Up-cycling of Waste A4 Papers into a $CaCO_3$/Biochar Nanocomposite for Wastewater Purification: Efficiency, Mechanism and Biotoxicity Evaluation

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1. **Materials**

The chemicals are used without further purification. The deionized water was prepared in the laboratory. A4 paper purchased from Deli Group Co., Ltd. Peroxymonosulfate and L-histidine were purchased from Anhui Zesheng Technology Co., Ltd. Tetracycline, chlortetracycline hydrochloride, sodium bicarbonate (AR, 99.8%), potassium sulfate (AR, 99%) were obtained from Shanghai Macklin Biochemical Co., Ltd. Oxytetracycline was obtained from Tianjin Xiensi Biochemical Technology Co., Ltd. Ethanol purchased from China National Pharmaceutical Group Chemical Reagent Co., Ltd. Trichloromethane purchased from Chengdu Cologne Chemical Co., Ltd. T-butanol purchased from Shanghai Aladdin Biochemical Co., Ltd. Sodium chloride (AR) purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium nitrate (AR, 99%) purchased from Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd. Humic acid (70%) purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

2. **Characterization**

UV-vis spectra were conducted on Metash UV-8000S. The X-ray powder diffractometer was conducted on SmartLab 9kW. The morphology of the catalyst was observed by scanning electron microscopy (Thermo Fisher Scientific FlB-SEM GX4 (10.16.0.97)) and the morphology of the catalyst after cycling was observed by scanning electron microscopy (ZEISS GeminiSEM 300, Germany). Scanning transmission electron microscopy and energy dispersive spectroscopy (EDS) were performed on Talos (10.16.0.199). X-ray photoelectron spectroscopy (XPS) was performed on Thermo Fisher NEXSA (USA). Laser confocal Raman spectroscopy was performed on Renishaw in Via (10.16.0.143). The extended multi station surface area and aperture analyzer was

conducted on ASAP-2460. The infrared spectrometer was performed on NICOLET 5700. High resolution mass spectrometry was performed at Thermo Scientific Q Exactive (USA). Electron paramagnetic resonance (EPR) spectroscopy was performed on the Bruker-A300/E500 (Germany).

3. Seed germination experiments

Wheat seeds were obtained from the local market. The seeds (50) were placed on each Petri dish. A piece of suitably sized filter paper was put into it. 10 mL of TC (40 mg/L) and TC degraded aqueous solution was added into the petri dish, respectively. At regular intervals, the same volume (10 mL) of TC and TC degraded aqueous solution were slowly added to the petri dish. The seed contained in petri dishes were incubated in the alternating dark and light at 25 ℃ for 3 days. The control group was treated with deionized water. Afterward, deionized water (10 mL) was added daily to maintain sufficient moisture content for germination and the germination percentage was recorded. All tests were repeated three times.

4. The electron transfer between TC and PMS

Firstly, CCBN-400 was coated on conductive glass (FTO) using naphthol and ethanol solution as binders and dried. Then, a calomel electrode was used as the reference electrode, a platinum plate as the counter electrode, the treated conductive glass (FTO) as the working electrode, and 0.05M Na_2SO_4 as the electrolyte to construct a three electrode system. Inject PMS solution into the solution within 200 s. Add TC solution to the solution at 400 s and observe the change in current.

All measurements were performed on an electrochemical analyzer (Interface 1010E, America).

The GOP system was conducted in two half-cells, one containing TC and the other containing PMS. The two half-cells were connected by an agar salt bridge, and an ammeter is connected to the processed carbon paper. Both the salt bridge and the electrodes were immersed in the half-cells, with one half-cell containing tetracycline (TC cell) and the other half-cell (PMS cell) buffered with 0.02 M acetic acid buffer solution at pH=5. PMS was added to the PMS cell to initiate the reaction when the current dropped close to equilibrium. The relative current changes were monitored throughout the entire GOP reaction process.

