Supplementary material

Enhanced peroxymonosulfate activation by polydopamine-decorated $CoMoO_4$ composite towards efficient decomposition of tetracycline hydrochloride in wastewater

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Text S1. Materials

Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2·6H_2O$), tris (hydroxymethyl) aminomethane, ammoniumheptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}·4H_2O$), dopamine hydrochloride (DA), humic acid (HA), tetrazolium (NBT), terephthalic acid (TA), tetracycline hydrochloride (TCH), sulfamethoxazole (SMX), phenol (PE), bisphenol A (BPA), rhodamine B (RhB) and methylene blue (MB) were purchased from Shanghai Macklin Chemical Reagent Co.Ltd, China. L-Histidine (L-His), ethanol (EtOH), tert-butyl alcohol (TBA), p-benzoquinone (p-BQ), potassium peroxymonosulfate (PMS, $2KHSO_5·KHSO_4·K_2SO_4$) were obtained from Shanghai Aladdin Biochemical Technology Co. Anhydrousethanol (EtOH), sodium bicarbonate, ($NaHCO_3$), potassium dihydrogen phosphate, (KH_2PO_4), potassium chloride, (KCl), potassium sulfate (K_2SO_4), and sodium nitrate ($NaNO_3$) were purchased from Tianjin Compagno Chemical Reagent Co.Ltd. Sodium hydroxide (NaOH) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd., China. Hydrogen peroxide (30% aqueous solution) was obtained from Shanghai Hushi Chemical Co.Ltd., China. The purity of the above reagent

reached the analytical level and no further purification was required. Unless otherwise noted, the water used for dissolution was deionized water.

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, SU1510, Japan). The characteristic functional groups of the catalysts were identified by Fourier transform infrared spectroscopy (FT-IR) with a Nicolet 6700 instrument (USA). 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.

