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Liping Wang

wanglp_csu@163.com

Qujing Normal University

Ziyun Zhang

Qujing Normal University

Chunyan Gao

Qujing Normal University

Zhicong Li

Qujing Normal University

Zhijuan Wang

Qujing Normal University

yingchun Miao

Qujing Normal University

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MOF-derived S-scheme CuFe₂O₄/CuO/C heterojunctions with broad-spectrum response for efficient and stable tetracycline degradation

Liping Wang*, Ziyun Zhang, Chunyan Gao, Zhicong Li, Zhijuan Wang*, Yingchun Miao*

Yunnan Key Laboratory of Crystalline Porous Organic Functional Materials, College of Chemistry and Materials Engineering, Qujing Normal University, Qujing, 655011, Yunnan Province, PR China

*Corresponding author, e-mail: wanglp_csu@163.com

Contributing authors: 253432678@qq.com; 18835776@qq.com; 283894449@qq.com;
273928656@qq.com; 398836242@qq.com

Abstract

The widespread application of tetracycline antibiotics (TCs) in medical treatment and livestock breeding has caused their pervasive accumulation in aquatic environments, thereby posing severe risks to ecosystems and public health. Photocatalysis stands out as an eco-friendly and sustainable technique for the removal of organic contaminants from aquatic environments. Herein, CuFe₂O₄/CuO/C heterostructures were synthesized through a facile and scalable calcination route with CuFe-based Prussian blue analogue as the precursor. The as-prepared composites exhibit broad light absorption spanning the 200-800 nm region. The composite calcined at 400 °C shows optimal catalytic activity, achieving 95.9% TC removal efficiency under visible light irradiation, and remains above 90% removal after 10 cycles, verifying outstanding structural stability and reusability. In addition, the composite possesses favorable TC elimination capacity across a wide pH window of 3-9, and common anions have negligible effects on the photocatalytic TC degradation over the CuFe₂O₄/CuO/C heterostructure. Comprehensive characterizations reveal that the excellent performance of the CuFe₂O₄/CuO/C heterostructure arises from the synergistic interplay of optimized crystallinity, carbon conductive network, tight interface and favorable surface properties. Radical trapping experiments and electron paramagnetic resonance (EPR) analyses confirm that superoxide radicals ($\cdot\text{O}_2^-$) and photogenerated holes (h^+) act as the dominant active species, whereas hydroxyl radicals ($\cdot\text{OH}$) played only a minor role. Combined with *in situ* irradiated X-ray photoelectron spectroscopy (XPS) measurements and band structure analysis, these findings support an S-scheme charge transfer mechanism, where photogenerated electrons accumulate in the conduction band of CuFe₂O₄ to facilitate O₂ reduction to $\cdot\text{O}_2^-$, while holes are reserved on the valence band of CuO to directly degrade TC molecules. This work offers a facile scale-up strategy to construct efficient and durable S-scheme CuFe-based photocatalysts, which can serve as a promising candidate for practical antibiotic wastewater remediation.

Keywords: S-scheme heterojunction, CuFe₂O₄/CuO/C, broad-spectrum response, reusability, tetracycline degradation

1 Introduction

The rapid expansion of pharmaceutical manufacturing and intensive livestock-breeding industries has led to persistent accumulation of organic pollutants in aquatic environments. Among these contaminants, tetracycline (TC) antibiotics exert an ever-increasing severe threat to ecological safety

and human health [1]. The accumulation of these contaminants not only induces microbial toxicity but also promotes the spread of antibiotic resistance genes, exacerbating the global antimicrobial resistance crisis [2]. Owing to their stable molecular architectures, such organic pollutants resist complete mineralization by conventional treatment processes, including adsorption [3], biodegradation [4], and chlorination [5]. As an advanced oxidation process that operates under mild conditions and produces no secondary solid waste, photocatalysis has emerged as a green technology for waterborne organic pollutant remediation [6]. The efficacy and practicality of this approach are governed by the performance of the photocatalyst [7]. Accordingly, the development of efficient, recyclable, and visible-light-active photocatalysts represents a major priority in current environmental catalysis research [8].