4. Physical characterizations and experimental spectra (Fig. S1-S14 and table S1)

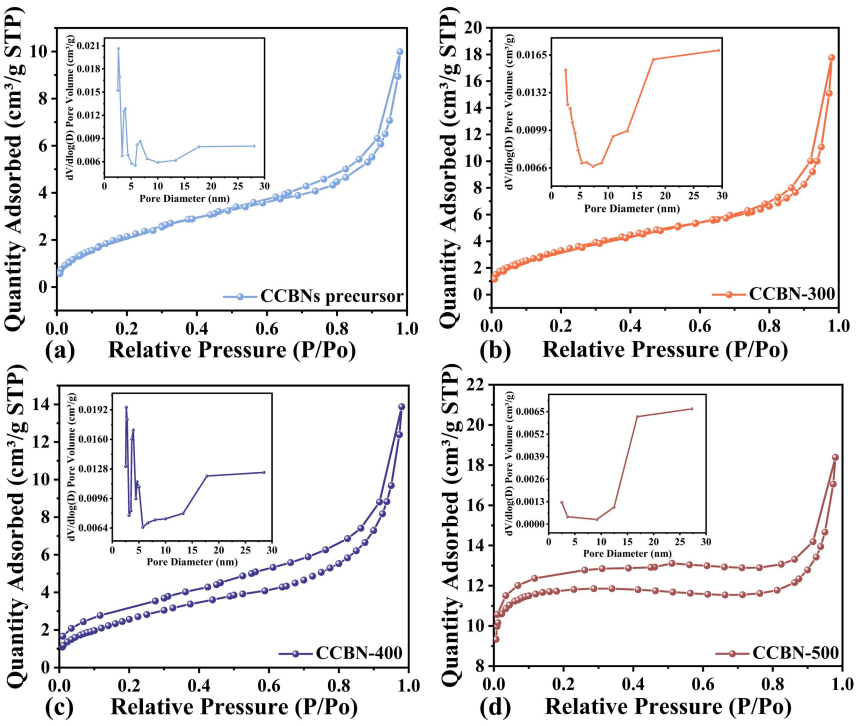

Figure S1. BET of (a) CCBN precursor, (b) CCBN-300, (c) CCBN-400 and (d) CCBN-500.

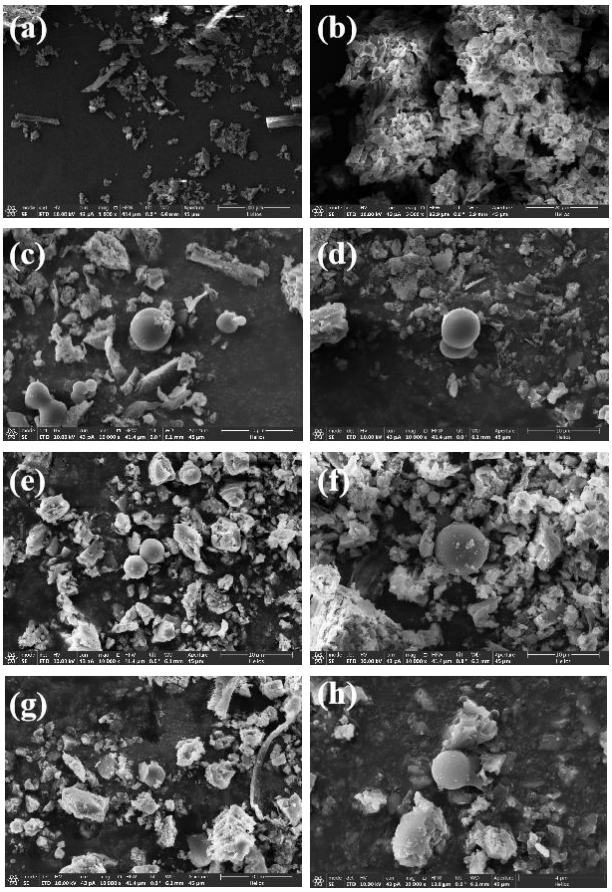

Figure S2. SEM of (a) & (b) CCBN precursor, (c) & (d) CCBN-300, (e) & (f) CCBN-400 and (g) & (h) CCBN-500.

