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Carbon nanotube as a nanocatalyst and nanoreactor for efficient treatment of actual pharmaceutical wastewater *via* $CaSO_3$ activation

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1. **Materials.**

The chemicals are used without further purification. The deionized water was prepared in the laboratory. Carbon nanotubes (CNTs) was purchased from 3A Materials Co., Ltd; Sodium sulfite ($NaSO_3$) was purchased from Aladdin chemical reagent Co., Ltd; Calcium sulfite ($CaSO_3$) was purchased from Aladdin chemical reagent Co., Ltd; Tetracycline (TC), Humic acid (HA), Sodium bicarbonate ($NaHCO_3$), Sodium bisulfite ($NaHSO_3$) and Tert-Butanol (TBA) were purchased from Shanghai Macklin Biochemical Co., Ltd; Oxytetracycline (OTC) and Chlortetracycline (CTC) were purchased from Dr. ehrenstorfer Co., Ltd; Perchloric acid was purchased from Chron Chemicals Co., Ltd; Sodium hydroxide (NaOH) and Sodium chloride (NaCl) were purchased from Kermel Co., Ltd; Sodium dihydrogen phosphate dihydrate (NaH_2PO_4) was purchased from Shanghai Hushi Co., Ltd; Sodium nitrate ($NaNO_3$) was purchased from Innochem Co., Ltd; Furfuryl alcohol (FFA) was purchased from Rhawn Reagent Co., Ltd. Silver nitrate ($AgNO_3$) was purchased from Sigma Aldrich Co., Ltd.

2. Characterization

Transmission electron microscopy (TEM) was performed with a JEOL jem-f200 microscope operated. The morphologies of the catalysts were observed by scanning electron microscopy (SEM, JSM-7500F). X-ray diffraction (XRD) analyses were measured on a SmartLab. X-ray photoelectron spectrometry (XPS) was performed on a AXIS Supra. Electron paramagnetic resonance (EPR) spectroscopy was conducted on a Bruker A300. Fourier transform infrared spectrometer (FT-IR) were measured on Frontier NIR. Raman was performed on a Thermo Scientific DXR . High resolution mass spectrum (HR-MS) was measured on a Q Exactive. UV-vis was tested by PerkinElmer Lambda 25.

3. Experimental Procedures.

In a typical procedure, 2 mg of $CaSO_3$ had been added into TC solution (20 mg/L, 40 mL) in a test tube at 30 °C. Then, TC degradation was activated by adding CNT (8 mg). During the reaction, a 3 mL of reaction solution had been extracted out at determined intervals. It was filtered by 0.22 μm film, and immediately tested by UV-vis. In the quenching experiments, TBA, EtOH, FFA and $CHCl_3$, respectively, was injected into the reaction medium, and the TC degradation was carried out at the same condition. Cycle experiment: The CNT was collected by the simple filtration, washed with hydrochloric acid solution for next cycle.

The degradation rate was calculated as:

Degradation rate (%) = $\frac{C_0-C_t}{C_0} \times 100\%$

where C_0 and C_t are the initial and final pollutant concentration determined on UV absorbance value.

4. Seed germination experiments

Seeds of wheat were collected from the local market. The seeds (50) were placed on each Petri dish. A piece of suitably sized filter paper was put into it. Five mL of TC (50 mg/L of TC) and an TC degraded aqueous solution (50 mg/L of TC, 0.5 g/L of CNT and 0.125 g/L of $CaSO_3$ at 30 °C) was added into the petri dish, respectively. The seed contained in petri dishes were incubated in the dark at 25 °C for 3 days. The control group was treated with distilled water. Afterward, distilled water (2 mL) was added daily to maintain sufficient moisture content for germination and the germination percentage was recorded. All tests were repeated three times.

