Supplementary Information

Direct Z-scheme P-TiO_2/g-C_3N_4 Heterojunction for the Photocatalytic Degradation of Sulfa Antibiotics

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Text S1. Characterization

X-ray diffraction (XRD) was performed on a Bruker D8 diffractometer with Cu-Kα(λ = 0.15406 nm) at 45 kV and 40 mA as the radiation source. Diffraction patterns were collected in the 2θ range of 5~90°. The morphologies of the synthesized photocatalysts samples were characterised using scanning electron microscope (SEM, JSM-6701F, JEOL, Japan) and transmission electron microscopy (TEM, JEM-2100F, Hitachi, Japan) operating at 5kV. The elemental composition of the synthesized samples was obtained by X-ray photoelectron spectroscopy (XPS) (XPS, ESCALAB 250Xi, ThermoFisher Ltd., USA). UV–vis diffuse reflectance spectra (DRS) were observed via a LAMBDA 1050 spectrophotometer (PerkinElmer, USA) from 200~800 nm. The transient photocurrent responses, Electrochemical impedance spectroscopy (EIS) spectra and Mott-Schottky plots were detected by an electrochemical workstation (CHI 760E, Shanghai Chenhua Instrument Co., China) with a standard three-electrode cell including a photocatalyst working electrode, a Pt wire counter electrode, and a standard saturated calomel electrode (SCE) as reference electrode.

Text S2. Photocatalytic activity

Experiments on the degradation of antibiotic by photocatalysts were performed in a quartz sleeve photoreactor, which was placed on a magnetic stirrer at a rotation speed of 350 rpm. The experiments use the Xe lamp (YM-GHX-XE-300) to simulate the irradiation of sunlight, 20 mg of the photocatalysts were added to 50 mL of the four mixed sulfonamide antibiotics solution (10 mg·L^{-1}) in a quartz photoreactor. The initial pH was adjusted with 1 M HCl or NaOH. After adsorption–desorption equilibrium was achieved by 30 min of stirring in darkness carry out photocatalytic degradation experiments. Moreover, approximately 3 mL of the suspensions were sampled at decided time intervals, followed by filtering with syringe membrane filters (0.22 μm) to remove catalyst particulates. The concentration of antibiotics was determined by LC-MS (LC: Agilent Technologies 1290 Infinity; MS: AB SCIEXQTRAP 6470, Agilent, USA).

The degradation rate of antibiotics is shown in Eq (1):$Y = (1 - C_t/C_0) \times 100\%$ Eq (1)

In the formula, where Y is the degradation rate of the antibiotic; C_0 is initial concentration of four mixed sulfonamide antibiotics; C_t is the time dependent concentration of four mixed sulfonamide antibiotics.

Text S3. Reusability and stability of photocatalyst

The solution after photocatalytic reaction was collected in the centrifugal tube, and the light yellow precipitate was obtained after centrifugation. The precipitate was dried at 80℃ and then ground for use. Finally, the dried photocatalyst is added to the sulfa mixture for reuse.

Text S4. The quenching experiment

The active substances in the photocatalytic reaction system, including photoinduced holes (h^+), photoinduced electrons (e^-), hydroxyl radical (·OH) and superoxide radical ($\cdot O_2^-$), may participate in the photocatalytic process. The active substances ·OH, e^-, $\cdot O_2^-$ and h^+ were quenched by isopropanol (IPA), potassium dichromate ($K_2Cr_2O_7$), N_2 and sodium oxalate ($Na_2C_2O_4$) to explore the beneficial active substances produced in the reaction system.

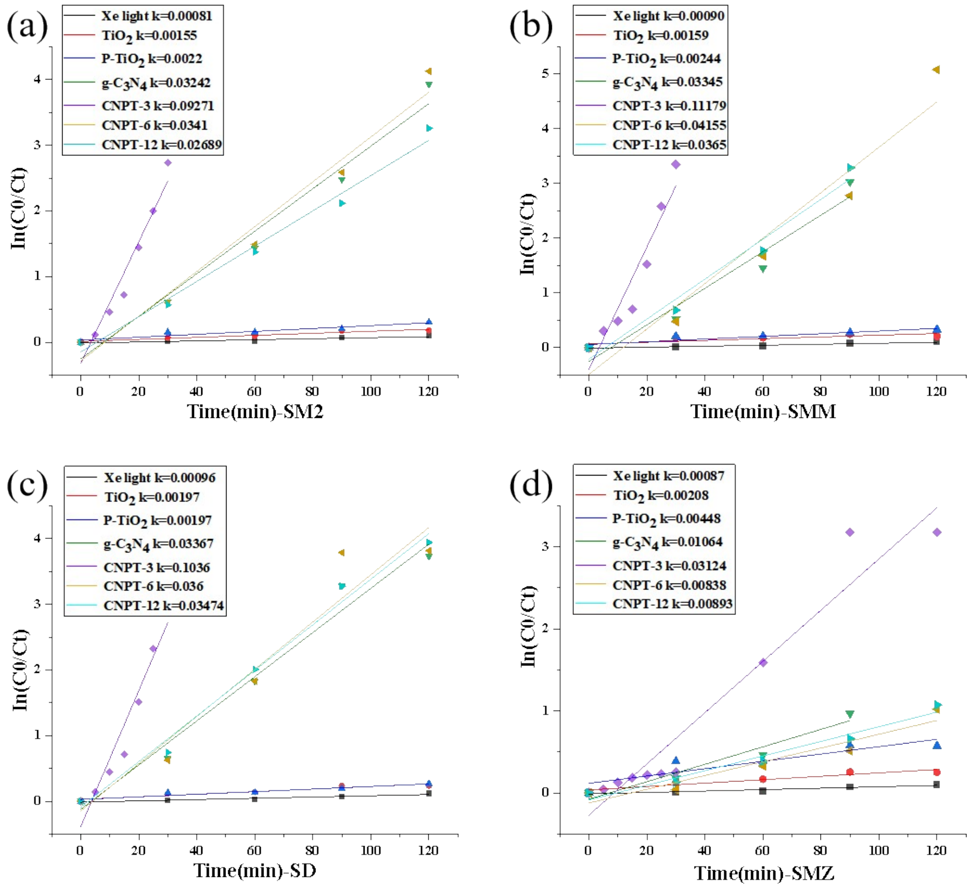


Fig.S1 Pseudo first-order rate constants of (a)SM2;(b)SMM;(c)SD;(d)SMZ.

