Supplementary Information (SI) for New Journal of Chemistry.

Supplementary material

$CeO_2/CuCo_2S_4$ composite for peroxymonosulfate activation to enhanced elimination of tetracycline hydrochloride

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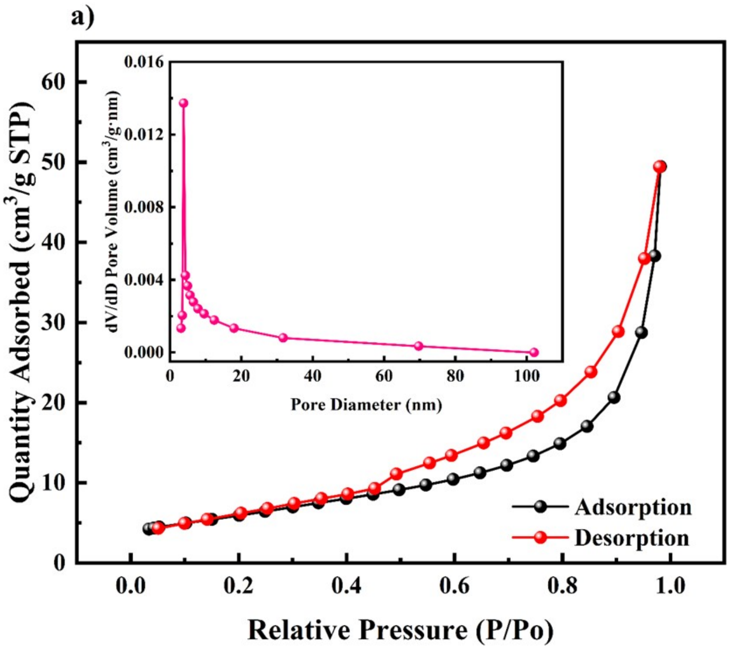
Text S1. Reagents

All chemicals used in this study were of analytical grade and used without further purification. Anhydrous citric acid ($C_6H_8O_7$), potassium peroxymonosulfate ($KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$), and L-histidine ($C_6H_9N_3O_2$) were purchased from Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Tetracycline hydrochloride (TCH, $C_{22}H_{25}ClN_2O_8$), copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), cerium(III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$), p-benzoquinone (p-BQ, $C_6H_4O_2$), potassium dihydrogen phosphate (KH_2PO_4), humic acid (HA), sodium thiosulfate ($Na_2S_2O_3$), and sodium nitrate ($NaNO_3$) were supplied by Macklin Biochemical Co., Ltd (Shanghai, China). Thiourea (CH_4N_2S), ethylene glycol ($C_2H_6O_2$), tert-butanol (TBA, $C_4H_{10}O$), ethanol (EtOH, C_2H_5OH), potassium sulfate (K_2SO_4), sodium bicarbonate ($NaHCO_3$), bisphenol A (BPA), phenol (PE), and sulfamethoxazole (SMX) were obtained from Kermel Chemical Reagent Co., Ltd (Tianjin, China). Potassium chloride (KCl) was purchased from Tianjin Guangfu Technology Development Co., Ltd (Tianjin, China). Rhodamine B (RhB) and methylene blue (MB) were provided by Guangfu Fine Chemical Research Institute (Tianjin, China). All solutions were prepared with deionized water (DIW).

Text S2. Characterization and measurement

The crystal structure of the samples was analyzed using an X-ray diffractometer (XRD, SHIMADZU X-6100, Japan). Surface morphology and elemental composition were characterized by field-emission scanning electron microscopy (SEM, JSM-7800F, Japan) coupled with energy-dispersive spectroscopy (EDS, X-Max50, UK). The chemical states of elements were compared before and after reaction using X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA), while the reaction species during the reaction were detected by electron paramagnetic resonance spectroscopy (EPR, Bruker EMXplus, Germany). Electrochemical performance was tested using an electrochemical workstation (CS315H, Wuhan, China). The TCH concentration was analyzed by a UV-visible spectrophotometer (UV-vis, MAPADA UV-1150, China). The pH value of the solution was determined using a pH meter (phs-25-3E, China). The Brunauer-Emmett-Teller (BET) surface area, pore size, and pore volume were determined on Quantachrome (NOVA200E, United States) at 77.35K. The total organic carbon (TOC) concentrations were tested using the TOC-VCPH Total Organic Carbon Analyzer (Shimadzu, Japan).