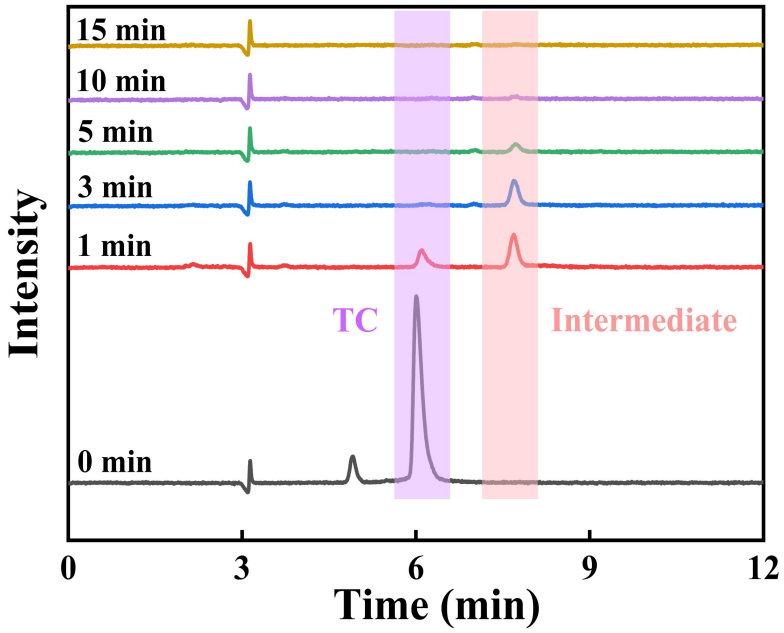

Figure S3. HPLC spectrum of TC degradation over CCBN-400/PMS system.

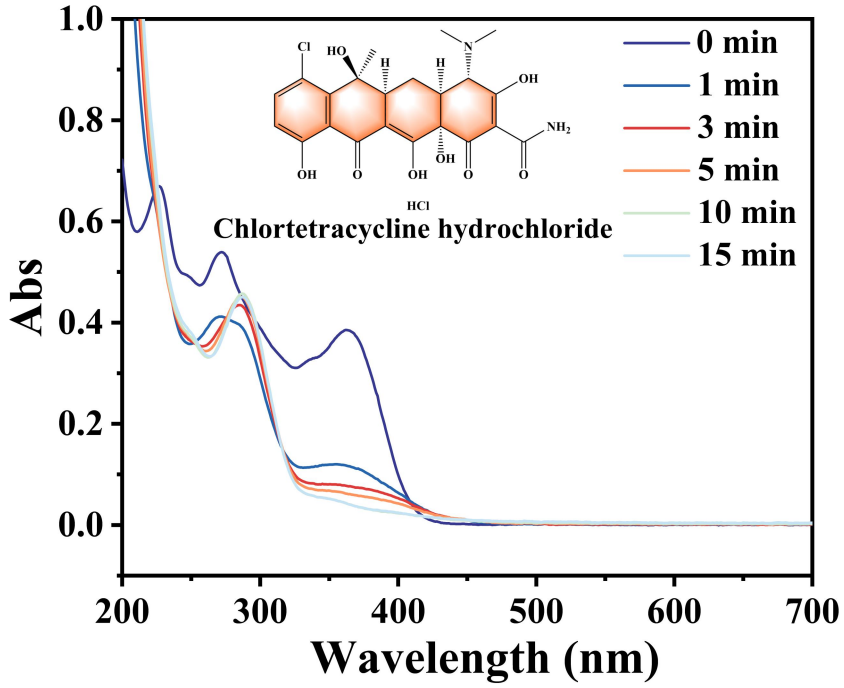

Figure S4. CTC degradation over CCBN-400/PMS.

