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Electronic Supplementary Information

Degradation of Tetracycline over Carbon Nanosheet: High Efficiency, Mechanism and Biotoxicity Assessment

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1. Chemicals and reagents

Reactive Red 2 comes from Shanghai Hawn chemical reagent Co., Ltd., oxytetracycline (OTC) from Tianjin Heowns Biochemical Co., tetracyclines (TC) and chlortetracycline (CTC) from Shanghai Macklin Biochemical Co., peroxymonosulfate ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, PMS) from Shanghai Annege Saen Chemical Technology Co., Ltd, and sodium hydroxide (NaOH) from Tianjin cameo chemical reagent co., LTD.

2. Characterization techniques

XRD analysis was carried out on a Rigaku Ultima IV. The morphologies of the catalysts were observed by scanning electron microscopy (SEM, HITACHI, SU8020) and transmission electron microscopy (TEM) was recorded on a Tecnai F-20 electron microscope (JEOL 2100F, Netherlands) at an accelerating voltage of 200 kV. XPS surface analysis was performed in an ultra-high vacuum (UHV) chamber by using a Thermo Scientific Escalab 250XI (Thermo Fischer, USA). The textural properties of catalysts were tested by N_2 sorption isotherms on a Micrometrics Tristar II 3020. Electron paramagnetic resonance (EPR) spectroscopy was conducted on a Bruker EMXnano. UV-vis. analysis was performed by using a Shimadzu UV-1900. Energy Dispersive Spectrometer (EDS) Mapping were performed with a TECNAI F-20 microscope (JEOL 2100F) operated at 200 kV. Fourier Transform Infrared Spectrometer (FTIR) of the catalysts was recorded on a PE·Fourier Transform, USA. Atomic Force Microscope (AFM) of the catalysts was studied on a BRUKER Dimension. Raman spectra the of catalysts were measured on a Thermo Scientific DXR.

3. Synthesis of GCN

First, 1 g of Reactive Red 2 was calcined at 550 °C and 600 °C, respectively, in a tubular furnace with the heating rate of 2.5 °C/min for 4 h. After the reaction was completed, the medium was cooled down to room temperature with a cooling rate of 2.5 °C/min. Then, the residue was collected and washed three times with deionized water and then dried at 60 °C under vacuum oven for 24 h. The final products were denoted as GCN-550 and GCN-600, corresponding to the

calcination temperature of 550 ºC and 600 ◦C, respectively. The yield of GCN-550 and-600 catalyst is 18 % and 10 %, respectively.

4. Catalytic activity study

In a typical experiment, 0.5 g/L of GCN-600 was added into a 100 mL round-bottom flask containing 20 mg/L of TC solution (50 mL). Then, 0.5g/L of PMS was added into the mixture. Among them, 2 mL of reaction sample was withdrawn from the solution using a syringe and was immediately analyzed by UV-vis. For the recycling experiments, the catalyst of GCN was collected and separated by sample filtration, and the separated GCN catalyst was desorbed by washing 3 times with 2 M NaOH solution and deionized water to regenerate the GCN catalyst. then dried at 60 ◦C under a vacuum drying oven for 24 h. The next degradation experiment was conducted with the addition of a fresh TC solution and PMS.

5. Ethics statement

All zebrafish husbandry and experimental procedures were performed in accordance with the Guiding Principles for the Care and Use of Laboratory Animals, and were reviewed and approved by the Animal Care Committee of Lanzhou University (Ethic approval ID No. EAF2020007). All efforts were taken to minimize animal suffering.

6. Zebrafish

Zebrafish wild-type AB strains were raised according to standard husbandry protocols[58] at 28 °C and a constant photoperiod of 14:10 h (light: dark). The zebrafish were fed twice daily with newly-hatched brine shrimp. Zebrafish embryos were obtained from the adults that segregated by sex in mating tanks overnight. Spawning was induced in the next morning by light stimulation. Fertilized healthy embryos were collected within one hour after the light was switched on and were washed with the standard zebrafish E3 culture medium. The embryos at 2 hrs post-fertilization (hpf) were examined under a dissecting microscope (Olympus); normally developed embryos were selected for further experiments.

7. Zebrafish developmental toxicity assays

Zebrafish embryos were exposed to TC or its degradation product at various concentrations diluted in the E3 medium at 28.5 °C, and observation was continuously conducted at different developmental stages ranging from 3 hpf to 140 hpf. The medium was refreshed every day during the entire exposure period. Phenotypic development was recorded and analyzed under a stereomicroscopy (Olympus). The control and treatment of each group was carried out using 50 embryos per condition, and each experiment was repeated at least three times.

Locomotor activity was monitored using a DanioVision Video-Tracking system (Noldus, Netherlands). Larval swimming behavior was monitored in response to vibration stimulations (every 30 seconds). The behavior parameters like distance traveled, velocity, acceleration etc. were recorded and analyzed in the whole experimental process or in every min.

8. Characterization of catalysts

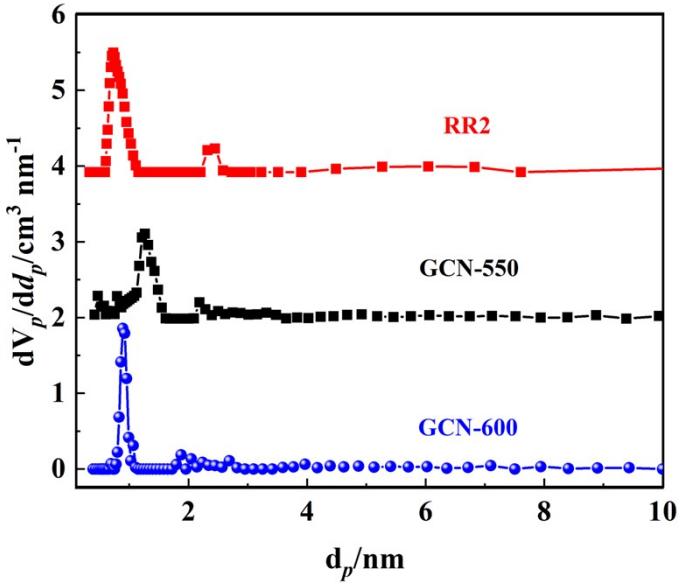

Figure S1. Pore size distributions of RR2, GCN-550 and GCN-600.

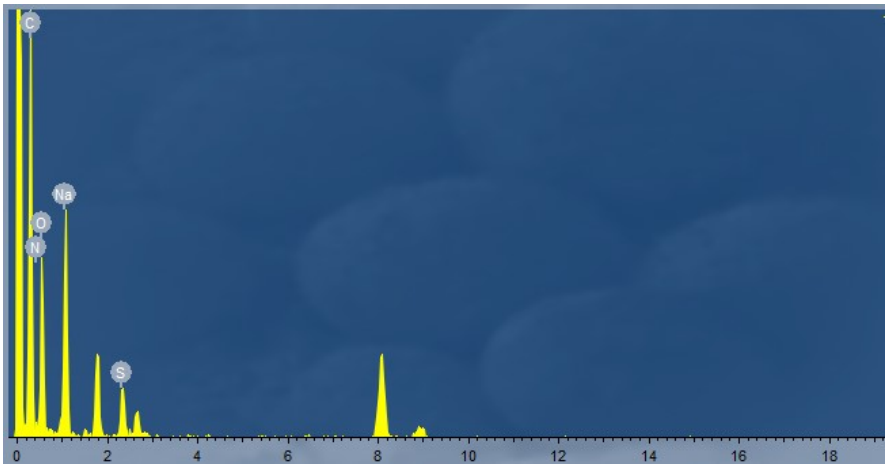

Figure S2. EDX sum spectrum of GCN.