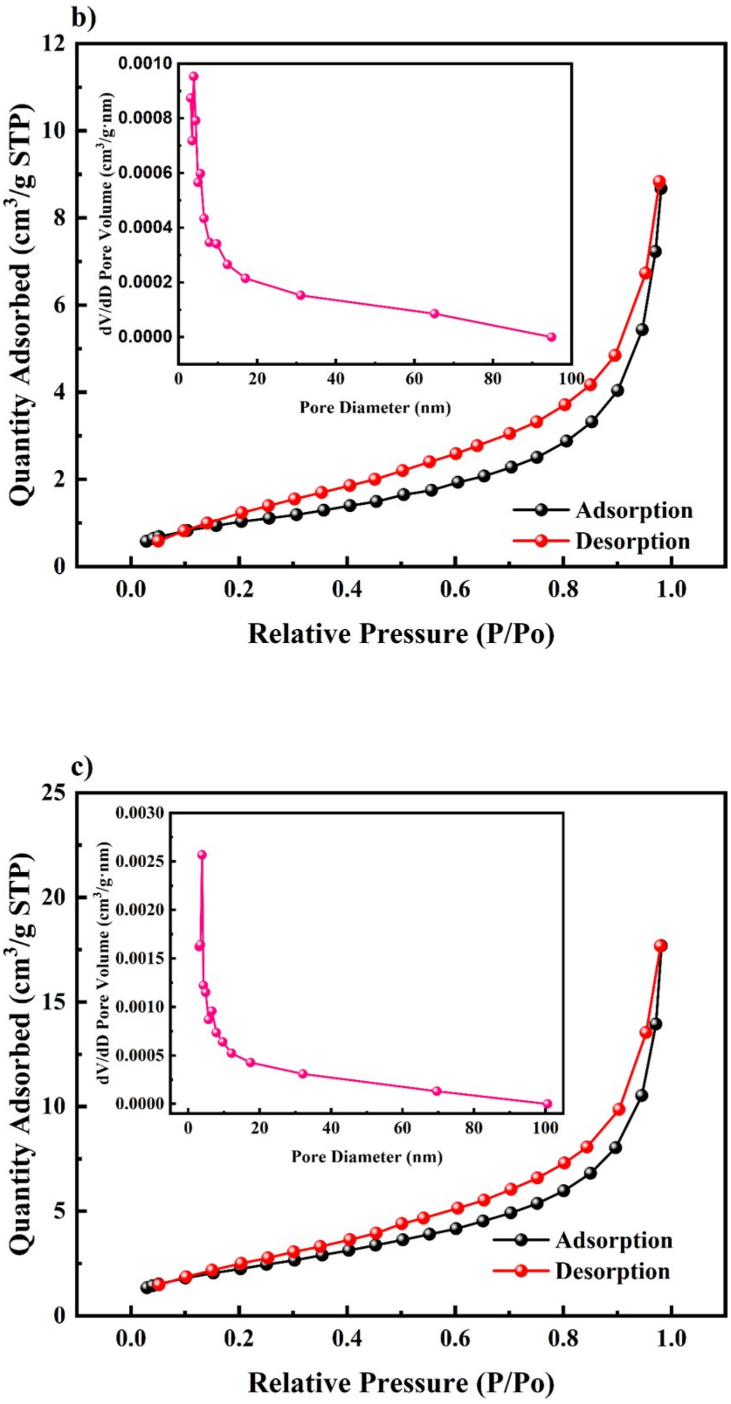


Fig. S1. N_2 sorption–desorption isotherms and the corresponding pore size distribution curves of CeO_2 (a), $CuCo_2S_4$ (b), and 0.5- CeO_2/ $CuCo_2S_4$ (c).