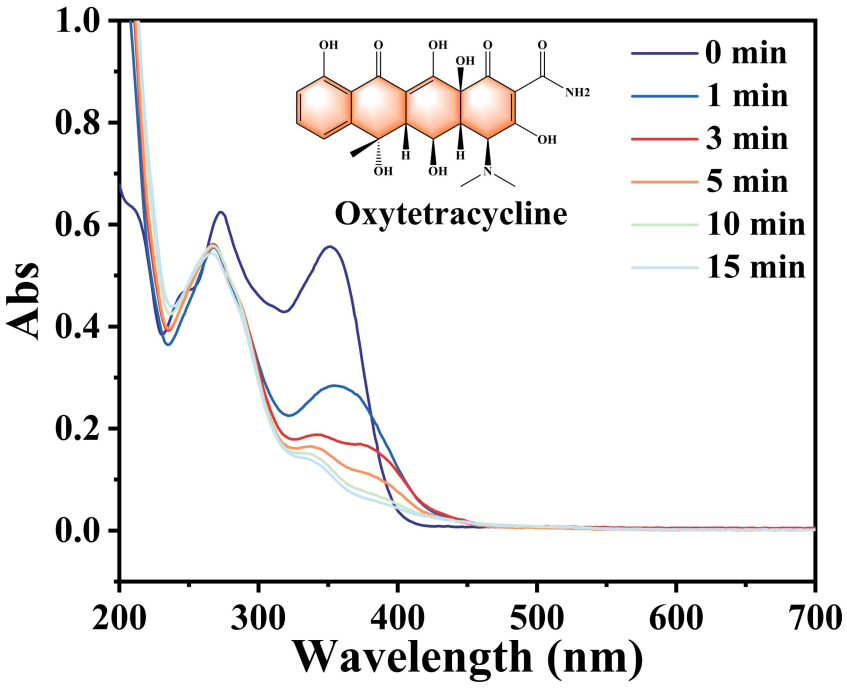

Figure S5. OTC degradation over CCBN-400/PMS.

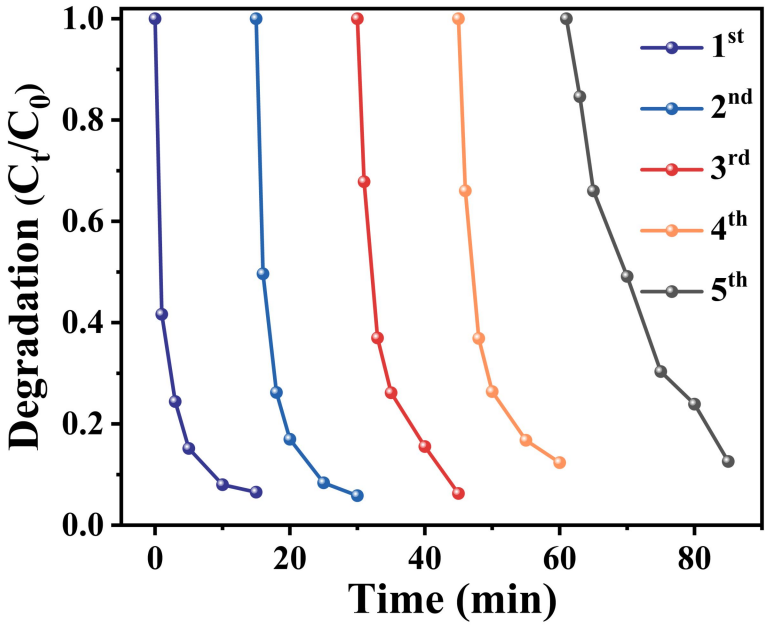

Figure S6. Stability of CCBN-400 in TC degradation. Condition: 20 mg/L of TC, 0.1 g/L of PMS and 0.5 g/L of CCBN-400 at 30 ºC.