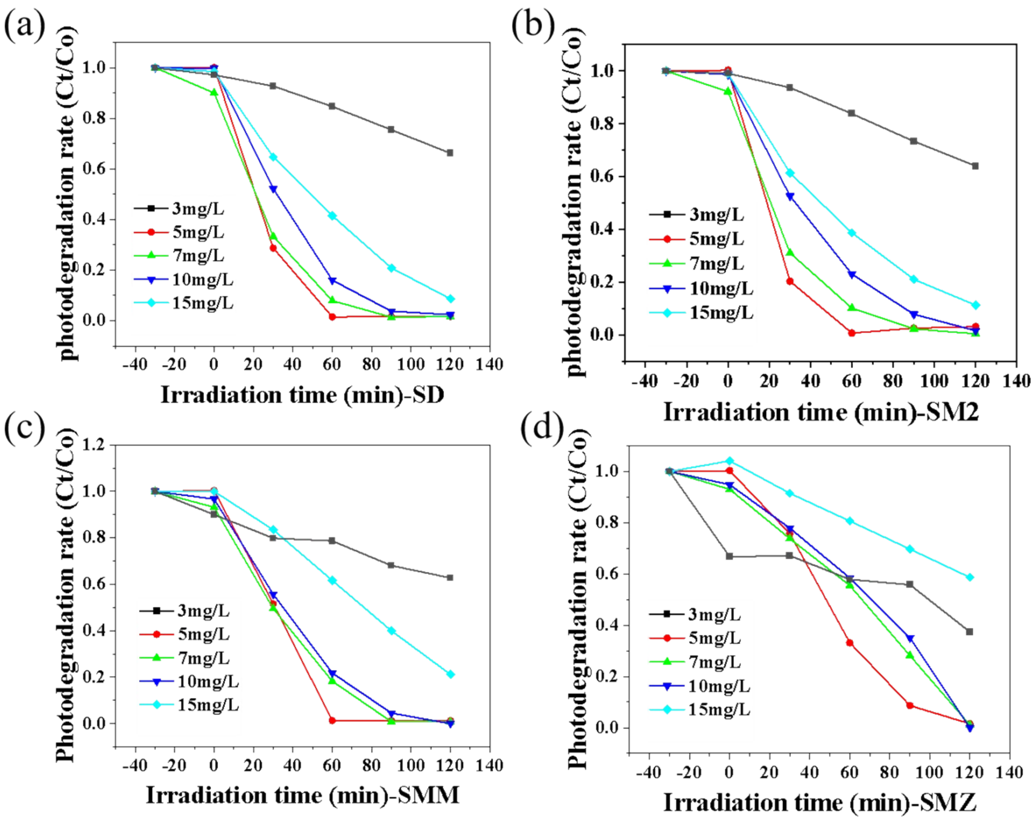


Fig.S2 Effect of different initial concentrations of antibiotics on photocatalytic degradation efficiency: a) SD, b) SM2, c) SMM, d) SMZ.

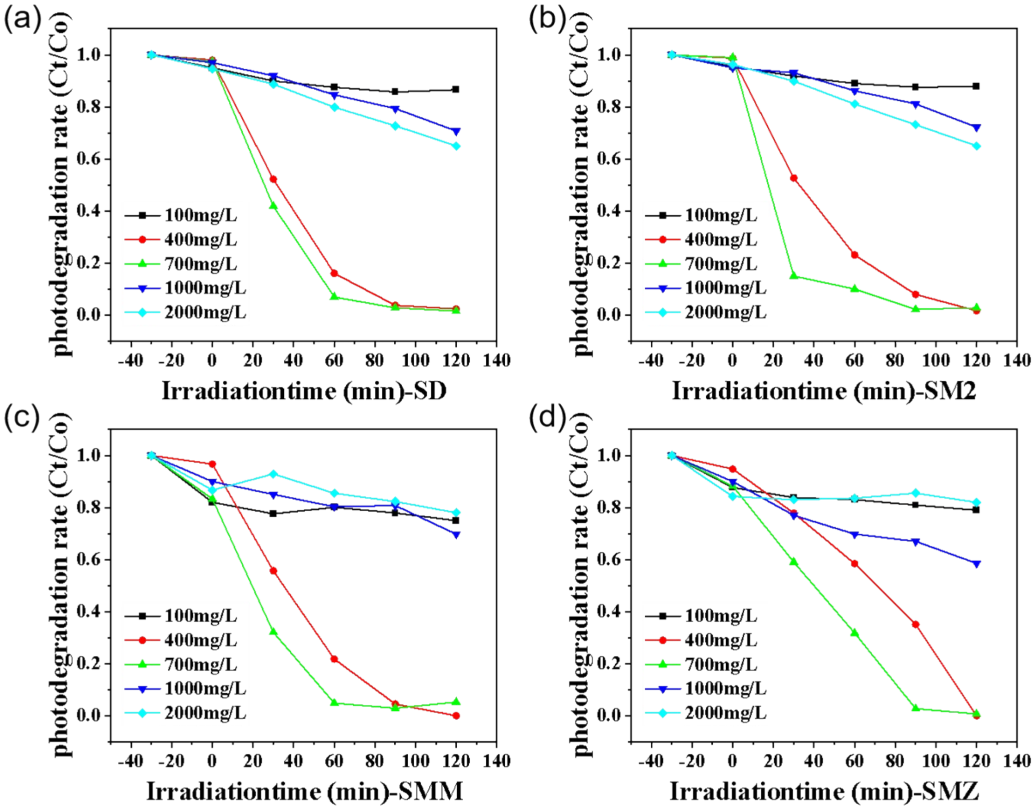


Fig.S3 Effect of different concentrations of photocatalytic materials on mixed sulfonamides antibiotics: a) SD, b) SM2, c) SMM, d) SMZ.