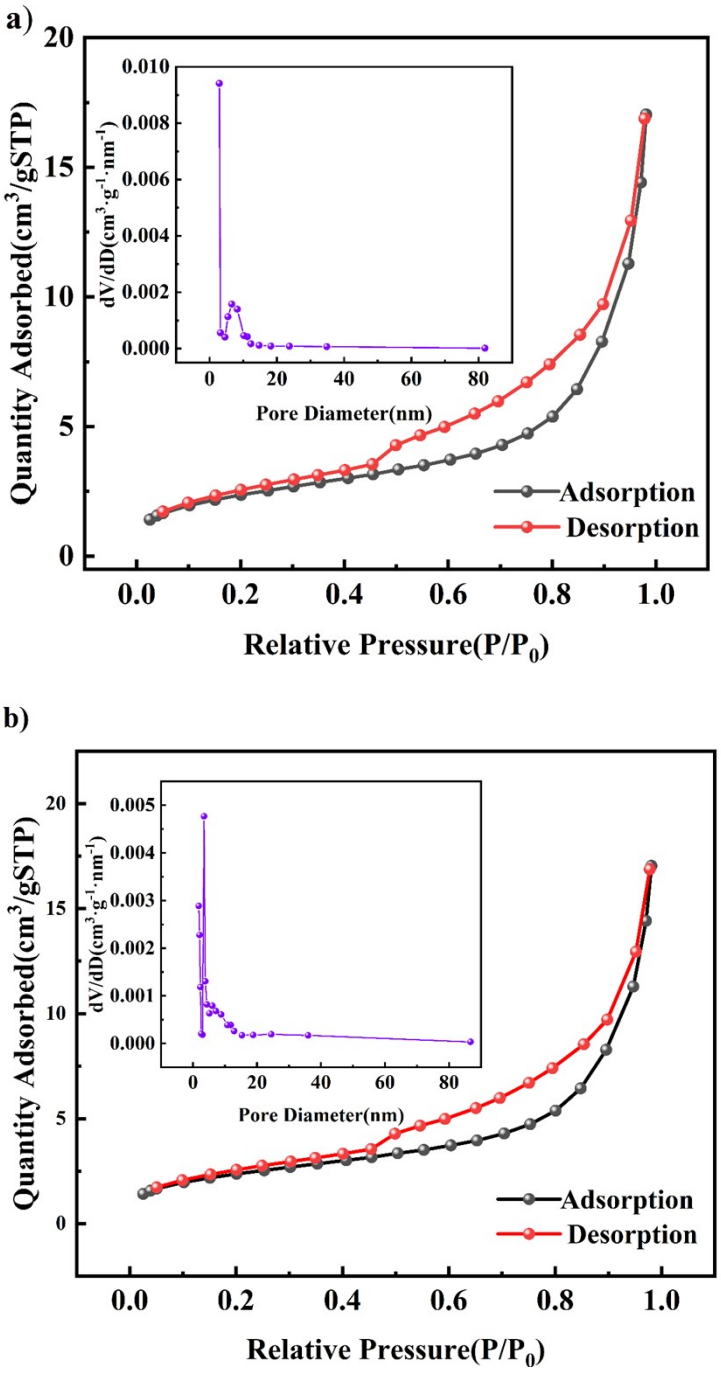


Fig. S1 N_2 sorption–desorption isotherms and the corresponding pore size distribution curves of $CoMoO_4$ (a), PDA@$CoMoO_4$ (b)

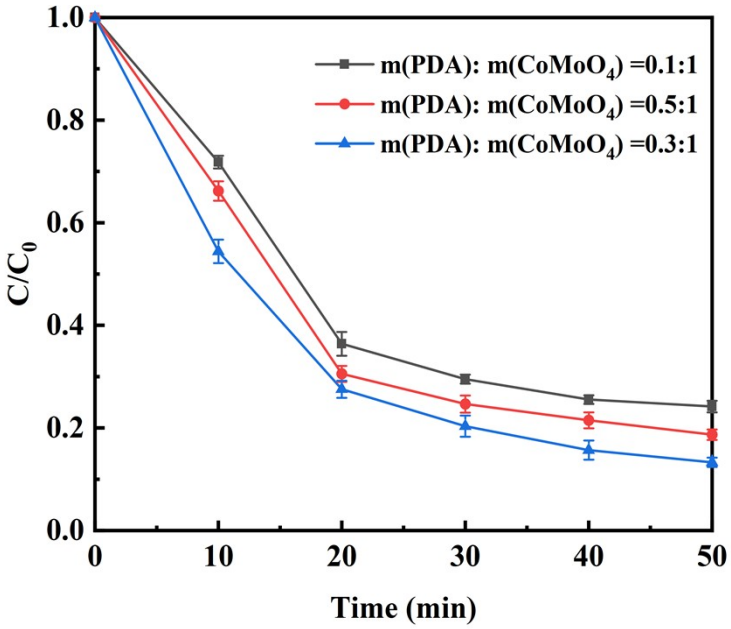


Fig. S2 The influence of quality ratio of PDA and $CoMoO_4$ on the TCH decomposition, Experimental conditions: $[PDA@CoMoO_4]_0$ = 60 mg/L, $[TCH]_0$ = 15 mg/L, $[PMS]_0$ = 0.6 mM, initial pH unadjusted (5.4), temperature 25℃