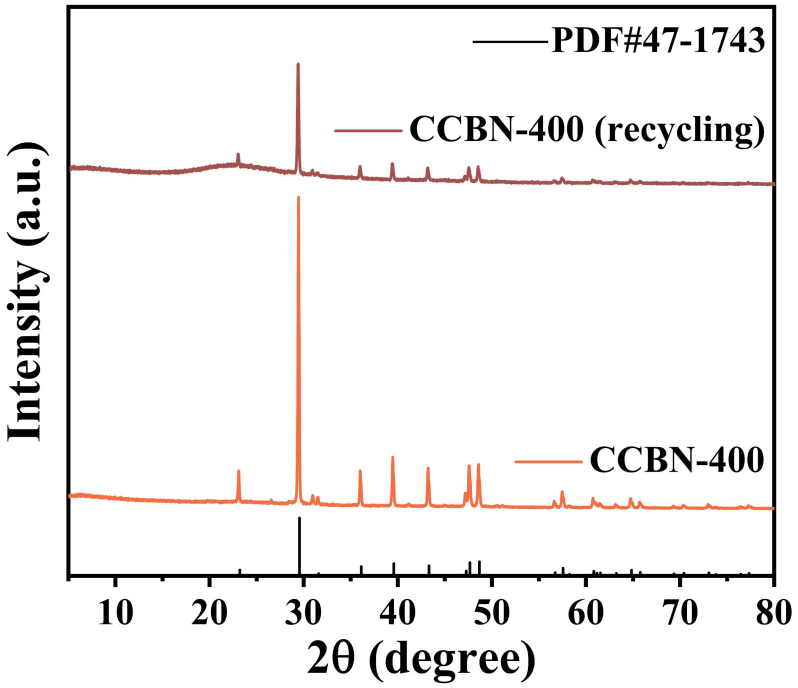

Figure S7. XRD of 5th reused CCBN-400.

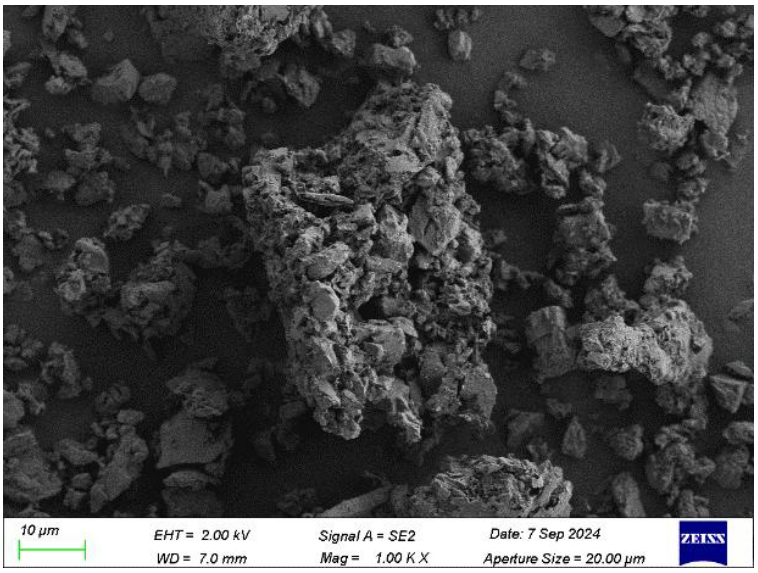

Figure S8. SEM of 5th reused CCBN-400.