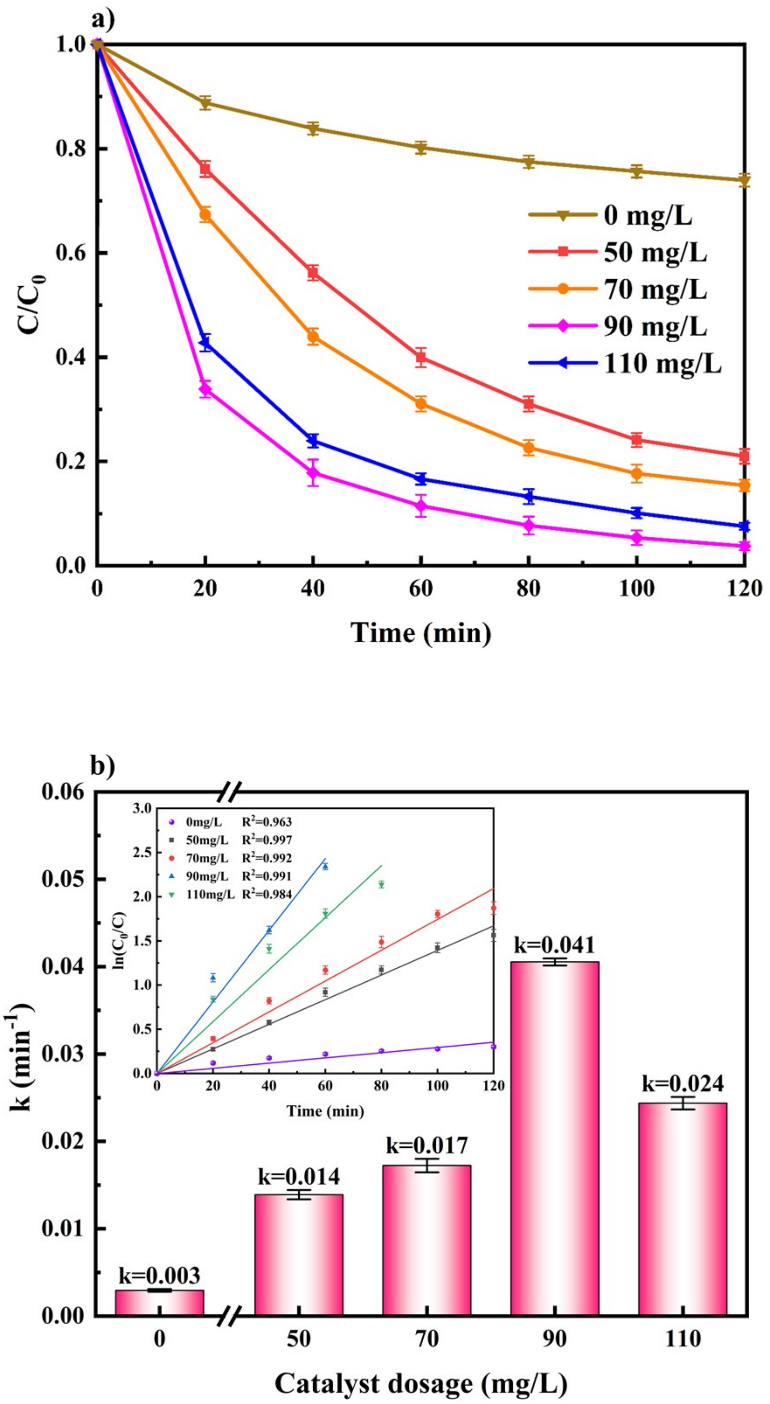


Fig. S2. (a) Effect of catalyst concentration on TCH degradation efficiency, and (b) its reaction kinetics (Experimental conditions: [TCH] = 15 mg/L, [PMS] = 0.9 mM, initial pH unadjusted (5.6), temperature = 20°C.)