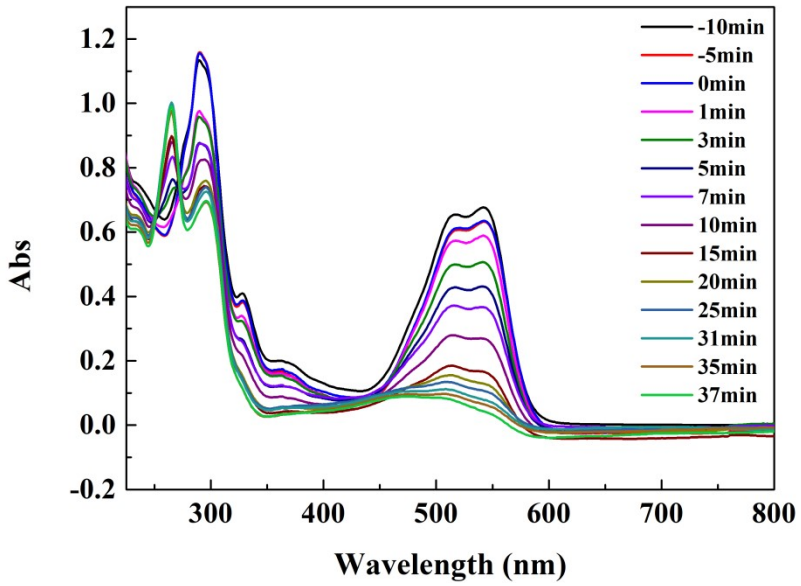

Figure S3. Degradation of RR2. Reaction conditions: 0.5 g/L of GCN, 0.5 g/L of PMS, 50 mg/L of RR2 (50 mL), 30℃.

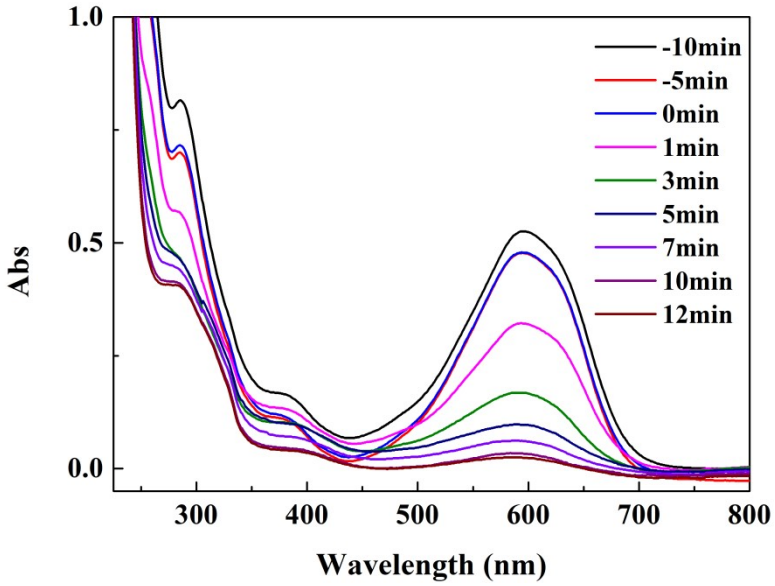

Figure S4 Degradation of RB19. Reaction conditions: 0.5 g/L of GCN, 0.5 g/L of PMS, 50 mg/L of RB19 (50 mL), 30℃.

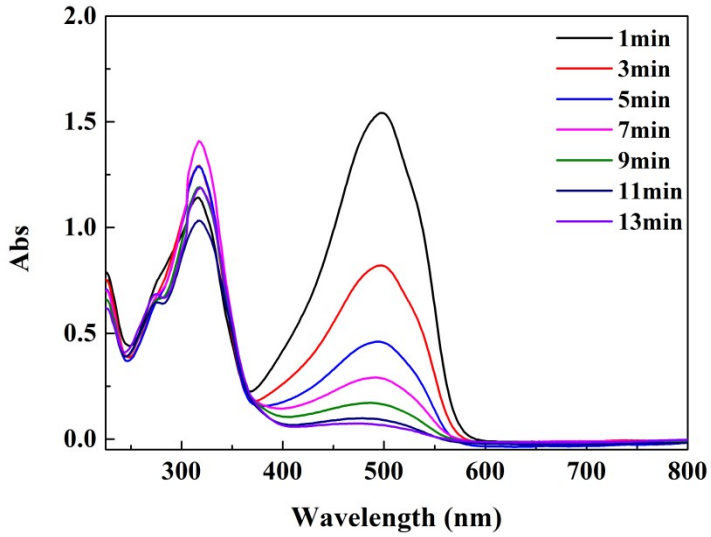

Figure S5. Degradation of MO. Reaction conditions: 0.5 g/L of GCN, 0.5 g/L of PMS, 50 mg/L of MO (50 mL), 30℃.

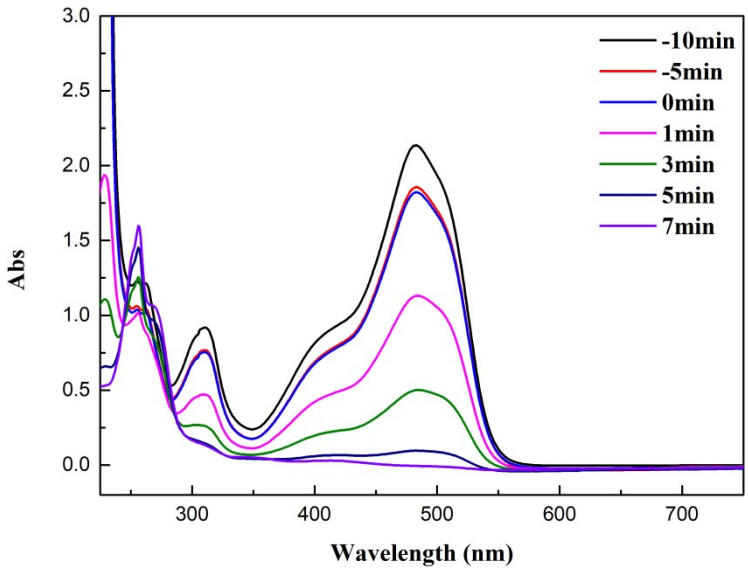

Figure S6. Degradation of AO7. Reaction conditions: 0.5 g/L of GCN, 0.5 g/L of PMS, 50 mg/L of AO7 (50 mL), 30℃.

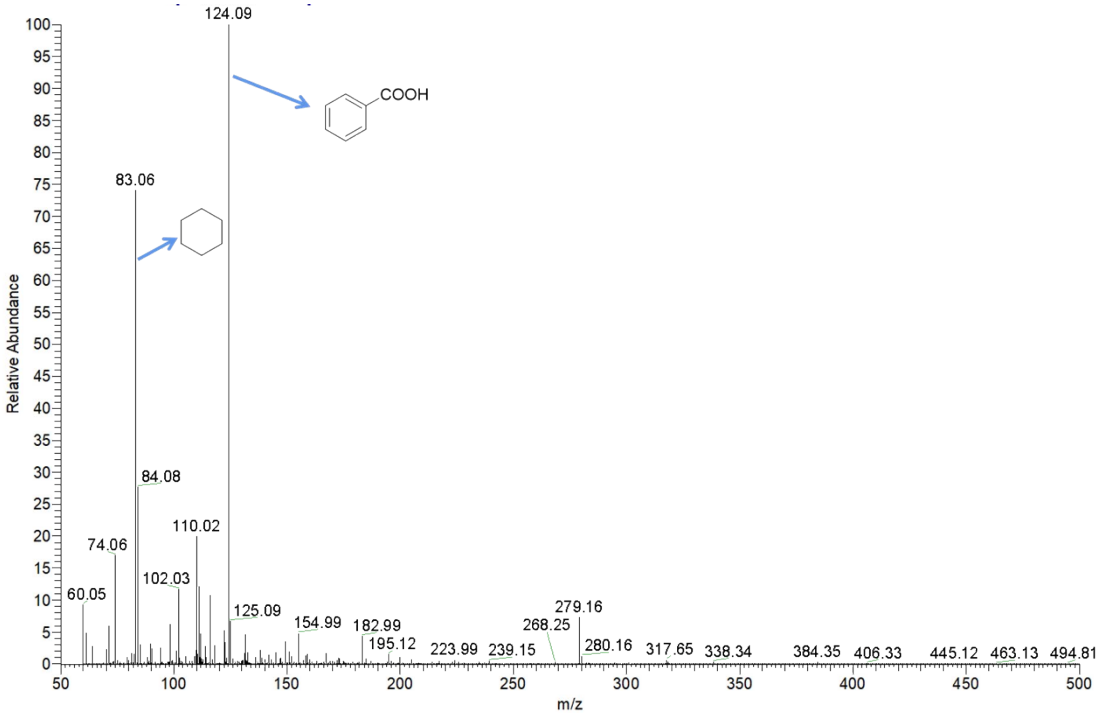

Figure S7. The HR-MS of the product after TC degradation

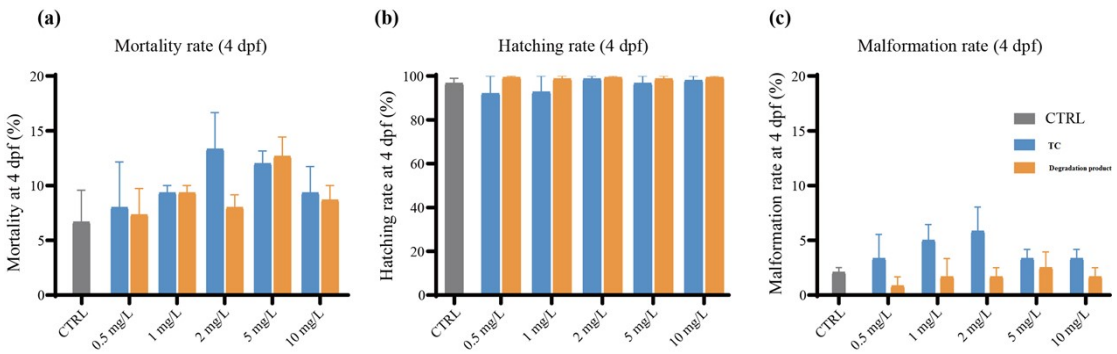

Figure S8. Effects of TS and its post-degradation product exposure on the (a) survival, (b) hatching and (c) malformation of zebrafish larvae at 4 dpf.

