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Supporting Information

Efficient degradation of tetracycline via peroxymonosulfate activation by phosphorus-doped biochar loaded with cobalt nanoparticles

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Text S1. Chemicals and reagents

Sunflower seeds were purchased from a supermarket in Taiyuan, Shanxi province. After cleaning the sunflower husks with tap water, deionized water was added and heated at 80 ℃ for 4 h. After cooling, the husks were left submerged for 12 h to remove the residual chemicals. Subsequently, the soaked husks were placed in an oven at 60 ℃ for drying, followed by grinding through a 60 mesh sieve, and the ground husk was collected for later use. All the chemicals were of high-purity grade; therefore, there was no need for further purification before use. PMS ($KHSO_5$ Å 0.5 $KHSO_4$ Å 0.5 K_2SO_4), TCH, tert butanol (TBA), p-benzoquinone (p-BQ) L-histidine (L-His), H_2SO_4, NaOH, and other raw materials were sourced from Aladdin Corporation, China. Other chemicals, including hexahydrate and cobalt nitrate, 5,5-dimethyl-1-pyrroline N-oxide (DMPO), 2,2,6,6-tetramethylpiperidine, chromatographically pure methanol, ethanol, and acetonitrile were purchased from China National Pharmaceutical Chemical Reagent Co., Ltd. Deionised water was used throughout the study.

Text S2. Characterizations

The morphology and structure of Co NP-PBC were analysed in detail using a FEI Talos F200S transmission electron microscopy (TEM). The surface chemical composition and elemental composition of Co NP-PBC were determined by X-ray photoelectron spectroscopy (XPS) on a Thermo Scientific K-Alpha+ XPS spectrometer. The defect structures of BC, PBC, and Co NP-PBC were determined

using a HORIBA LabRAM HR Evolution Raman spectrometer. The electrochemical measurements were performed using a CHI 660E workstation. Intermediate TCH was detected using High performance liquid chromatography tandem mass spectrometry (HPLC-MS). Electron paramagnetic resonance (EPR) spectroscopy was used to detect the free radicals in the Co NP-PBC/PMS system. Toxicity analysis software (TEST version 5.1.2) was used to assess the risk of developing TC and its intermediates.