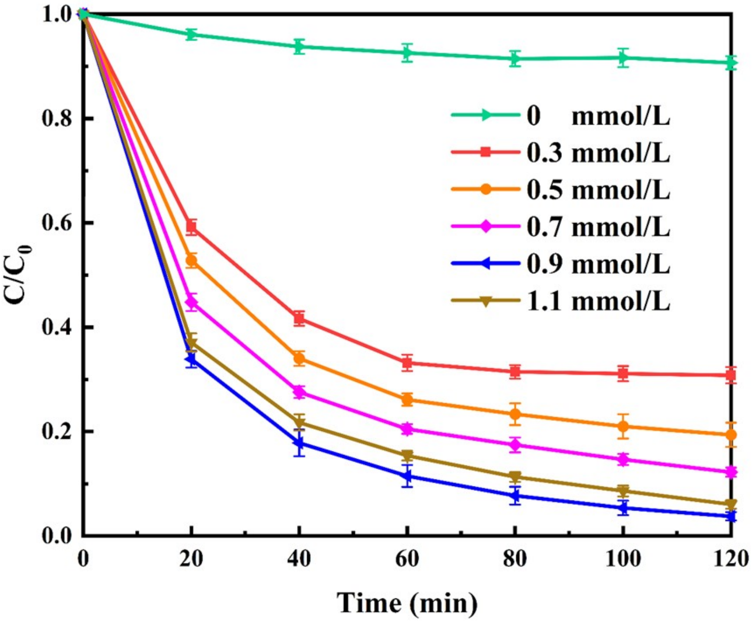
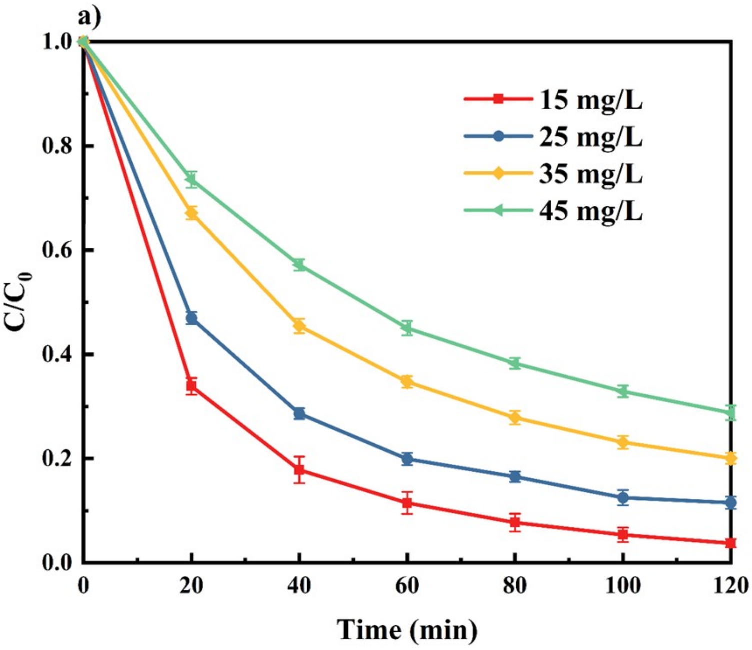


Fig. S3. Effect of PMS concentration on the efficiency of TCH degradation (Experimental conditions: [TCH] = 15 mg/L, [0.5-$CeO_2/CuCo_2S_4$] = 90 mg/L, initial pH unadjusted (5.6), and temperature = 20°C.)