CuFe₂O₄ features a narrow bandgap that enables visible light absorption, combined with low cost, excellent chemical stability, and intrinsic ferromagnetism, making it an attractive semiconductor photocatalyst [9]. Consequently, it has been widely adopted for various applications, including hydrogen evolution [10], CO₂ reduction [11], organic synthesis [12], Cr(VI) reduction [13], sterilization [14], and the photocatalytic degradation of organic pollutants, such as dyes, antibiotics, herbicides, and nitrogen-containing heterocyclic compounds [15]. However, the application of pristine CuFe₂O₄ is hindered by its inherent drawbacks, namely severe magnetic agglomeration, fast charge carrier recombination, and poor photon utilization. As a result, the bare material fails to deliver the photocatalytic activity needed for water remediation. To overcome these limitations, numerous modification strategies have been developed. These include elemental doping to introduce lattice impurity energy levels and modulate band alignment [16], carbonaceous material hybridization to build conductive networks for fast electron migration [17], noble metal deposition to broaden the light response range [18], MOF-confined engineering to inhibit particle aggregation and enrich organic contaminants [19], conducting polymer coating to construct electron transport channels [20], inert interlayer coating to alleviate metal ion leaching and photocorrosion [21], and heterojunction construction by coupling two or more semiconductors to create Z-scheme or S-scheme interfaces for efficient charge separation [22]. Among these approaches, heterojunction construction is regarded as the most effective method for enhancing the photocatalytic performance of CuFe₂O₄.

To date, most reported CuFe₂O₄-based heterojunctions still rely on cumbersome multi-step procedures. The most commonly adopted method involves physically mixing pre-synthesized CuFe₂O₄ particles with other semiconductor components via sonication and/or mechanical grinding, followed by high-temperature annealing to form heterojunctions, as reported by CuO/CuFe₂O₄/g-C₃N₄ [23], WO₃/CuFe₂O₄ [24], Bi₂Te₃/CdS/CuFe₂O₄ [25], CuFe₂O₄/Bi₂O₃ [26], CuFe₂O₄/ZnIn₂S₄ [27], CuFe₂O₄/SnS₂ [28], BiOCl/BiOBr/CuFe₂O₄ [29], and ZIF-8/g-C₃N₄/CuFe₂O₄ [30]. However, this physical assembly merely creates loose interfacial contact, resulting in large interfacial resistance and severe carrier recombination. To address the weak interfacial adhesion, an *in situ* growth strategy has been proposed, wherein a second semiconductor phase is directly grown onto the surface of prefabricated CuFe₂O₄ particles, as demonstrated in FeOOH QDs/CuFe₂O₄ [31], CuFe₂O₄@NH₂-MIL-125(Ti) [32], CuFe₂O₄/AgBr [33], CuFe₂O₄-MoS₂@BC [34], CuFe₂O₄/CuS [35], CuFe₂O₄@ZnFe₂O₄ [36], and gCN/CuFe₂O₄/MoS₂ [37]. Nevertheless, the stepwise *in situ* growth cannot eliminate magnetic agglomeration of CuFe₂O₄ particles, which inevitably covers the abundant active sites. As an alternative, a reverse growth strategy has been developed, in which CuFe₂O₄ is grown onto pre-synthesized semiconductor substrates, as represented by CuFe₂O₄/C/SiO₂ [38], CuFe₂O₄@LBC [39], CuFe₂O₄@BC [40]. This method effectively suppresses CuFe₂O₄ aggregation.

However, the reverse-loaded composites are prone to light-shielding effects caused by excessive secondary phases, which reduce photon capture efficiency. In addition, existing systems commonly suffer from limited recyclability and leaching of metal ions under prolonged irradiation. Therefore, there is an urgent need to develop novel CuFe_2O_4 -based photocatalysts that meet the requirements of facile and scalable preparation, robust interfacial bonding, and long-term stability.