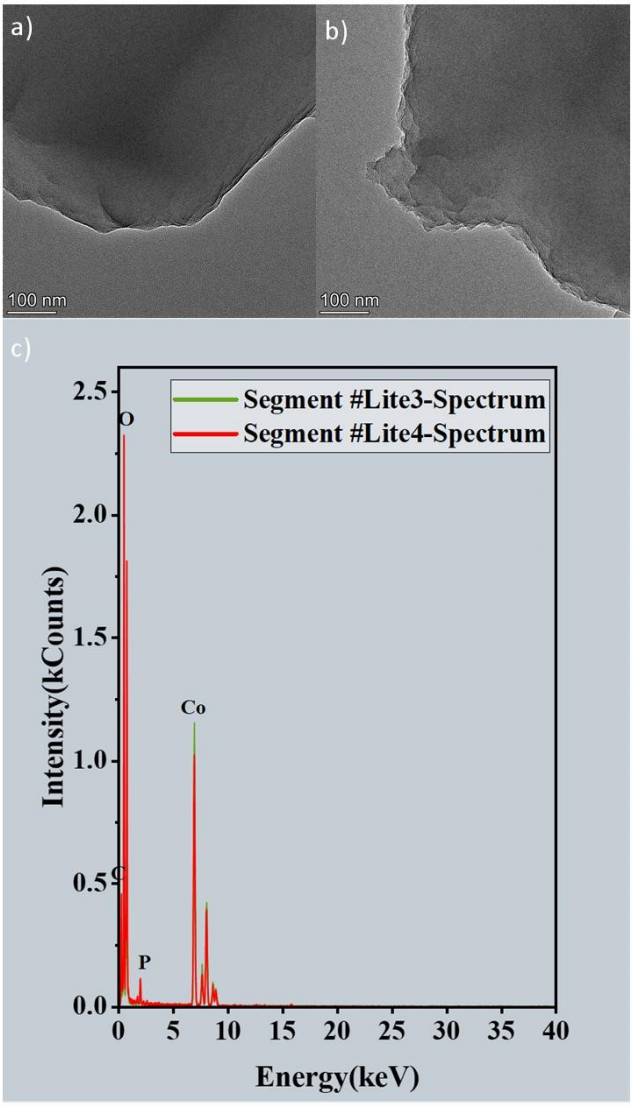

Fig. S1. (a) TEM of BC, (b) TEM of PBC

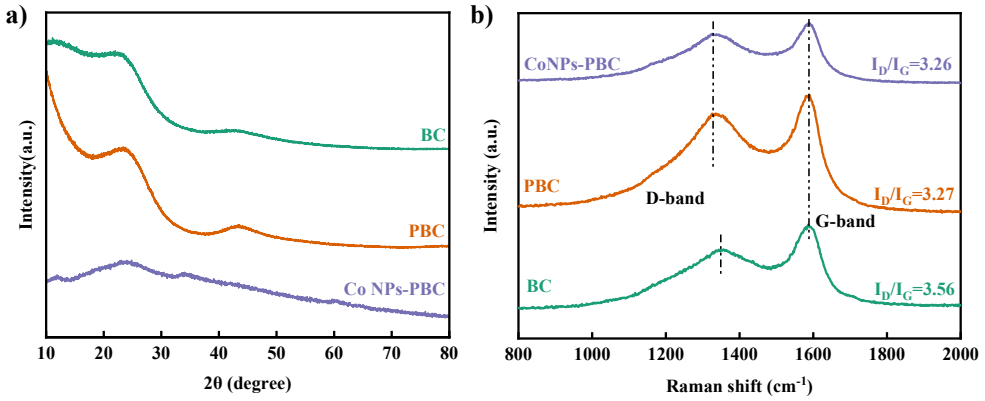

Fig. S2. (a) XRD of BC, PBC, Co NP-PBC; (b) Raman spectra of BC, PBC, Co NP-PBC

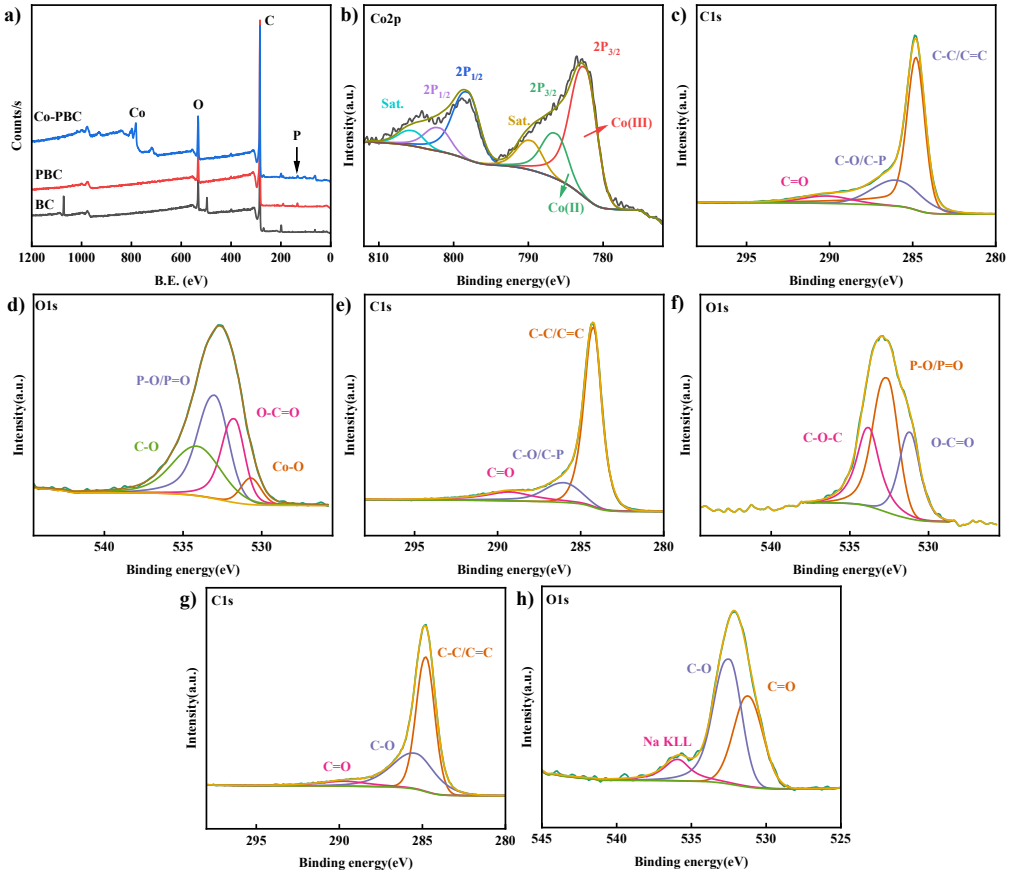

Fig. S3. (a) Total XPS spectra of BC, PBC, and Co NPs-PBC (b-d) Co 2p, C1s, and O1s spectra of Co NP-PBC (e-f) C1s, and O1s spectra of PBC; (g-h) C1s, and O1s spectra of BC