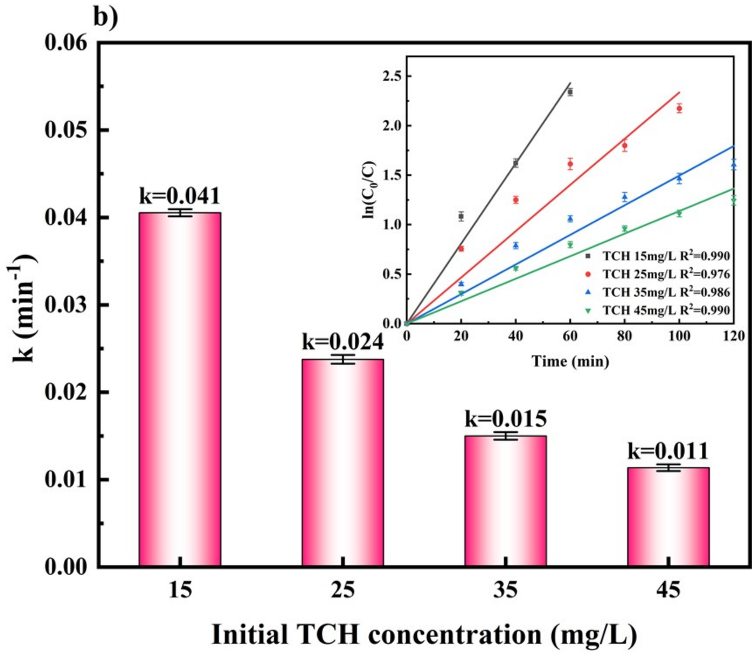
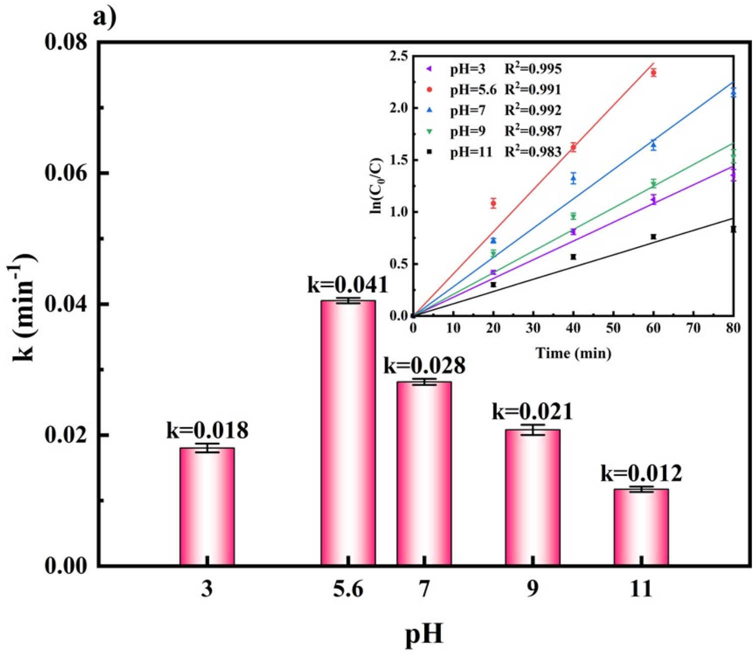


Fig. S4. (a) The effect of initial TCH concentration on degradation, and (b) its reaction kinetics (Experimental conditions: [PMS] = 0.9 mM, [0.5-$CeO_2/CuCo_2S_4$] = 90 mg/L, initial pH unadjusted (5.6), and temperature = 20°C).