Prussian blue analogues (PBAs), a subclass of MOFs characterized by periodically arranged metal ions and cyanide bridges, have emerged as versatile precursors for metal oxide composites [41]. Upon calcination at moderate temperatures, PBA precursors undergo transformation into multi-metal oxide heterostructures, accompanied by the *in situ* decomposition of cyanide groups to form continuous conductive carbon networks. The atomic-level homogeneity of metal ions ensures uniform oxide distribution [42]. The self-sacrificial template effect preserves morphological integrity, and the incorporated carbon species facilitate charge transport and light harvesting [43]. Furthermore, the method is both operationally simple and readily scalable, rendering it amenable to practical implementation [44]. Given these advantages, the PBA-derived strategy presents a compelling route for overcoming the limitations of conventional fabrication techniques and realizing heterojunctions with robust, well-defined interfaces. In this work, CuFe-PBA was employed as a single-source precursor to fabricate S-scheme $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ ternary heterojunctions via one-step calcination process. The synthesis procedure avoids tedious multi-step impregnation and secondary coating. The calcination temperature was adjusted to balance crystallinity, residual carbon content, and interfacial bonding strength. TC was selected as representative organic pollutant to evaluate the photocatalytic performance of the resulting composites. Comprehensive characterizations were carried out to analyze the microstructure, optical properties, and charge transfer behavior. Band structure calculation, radical scavenging experiments, electron paramagnetic resonance spectroscopy, and *in situ* irradiated X-ray photoelectron spectroscopy were combined to elucidate the S-scheme carrier migration pathway, and the mineralization pathway of TC was proposed from intermediate analysis. Cyclic degradation tests were performed to verify recyclability and long-term stability. Collectively, this work demonstrates a facile, self-sacrificial PBA-templated approach for the construction of S-scheme heterojunctions, offering both a theoretical framework and a technical reference for the design of visible-light-driven photocatalysts for organic wastewater remediation.

2 Experimental section

2.1 Materials

All reagents were purchased from commercial suppliers and used as received. Copper(II) acetate monohydrate ($(\text{CH}_3\text{COO})_2\text{Cu}\cdot\text{H}_2\text{O}$, 98.0%) was sourced from Reagent No.1 Factory of Shanghai Chemical Reagent Co., Ltd.. Potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$, 99.5%), sodium citrate ($\text{C}_6\text{H}_5\text{O}_7\text{Na}_3$, 98%), sodium chloride (NaCl), and sodium sulfate anhydrous (Na_2SO_4 , 99%) were obtained from Shanghai Aladdin Biochemical Technology Co.. Ethylenediaminetetraacetic acid disodium salt ($\text{EDTA}\cdot 2\text{Na}$, 99%) were supplied by Tianjin Fengchuan Chemical Reagent Technology Co.. Tetracycline (TC, 90%), p-benzoquinone (BQ, 99%), sodium nitrate (NaNO_3), sodium bicarbonate (NaHCO_3), sodium phosphate monobasic (NaH_2PO_4), humic acid (HA), and tert-butanol (TBA, 99.5%) were acquired from Shanghai Titan Scientific Co., Ltd.. Ethanol ($\geq 99.7\%$) and acetone ($\geq 99.5\%$) were sourced from Chengdu Kelong Chemicals Co., Ltd.