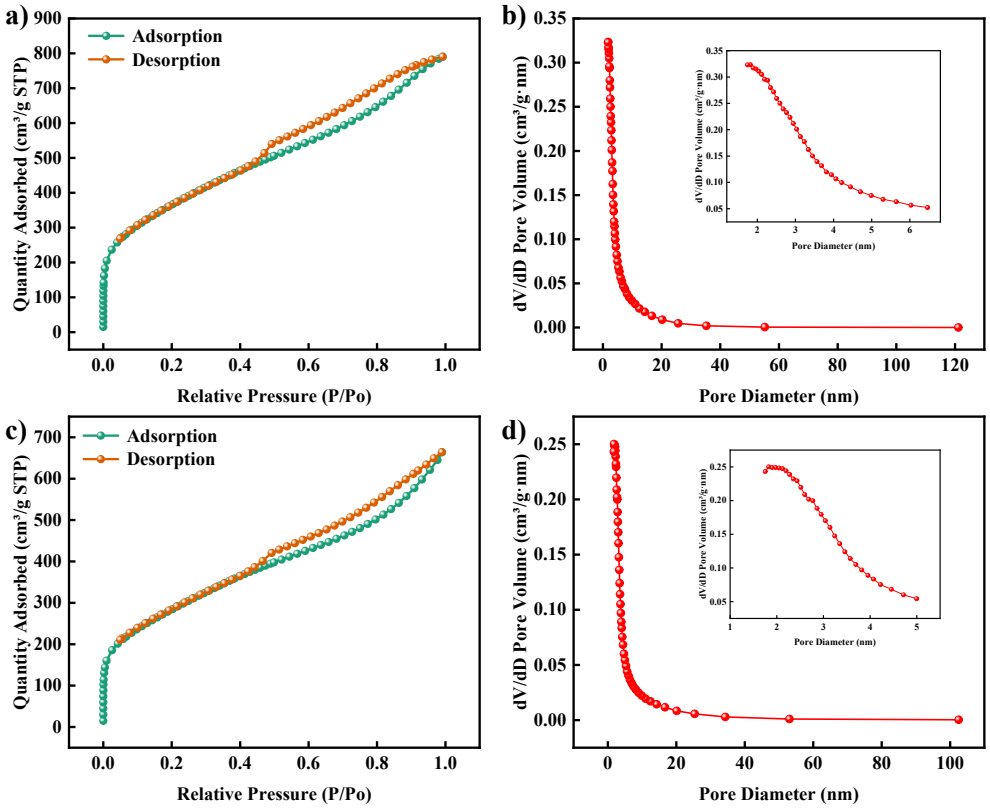

Fig. S4. N_2 adsorption desorption curves and pore size distributions for (a,b) PBC, (c,d) Co NP-PBC catalysts.

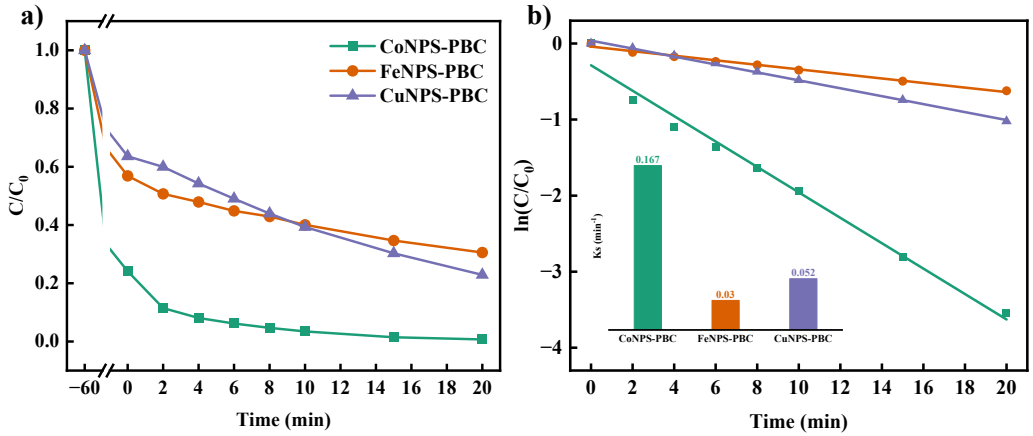

Fig. S5. (a) The degradation efficiency of TCH and (b) its corresponding reaction kinetics coefficients by catalysts loaded with different metals.