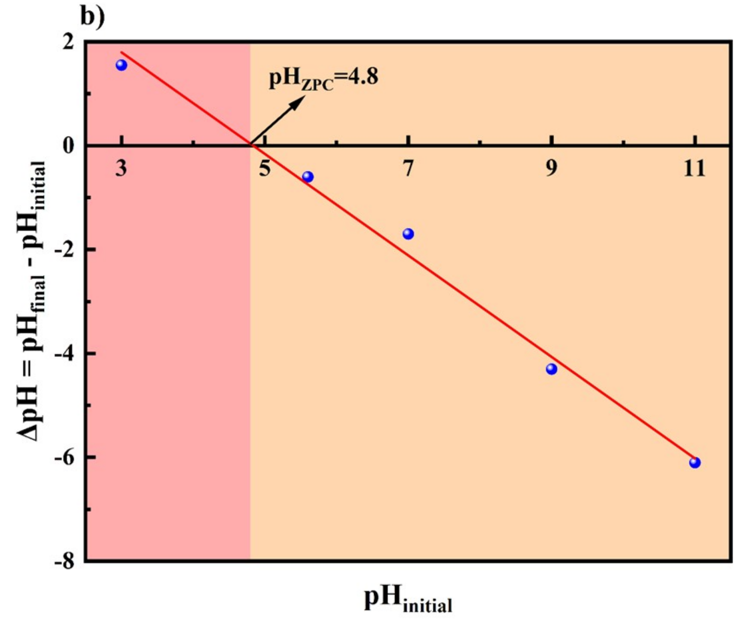


Fig. S5. (a) Corresponding constant rate (k), (b) the point of zero charge of 0.5-$CeO_2/CuCo_2S_4$. (Experimental conditions: [TCH] = 15 mg/L, [PMS] = 0.9 mM, [0.5-$CeO_2/CuCo_2S_4$] = 90 mg/L, temperature = 20℃.)

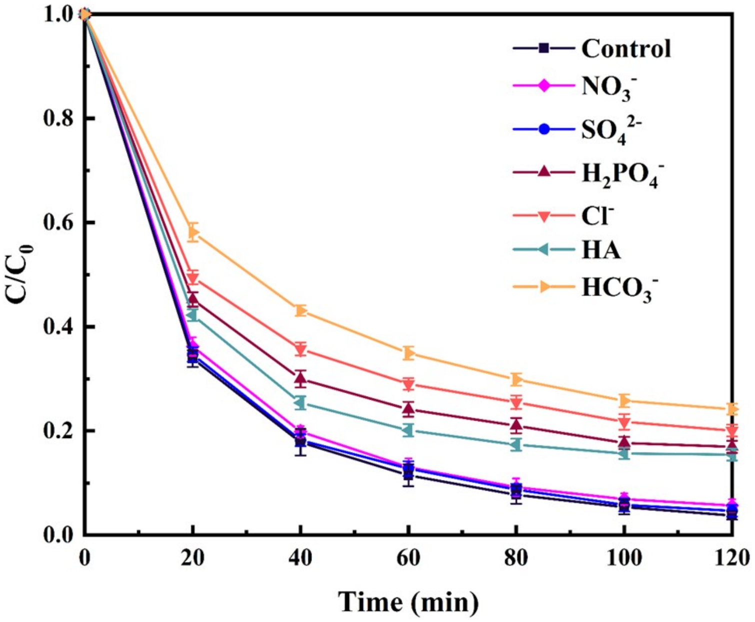


Fig. S6. The influence of inorganic anions and humic acids on the degradation effect of TCH (Experimental conditions: [TCH] = 15 mg/L, [PMS] = 0.9 mM, [0.5-$CeO_2/CuCo_2S_4$] = 90 mg/L, [Anion] = 5 mM, [HA] = 20 mg/L, initial pH unadjusted (5.6), temperature = 20℃.)