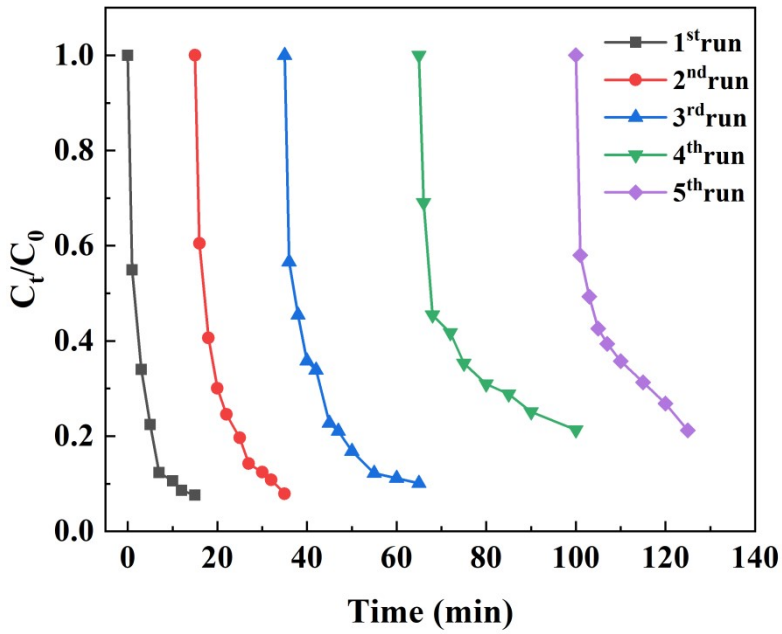

Figure S9. Cycling runs in the degradation of TC, reaction condition: 20 mg/L of TC, 0.5 g/L of PMS and 0.5 g/L of GCN, at 30 °C

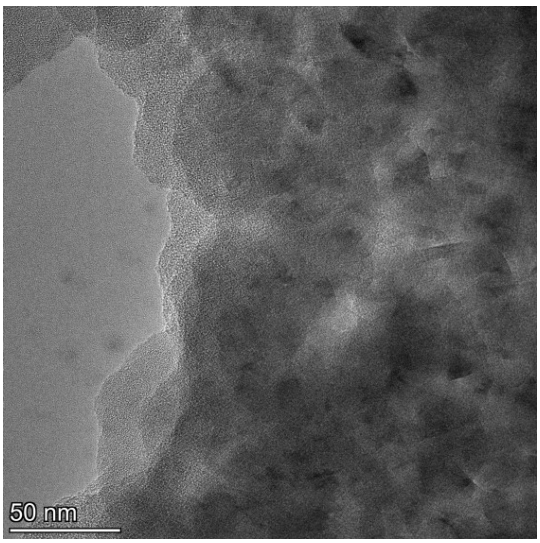

Figure S10. The TEM image of 5th reused GCN.

9. **Table. S1.** Comparison of catalytic activities with literature examples for degradation of TC

Entry	TC	Catalyst	PMS	Other additive	Yield (%)	Time
1	20 mg/L	GCN (0.5 g/L)	0.5g/L	-	96	15 min
2[48]	10 mg/L	Co-C_3N_4 (0.2 g/L)	200 mg/L	light	97.77	60 min
3[55]	20 mg/L	SMC-K (0.1 g/L)	0.3 g/L	PH=7	99.18	60 min
4[49]	20 mg/L	MoS_2/Ag/g-C_3N_4 (0.2 g/L)	0.1 mM	light (pH=5.5)	98.9	50 min
5[53]	80 mg/L	CuO-$BiVO_4$ (0.2 g/L)	2 mM	light	100	50 min
6[20b]	50 mg/L	FMO-46 (0.4 g/L)	0.4 g/L	PH=5.11	94.3	80 min
7[50]	45 μM	CuO@C-550 (0.2 g/L)	1 mM	-	99.82	40 min
8[56]	20 mg/L	C_3N_4/Na-$BiVO_4$ (0.2 g/L)	0.5 mM	light (pH=5)	98.2	40 min
9[46]	30 mg/L	25%MIL-53(Al) (0.2 g/L)	0.3 g/L	-	94	120 min
10[51]	30 mg/L	CoFeLa·LDH_2 (0.05 g/L)	1.0 mM	pH=5.4	90.1	10 min
11[54]	10 mg/L	F-Ni100 (0.2 g/L)	20 mg/L	pH=7	70.94	120 min
12[52]	20 mg/L	BFO-u (1 g/L)	10 g/L	light	98.6	20 min
13[47]	40 mg/L	MoO_3/Bi_2O_3/g-C_3N_4(0.6 mg/L)	4 mM	light (pH=6)	98	120 min
14[59]	20 mg/L	PFSC-900 (0.4 g/L)	0.3 g/L	pH=5.4	90.91	120 min
15[57]	40 mg/L	5% Co/$BiVO_4$ (0.2 g/L)	5 mM	light	100	25 min
16[58]	40 mg/L	CuHNPs-7.5 (0.2 g/L)	0.45 mM	light (pH=5.5)	97.8	30 min
17[13]	20 mg/L	3D$CoFe_2O_4$/ N-rGA (0.1 g/L)	0.3 g/L	pH=11	93.5	300 min

10. UV-vis. spectra of TC degradation in Figure 8a.

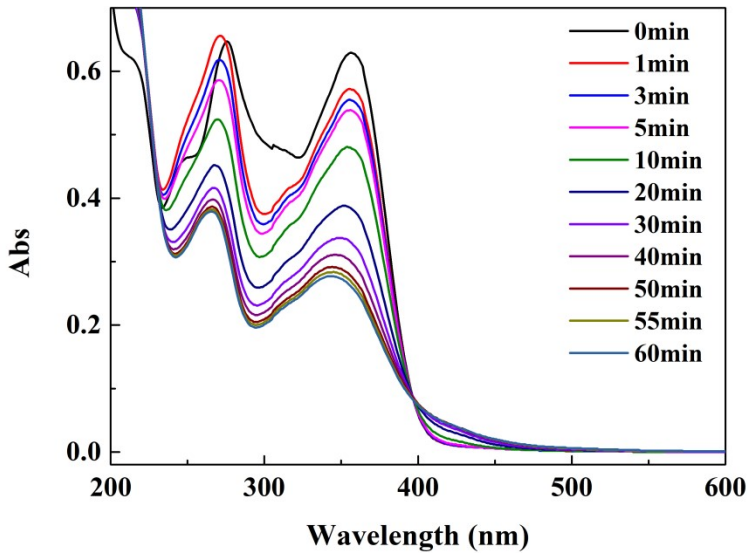

Figure S11. Degradation of TC. Reaction conditions: 0 g/L of GCN, 0.5 g/L of PMS, 20 mg/L of TC (50 mL), 30℃.

