Supporting Information

Efficient Degradation of Tetracycline via Cobalt Phosphonate-Activated Peroxymonosulfate: Mechanistic Insights and Catalytic Optimization

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Materials

The chemicals and reagents used in this experiment are analytical-grade and used directly. $Co(NO_3)_2•6H_2O$ (99%), phenylphosphonic acid ($C_6H_7O_3P$, 99%), N, N-Dimethylformamide (DMF, C_3H_7NO) were purchased from Aladdin Industrial Co (Shanghai, China). HCl-Tetracycline (TC, ≥98%), PMS ($KHSO_5•0.5KHSO_4•0.5 K_2SO_4$, 42%~46%), Ethylene Diamine Tetraacetic Acid (EDTA, $C_{10}H_{16}N_2O_8$, 99%),

benzoquinone (BQ, 99%) and Isopropanol (IPA, AR) were provided from Shanghai Macklin Biochemical Technology Co., Ltd (China). Methanol (CH_3OH, AR), Anhydrous ethanol (C_2H_5OH, AR) were provided from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

Characterization Methods

The microstructural morphology of the samples was examined using a cold field-emission scanning electron microscope (SEM, Regulus 8100, Tokyo, Japan) at low magnification. Transmission electron microscopy (TEM, JEM-1400, 120 kV, JEOL, Tokyo, Japan) was employed to observe the microscopic morphology and structure of the materials. The crystal structure of the samples was qualitatively analyzed using a multi-functional horizontal X-ray diffraction (XRD, D/MAX-2500, Rigaku, Tokyo, Japan) instrument. Fourier-transform infrared spectroscopy (FT-IR) (Vertex 80 V, Bruker, Billerica, U.S.) was utilized to determine the structural features and functional groups of the samples. X-ray photoelectron spectroscopy (XPS, Thermo K-alpha, Thermo Fisher Scientific**,** Waltham, U.S.) was applied to analyze the surface elemental composition and valence states. The optical properties of the materials were characterized using ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS, Lambda 950, PerkinElmer, Waltham, U.S.), enabling an analysis of their optical response characteristics. Liquid chromatography-mass spectrometry (HPLC/MS, Ultimate 3000 UHPLC -Q Exactive, Thermo Fisher Scientific**,** Waltham, U.S.): Characterization of degradation intermediates to infer possible degradation pathways.

Photocatalytic Activation of PMS for TC Degradation

The photocatalytic experiments were conducted as follows: A 500 mg/L stock solution of TC was prepared, and the desired concentration was obtained by diluting the stock solution with deionized water in a 50 mL volumetric flask. The solution was then transferred to a beaker and mixed with the catalyst. The beaker was placed on a magnetic stirrer inside a dark box, and the reaction was allowed to proceed in the dark for 20 min. A 3 mL aliquot of the solution was collected, after which PMS was added. Upon turning on the light source, samples (3 mL each) were extracted at 1 min intervals for 6 min. The collected samples were filtered through a membrane into test tubes and analyzed using liquid chromatography. The residual concentration of TC was analyzed by UV-vis spectrophotometer. The degradation efficiency formula is as follows.

$$\text{Degradation efficiency} = \frac{C_0 - C_t}{C_0} \times 100\%$$

For free radical quenching experiments, $SO_4^{\bullet-}$, $^{\bullet}OH$, $O_2^{\bullet-}$ and $^1O_2$ were quenched by the addition of IPA (200 mM), BQ (10 mM) and EDTA (10 mM), respectively. To study the effect of typical anions on TC in a deionised water environment, solutions of NaCl, $NaHCO_3$, NaH_2PO_4 and $NaCO_3$ were added at a concentration of 5.0 mM.

The CoP-3 composites were collected by centrifugation of the remaining solution. The collected CoP-3 composites were used for subsequent experiments without any treatment. Samples were collected at the end of the experiment to determine the concentration of TC and the degree of degradation. Cyclic experiments were conducted in four rounds, each lasting 6 min.

Electrochemical Performance Characterization

Electrochemical performance measurements were conducted using a three-electrode system. The counter electrode was a platinum wire, the reference electrode was an Ag/AgCl electrode, and the working electrode consisted of ITO conductive glass coated with the sample. A 1.5 M Na_2SO_4 solution was used as the electrolyte. The measurements were performed using a CHI760E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China).