5. **Catalytic performance and Physical characterization of nanocatalysts (Fig. S1-S9)**

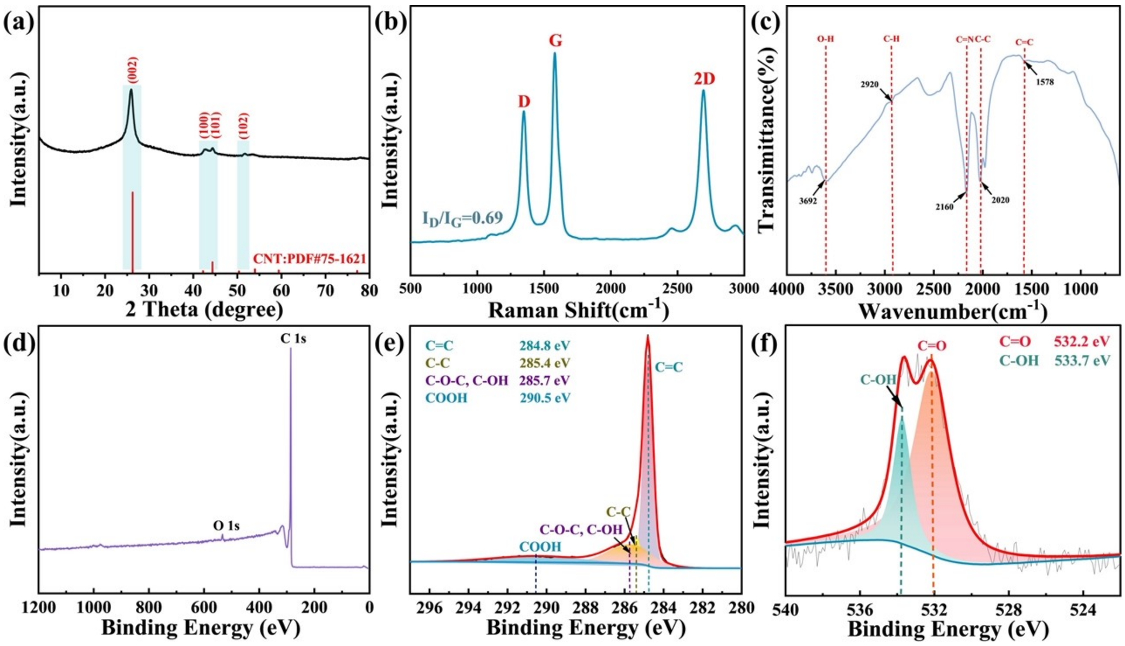

Figure S1. (a) XRD, (b) Raman spectra, (c) FT-IR, (d) Sum, (e) C 1s and (f) O 1s XPS of CNTs.

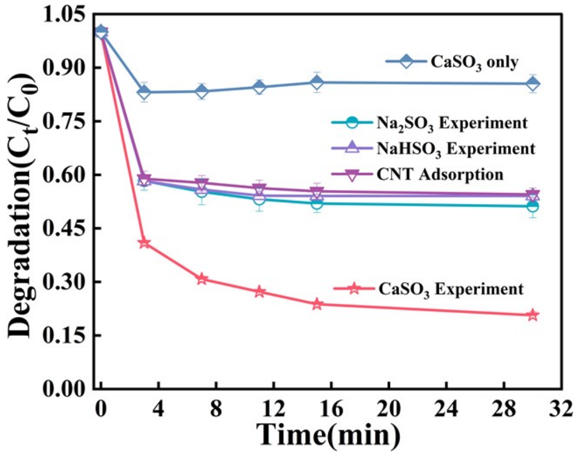

Figure S2. TC adsorption by only CNT, degradation by only $CaSO_3$ and comparison of TC degradation catalyzed by CNT with $CaSO_3$, Na_2SO_3 and $NaHSO_3$. respectively. Reaction Conditions: 0.2 g/L of CNTs, 0.05 g/L of sulfites and 20 mg/L of TC at 30 ℃.