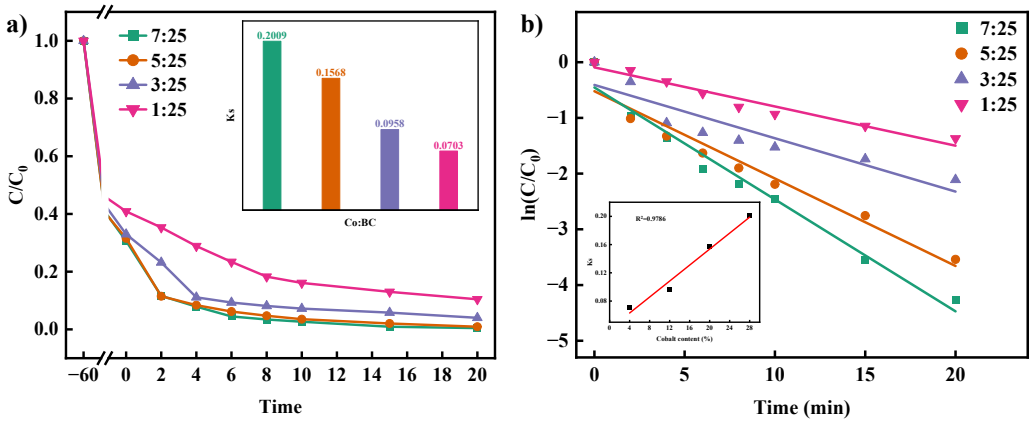

Fig. S6. (a) The effect of different cobalt doping on the degradation efficiency of TCH and its reaction kinetic parameters, (b) Fitting of first-order reaction kinetic parameters of cobalt with different doping amounts and correlation between cobalt dosage and reaction kinetic parameters

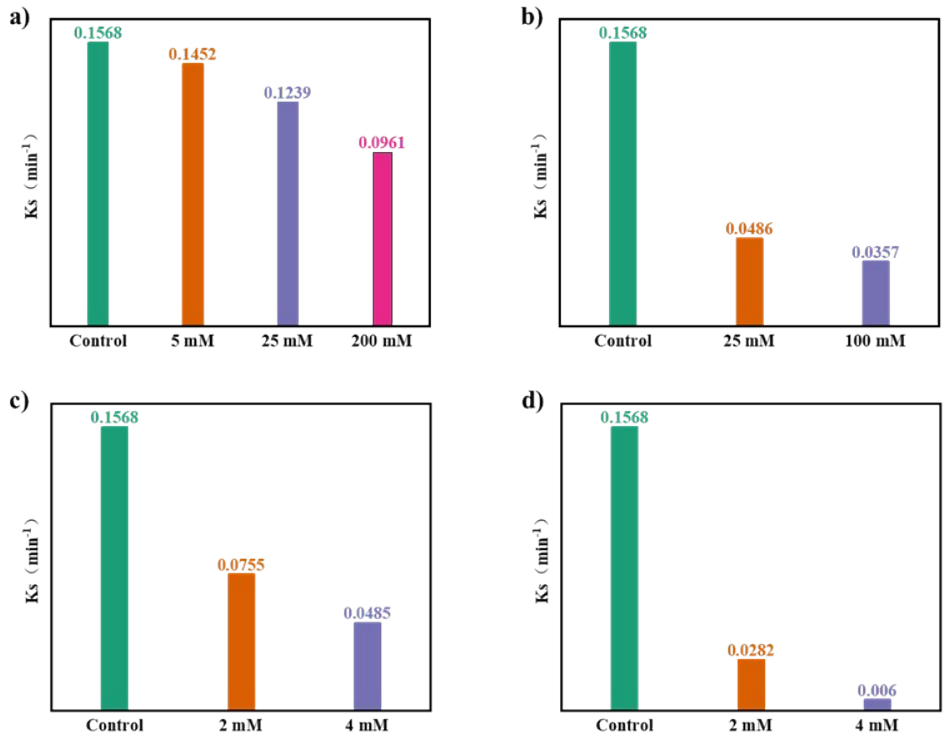

Fig. S7. Effects of different kinds of quenching agents on the first-order reaction kinetic coefficients of TCH degradation, (a) MeOH, (b) TBA, (c) p-BQ, (d) L-his.