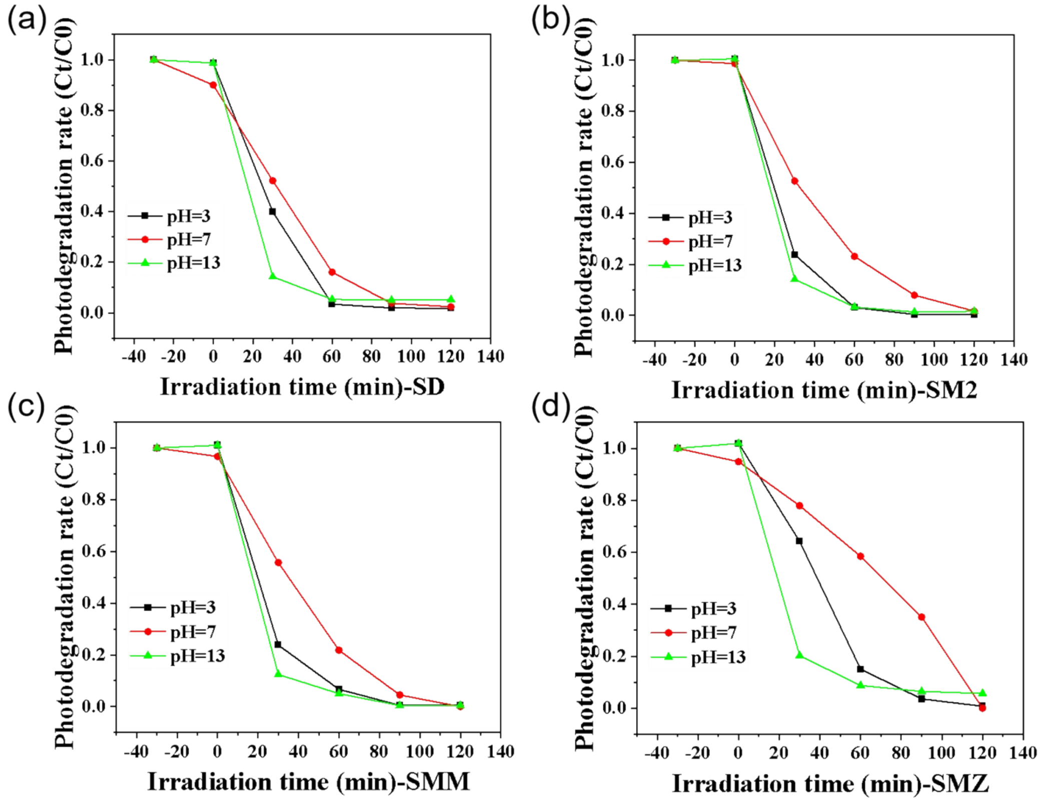


Fig.S4 Effect of pH of different solution on photocatalytic degradation: a) SD, b) SM2, c) SMM, d) SMZ.

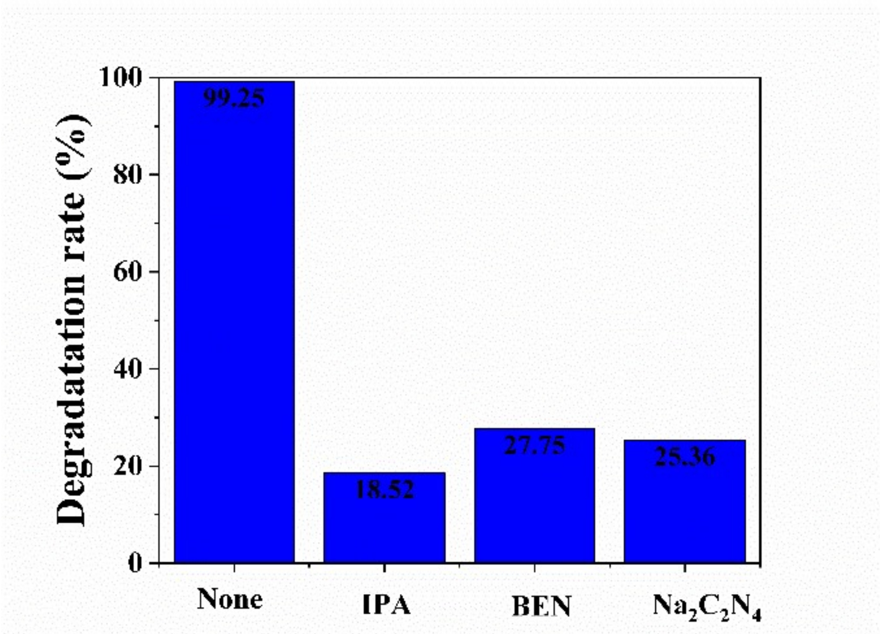


Fig. S5. Quenching experiment for the active substance.

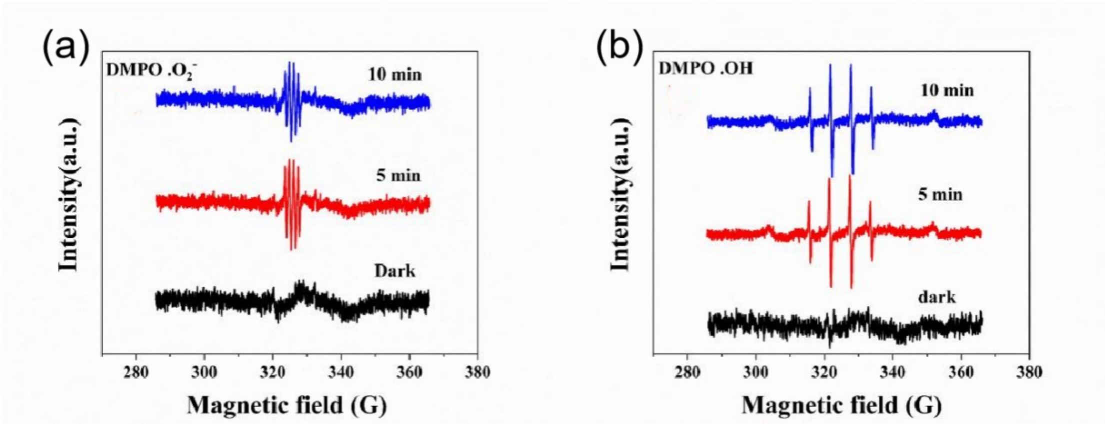


Fig.S6 ESR spectra of DMPO spin-trapping over CNPT-3: a) DMPO·O^{-2}; b) DMPO·OH.