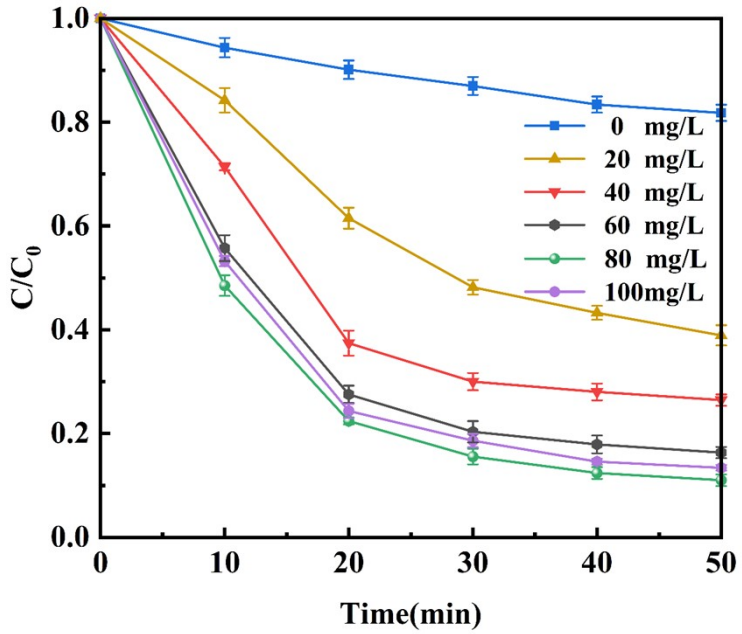


Fig. S3 Influence of catalyst dose on TC degradation, reaction conditions: $[TCH]_0$ = 15 mg/L, $[PMS]_0$ = 0.6 mM, initial pH = 5.4, 25℃.

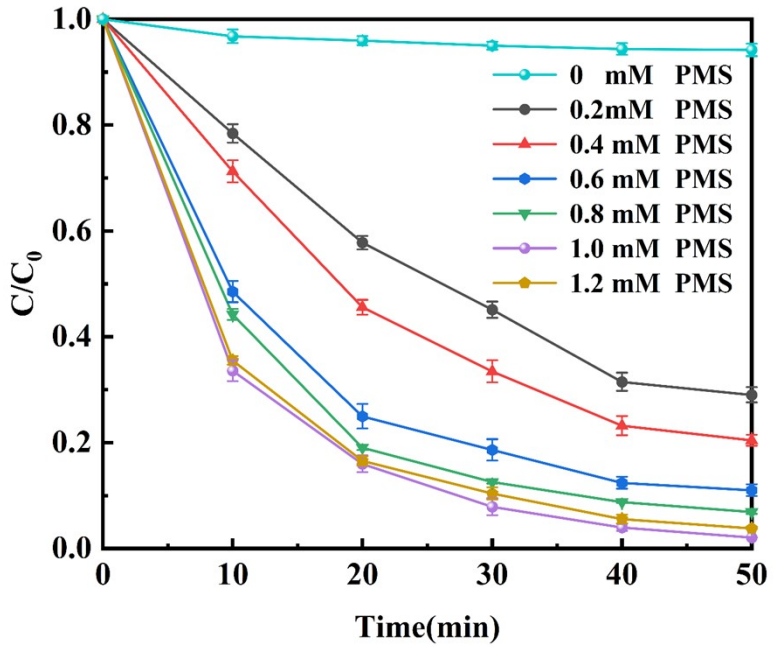
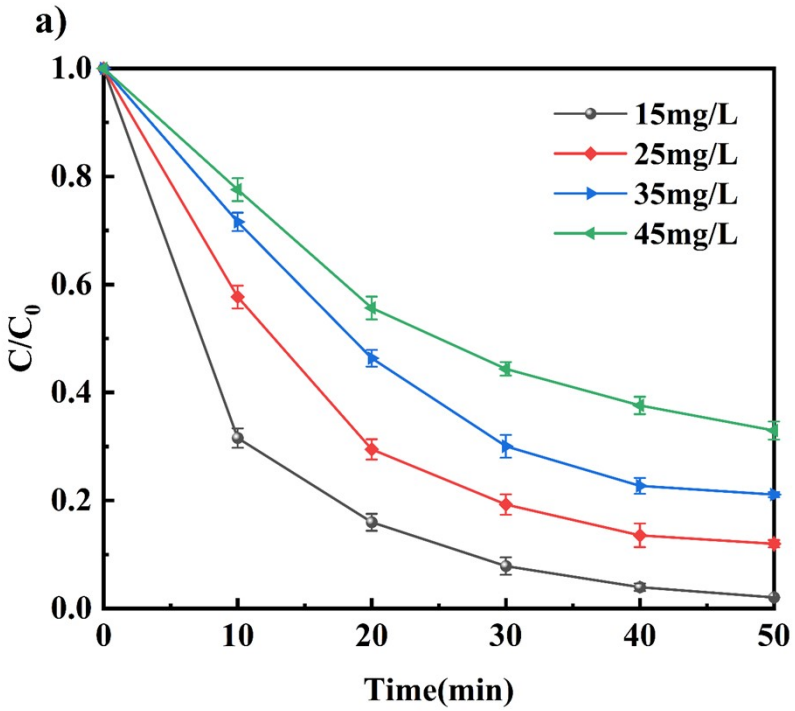