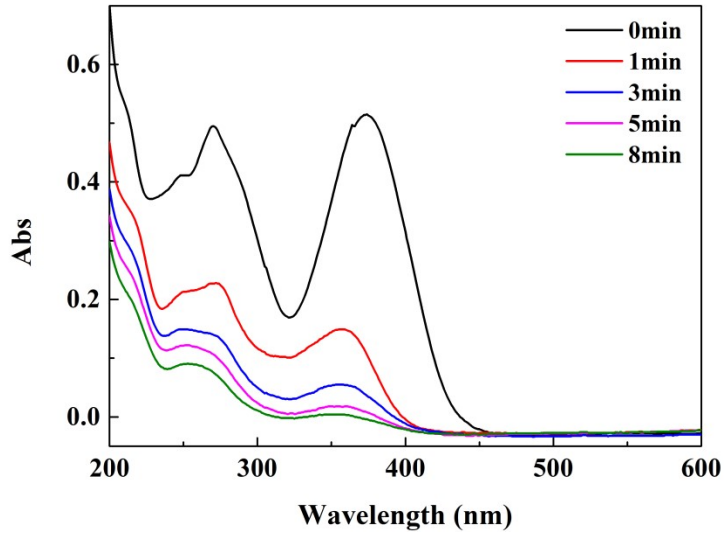

Figure S12. Degradation of TC. Reaction conditions: Reaction conditions: 0.75 g/L of GCN, 0.5 g/L of PMS, 20 mg/L of TC (50 mL), 30℃.

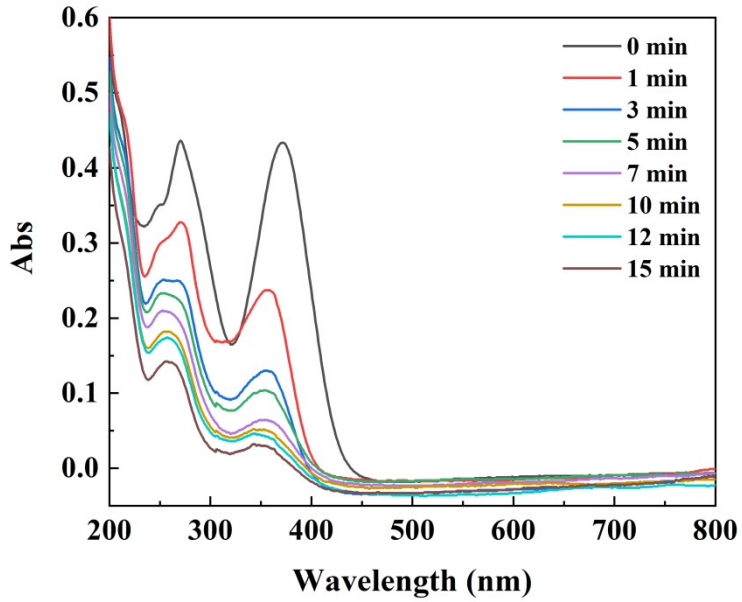

Figure S13. Degradation of TC. Reaction conditions: 0.5 g/L of GCN, 0.5 g/L of PMS, 20 mg/L of TC (50 mL), 30℃.

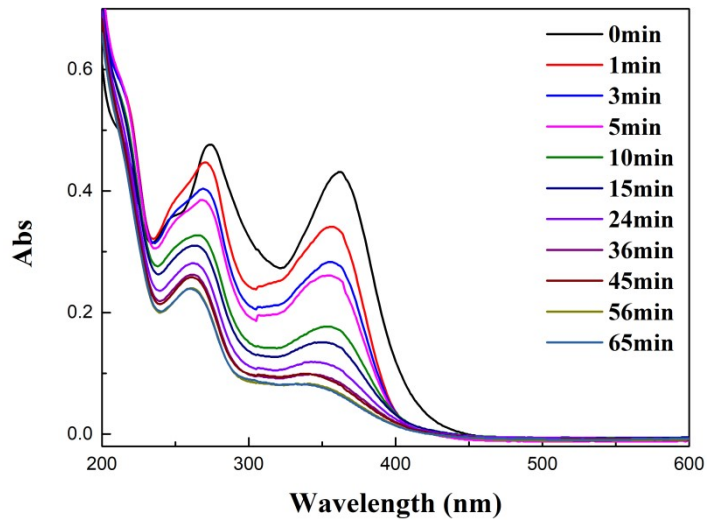

Figure S14. Degradation of TC. Reaction conditions: 0.25 g/L of GCN, 0.5 g/L of PMS, 20 mg/L of TC (50 mL), 30℃.

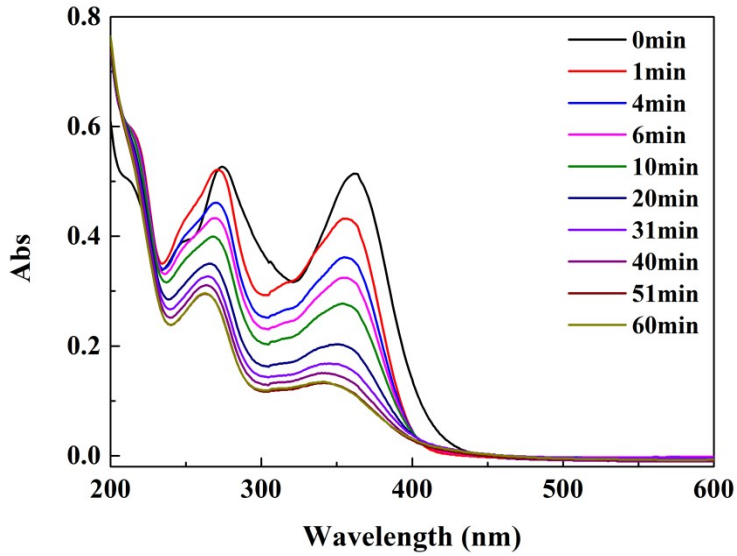

Figure S15. Degradation of TC. Reaction conditions: 0.126 g/L of GCN, 0.5 g/L of PMS, 20 mg/L of TC (50 mL), 30℃.

11. UV-vis. spectra of TC degradation in Figure 8b.

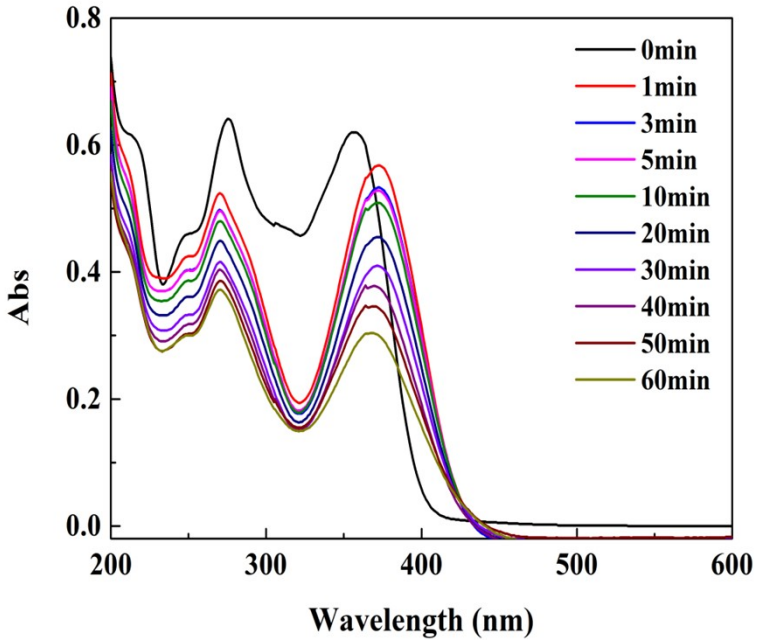

Figure S16. Degradation of TC. Reaction conditions: 0.5 g/L of GCN, 0 g/L of PMS, 20 mg/L of TC (50 mL), 30℃.

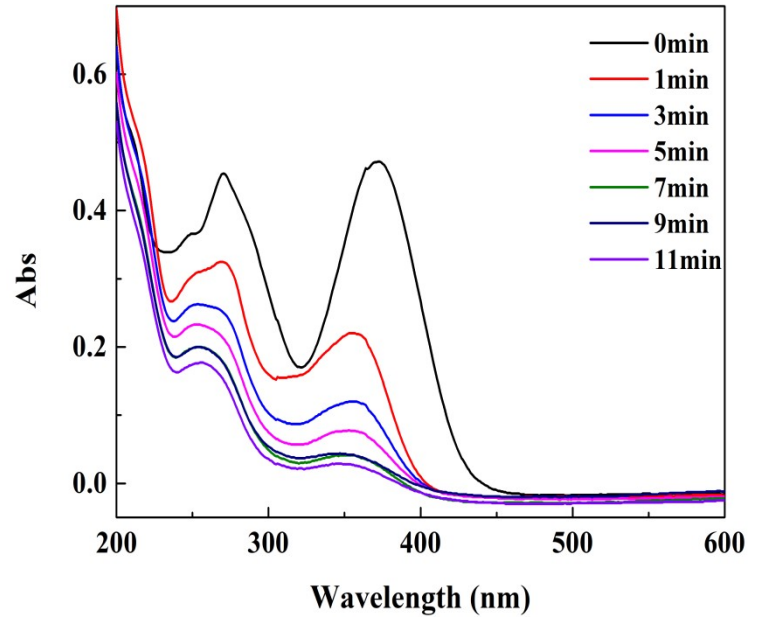

Figure S17. Degradation of TC. Reaction conditions: 0.5 g/L of GCN, 0.75 g/L of PMS, 20 mg/L of TC (50 mL), 30℃.