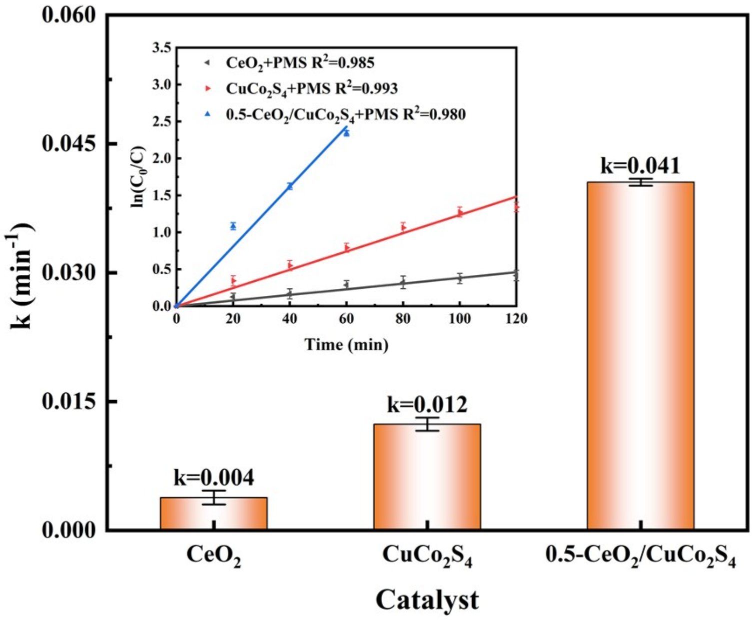


Fig. S7. The reaction rate constants (k) of TCH degradation in different systems. (Experimental conditions: [TCH] = 15 mg/L, [PMS] = 0.9 mM, [CeO_2] = 20 mg/L, [$CuCo_2S_4$] = 70 mg/L, [0.5-CeO_2/$CuCo_2S_4$] = 90 mg/L, initial pH unadjusted (5.6), and temperature = 20°C).

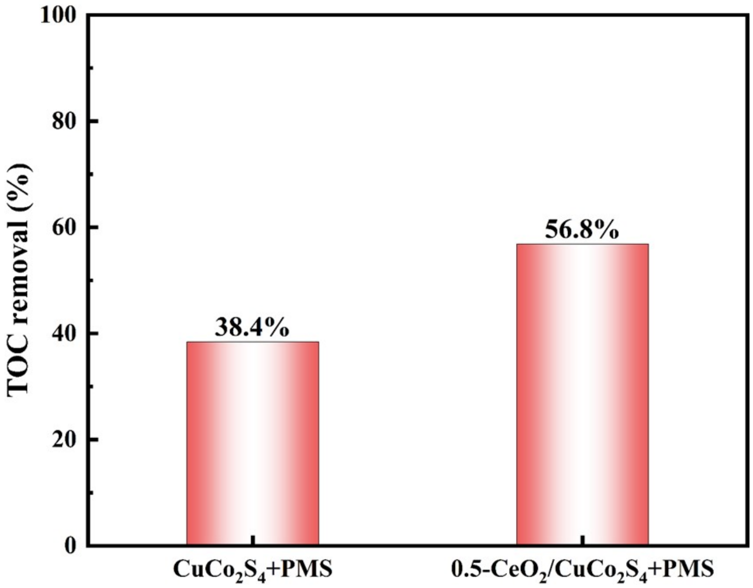


Fig. S8. TOC removal efficiency (Experimental conditions: [TCH] = 15 mg/L, [PMS] = 0.9 mM, [$CuCo_2S_4$] = 70 mg/L, [0.5-CeO_2/$CuCo_2S_4$] = 90 mg/L, initial pH unadjusted (5.6), and temperature = 20°C).