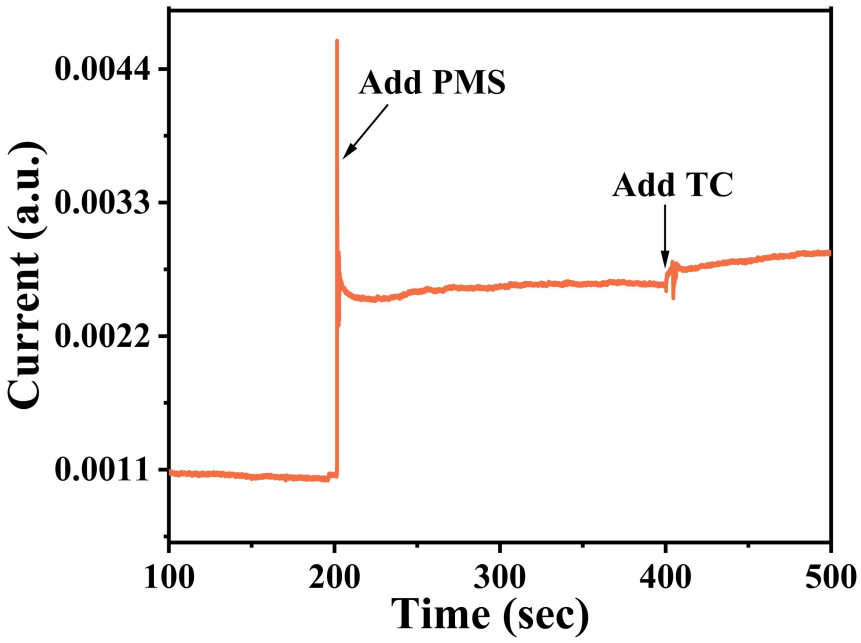

Figure S9. Chronoamperometry study of CCBN-400 for current response with injection of PMS and TC.

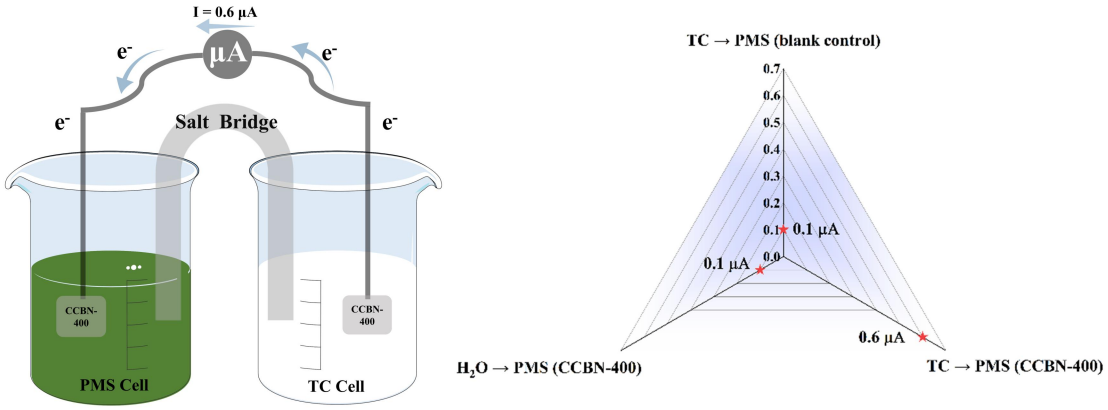

Figure S10. A GOP system setup with PMS and TC were present separately in the two half cells, and current flowing from the TC cell to the PMS cell in the GOP system.

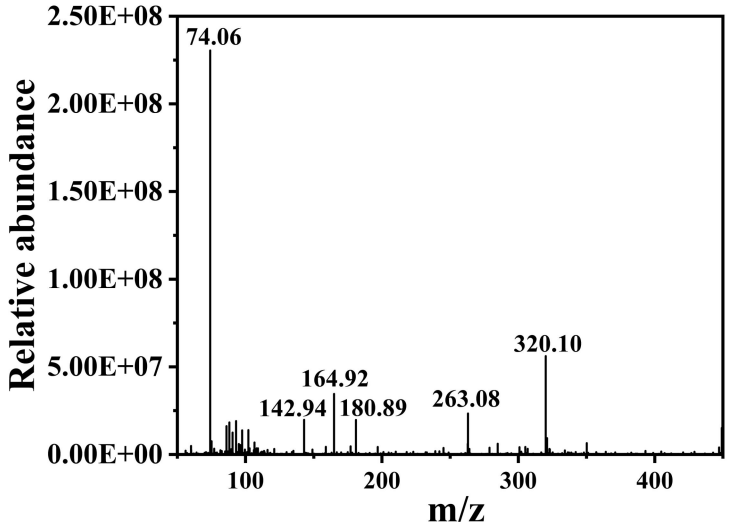

Figure S11. The HR-MS of degraded TC solution.