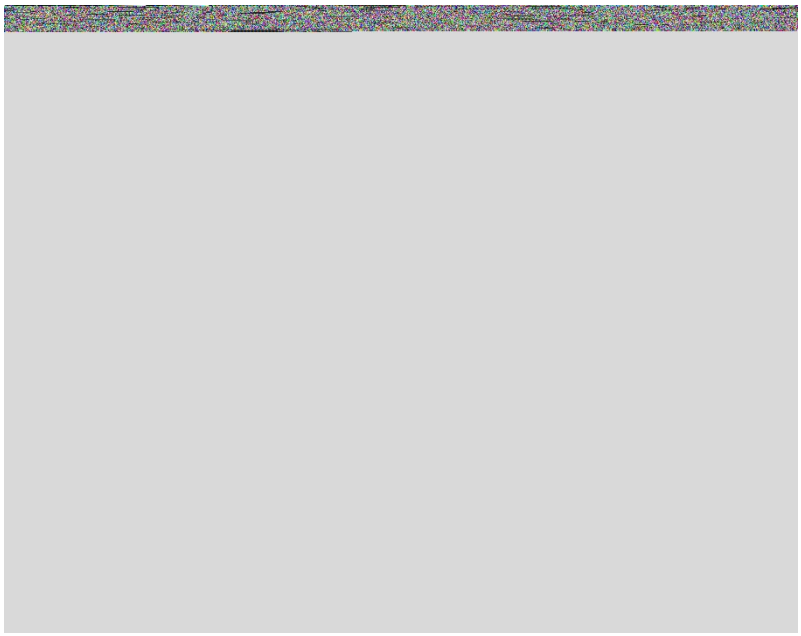

Figure S18. Degradation of TC. Reaction conditions: 0.5 g/L of GCN, 0.5 g/L of PMS, 20 mg/L of TC (50 mL), 30℃.

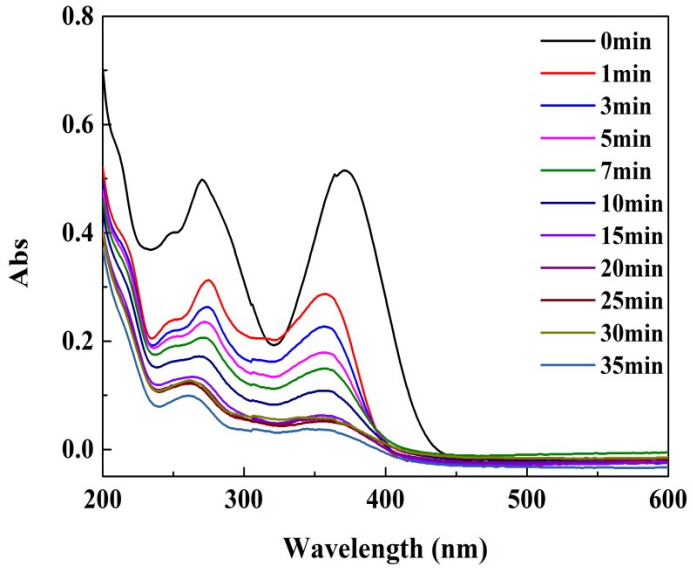

Figure S19. Degradation of TC. Reaction conditions: 0.5 g/L of GCN, 0.25 g/L of PMS, 20 mg/L of TC (50 mL), 30℃.

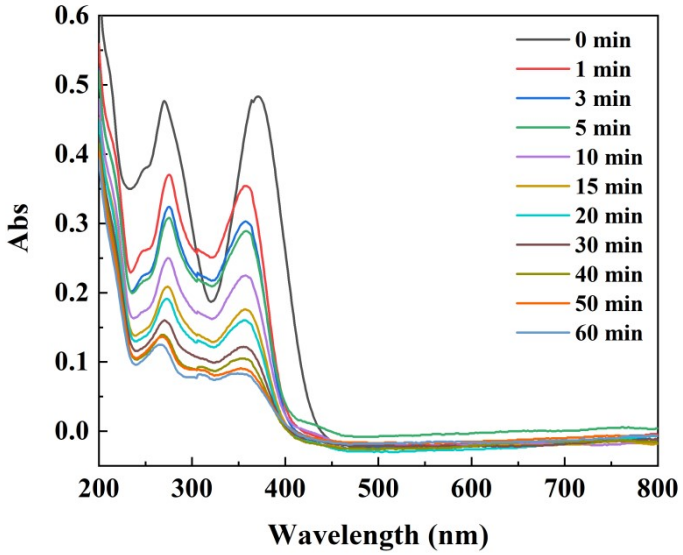

Figure S20. Degradation of TC. Reaction conditions: 0.5 g/L of GCN, 0.126 g/L of PMS, 20 mg/L of TC (50 mL), 30℃.

12. UV-vis. spectra of TC degradation in Figure 8c.

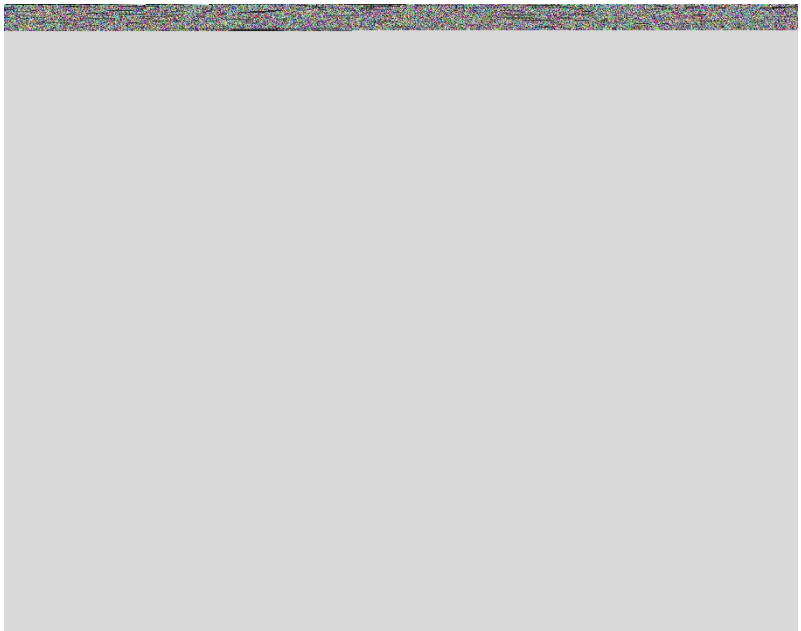

Figure S21. Degradation of TC. Reaction conditions: 0.5 g/L of GCN, 0.5 g/L of PMS, 20 mg/L of TC (50 mL), 30℃.

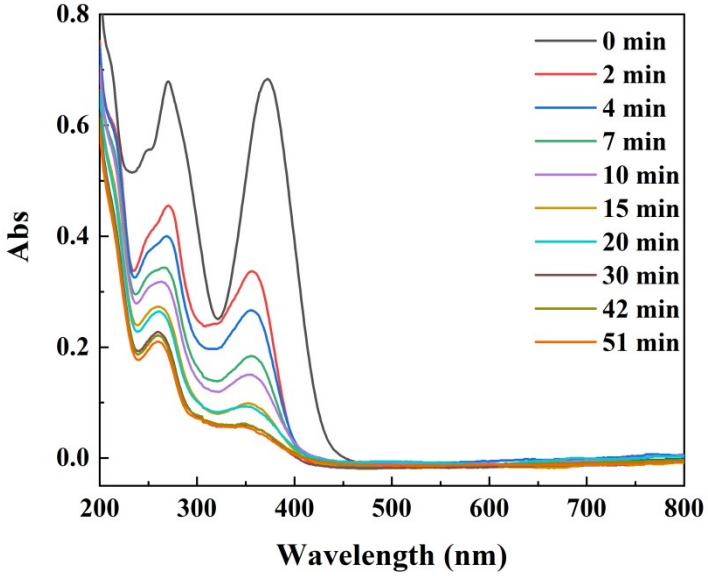

Figure S22. Degradation of TC. Reaction conditions: 0.5 g/L of GCN, 0.5 g/L of PMS, 25 mg/L of TC (50 mL), 30℃.

