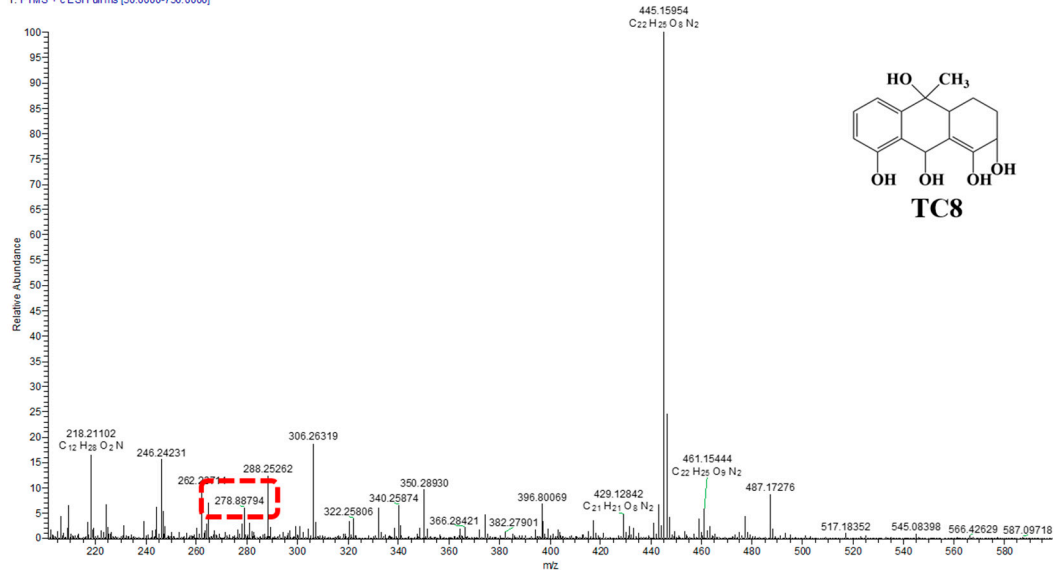
TB-3_20230224090712 #1224-5448 RT: 2.98-13.01 AV: 192 SB: 53 13.49-14.93, 15.68-17.03 NL: 4.88E5
T: FTMS + c ESI Full ms [50.0000-750.0000]



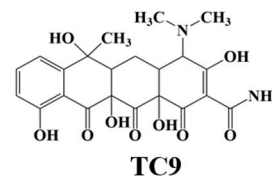
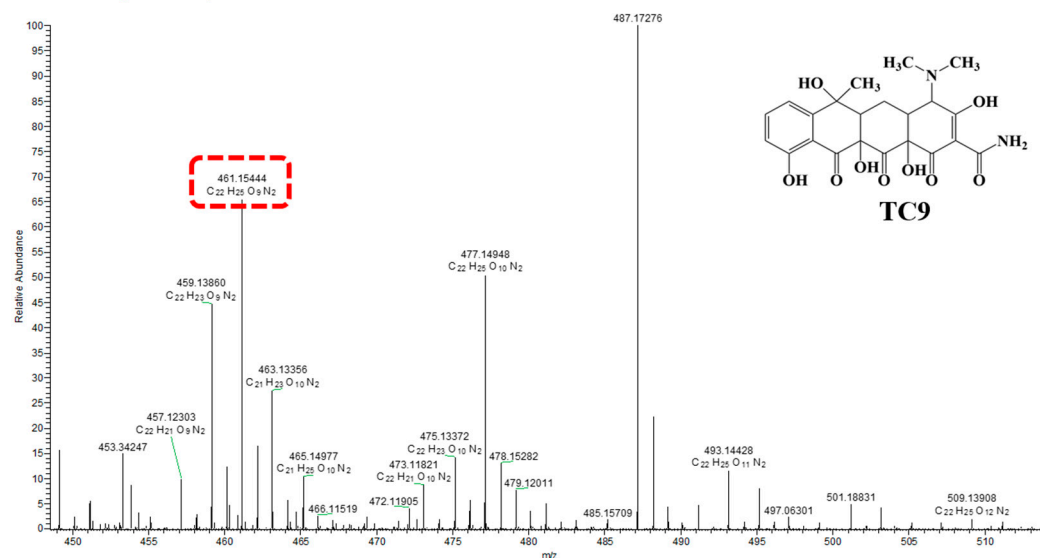
TB-3_20230224090712 #1224-5448 RT: 2.98-13.01 AV: 192 SB: 53 13.49-14.93, 15.68-17.03 NL: 4.88E5
T: FTMS + c ESI Full ms [50.0000-750.0000]