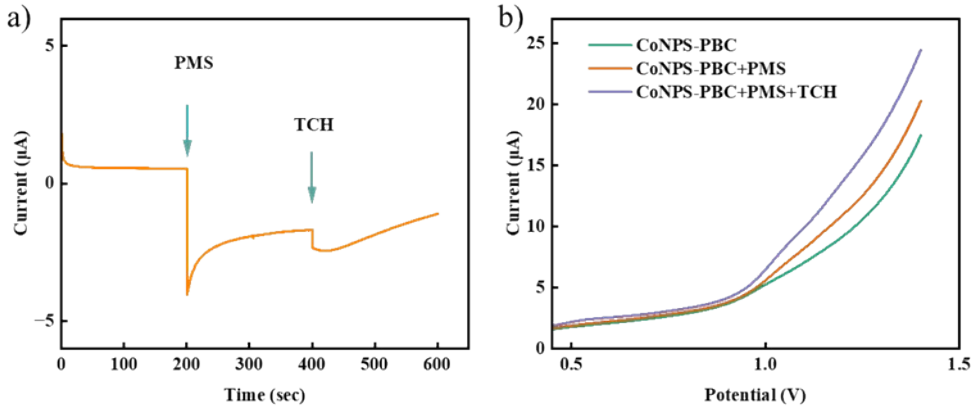

Fig. S8. (a) Current response of PMS and TCH added to Co NPs-PBC/PMS system, (b) LSV under different conditions