Fig. S4 Influence of PMS dosage on TCH degradation. reaction conditions: $[PDA@CoMoO_4]_0$ = 80 mg/L, $[TCH]_0$ = 15 mg/L, initial pH = 5.4, 25℃.



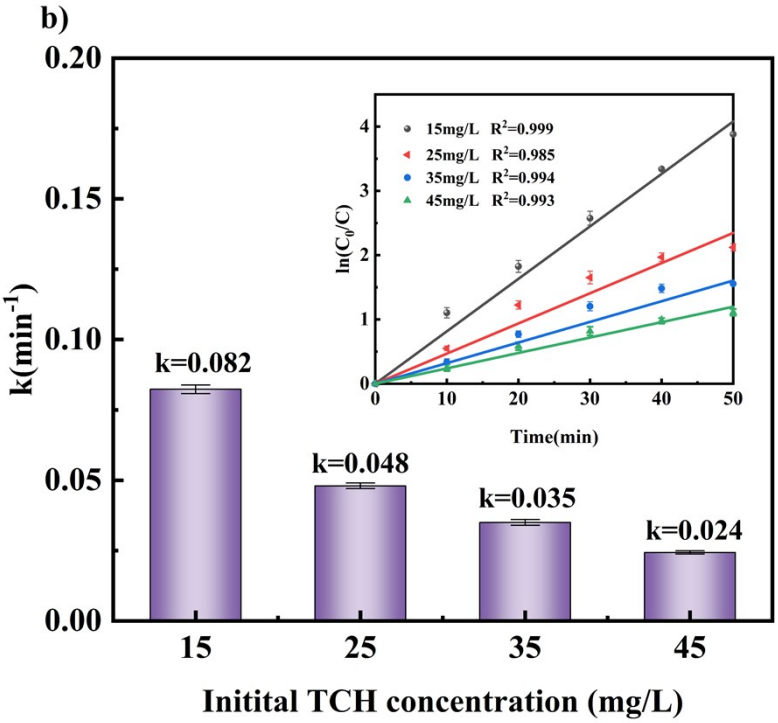


Fig. S5 (a) Influence of initial TCH concentration on TCH removal and (b) its kinetics, reaction conditions: $[PDA@CoMoO_4]_0$ = 80 mg/L, $[PMS]_0$ = 1.0 mM, initial pH = 5.4, 25℃.