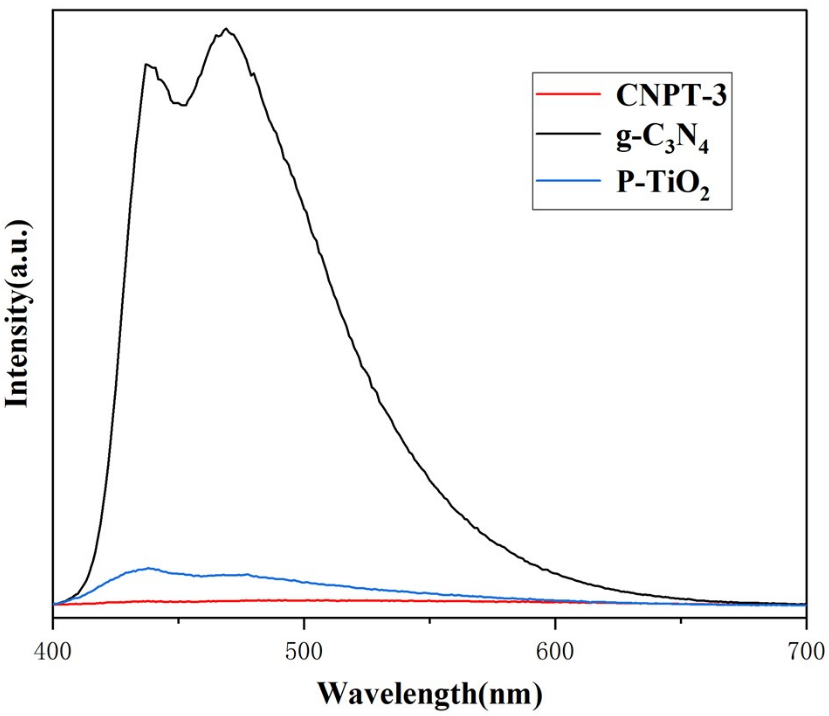


Fig.S7 PL Spectra Excited of Photocatalytic Materials

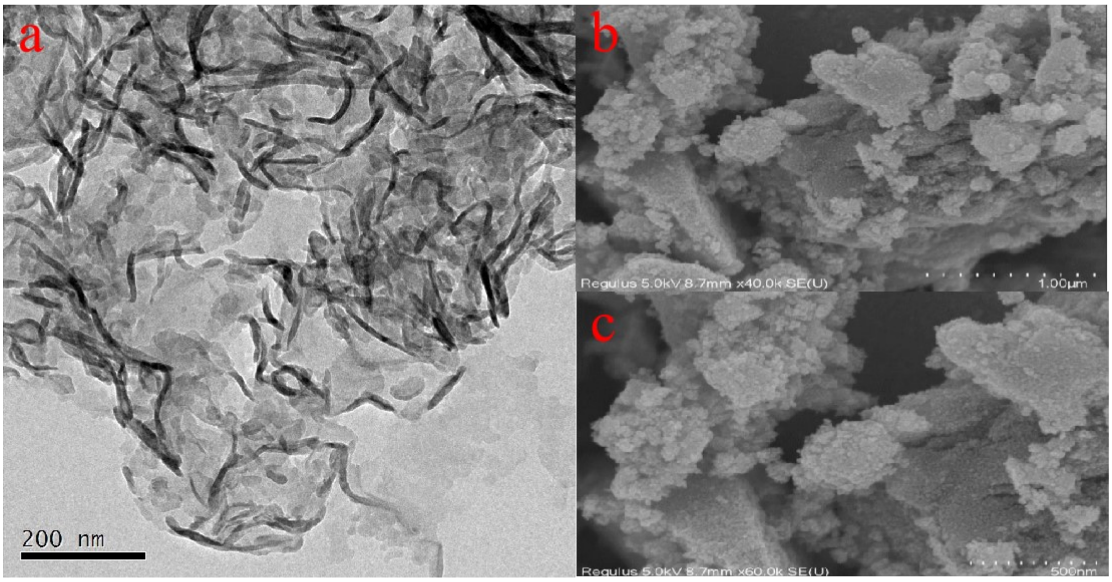
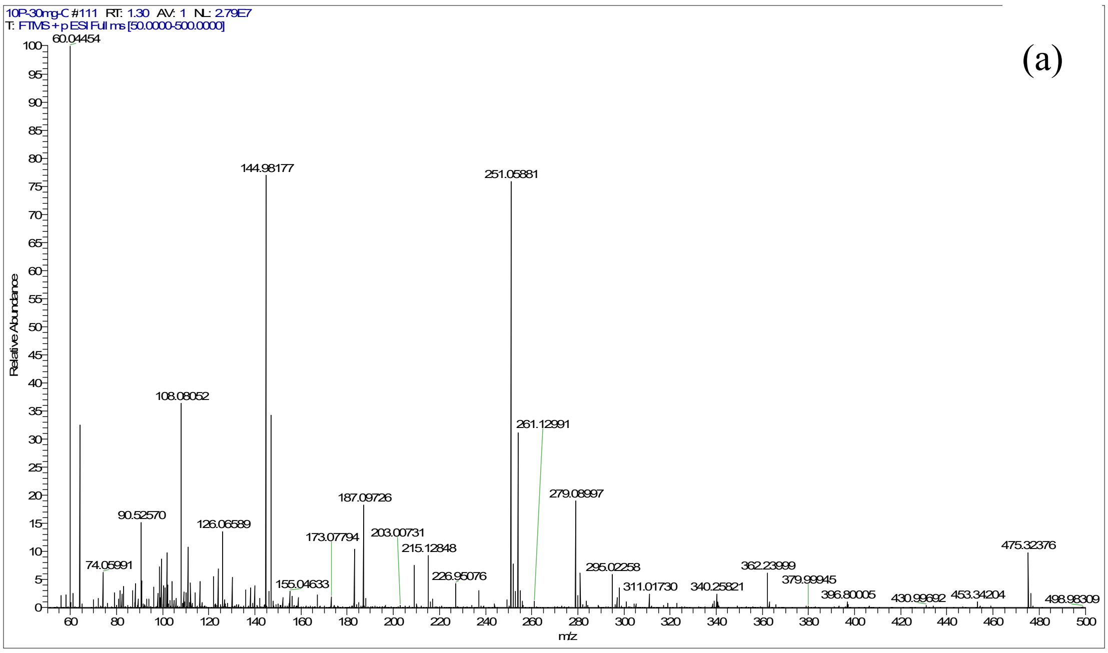
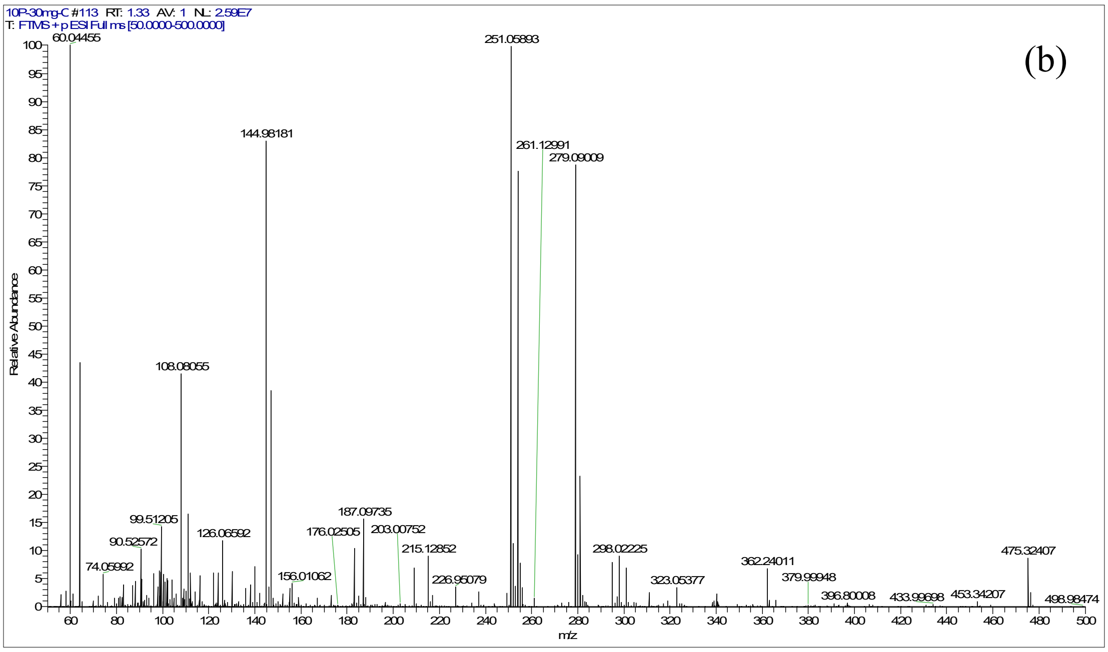


Fig. S8 (a) g-C_3N_4 and (b) (c) P-TiO_2 photocatalytic material SEM.