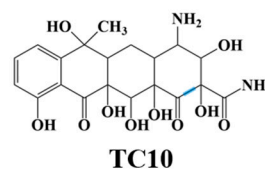
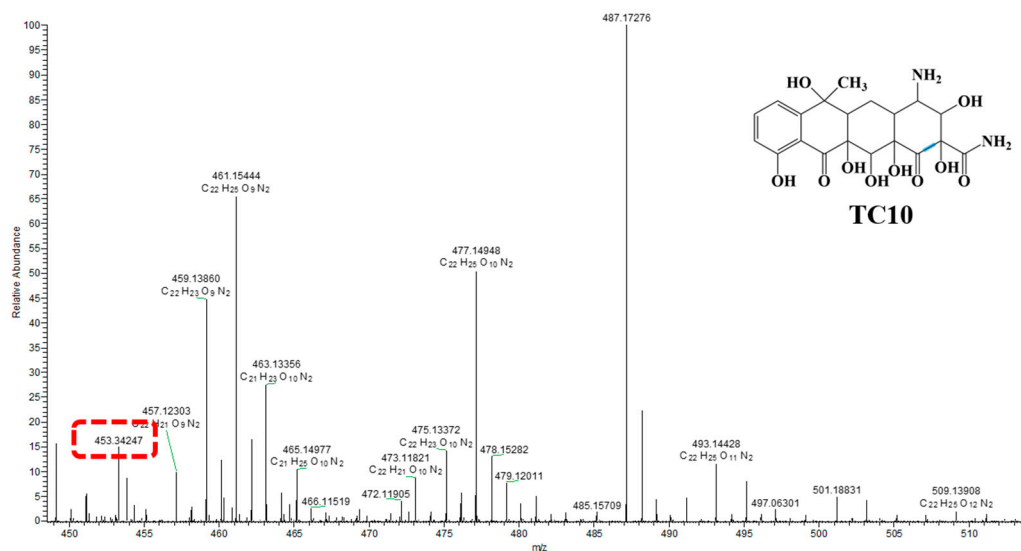
TB-3_20230224090712 #1224-5448 RT: 2.98-13.01 AV: 192 SB: 53 13.49-14.93, 15.68-17.03 NL: 5.07E5
T: FTMS + c ESI Full ms [50.0000-750.0000]