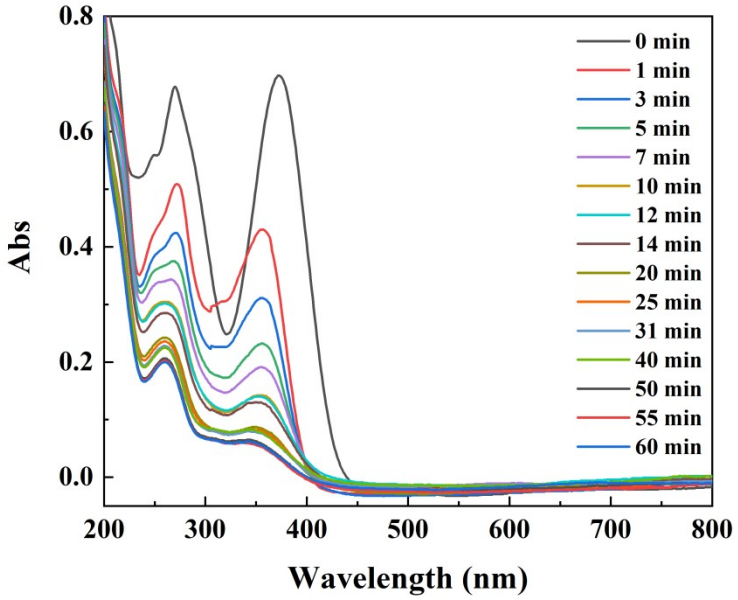

Figure S23. Degradation of TC. Reaction conditions: 0.5 g/L of GCN, 0.5 g/L of PMS, 30 mg/L of TC (50 mL), 30℃.

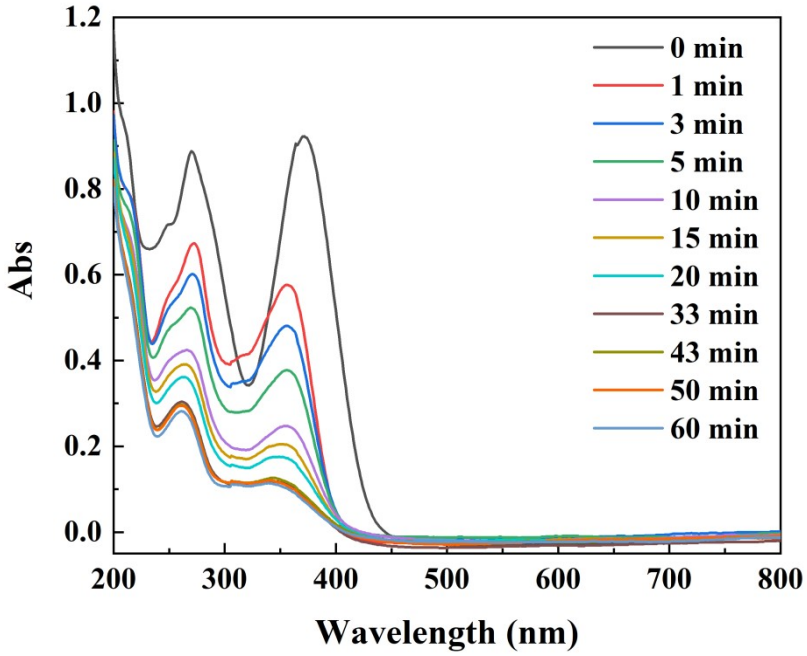

Figure S24. Degradation of TC. Reaction conditions: 0.5 g/L of GCN, 0.5 g/L of PMS, 35 mg/L of TC (50 mL), 30℃.

13. UV-vis. spectra of TC degradation in Figure 8d.

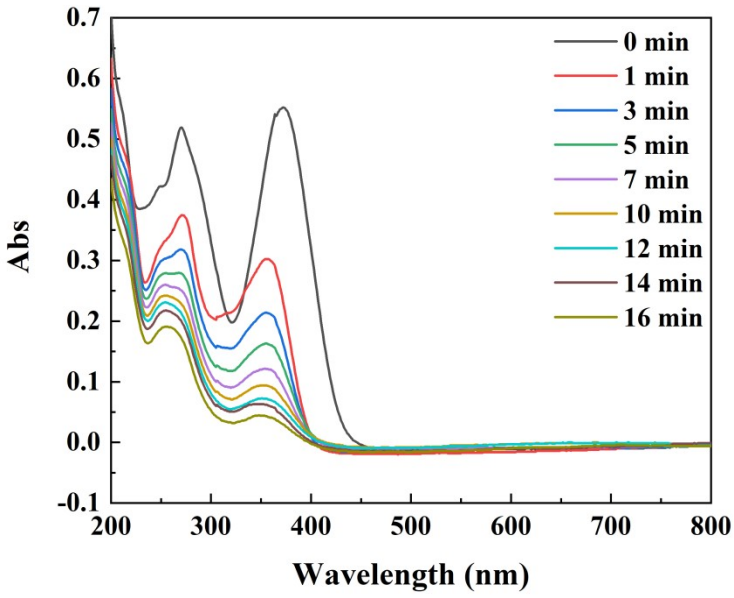

Figure S25. Degradation of TC. Reaction conditions: 0.5 g/L of GCN, 0.5 g/L of PMS, 20 mg/L of TC (50 mL), 293.15 K.

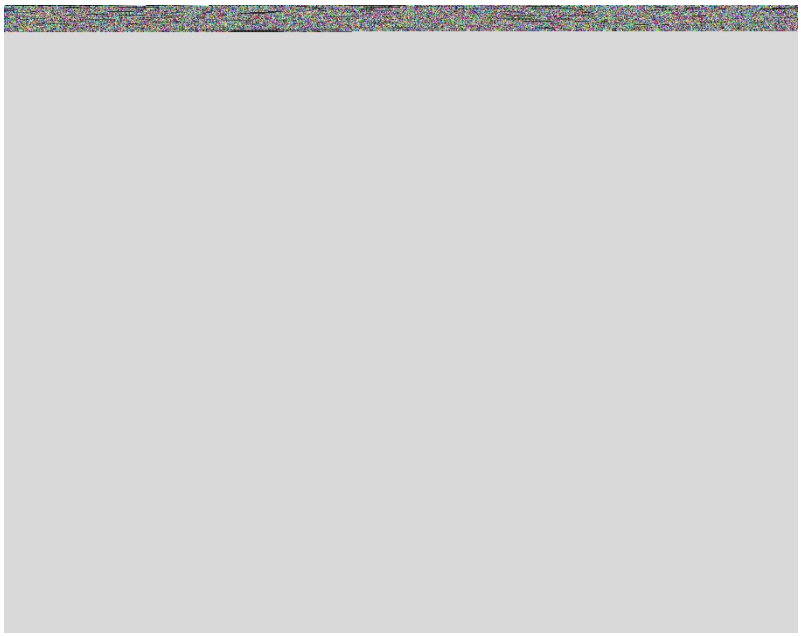

Figure S26. Degradation of TC. Reaction conditions: 0.5 g/L of GCN, 0.5 g/L of PMS, 20 mg/L of TC (50 mL), 303.15 K.

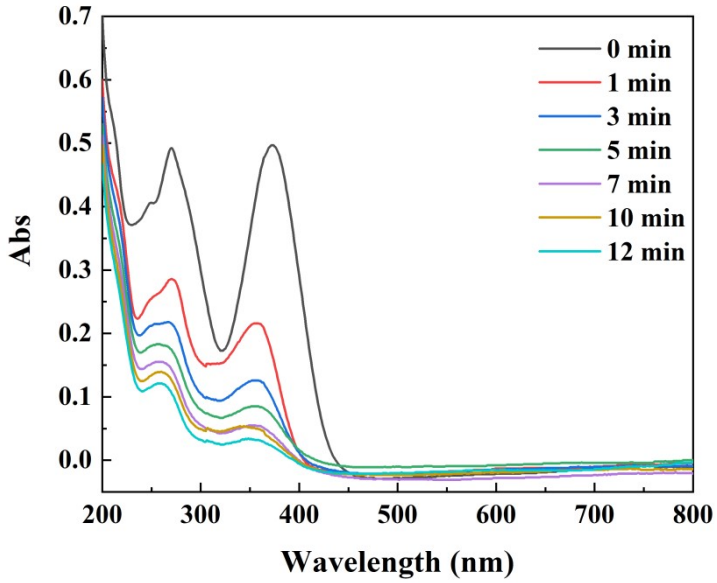

Figure S27. Degradation of TC. Reaction conditions: 0.5 g/L of GCN, 0.5 g/L of PMS, 20 mg/L of TC (50 mL), 313.15 K.

