Electronic Supplementary Information (ESI)

Constructing electron-deficient Co centers into lattice of oxygen-vancancy-rich CuO for improved PMS activation and contaminant degradation

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Text S1. Chemicals and reagents

Ethylsilicate (AR, TEOS), Methanol (99.9%, CH₃OH), Tert-butanol (99.5%, TBA), L-histidine (99%, L-his), P-benzoquinone (98%, PBQ), ethylsilicate (AR, TEOS), dopamine hydrochloride (98%, C₈H₁₂ClNO₂), cobalt nitrate hexahydrate (98%, Co(NO₃)₂·6H₂O), 2-methylimidazole (99.9%, C₄H₆N₂), tris (hydroxymethyl) aminomethane (NH₂C(CH₂OH)₃), Hydrochloric acid (HCl), Potassium peroxymonosulfate complex salt (PMS), P-benzoquinone (98%, p-BQ) and ethanol absolute were obtained by Energy Chemicals Co., Ltd. Oxytetracycline (98%, OTC), tetracycline (CP, TC), carbamazepine (99%, CBZ) and norfloxacin (CP, NFX) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Ammonium hydroxide (AR, NH₃·H₂O) was purchased from Chinasun Specialty Products Co., Ltd. Sodium carbonate (AR, Na₂CO₃), sodium bicarbonate (99.5%, Na₁CO₃), sodium sulphate (99.5%, Na₂SO₄) and sodium hydroxide (AR, NaOH) were obtained from Shanghai Aladdin Industrial Co., Ltd. All the chemicals were used without further purification. Dicopper hydroxide phosphate (Cu(OH)₂PO₄) was obtained from Zhenjiang Fuyuancheng Technology Co., Ltd.

Text S2. Synthesis of catalysts

The acquired $Cu(OH)_2PO_4$ was modified using a metal-doped dopamine strategy. Specifically, 0.25 g of $Cu(OH)_2PO_4$ was added to 60 ml of Tris solution and sonicated for 20 minutes, then 0.25 g of dopamine and 0.5 mmol of cobalt nitrate hexahydrate were added with stirring for 12 h. The resulting mixture underwent washing with ethanol and water. The precipitate obtained post-centrifugation was dried at 70 °C and then treated at different temperatures (500, 600, and 700 °C) in a tube furnace at a rate of 5 °C min⁻¹, followed by a 3-h calcination under air atmosphere. The final sample obtained was Cu-Co-700.

In addition to these experiments, several control comparison samples were prepared. In one such example, $Cu(OH)_2PO_4$ was altered to SiO₂, while maintaining all other conditions constant, thus yielding Si-Co-700. In another example, the dopamine-coating strategy was cancelled, other conditions being unchanged, to obtain the material Cu-700.

Text S3. Characterizations

The morphology and structure of the sample were examined using field emission scanning electron microscopy

(SEM, Zeiss, Germany) and high-resolution transmission electron microscopy (HR-TEM, JEOL, 2100 F, Japan). The chemical states of the surface elements were identified using X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, Kanagawa, Japan). Various catalyst structures were analyzed using a K α -ray diffractometer (XRD-6000X, Shimadzu Corporation, Tokyo, Japan) ($\lambda = 1.54178A$). Excitation-emission-matrix spectroscopy (EEM) was performed using an F-4700 FL spectrophotometer to assess the degree of change in contaminants during degradation. Open circuit voltage (OCP), linear scanning voltammetry (LSV), electrochemical impedance (EIS), and cyclic voltammetry (CV) were investigated on a CHI 760 E electrochemical workstation using a standard three-electrode method with a Pt electrode as the counter electrode and an Ag/AgCl electrode as the reference electrode.

Text S4. Catalytic performance assessment

In order to systematically evaluate the effectiveness of various catalysts for the degradation of pollutants, experiments were carried out for the catalytic degradation of NFX using PMS as an oxidant. Initially, the starting concentrations of PMS and the catalyst were established at 0.2 g·L⁻¹. The concentration of NFX following degradation was then monitored in real time using a UV spectrophotometer. This was achieved by initially dispersing PMS in a 20 ppm NFX solution and subsequently recording the concentration, followed by the addition of catalyst and the subsequent recording of the NFX concentration at regular intervals. The optimal catalyst was optimised by varying the PMS dosage, the catalyst dosage and the NFX concentration. The optimised catalyst was then subjected to NFX degradation experiments with different pollutants, different water quality and related stability tests while keeping other conditions unchanged. In order to further investigate the reaction mechanism of NFX degradation under the optimal conditions, free radical bursting experiments were conducted, which were achieved by adding a bursting agent to the normal experimental process.



Figure S1 SEM images of (a) Cu(OH)₂PO₄ and (b) Cu-Co-700.



Figure S2 (a) Wide-angle XRD patterns of Cu-Co-N-700 and Cu-Co-x. (b) Wide-angle XRD patterns of Cu-Co-700 , used Cu-Co-700, and Cu(OH)₂PO₄.



Figure S3 Analysis of the electrochemical active surface area (ECSA): Cyclic voltammetric curves for different scan rates (20-160 mV s⁻¹) and (a) Cu-Co-700, (b) Si-Co-700 and (c) Cu-700 samples in the range from 0.9 to 1.3 V vs. RHE.



Figure S4 $\ln(C_0/C)$ versus reaction time of NFX degradation over various catalysts; Reaction conditions: [NFX]=20 mg·L⁻¹, [PMS]=0.2 g·L⁻¹, [catalyst]=0.2 g·L⁻¹.