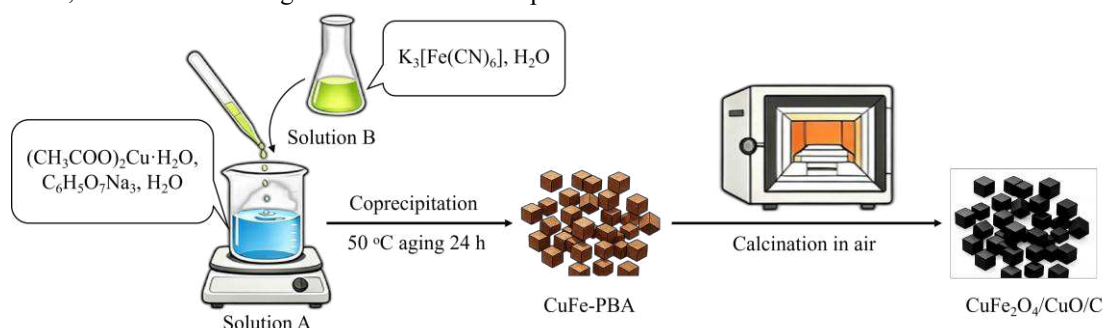
2.2 Synthesis of CuFe-PBA

CuFe-PBA was synthesized via a simple coprecipitation method. In a typical procedure, Solution A was prepared by dissolving $(\text{CH}_3\text{COO})_2\text{Cu}\cdot\text{H}_2\text{O}$ (4.50 mmol) and $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3$ (9.00 mmol) in 150 mL

ultrapure water under continuous stirring. Solution B was prepared by dissolving $K_3[Fe(CN)_6]$ (6.75 mmol) in 150 mL ultrapure water. Subsequently, Solution B was introduced dropwise into Solution A under vigorous stirring, immediately yielding the formation of a colored precipitate. After complete addition, the mixture was stirred for another 30 min and then aged at 50 °C for 24 h in a static incubator. The resulting precipitate was collected by centrifugation, washed sequentially with ultrapure water, ethanol, and acetone to remove residual precursors and byproducts, and finally dried at 50 °C overnight. Finally, the purified material was dried at 50 °C overnight. The final powder, denoted as CuFe-PBA (Scheme 1), was kept in a desiccator to prevent moisture absorption.

2.3 Synthesis of $CuFe_2O_4/CuO/C$

$CuFe_2O_4/CuO/C$ composites were obtained by calcining the CuFe-PBA precursor in air. In a typical run, approximately 0.3 g of CuFe-PBA was heated in a muffle furnace to the target temperature (300, 350, 400, 450, or 500 °C) at a ramping rate of 2 °C/min, held for 2.5 h, and then allowed to cool naturally to room temperature. The resulting products (Scheme 1) were labeled as T300, T350, T400, T450, and T500 according to the calcination temperature.



Scheme 1 Synthesis of $CuFe_2O_4/CuO/C$ composites from CuFe-PBA precursors

2.4 Characterizations

X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV X-ray diffractometer using $Cu\ K\alpha$ radiation ($\lambda = 1.5406\ \text{\AA}$). Thermogravimetric (TG) analysis was performed on a Netzsch STA 449 F3 simultaneous thermal analyzer. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Scientific K-Alpha X-ray spectrometer. Scanning electron microscopy (SEM) images were acquired using a ZEISS Sigma 300 electron microscope. High-resolution transmission electron microscopy (HRTEM) characterization and energy-dispersive spectroscopy (EDS) elemental mapping were performed on a Thermo Scientific Talos F200X transmission electron microscope. Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) spectra were recorded on a Shimadzu UV-3600i Plus spectrophotometer. Photoluminescence (PL) spectra were obtained on an Edinburgh FLS1000 fluorescence spectrometer. Water contact angle (WCA) measurements were carried out on a SCI4000D goniometer (Beijing Global Hengda Technology Co., Ltd., China). Electron paramagnetic resonance (EPR) signals were collected on a Bruker EMXplus-6/1 spectrometer. *In situ* irradiated XPS measurements were carried out on a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer. Liquid chromatography-mass spectrometry (LC-MS) analysis for intermediate identification was conducted on a Ultimate 3000 UHPLC-Q-Exactive mass spectrometer.

2.6 Electrochemical tests

Transient photocurrent response, electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV) measurements were performed on a CHI760E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China) using a conventional three-electrode system with a saturated calomel electrode (SCE) as the reference electrode.