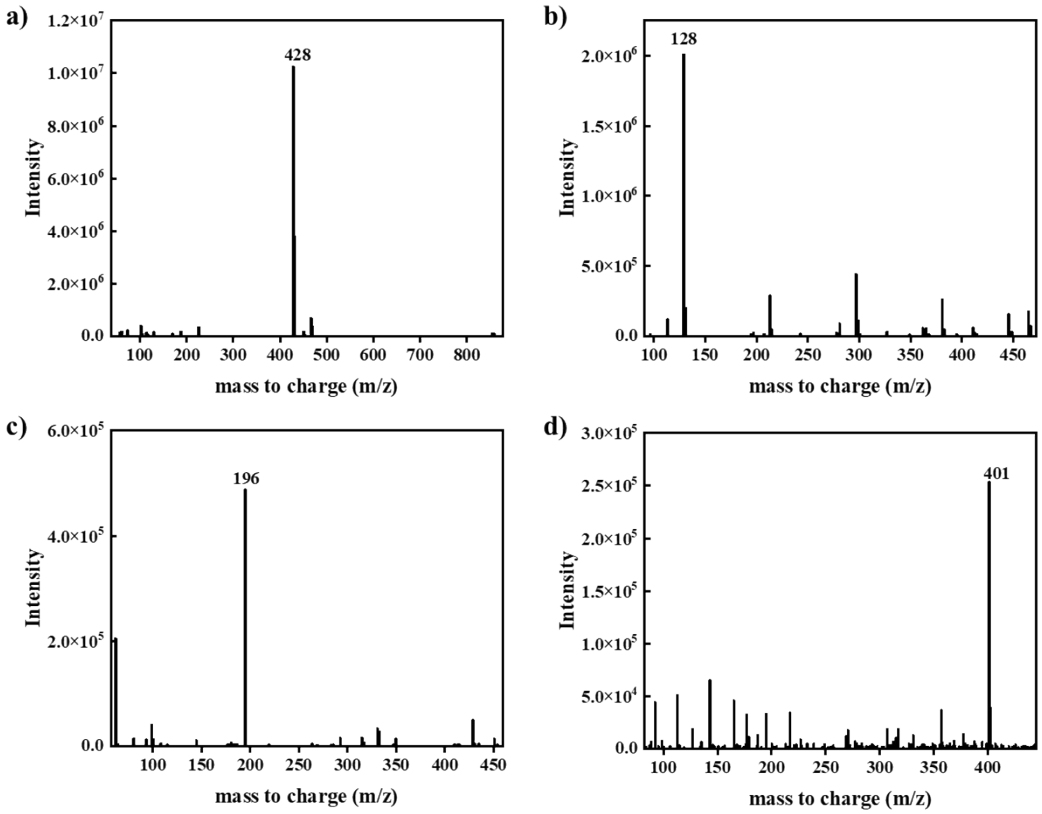

Fig. S9. The m/z and retention time of TCH degradation intermediates

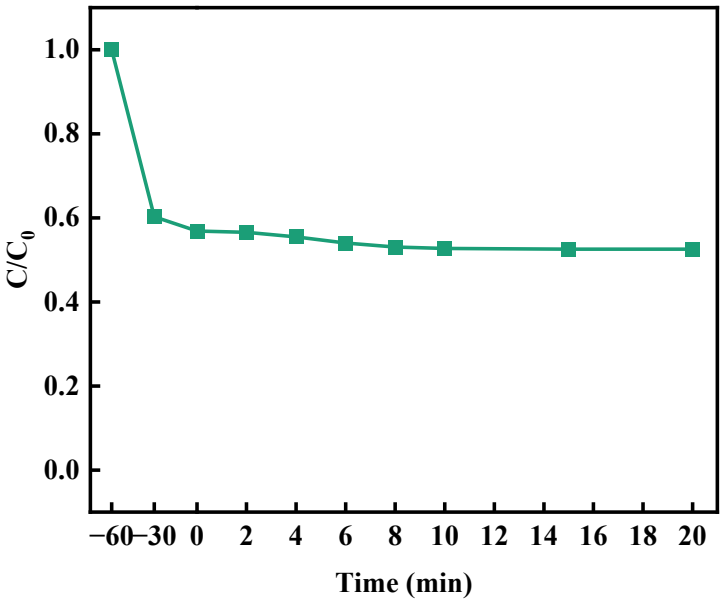

Fig. S10. Co NPs-PBC reuse degradation of TCH.

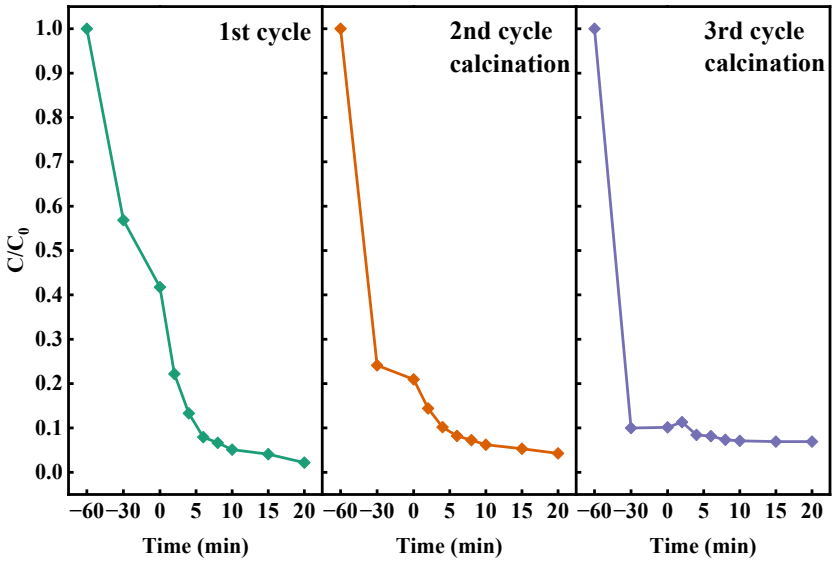

Fig. S11. Reusability Experiment of CPBC.