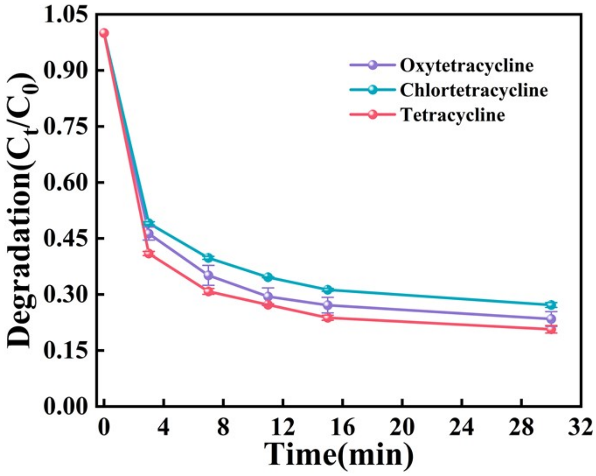

Figure S3. CNT catalyzed degradation of CTC, OTC, and TC *via* $CaSO_3$ activation. Reaction Conditions: 0.2 g/L of CNTs, 0.05 g/L of sulfites and 20 mg/L of pollutants at 30 ℃.

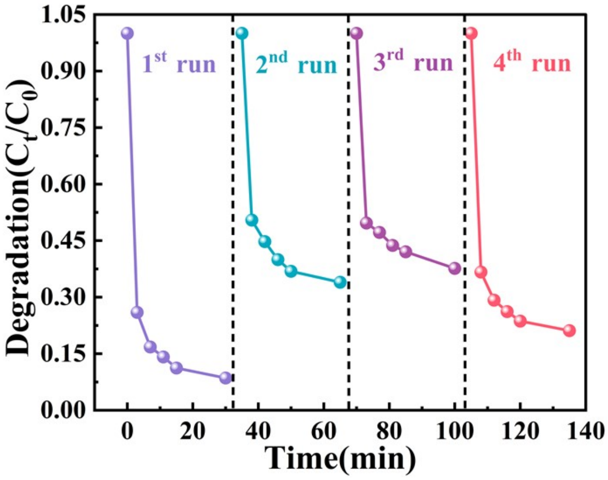

Figure S4. Stability of CNT in TC degradation. Reaction Conditions: 0.3 g/L of CNTs, 0.05 g/L of sulfites and 20 mg/L of TC at 30 ℃.