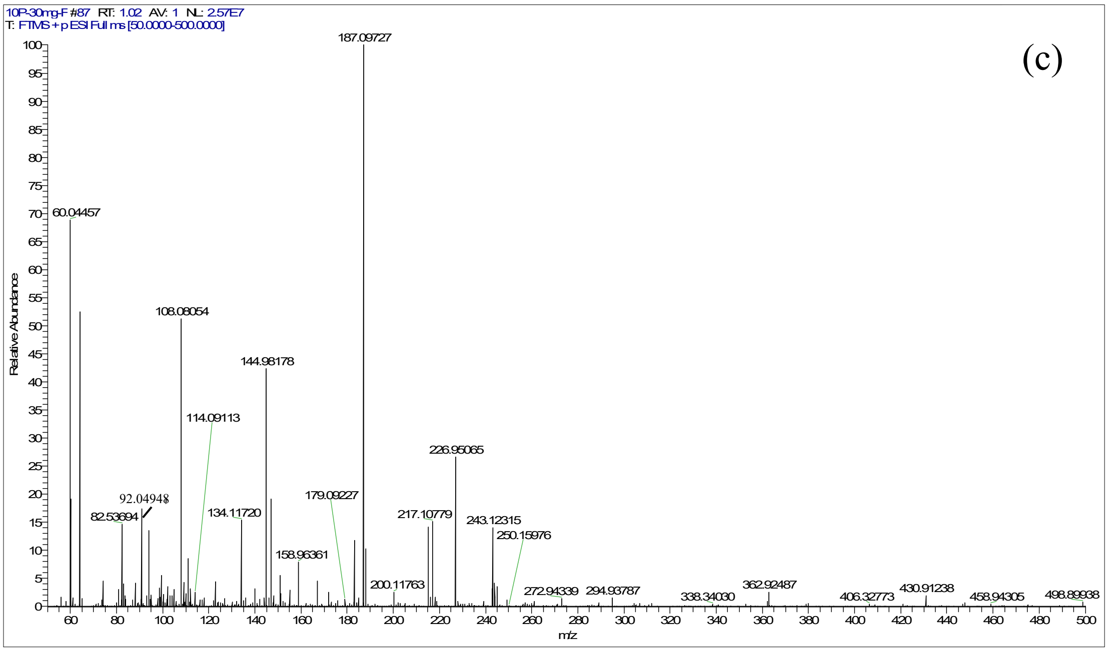
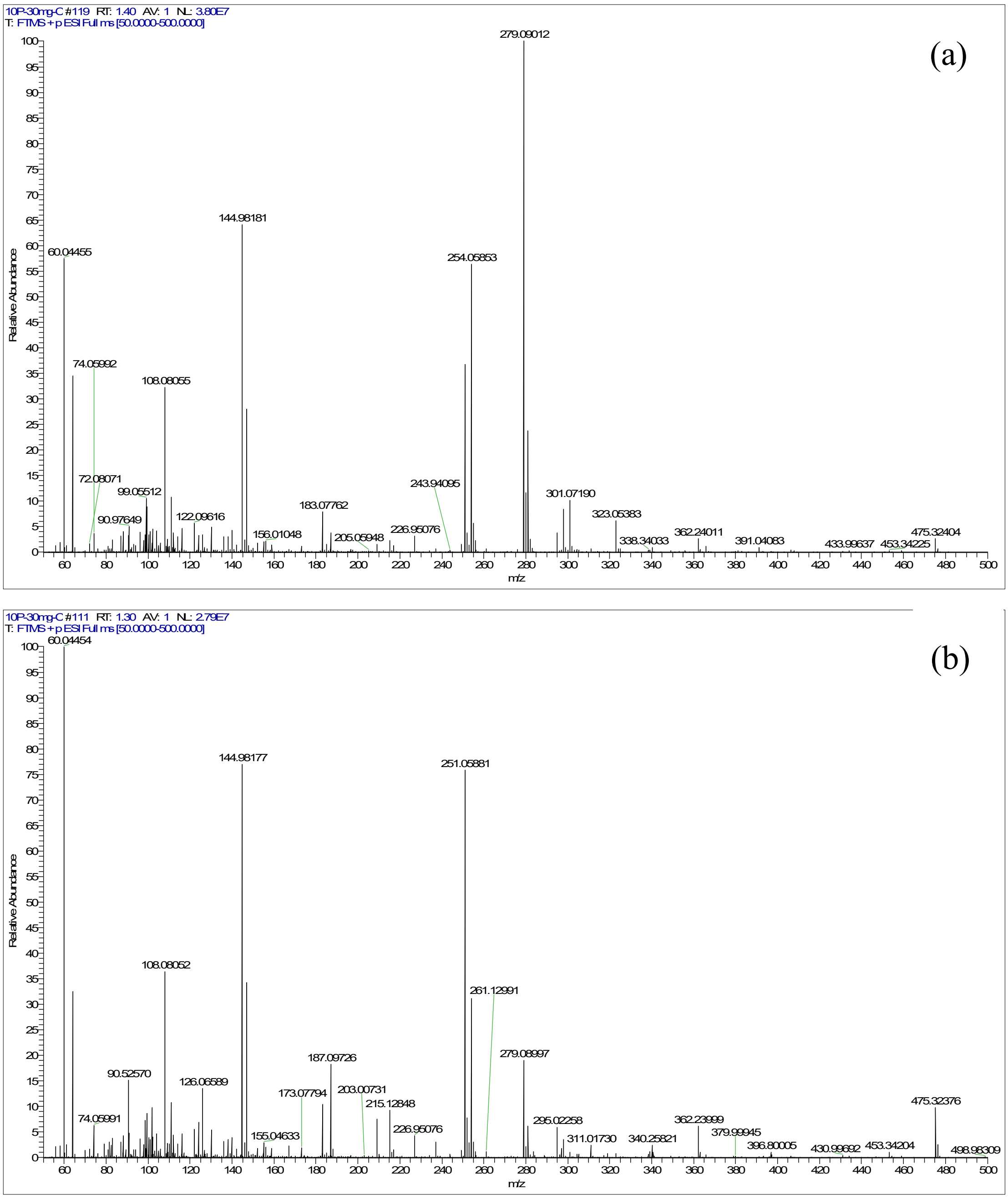