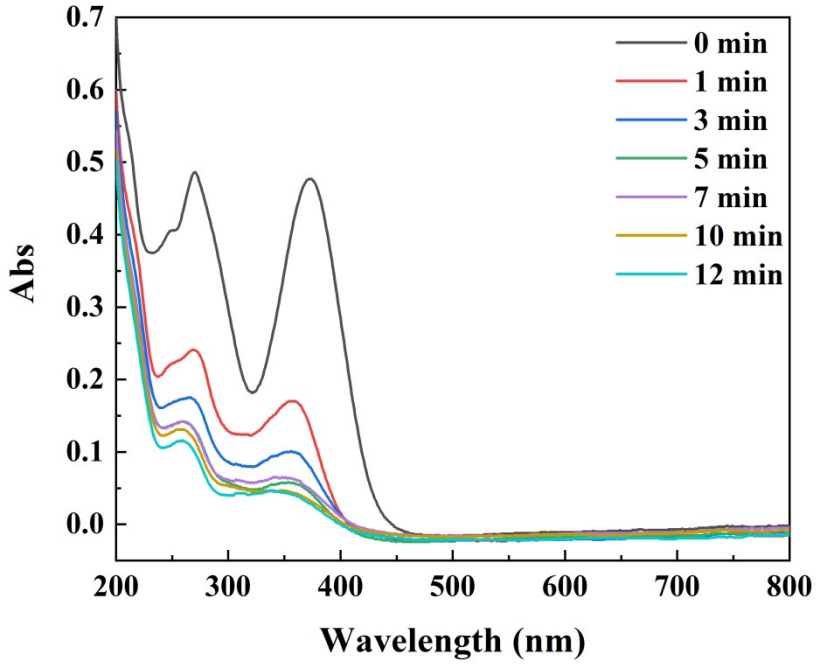

Figure S28. Degradation of TC. Reaction conditions: 0.5 g/L of GCN, 0.5 g/L of PMS, 20 mg/L of TC (50 mL), 323.15 K.

14. UV-vis. spectra of TC degradation in Figure 9a.

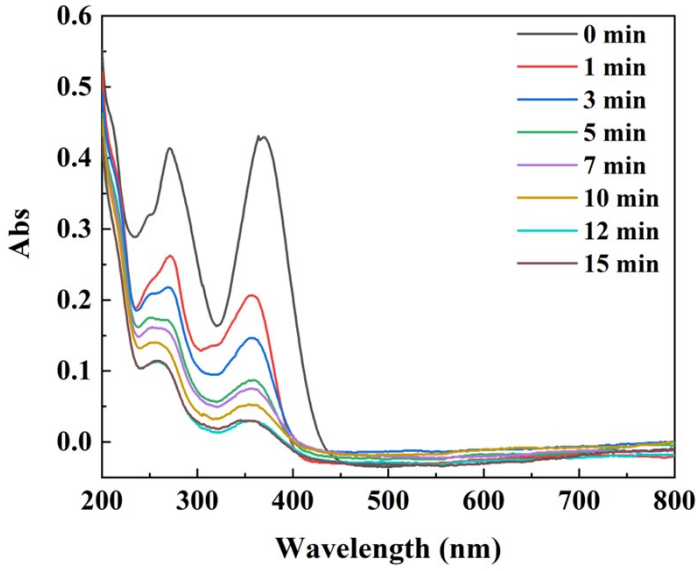

Figure S29. TC (20 mg/L, 50 mL), GCN (0.5 g/L), PMS (0.5 g/L), and TBA (3.2 mM), 30℃

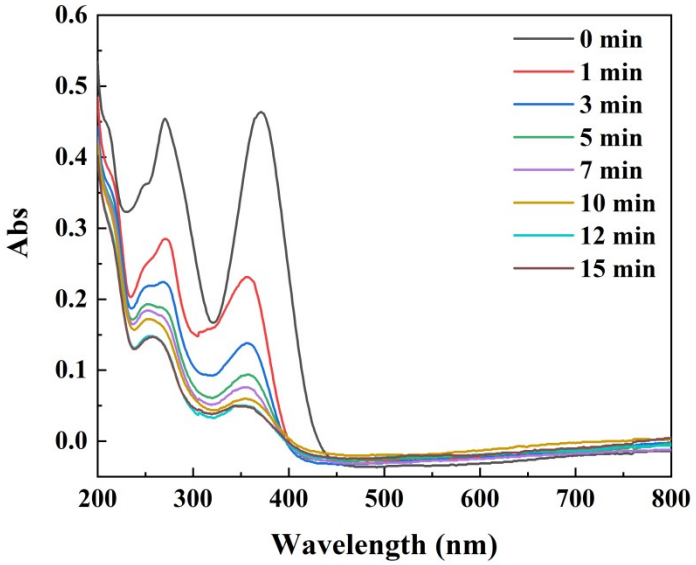

Figure S30. TC (20 mg/L 50 mL), GCN (0.5 g/L), PMS (0.5 g/L), EtOH (3.2mM), 30℃

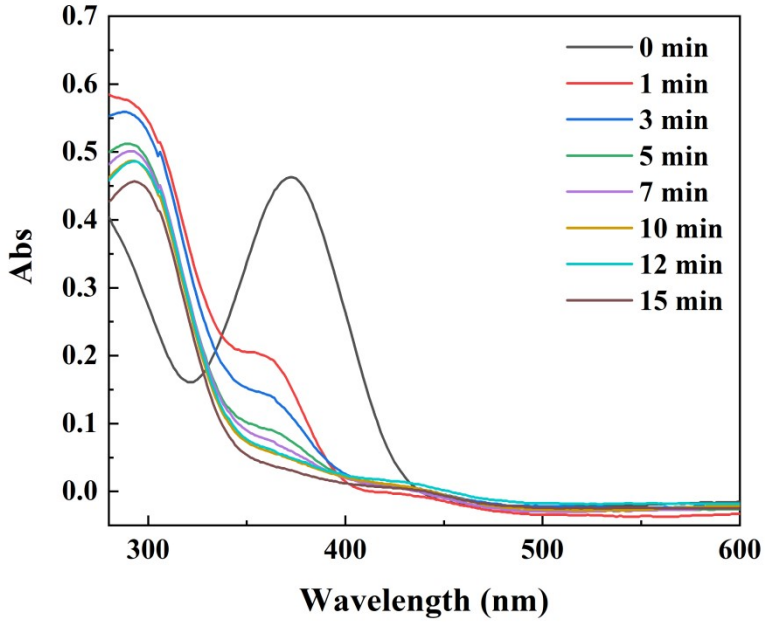

Figure S31. TC (20 mg/L 50 mL), GCN (0.5 g/L), PMS (0.5 g/L), BQ (1.6 mM). 30℃

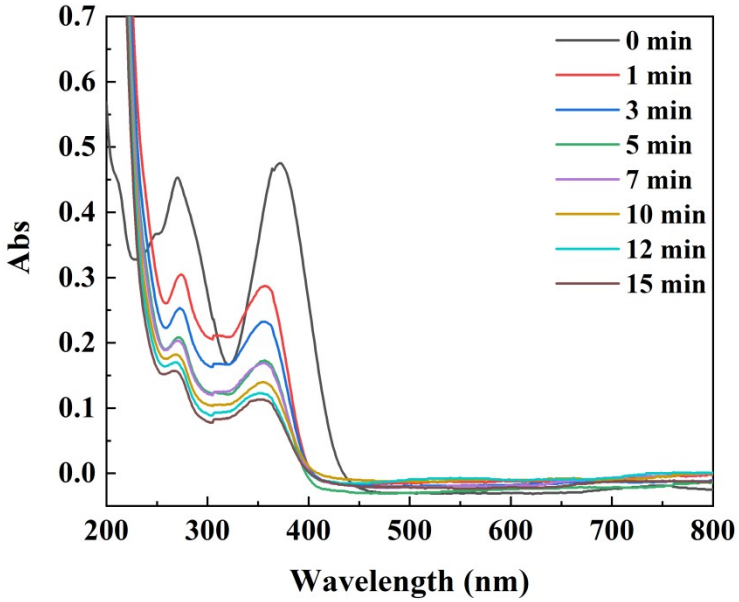

Figure S32. TC (20 mg/L 50 mL), GCN (0.5 g/L), PMS (0.5 g/L), NaN_3 (1.6 mM). 30℃