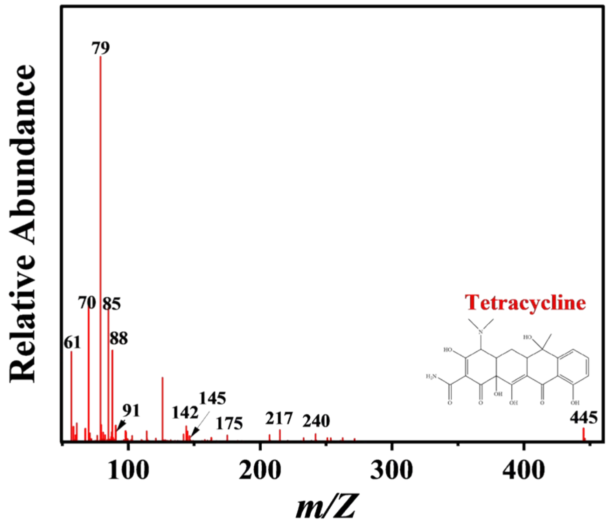

Figure S5. HR-MS of degraded TC solution

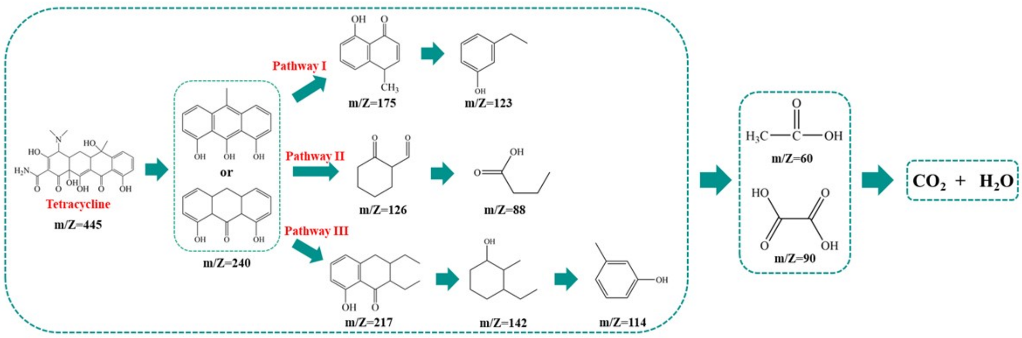

Figure S6. The possible TC degradation pathways over CNTs/$CaSO_3$ system.

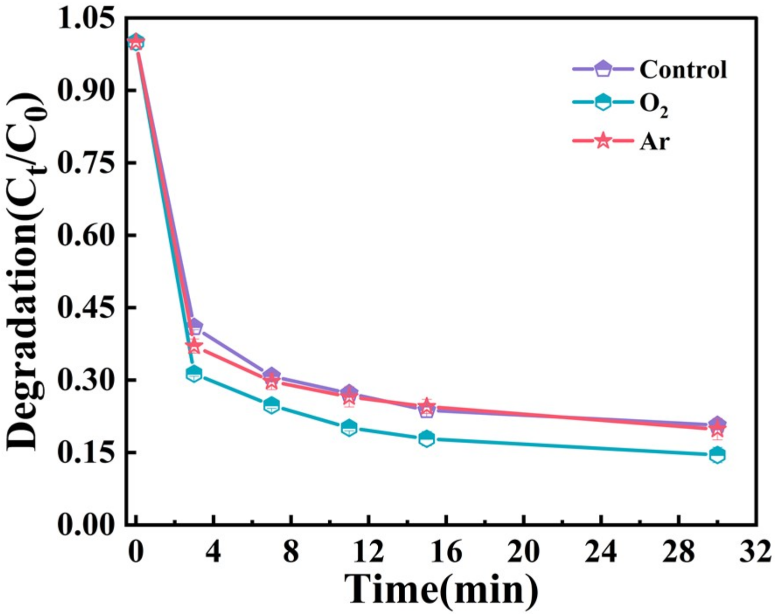

Figure S7. TC degradation was carried out at air and O_2 atmosphere, respectively. Reaction Conditions: 0.2 g/L of CNTs, 0.05 g/L of sulfites and 20 mg/L of TC at 30 °C.