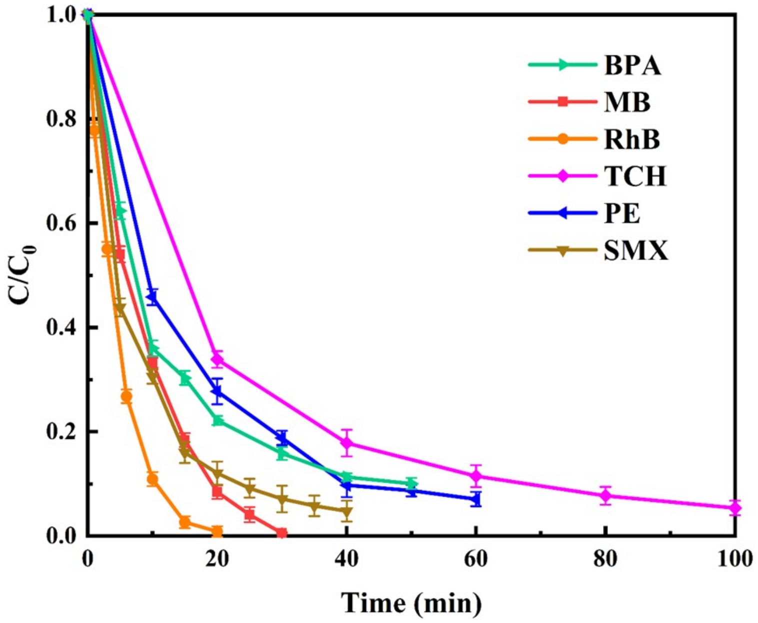


Fig. S9 0.5-$CeO_2/CuCo_2S_4$ composite catalyst utility experiment (Experimental conditions: [Contaminant] = 15 mg/L, [PMS] = 0.9 mM, [0.5-$CeO_2/CuCo_2S_4$] = 90 mg/L, initial pH unadjusted (5.6), and temperature = 20°C.)

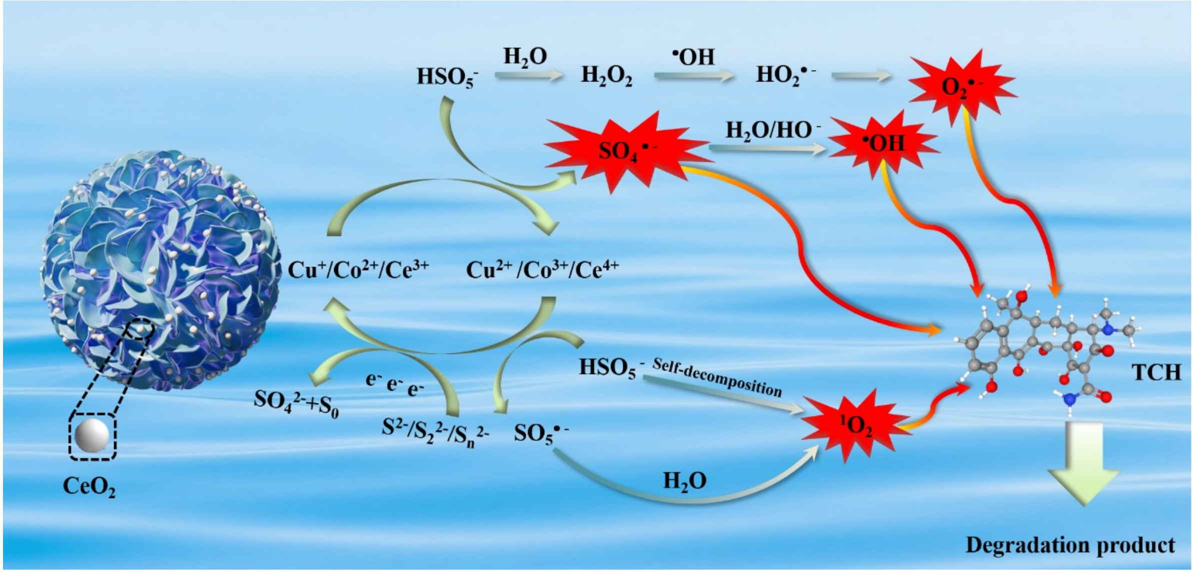


Fig. S10The possible synergistic mechanisms of 0.5-$CeO_2/CuCo_2S_4$.

Table S1. The structural parameters of the sample preparation

Sample	Specific Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Mesopore Diameter (nm)
CeO_2	21.50	0.077	14.23
$CuCo_2S_4$	3.79	0.013	14.16
0.5-CeO_2/$CuCo_2S_4$	8.37	0.027	13.08

Table S2. Comparison of activation energies of multiphase catalytic systems.

Catalyst	Organics	Ea (kJ/mol)	Ref.
FePc@PAN	TCH	64.41	1
Fe_2O_3	Rhodamine B	69.2	2
3D nitrogen-doped graphene aerogels (NGA)	ibuprofen	78.8	3
nitrogen-doped graphene (NG)	phenol	96.6	4
$CoFe_2O_4$/TNTs	MB	70.56	5
graphene oxide	phenol	84.0	6
MgCoAl	MB	70.81	7
CeO_2/$CuCo_2S_4$	TCH	56.6	This work

Reference

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