15. UV-vis. spectra of TC degradation in Figure S5.

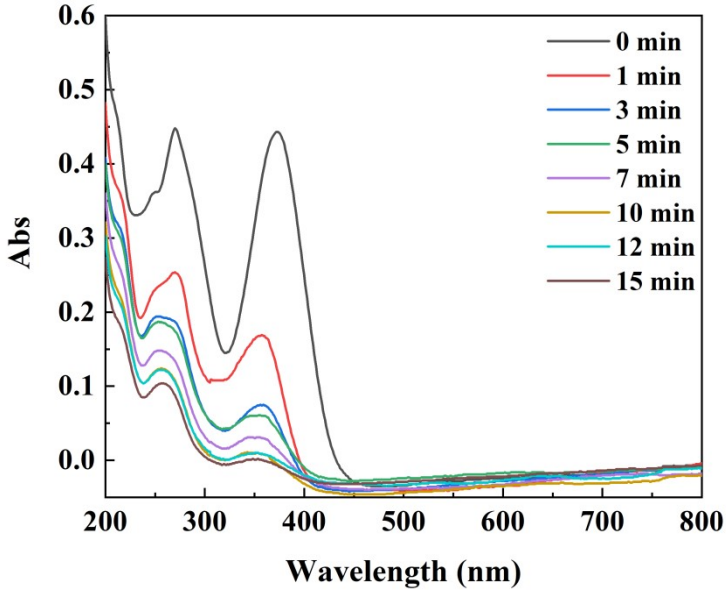

Figure S33. UV/Vis spectra of TC degradation for 1st run. Reaction conditions: TC (20 mg/L 50

mL), GCN (0.5 g/L), PMS (0.5 g/L), 30℃

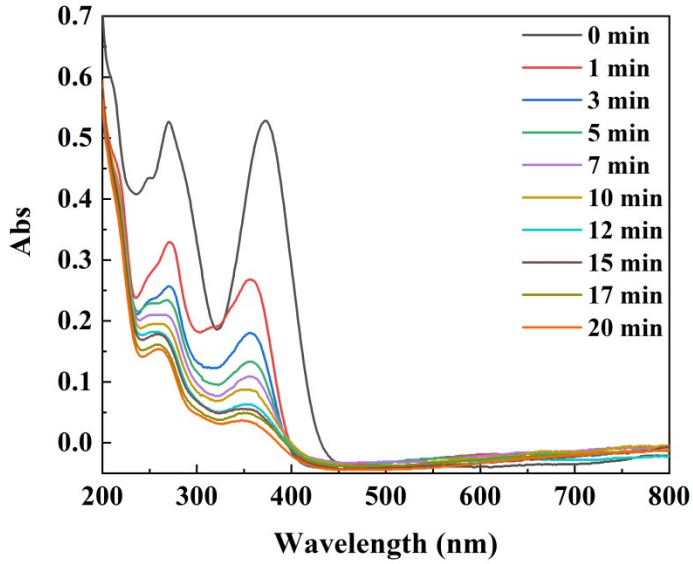

Figure S34 UV/Vis spectra of TC degradation for 2nd run. Reaction conditions: TC (20 mg/L 50 mL), GCN (0.5 g/L), PMS (0.5 g/L), 30℃

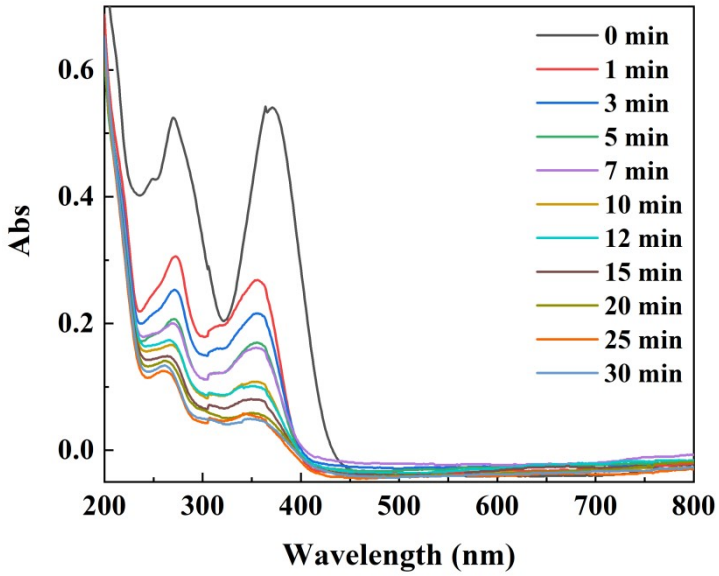

Figure S35. UV/Vis spectra of TC degradation for 3rd run. Reaction conditions: TC (20 mg/L 50 mL), GCN (0.5 g/L), PMS (0.5 g/L), 30℃

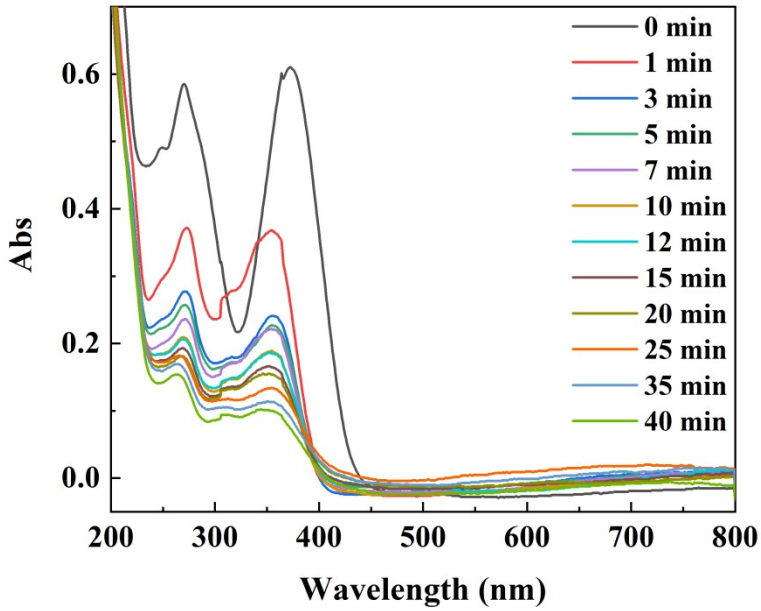

Figure S36. UV/Vis spectra of TC degradation for 4th run. Reaction conditions: TC (20 mg/L 50 mL), GCN (0.5 g/L), PMS (0.5 g/L), 30℃

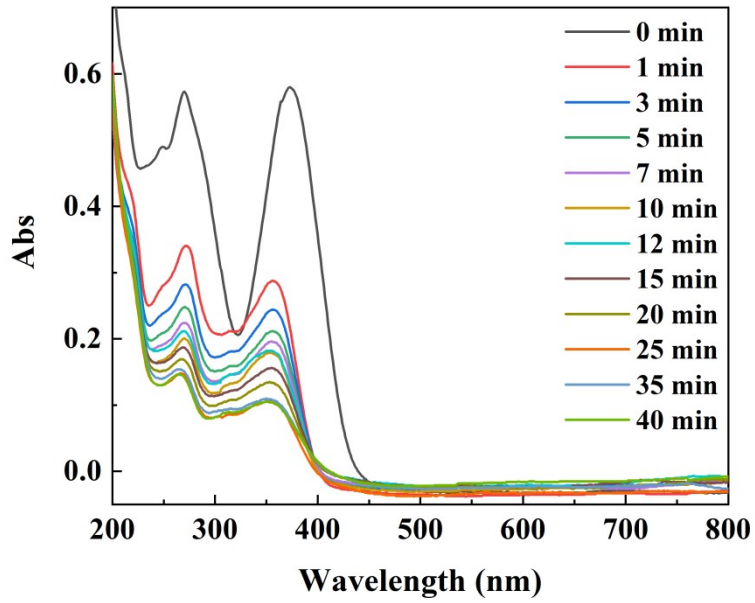

Figure S37 UV/Vis spectra of TC degradation for 5th run. Reaction conditions: TC (20 mg/L 50 mL), GCN (0.5 g/L), PMS (0.5 g/L), 30℃