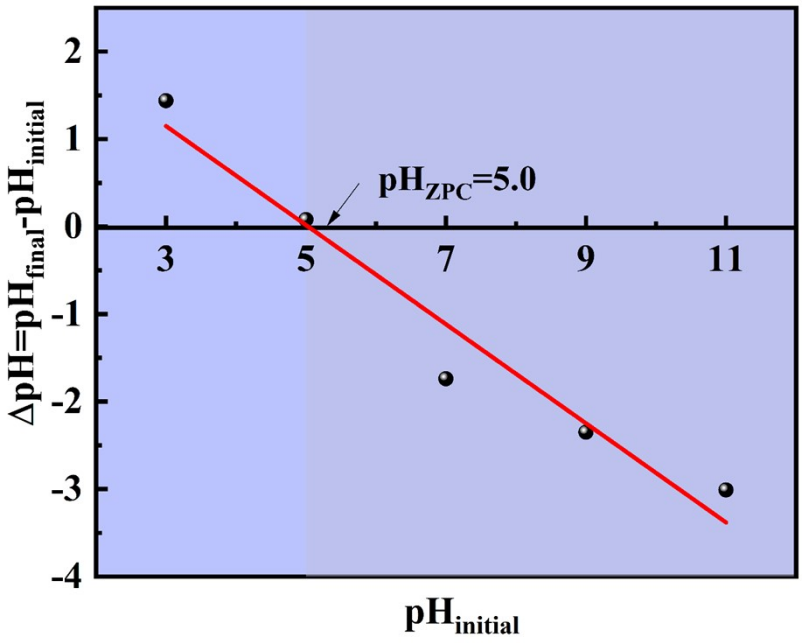


Fig. S6 Point of zero charge of $PDA@CoMoO_4$

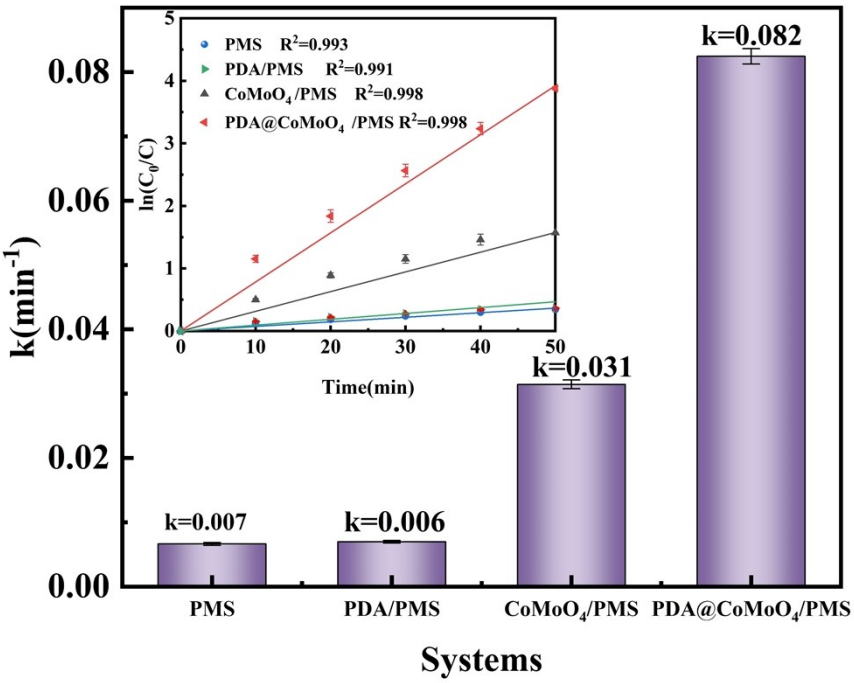


Fig. S7 The reaction rate constants (k) of TCH degradation in different systems, reaction conditions: $[TCH]_0$ = 15 mg/L, $[PDA@CoMoO_4]_0$ = 80 mg/L, $[PMS]_0$ = 1.0 mM, initial pH = 5.4, 25℃.