Fig. S9 Mass spectra of the Possible identified intermediates by GC–MS analyses at different illumination intervals of Sulfadiazine (a) 0 min, (b) 60 min, (c) 120 min.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(a)
Relative Abundance
m/z
279.09012
144.98181
60.04455
254.05853
74.05992
108.08055
72.08071
99.05512
90.97649
122.09616
156.01048
183.07762
205.05948
226.95076
243.94095
301.07190
323.05383
338.34033
362.24011
391.04083
433.99637
453.34225
475.32404
10P-30mg-C #111 RT: 1.30 AV: 1 NL: 2.79E7
T: FTMS + p ESI Full ms [50.0000-500.0000]
(b)
Relative Abundance
m/z
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251.05881
108.08052
261.12991
279.08997
187.09726
90.52570
126.06589
173.07794
203.00731
215.12848
74.05991
155.04633
226.95076
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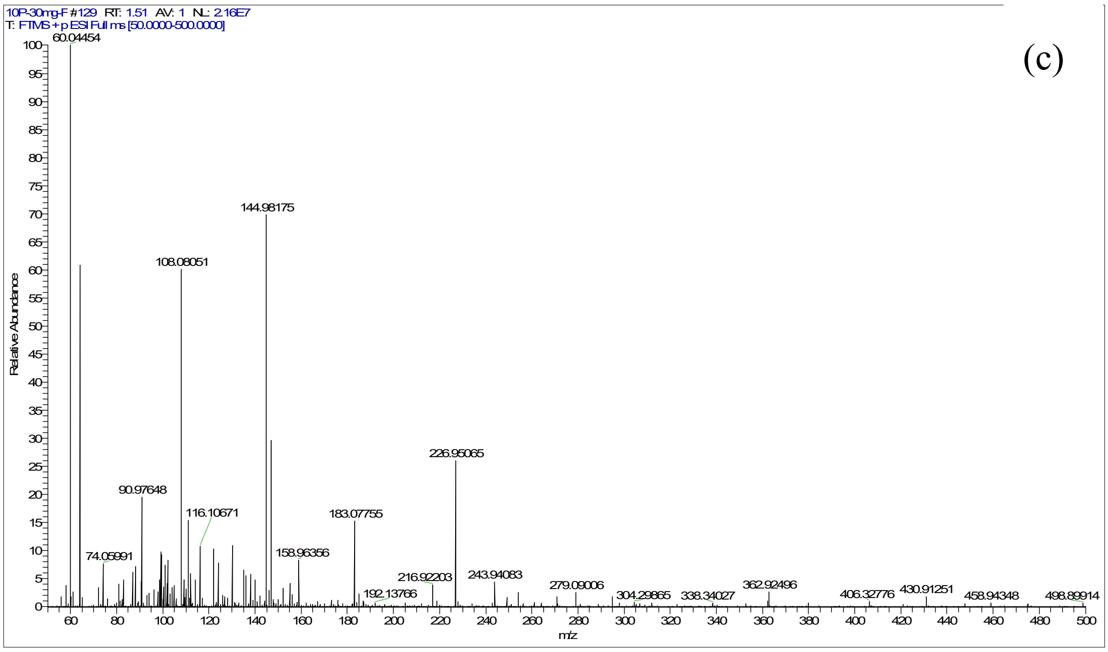
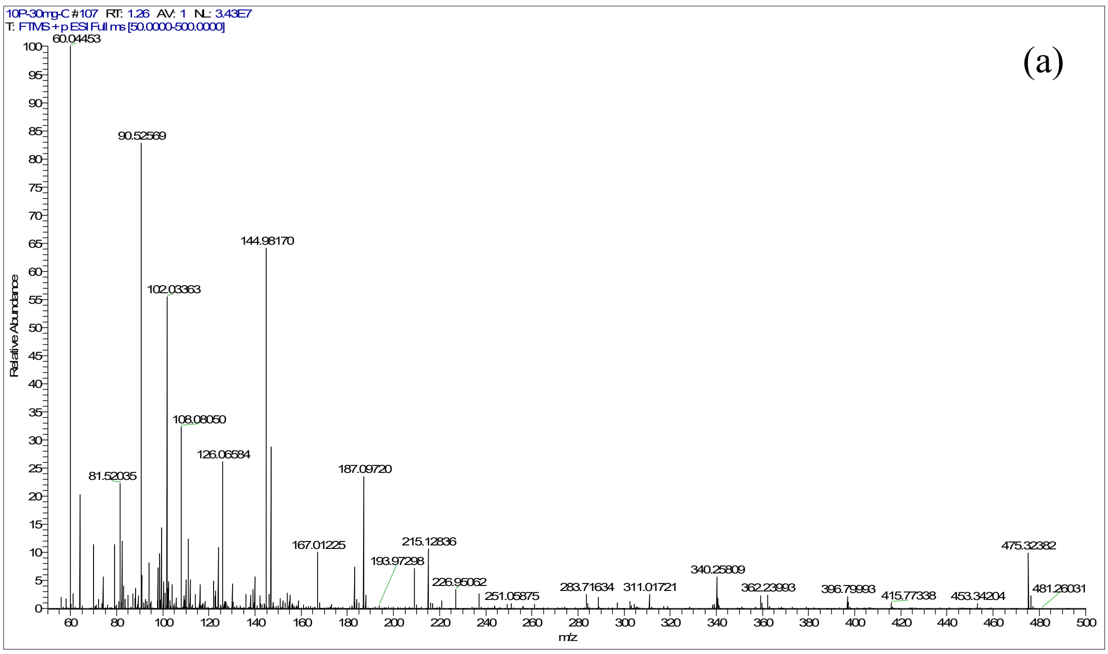
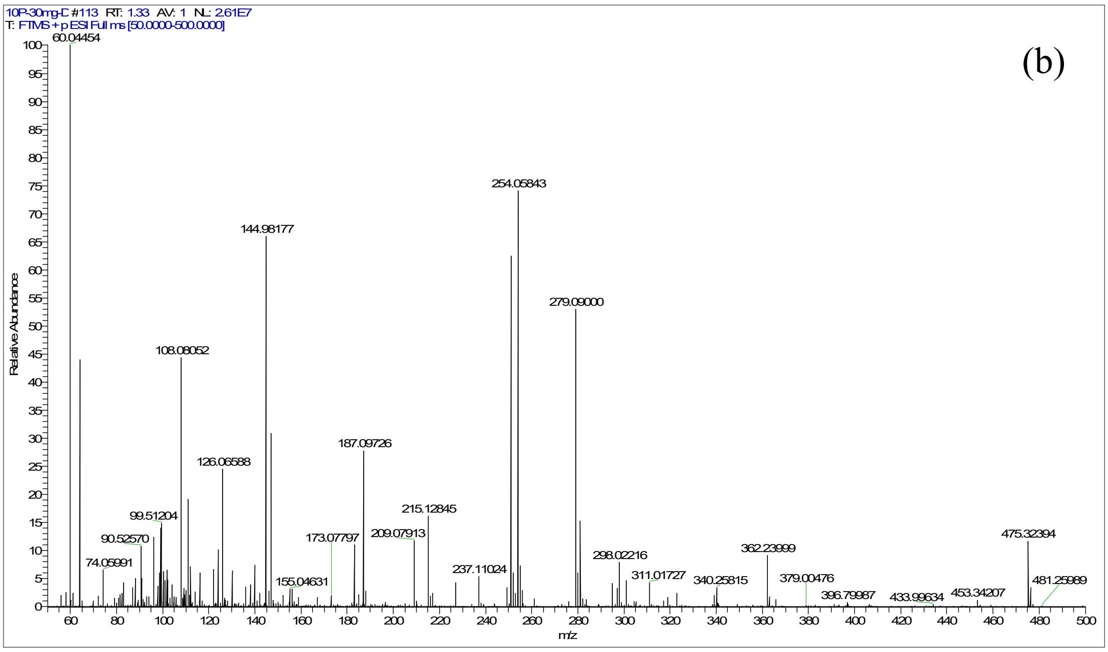