To prepare the working electrode, 5 mg of the sample was dispersed uniformly in 1 mL of anhydrous ethanol, followed by the addition of 10 μL of Nafion solution. The mixture was thoroughly homogenized and drop-cast onto a clean ITO conductive glass substrate (20 mm×50 mm×1.1 mm). The glass was air-dried at room temperature and subsequently oven-dried until the ethanol completely evaporated, yielding the ITO working electrode.

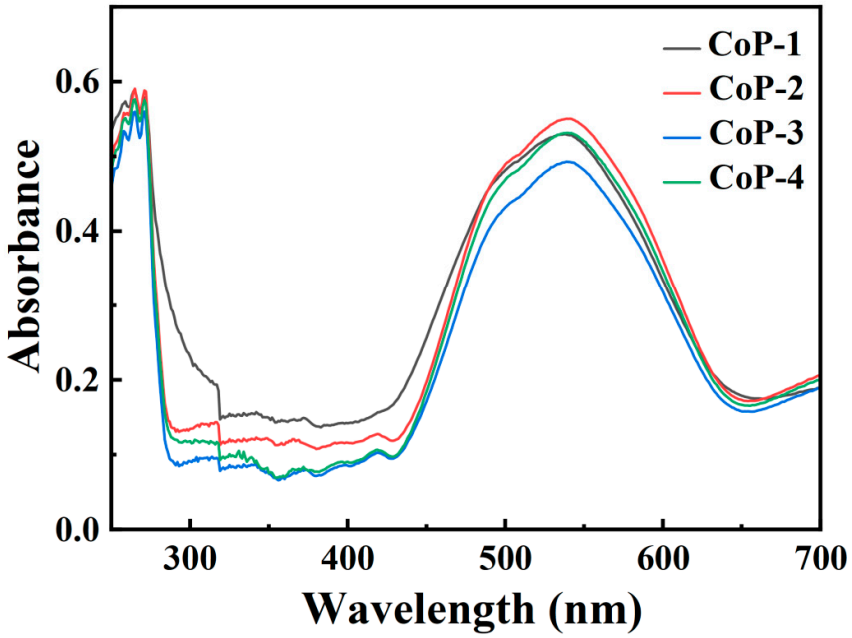


Figure S1. UV-vis DRS spectra of CoP-X samples

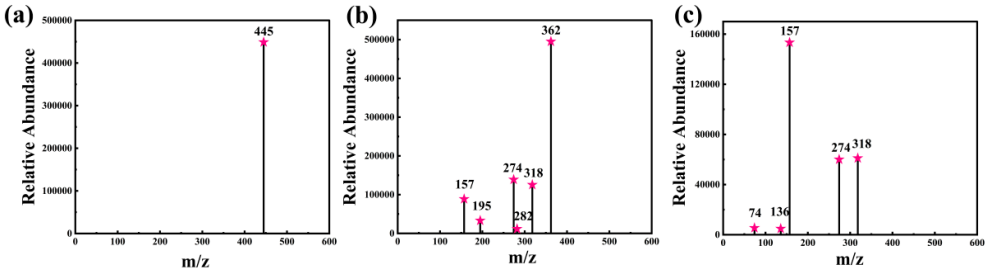


Figure S2. Mass spectra of TC and transformation products at 0 min (a), 1.0 min (b), 6.0 min (c).

Table S1. Comparison of catalytic effects among homogeneous catalysts

Catalysts	TC concentration	Conditions	Removal efficiency	Rate constant k_1 (min^{-1})	Ref.
Co−CN/PMS	10 mg/L	[Cat.] = 0.5g/L, [PMS] = 0.8 mM	99.3% in 24 min	0.149	[68]
FMDS-3/PMS	10 mg/L	[Cat.] = 0.2 g/L, [PMS] = 3.0 mM	89.0% in 60 min	0.0766	[63]
$MnFe_2O_4$/ZIF-67	10mg/L	[Cat.] = 0.1 g/L, [PMS]=0.3285 mM	84.9% in 30 min	/	[67]
CoMnSi	10 mg/L	[Cat.] = 1.0 g/L, [PMS] = 6.39 mM	95.1% in 40 min	0.078	[66]
$BiFeO_3$	10 mg/L	[Cat.] = 0.2g/L, [PMS] = 3.942mM	83.60% in 20 min	0.177	[65]
CoP-3	10 mg/L	[Cat.] = 0.1g/L, [PMS] = 1.314mM	90.7% in 6 min	0.989	This work