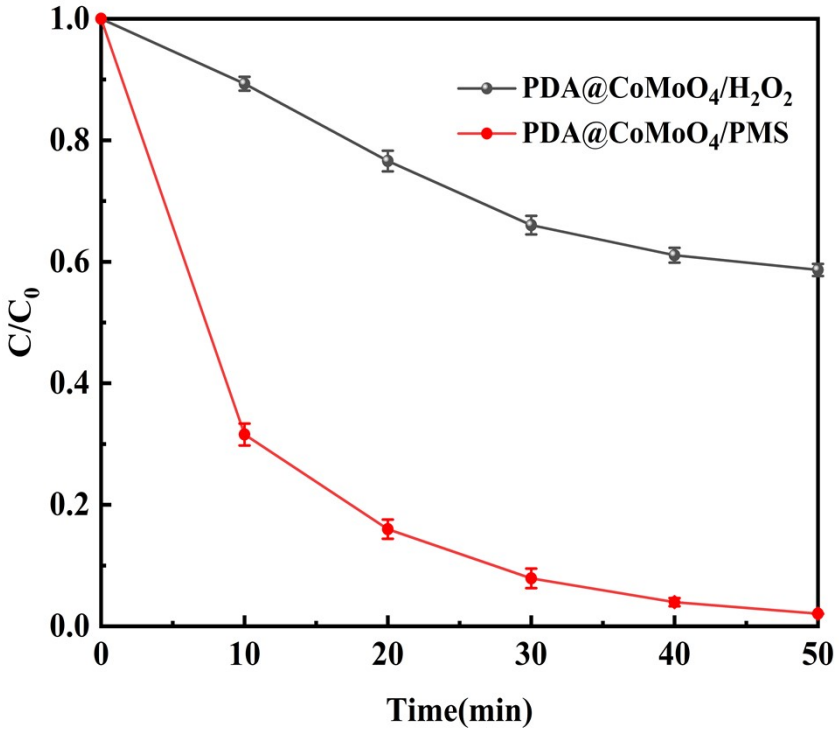


Fig. S8. Degradation of TCH in $PDA@CoMoO_4/H_2O_2$ system and $PDA@CoMoO_4$/PMS system, experimental conditions: $[PDA@CoMoO_4]$ = 80 mg/L, $[H_2O_2]$ = 1.0 mM, [PMS] = 1.0 mM, [TCH]= 15 mg/L, initial pH unadjusted (5.4), temperature = 25℃.

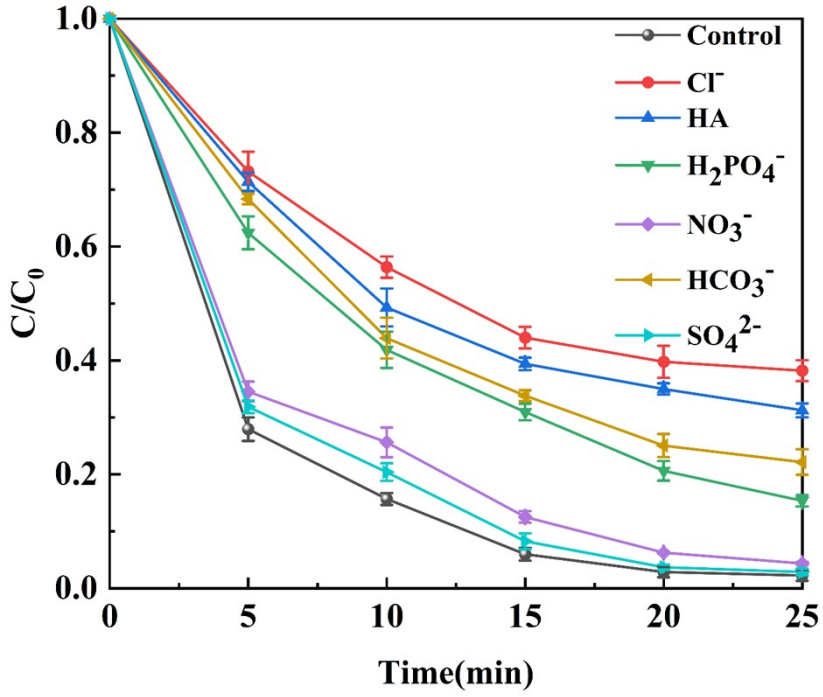


Fig. S9. Effects of different anions and humic acids on the degradation of TCH, reaction conditions: $[TCH]_0$ = 15 mg/L, $[PDA@CoMoO_4]_0$ = 80 mg/L, $[PMS]_0$ = 1.0 mM, initial pH = 5.4, 25℃.