Fig. S10 Mass spectra of the Possible identified intermediates by GC–MS analyses at different illumination intervals of Sulfamethazine (a) 0 min, (b) 60 min, (c) 120 min.





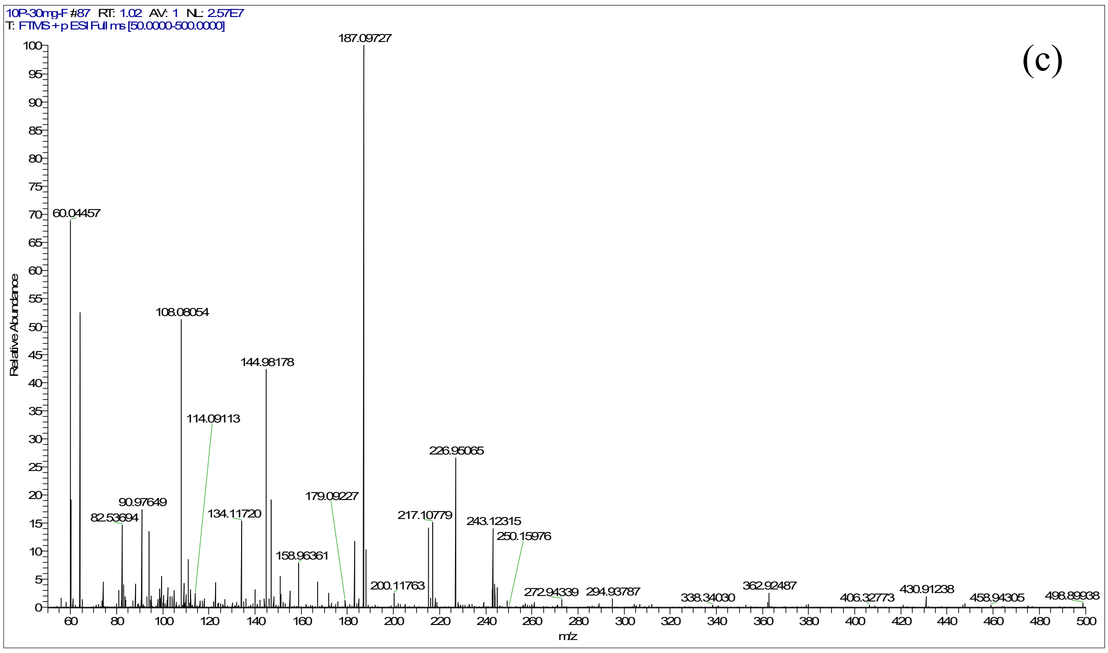
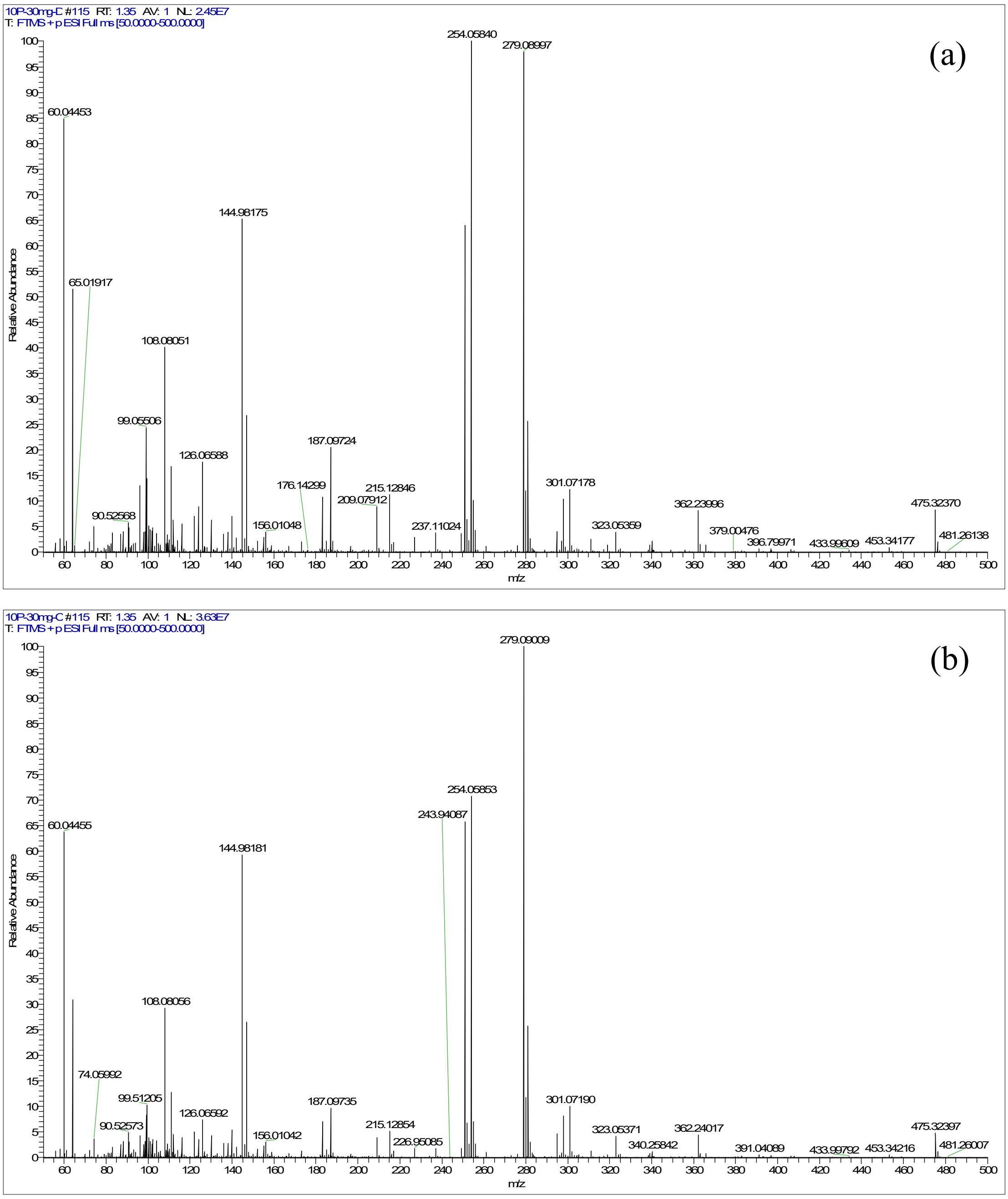