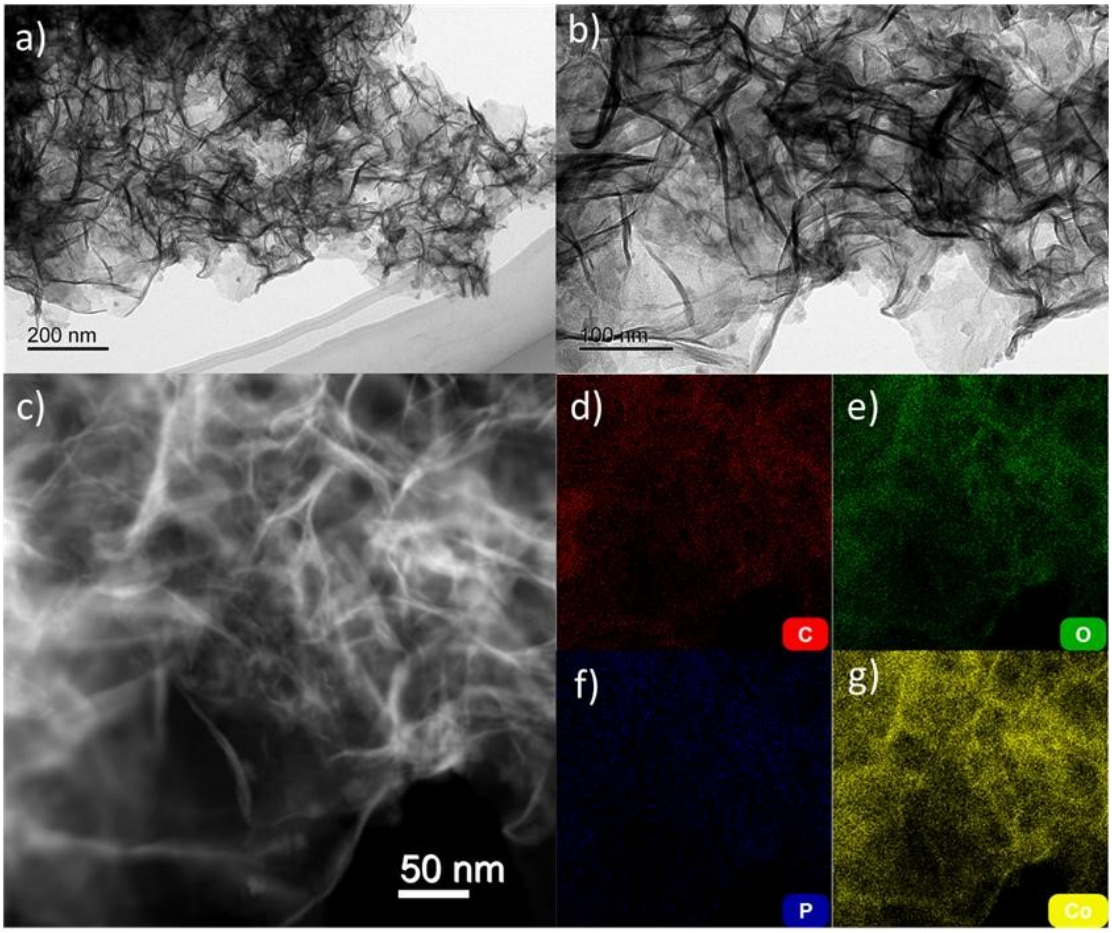

Fig. S12. TEM of CPBC after three cycles

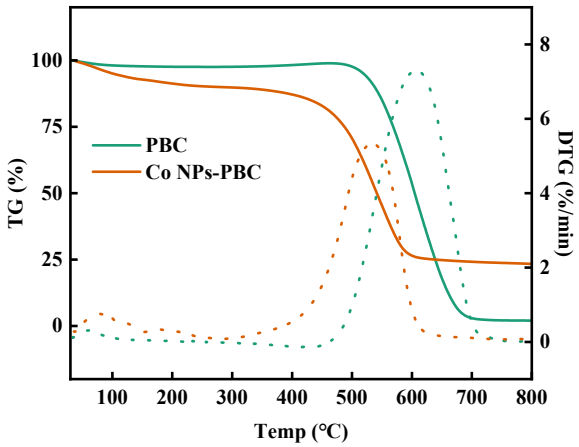

Fig. S13. Thermogravimetry of PBC, Co NP-PBC

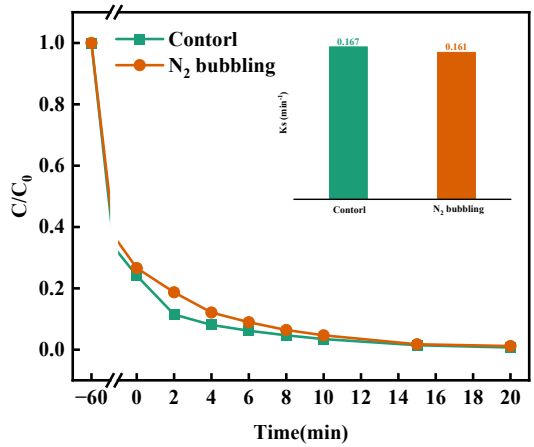

Fig. S14. Degradation of TCH under different gas conditions

Table. S1. Condensed Fukui Function of TCH

Atom	q(N)	q(N+1)	q(N-1)	f -	f 0
1(O)	-0.2184	-0.2478	-0.2121	0.0064	0.0178
2(O)	-0.2072	-0.2193	-0.2012	0.0060	0.0091
3(O)	-0.2307	-0.3044	-0.2092	0.0214	0.0476
4(O)	-0.1719	-0.1864	-0.1422	0.0296	0.0221
5(O)	-0.1557	-0.2171	-0.1363	0.0194	0.0404
6(O)	-0.2491	-0.2801	-0.1980	0.0511	0.0411
7(O)	-0.1718	-0.1961	-0.1478	0.0240	0.0242
8(O)	-0.3112	-0.3388	-0.2342	0.0770	0.0523
9(N)	-0.1019	-0.0994	0.0114	0.1133	0.0554
10(N)	-0.1548	-0.1628	-0.1244	0.0303	0.0192
11(C)	-0.0204	-0.0217	-0.0203	0.0001	0.0007
12(C)	-0.0248	-0.0279	-0.0208	0.0040	0.0035
13(C)	-0.0539	-0.0562	-0.0503	0.0036	0.0029
14(C)	0.0757	0.0654	0.0753	-0.0004	0.0049
15(C)	0.0131	0.0105	0.0248	0.0117	0.0072
16(C)	0.0901	0.0882	0.0906	0.0005	0.0012
17(C)	-0.0596	-0.0808	-0.0385	0.0211	0.0212
18(C)	0.1228	0.0380	0.1247	0.0020	0.0434
19(C)	0.0918	0.0927	0.1132	0.0214	0.0103
20(C)	0.0156	-0.0159	0.0176	0.0020	0.0167
21(C)	0.1388	0.1318	0.1449	0.0061	0.0066
22(C)	0.1270	0.0484	0.1395	0.0125	0.0455
23(C)	-0.0538	-0.0754	-0.0324	0.0214	0.0215
24(C)	-0.0279	-0.0397	-0.0177	0.0102	0.0110
25(C)	-0.0911	-0.0988	-0.0865	0.0046	0.0062
26(C)	-0.0485	-0.0740	-0.0283	0.0201	0.0228
27(C)	-0.0442	-0.0477	-0.0184	0.0258	0.0146
28(C)	-0.0433	-0.0479	-0.0202	0.0231	0.0138
29(C)	0.0942	0.0619	0.1122	0.0180	0.0251
30(C)	0.1613	0.1553	0.1801	0.0188	0.0124
31(C)	-0.0182	-0.0810	0.0061	0.0244	0.0436
32(C)	-0.0663	-0.0972	-0.0499	0.0164	0.0236