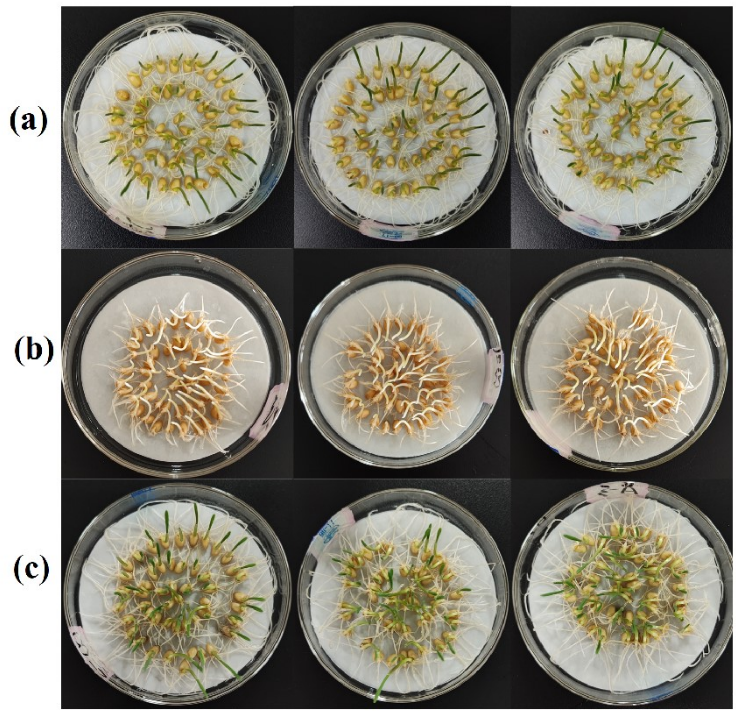

Figure S8. Photographs of wheat seeds with (a) ultrapure water, (b) TC aqueous solution (50 mg/L) and (c) degraded TC aqueous solution under 3 days.

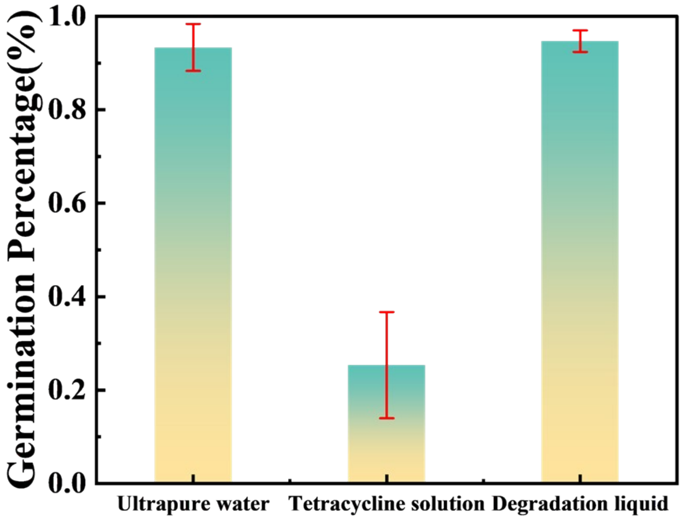

Figure S9. Germination rate of wheat seeds treated with (a) ultrapure water, (b) TC aqueous solution (50 mg/L) and (c) degraded TC aqueous solution under 3 days.

Table S1. Comparison of the catalytic activity of CNT/$CaSO_3$ system with other reported catalytic systems for TC degradation.

Entry	$C_{(TC)}$ (mg/L)	Catalyst (g/L)	Oxidant	Another additive	Degradation efficiency	Time/min	Ref.
1	**20**	**CNT (0.2)**	**$CaSO_3$ (0.05 g/L)**	**—**	**80%**	**30**	**This work**
2	50	CB (0.05)	PDS (1 g/L)	pH=5	52%	40	S1
3	20	P-C_3N_4 (0.2)	PMS (6 mM)	—	77%	60	S2
4	20	F, N-CM (0.02)	PMS (0.1 g/L)	—	80%	60	S3
5	20	SSB1000 (1)	PS (6 mM)	—	100%	15	S4
6	10	40% C-BN (0.6)	PMS (0.8 g/L)	pH=7	99%	45	S5
7	20	CNC (0.25)	PS (2 mM)	Light	82%	60	S6
8	15	BC-OH-700 (0.2)	PMS (1 mM)	pH=7	100%	60	S7
9	10	MCHS (0.01)	PS (0.5 mM)	—	95%	180	S8
10	10	N/O-C-8 (0.1)	PDS (0.18 mM)	—	100%	30	S9
11	20	BCNT-5 (0.2)	PMS (0.5 mM)	—	78%	180	S10
12	100	CCBC (0.2)	PDS (1 g/L)	—	83%	180	S11
13	10	Fe (IV) (0.0075)	$CaSO_3$ (100 μM)	pH=7	100%	0.5	S12
14	20	Co_3Cu_1-LDHs (0.1)	$CaSO_3$ (2 mM)	—	90%	60	S13

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