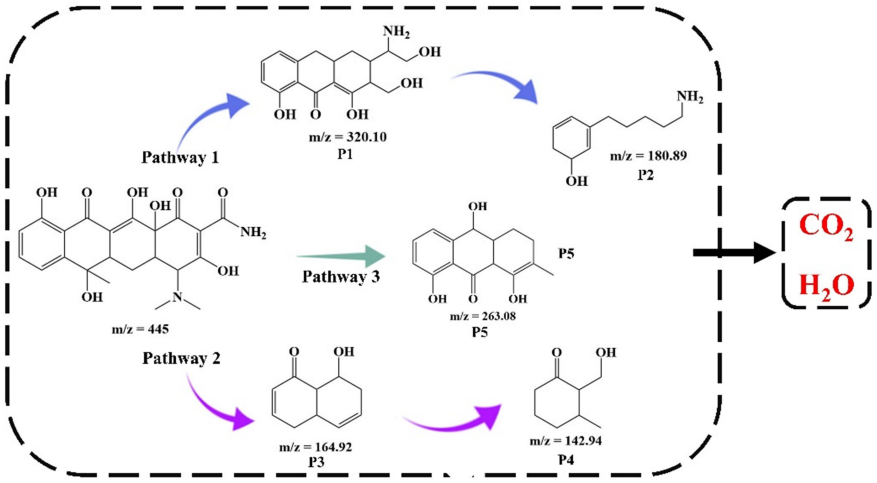

Figure S12. Proposed TC degradation pathways over CCBN-400/PMS system

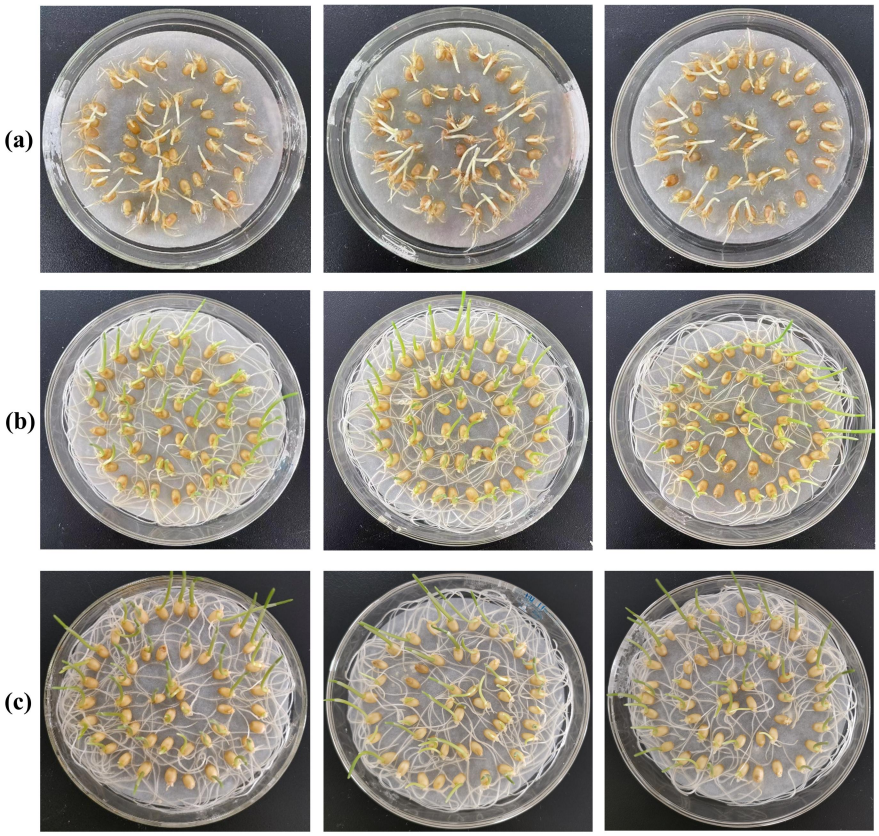

Figure S13. Phenotype of representative wheat seeds cultivated by (a) TC aqueous solution (40 mg/L), (b) degraded TC aqueous solution, and (c) deionized water at 3 days.