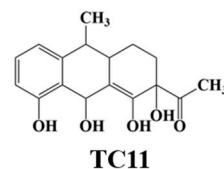
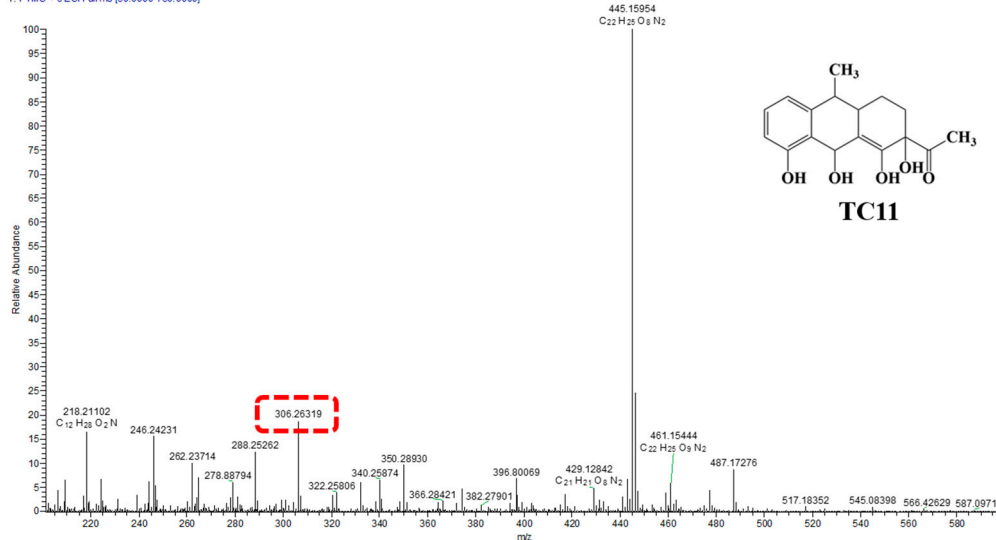
TB-3_20230224090712 #1224-5448 RT: 2.98-13.01 AV: 192 SB: 53 13.49-14.93 , 15.68-17.03 NL: 4.39E5
T: FTMS + c ESI Full ms [50.0000-750.0000]



TB-3_20230224090712 #1224-5448 RT: 2.98-13.01 AV: 192 SB: 53 13.49-14.93 , 15.68-17.03 NL: 4.39E5
T: FTMS + c ESI Full ms [50.0000-750.0000]



TB-3_20230224090712 #1224-5448 RT: 2.98-13.01 AV: 192 SB: 53 13.49-14.93 , 15.68-17.03 NL: 5.07E6
T: FTMS + c ESI Full ms [50.0000-750.0000]



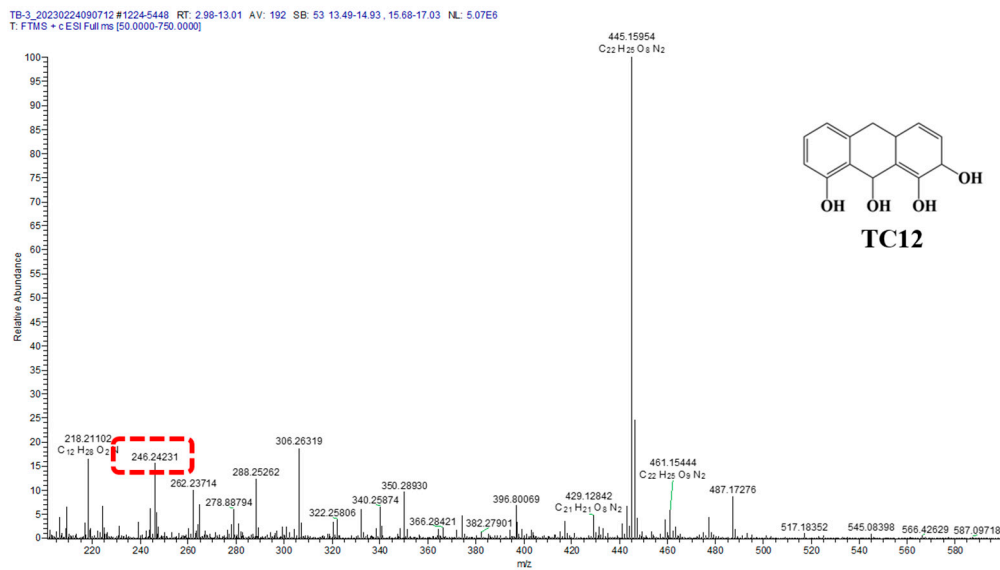


Figure S5. HPLC-MS spectra of the intermediates in the photocatalytic degradation of TC using TB-3.