Table. S2. Laplace Bond Order of TCH.

Bond	Laplace Bond Order	Bond	Laplace Bond Order
1 O — 14 C	0.3398	14 C — 18 C	0.9686
2 O — 16 C	0.3453	14 C — 19 C	0.9675
3 O — 18 C	0.8591	15 C — 21 C	1.0855
4 O — 19 C	0.5922	16 C — 20 C	1.059
5 O — 22 C	0.6429	16 C — 25 C	0.979
6 O — 21 C	1.1032	17 C — 18 C	1.4445
7 O — 29 C	0.533	17 C — 22 C	1.5066
8 O — 30 C	1.0542	19 C — 23 C	1.6892
9 N — 15 C	0.6945	20 C — 24 C	1.3538
9 N — 27 C	0.7445	20 C — 26 C	1.5397
9 N — 28 C	0.7379	21 C — 23 C	1.2215
10 N — 30 C	1.2373	22 C — 24 C	1.2663
11 C — 13 C	0.9229	23 C — 30 C	1.1058
11 C — 14 C	0.9496	24 C — 29 C	1.4141
11 C — 15 C	0.934	26 C — 31 C	1.5347
12 C — 13 C	0.9663	29 C — 32 C	1.5507
12 C — 16 C	0.9201	31 C — 32 C	1.5865
12 C — 17 C	1.004		

Table. S3. Toxicity Analysis of Different Intermediates.

Number	Oral rat LD_{50} mg/kg	Developmental toxicity		Mutagenicity		Bioconcentr-ation factor
		Predicted value	Predicted result	Predicted value	Predicted result	
TCH-444	1524.04	0.86	Developmental toxicant	0.60	Mutagenicity Positive	0.71
A1-401	1043.63	0.85	Developmental toxicant	0.70	Mutagenicity Positive	0.85
A2-345	2671.47	0.77	Developmental toxicant	0.92	Mutagenicity Positive	2.30
A3-192	2145.96	0.83	Developmental toxicant	0.49	Mutagenicity Negative	N/A
A4-113	3003.45	0.68	Developmental toxicant	0.11	Mutagenicity Negative	3.11
A5-108	263.68	0.60	Developmental toxicant	0.09	Mutagenicity Negative	11.34
A6-86	946.25	0.69	Developmental toxicant	0.39	Mutagenicity Negative	N/A
A7-166	N/A	0.73	Developmental toxicant	0.22	Mutagenicity Negative	N/A
A8-239	1518.86	0.78	Developmental toxicant	0.27	Mutagenicity Negative	0.89
A9-122	776.75	0.19	Developmental non-toxicant	0.00	Mutagenicity Negative	N/A
A10-196	435.95	0.64	Developmental toxicant	0.36	Mutagenicity Negative	0.54
A11-128	3101.63	0.80	Developmental toxicant	0.21	Mutagenicity Negative	2.76
A12-428	1420.42	0.84	Developmental toxicant	0.63	Mutagenicity Positive	1.01
A13-384	918.67	0.85	Developmental toxicant	0.86	Mutagenicity Positive	1.20
A14-192	N/A	0.68	Developmental toxicant	0.64	Mutagenicity Positive	10.63
A15-169	1070.61	0.72	Developmental toxicant	0.27	Mutagenicity Negative	0.13
A16-108	263.68	0.60	Developmental toxicant	0.09	Mutagenicity Negative	11.34
A17-56	64.96	0.64	Developmental toxicant	0.51	Mutagenicity Positive	N/A