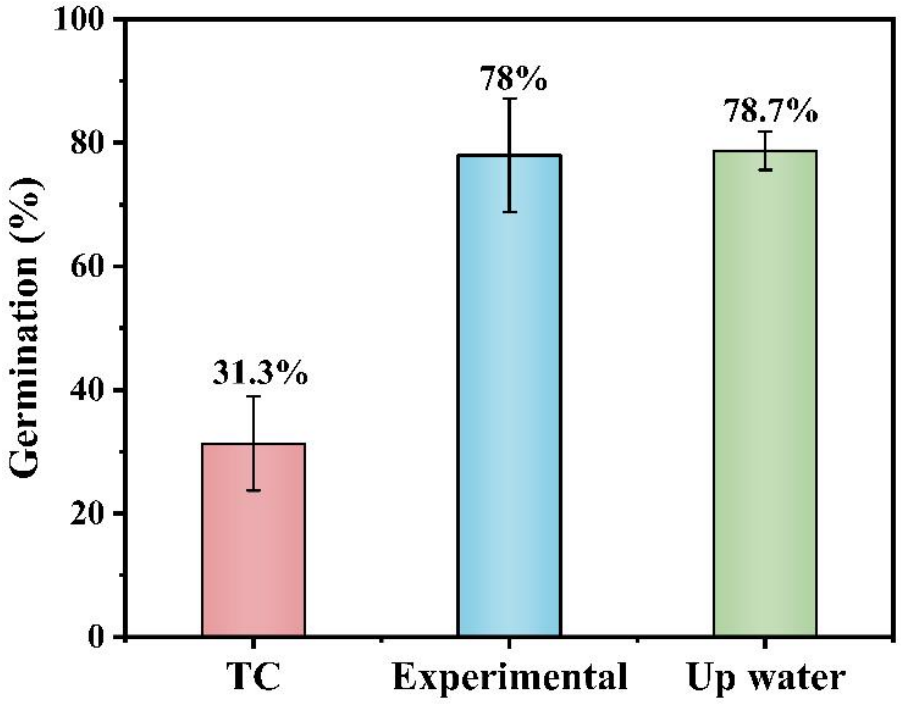

Figure S14. Germination of wheat seeds treated by TC solution, degraded TC solution and up water at 3 days.

Table S1. The degradation performance of CCBN-400/PMS with other systems for TC degradation

Catalyst	Pollutant (TC)	Reactant conditions	Time (min)	Degradation efficiency (%)	Ref.
CCBN-400	20 mg/L	[Catalyst] = 0.5 g/L [PMS] = 0.1 g/L	15	95.00	This work
Co_3O_4/CPANI	20 mg/L	[Catalyst] = 0.15 g/L [PMS] = 0.15 g/L	40	92.11	[S1]
Fe/Co-CNS-2	20 mg/L	[Catalyst] = 0.1 g/L [PMS] = 0.2 g/L	30	93.34	[S2]
Fe_3O_4/sep-70%	20 mg/L	[Catalyst] = 0.4 g/L [PMS] = 2.0 mM	60	90.12	[S3]
0.4 O–C_3N_4	20 mg/L	[Catalyst] = 0.2 g/L [PMS] = 4.0 mM	120	89.94	[S4]
CG@ZIF-67	20 mg/L	[Catalyst] = 0.1 g/L [PMS] = 1.0 mM	30	96.3	[S5]
D-FeTiO3/C	20 mg/L	[Catalyst] = 0.15 g/L [PMS] = 0.2 g/L	120	90	[S6]

Reference:

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[S6] X. Luo, L. Zhang, X. Gong, Y. Liu, J. Tian, Defect-enriched ilmenite-type catalyst derived from titanium dioxide slag for peroxymonosulfate activation in efffcient tetracycline removal, Chem. Eng. Sci., 2023, 280, 119068.