Fig. S11 Mass spectra of the Possible identified intermediates by GC–MS analyses at different illumination intervals of Sulfamonomethoxine (a) 0 min, (b) 60 min, (c) 120 min.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(a)
Relative Abundance
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65.01917
108.08051
99.05506
126.06588
187.09724
176.14299
215.12846
209.07912
301.07178
362.23996
475.32370
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156.01048
237.11024
323.05359
379.00476
396.79971
433.99609
453.34177
481.26138
10P-30mg-C #115 RT: 1.35 AV: 1 NL: 3.63E7
T: FTMS + p ESI Full ms [50.0000-500.0000]
(b)
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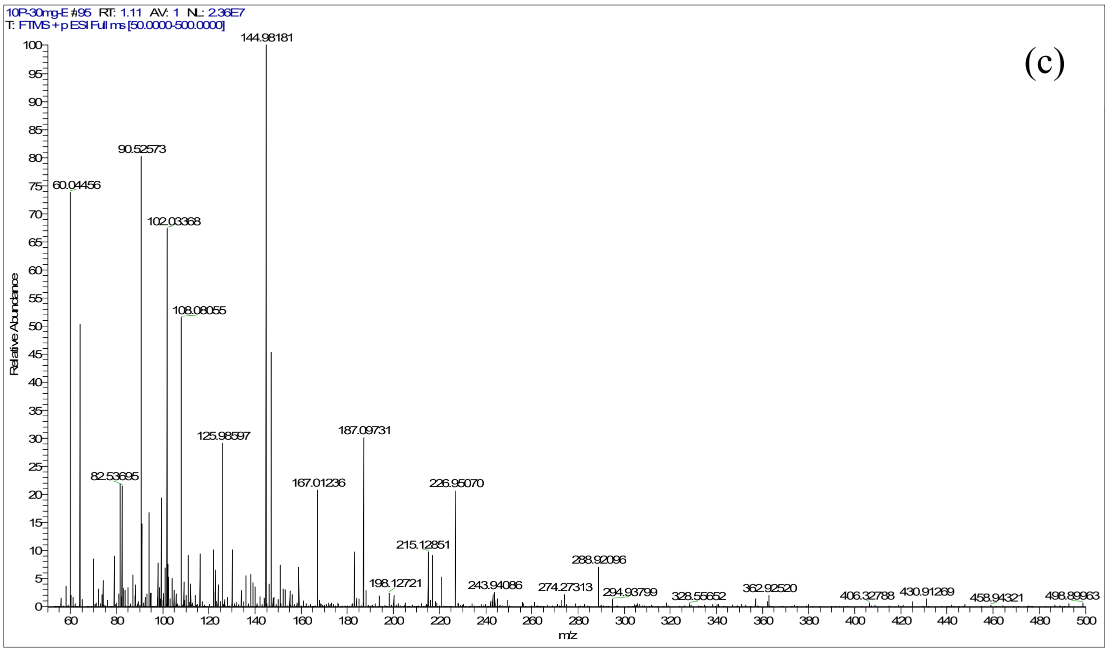

Fig. S12 Mass spectra of the Possible identified intermediates by GC–MS analyses at different illumination intervals of Sulfamethoxazole (a) 0 min, (b) 60 min, (c) 120 min.

Table.S1 The SAs concentration in different sewage

Types of antibiotics	Types of polluted water sources	Country	Concentration	Reference
Sulfamethoxazole	Effluent water	USA	18-910 ng/L	[1]
Sulfamethoxazole	Effluent water	Canada	519 ng/L	[2]
Sulfamethoxazole	Effluent water	Germany	300-1500 ng/L	[3]
Sulfamethoxazole	Surface water	USA	34-1020 ng/L	[4]
Sulfamethoxazole	Surface water	Germany	480 ng/L	[5]
Sulfamethoxazole	Surface water	China	3.68-529.4 ng/L	[6]
Sulfamethoxazole	Groundwater	USA	30-220 ng/L	[7]
Sulfamethoxazole	Groundwater	China	7.87-26.1 ng/L	[8]
Sulfadiazine	Pharmaceutical wastewater	Northern Croatia	3-20 μg/L	[9]
Sulfamethazine	Pharmaceutical wastewater	Northern Croatia	6.7-231 μg/L	[9]
sulfadiazine	Natural water	The Yellow River	0.017-196.16 ng/L	[10]
sulfamethoxazole	Natural water	The Yellow River	0.65-601.83 ng/L	[10]
sulfamethazine	WWTPs	Korea	1.64–1629 μg/L	[11]
sulfamethazine	WWTPs	China	35.0–45.0 μg/L	[11]

Table.S2 Comparison of SAs photocatalytic degradation efficiency by various photocatalysts.

Material	Dosage (g/L)	Initial concentration	Removal efficiency	References
g-C_3N_4/ZnO	0.65	Sulfamethoxazole 10 mg/L	96.91%, 80 min	[12]
P-TiO_2	1	sulfamethazine 10 mg/L	90.5%, 300min	[13]

Biochar/ TiO_2	5	Sulfamethoxazole 10 mg/L	91%, 360 min	[14]
Bisphenol S/g-C_3N_4/boron nitride quantum dots	0.25	Sulfadiazine 20 mg/L	100%, 60min	[15]
P-TiO_2/g-C_3N_4	0.4	Sulfadiazine Sulfamethazine Sulfamonomethoxine Sulfamethoxazole 10 mg/L	99.3%, 120min 99.6%,120min 99.1%,120min 99.0%,120min	This work

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