Tables

Table S1. The BET specific surface area (SBET) and pore volume of the samples.

Sample	SBET	Pore Volume
	(m ² g ⁻¹)	(cm ³ g ⁻¹)
TiO ₂ NPs	119.87	0.353
Bi ₂ O ₃	5.14	0.0357
TB-1	101.04	0.300
TB-2	90.38	0.287
TB-3	99.52	0.245
TB-4	83.12	0.212

Table S2. Kinetic fitting parameters of TC adsorption onto P25, TiO₂ NPs, and TB-3.

Model		Pseudo-First-Order		Pseudo-Second-Order	
Sample	q _e ^{exp} /	K ₁ /	R ² /	K ₂ /	R ²
	(mg·g ⁻¹)	(min ⁻¹)		(min ⁻¹)	

P25	10.05	-0.093	0.875	0.095	0.999
TiO ₂ NPs	17.04	-0.037	0.701	0.052	0.980
TB-3	33.99	-0.099	0.918	0.029	0.999

Table S3. Comparison of TC removal % with other TiO₂ and Bi₂O₃-based heterojunctions.

Catalysts	C ₀ (mg/L)	Dosage (mg/mL)	Reaction Time (min)	Removal (%)	Light	Ref.
Fe ₃ O ₄ /rGO/TiO ₂	20	20/50	330	92.6	UV	[1]
SrTiO ₃ /Bi ₂ O ₃	10	100/100	140	85	Visible light	[2]
N-TiO ₂ /AgI	10	100/200	105	72.5	Visible light	[3]
CPS@TiO ₂	10	10/50	120	90.1	420 nm	[4]
AgBr-TiO ₂ -Pal	20	25/50	90	89	Visible light	[5]
TiO ₂ NPs/Bi ₂ O ₃	50	30/50	60	80	Visible light	This work

Related References

1. Wang, W.; Xiao, K.; Zhu, L.; Yin, Y.; Wang, Z., Graphene oxide supported titanium dioxide & ferroferric oxide hybrid, a magnetically separable photocatalyst with enhanced photocatalytic activity for tetracycline hydrochloride degradation. *RSC Adv.* **2017**, 7 (34), 21287-21297.
2. Che, H.; Chen, J.; Huang, K.; Hu, W.; Hu, H.; Liu, X.; Che, G.; Liu, C.; Shi, W., Construction of SrTiO₃/Bi₂O₃ heterojunction towards to improved separation efficiency of charge carriers and photocatalytic activity under visible light. *J. Alloys Compd.* **2016**, 688, 882-890.
3. Thanh Tung, M.-H.; Dieu Cam, N.-T.; Van Thuan, D.; Van Quan, P.; Van Hoang, C.; Thu Phuong, T.-T.; Lam, N.-T.; Tam, T.-T.; Phuong Le Chi, N.-T.; Lan, N.-T.; Thoai, D.-N.; Pham, T.-D., Novel direct Z-scheme AgI/N-TiO₂ photocatalyst for removal of polluted tetracycline under visible irradiation. *Ceram. Int.* **2020**, 46 (5), 6012-6021.
4. Zhang, S.; Yin, Z.; Xie, L.; Yi, J.; Tang, W.; Tang, T.; Chen, J.; Cao, S., Facet engineered TiO₂ hollow sphere for the visible-light-mediated degradation of antibiotics via ligand-to-metal charge transfer. *Ceram. Int.* **2020**, 46 (7), 8949-8957.
5. Shi, Y.; Yan, Z.; Xu, Y.; Tian, T.; Zhang, J.; Pang, J.; Peng, X.; Zhang, Q.; Shao, M.; Tan, W.; Li, H.; Xiong, Q., Visible-light-driven AgBr-TiO₂-Palygorskite photocatalyst with

excellent photocatalytic activity for tetracycline hydrochloride. *J. Clean. Prod.* **2020**, 277.