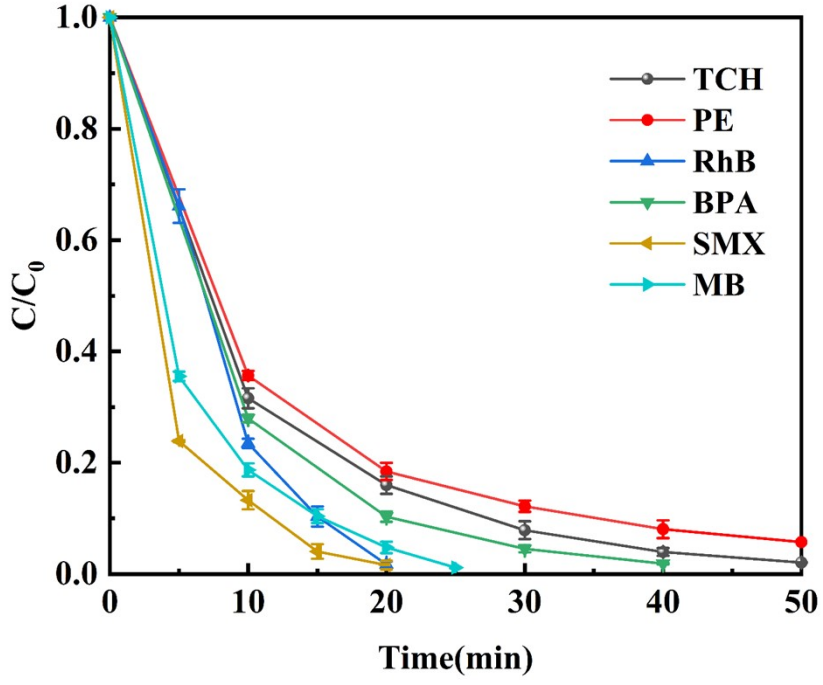


Fig. S10 Degradation effect of $PDA@CoMoO_4$ on different pollutants, reaction conditions: $[pollutant]_0$ = 15 mg/L, $[PDA@CoMoO_4]_0$ = 80 mg/L, $[PMS]_0$ = 1.0 mM, initial pH = 5.4, 25 ℃

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)
PDA@$CoMoO_4$	8.575	0.026	12.292
$CoMoO_4$	11.970	0.037	12.227

Table S2. Comparison of activation energies of multiphase catalytic systems

Catalyst	Organics	Ea(kJ/mol)	Ref.
$LaNiO_3$	Sulfamethoxazole	82.6	1
Co(II)-doped TiO_2	Ofloxacin	64.4	2
Co/SiO_2	Phenol	61.7-75.1	3
$FeCo_2O_4$-N-C	Methylene Blue	70.26	4
CoPc@PAN	Tetracycline Hydrochloride	66.9	5
Co/FA	Phenol	47.0	6
$CoFe_2O_4$/TNTs	Rhodamine B	70.56	7
CoP/CoO_x	Tetracycline	78.8	8
$CoMoO_4$	Methylene Blue	69.89	9
PDA@$CoMoO_4$	Tetracycline Hydrochloride	42.5	This work

Table S3. Comparison of catalytic performance.

Catalyst (g/L)	PMS (Concentration, mM)	Pollutants (Concentration, mg/L)	Removal Efficiency (reaction time)	Ref.
β-ADA@Fe_3O_4 (0.8)	0.3	SDZ (10)	54% (90min)	10
VC@Fe_3O_4 (0.8)	0.3	SDZ (10)	57% (90min)	11
FONC@PAC (0.5)	5	TC (1)	86.9% (90min)	12
Fe_3O_4@BC (0.4)	0.6	SMX (10)	82.0%(40min)	13
N-rGO-Ru (0.02)	1	SMX (25)	92% (120min)	14
$CoMoO_4$/AC (2)	2	MB (100)	90% (60min)	15
Fe_3O_4 (0.8)	0.2	APAP (10)	75% (120 min)	16
PDA@$CoMoO_4$ (0.8)	1	TCH (15)	98% (50min)	This work

Eqs. S1-S5

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (S1)$$

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \quad (S2)$$

$$^{\bullet}OH + SO_4^{\bullet-} \rightarrow HSO_5^- \quad (S3)$$

$$HSO_5^- + {}^{\bullet}OH \rightarrow SO_5^{\bullet-} + H_2O \quad (S4)$$

$$HSO_5^- + SO_4^{\bullet-} \rightarrow SO_5^{\bullet-} + SO_4^{2-} + H^+ \quad (S5)$$

Eqs. S6

$$HSO_5^- \xrightarrow{\Delta} SO_4^{\bullet-} + {}^{\bullet}OH \quad (S6)$$

Eqs. S6

$$k = A\exp(-Ea/RT) \quad (S7)$$

The activation energy of the reaction was calculated via Arrhenius formula (Eq. S7), where A represents the pre-exponential factor, Ea represents the reaction activation energy (kJ/mol), R represents the gas constant (8.314 J/(mol·K)) and T represents the absolute temperature (K).