Figure S5 The PMS usage effect on degradation process (a) versus ln (C_0/C) and reaction time (d) of Cu-Co-700 catalyst; Reaction conditions: [NFX] =20 mg·L⁻¹, [catalyst] =0.2 g·L⁻¹. The catalyst dosage effect on degradation process (b) and ln (C_0/C) versus reaction time (e) of Cu-Co-700; Reaction conditions: [NFX] =20 mg·L⁻¹, [PMS] =0.4 g·L⁻¹. The NFX concentration effect on degradation process curves (c) and ln (C_0/C) versus reaction time (f) on Cu-Co-700 catalyst; Reaction conditions: [PMS] =0.4 g·L⁻¹, [catalyst] =0.3 g·L⁻¹.



Figure S6 Time-dependent NFX degradation course curves and $\ln(C_0/C)$ versus reaction time over Cu-Co-700 with different anionic interferents. Reaction condition: $[NFX] = 20 \text{ mg} \cdot \text{L}^{-1}$, $[PMS] = 0.4 \text{ g} \cdot \text{L}^{-1}$, $[catalyst] = 0.3 \text{ g} \cdot \text{L}^{-1}$, $[anionic] = 1 \text{ mmol} \cdot \text{L}^{-1}$.



Figure S7 Quenching experimental results of NFX degradation of Cu-Co-700 using various quenching agents (a) and $\ln(C_0/C)$ versus reaction time of NFX degradation (b) using various quenching agents; Reaction conditions: [NFX]=20 mg·L⁻¹, [PMS]=0.4 g·L⁻¹, [catalyst]=0.3 g·L⁻¹.



Figure S8 (a) Time-dependent NFX degradation course curves over Cu-Co-700 using different reaction temperatures, and (b) corresponding kinetic fitting curves: $\ln(C_0/C)$ v.s. reaction time. Reaction condition: $[NFX] = 20 \text{ mg} \cdot \text{L}^{-1}$, $[PMS] = 0.4 \text{ g} \cdot \text{L}^{-1}$, $[catalyst] = 0.3 \text{ g} \cdot \text{L}^{-1}$. (f) Arrhenius plots derived from corresponding kinetic curves of Cu-Co-700: $\ln(k)$ v.s. T^{-1} .



Figure S9 NFX degradation course curves by Cu-Co-700 system in actual water samples; Reaction condition: [NFX] = $20 \text{ mg} \cdot \text{L}^{-1}$, [PMS] = $0.4 \text{ g} \cdot \text{L}^{-1}$, [catalyst] = $0.3 \text{ g} \cdot \text{L}^{-1}$.



Fig. S10 Reaction time dependent NFX degradation course curves of NFX degradation over Cu-Co-700 and the leachate; Reaction conditions: $[NFX]=20 \text{ mg} \cdot \text{L}^{-1}$, $[PMS]=0.2 \text{ g} \cdot \text{L}^{-1}$, $[catalyst]=0.2 \text{ g} \cdot \text{L}^{-1}$, [Leachate: NFX]=25 mL.



Figure S11 3D fluorescence spectra during waste water degradation process with Cu-Co-700. Reaction condition: $[PMS] = 0.4 \text{ g}\cdot\text{L}^{-1}$, $[catalyst] = 0.3 \text{ g}\cdot\text{L}^{-1}$.

NFX	Time	Conv.	Catalyst	Dosage (g·L ⁻¹)	PMS (g·L ⁻¹)	Rate	
						constant	Ref.
(mg·L ⁻¹)	(min)	(%)				k (min ⁻¹)	
20	12	89.9	Cu-Co-700	0.3	0.4	0.629	This work
20	90	97.5	NiCo ₂ O ₄ NS	0.4	0.18	0.488	[1]
3.2	45	95~	Co_3O_4 (@Fe_2O_3)	0.2	0.03	0.140	[2]
9.6	60	94.8	Co ₃ O ₄ @CNT	0.12	0.076	0.044	[3]
30	30	100	Fe_2O_3 @CoFe_2O_4	0.3	0.061	0.188	[4]
10	15	87	2-CZA	0.02	0.14	0.165	[5]
9.6	60	90.8	Co ₂ Fe ₂ O ₄ /OSC	0.5	0.22	0.05	[6]
32	20	100	Fe/Fe ₃ C@NG	0.1	0.15	0.22	[7]

Table S1. Comparison of NFX degradation based on optimal Cu-Co-700 and several comparative catalysts.

10	30	99.1	β-CD@Fe ₃ O ₄	0.4	0.608	0.158	[8]
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 Table S2. The following equations are concerned with anions and radicals:

$\cdot \mathrm{OH} + \mathrm{H}_{2}\mathrm{PO}_{4}^{-} \rightarrow \mathrm{OH}^{-} + \mathrm{H}_{2}\mathrm{PO}_{4}^{-} \cdot$	(1)
$\cdot \mathrm{OH} + \mathrm{HCO}_3^- \to \mathrm{CO}_3^- \cdot + \mathrm{OH}^-$	(2)
$\cdot \mathrm{OH} + \mathrm{CO}_3^{2\text{-}} \rightarrow \mathrm{CO}_3^{-\text{-}} + \mathrm{OH}^{-\text{-}}$	(3)
$\mathrm{SO}_4^{-\cdot} + \mathrm{HCO}_3^{-} \rightarrow \mathrm{CO}_3^{-\cdot} + \mathrm{HSO}_4^{-}$	(4)
SO_4 -· + CO_3 ²⁻ $\rightarrow CO_3$ -· + SO_4 ²⁻	(5)

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