Eqs. S8-S9

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + {}^{\bullet}OH \quad (S8)$$

$$HSO_5^- + OH^- \rightarrow H_2O + SO_5^{2-} \quad (S9)$$

Eqs. S10-S17

$$SO_4^{\bullet-} + NO_3^- \rightarrow NO_3^{\bullet} + SO_4^{2-} \quad (S10)$$

$$SO_4^{\bullet-} + HCO_3^- \rightarrow HCO_3^{\bullet} + SO_4^{2-} \quad (S11)$$

$$^{\bullet}OH + HCO_3^- \rightarrow CO_3^{\bullet-} + H_2O \quad (S12)$$

$$SO_4^{\bullet-} + Cl^- \rightarrow Cl^{\bullet} + SO_4^{2-} \quad (S13)$$

$$^{\bullet}OH + Cl^- \rightarrow HOCl^{\bullet-} \quad (S14)$$

$$Cl^{\bullet-} + Cl^- \rightarrow Cl_2^{\bullet-} \quad (S15)$$

$$SO_4^{\bullet-} + H_2PO_4^- \rightarrow HPO_4^{\bullet-} + HSO_4^- \quad (S16)$$

$$^{\bullet}OH + H_2PO_4^- \rightarrow HPO_4^{\bullet-} + H_2O \quad (S17)$$

Eqs. S18-S36

$$Co^{2+} + HSO_5^- \rightarrow Co^{3+} + SO_4^{\bullet-} + OH^- \quad (S18)$$

$$Mo^{4+} + 2HSO_5^- \rightarrow Mo^{6+} + 2SO_4^{\bullet-} + 2OH^- \quad (S19)$$

$Co^{3+} + HSO_5^- \rightarrow Co^{2+} + H^+ + SO_5^{\bullet-}$ (S20)

$Mo^{6+} + 2HSO_5^- \rightarrow Mo^{4+} + 2H^+ + 2SO_5^{\bullet-}$ (S21)

$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + H^+ + {}^{\bullet}OH$ (S22)

$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + {}^{\bullet}OH$ (S23)

$2SO_5^{\bullet-} + H_2O \rightarrow HSO_4^- + 1.5{}^1O_2$ (S24)

$HSO_5^- \rightarrow H^+ + SO_5^{2-}$ (S25)

$HSO_5^- + SO_5^{2-} \rightarrow SO_4^{2-} + HSO_4^- + {}^1O_2$ (S26)

$HSO_5^- + H_2O \rightarrow HSO_4^- + H_2O_2$ (S27)

$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet-}$ (S28)

$HO_2^{\bullet-} \rightarrow O_2^{\bullet-} + H^+$ (S29)

$2O_2^{\bullet-} + 2H_2O \rightarrow H_2O_2 + {}^1O_2 + 2OH^-$ (S30)

$O_2^{\bullet-} + {}^{\bullet}OH \rightarrow {}^1O_2 + OH^-$ (S31)

$Co^{3+} + HQ \rightarrow Co^{2+} + SQ + H^+$ (S32)

$Mo^{6+} + 2HQ \rightarrow Mo^{4+} + 2SQ + 2H^+$ (S33)

$Co^{3+} + SQ \rightarrow Co^{2+} + Q + H^+$ (S34)

$Mo^{6+} + 2SQ \rightarrow Mo^{4+} + 2Q + 2H^+$ (S35)

$Co^{3+} + Mo^{4+} \rightarrow Co^{2+} + Mo^{6+}$ (S36)

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