A catalyst ink was prepared by dispersing 10.0 mg of CuFe₂O₄/CuO/C composite in 1 mL of ethanol containing 10 µL of 5 wt% Nafion solution. For the photocurrent and CV measurements, a working electrode was constructed by drop-casting the ink onto a fluorine-doped tin oxide (FTO) glass substrate (1 cm × 2 cm), with a platinum sheet as the counter electrode. For EIS test, the working electrode was fabricated by coating the same ink onto a glassy carbon electrode (GCE, 3 mm diameter), using a platinum disk as the counter electrode.

2.7 Photocatalytic degradation experiments

Photocatalytic degradation experiments were conducted using a 300 W xenon lamp with a 420 nm cutoff filter as the simulated light source. Briefly, 100 mL TC aqueous solution was poured into a 200 mL beaker, followed by the addition of the as-prepared CuFe₂O₄/CuO/C composite. A set of batch experiments was designed to investigate TC removal performance with varying catalyst loadings, initial TC concentrations and solution pH values. Furthermore, the inhibitory influences of HA and common inorganic anions in actual water were also examined.

Prior to illumination, the suspension was magnetically stirred in the dark for 20 min to achieve adsorption-desorption equilibrium. At 20 min intervals, 4 mL aliquots were collected and filtered through a 0.22 µm syringe filter, and analyzed by a UV-vis spectrophotometer. The absorbance was recorded at 356 nm using deionized water as the blank reference. All measurements were conducted in triplicate, and average values were adopted to guarantee experimental accuracy. The TC removal efficiency and the reaction rate constant (*k*) were calculated according to equations (1) and (2), respectively, where η is the TC removal efficiency, C_0 and C_t represent the initial and residual absorbances at a given irradiation time, *k* is the reaction rate constant, and *t* is the irradiation time.

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

$$-\ln\left(\frac{C_t}{C_0}\right) = -kt \quad (2)$$

2.8 Radical trapping experiments

Radical trapping experiments were performed to identify the dominant active species involved in the photocatalytic TC degradation. In a typical procedure, 40.0 mg of CuFe₂O₄/CuO/C composite was suspended in 100 mL of TC solution (10 mg/L). Subsequently, BQ, EDTA-2Na, and TBA were separately introduced as scavengers for superoxide anion radicals ($\cdot\text{O}_2^-$), photogenerated holes (h^+), and hydroxyl radicals ($\cdot\text{OH}$), respectively. The suspension was magnetically stirred in the dark for 20 min to establish adsorption-desorption equilibrium, and then irradiated under a 300 W xenon lamp with continuous stirring. At given time intervals, aliquots were sampled and filtered, and the absorbance at 356 nm was measured using a UV-vis spectrophotometer. The TC removal efficiency was calculated to evaluate the contribution of each active species.

3 Results and discussion

3.1 Structural and morphological evolution

The crystal structures and thermal decomposition behavior of the CuFe-PBA were investigated by XRD and TG. As presented in Fig.1a, the XRD pattern can be indexed to the cubic Cu(Fe(CN)₆)_{0.67} phase (PDF#86-0513). The peaks at 15.1°, 17.6°, 24.9°, 29.3°, 35.6°, 39.9°, 43.9°, 51.1°, 54.6°, 57.8°, 66.6°, and 69.6° are assigned to the (111), (200), (220), (311), (400), (420), (422), (440), (442), (620), (640), and (642) planes, respectively. The absence of impurity peaks indicates the high phase purity of the as-prepared CuFe-PBA precursor. TG analysis was performed from 30 °C to 800 °C in air. As illustrated in Fig.1b, TG curve reveals a continuous weight loss with increasing temperature, while the

derivative thermogravimetric (DTG) curve exhibits two distinct exothermic peaks at approximately 106 °C and 194 °C. The weight loss can be divided into three stages, namely, the removal of physically adsorbed water below 126 °C, the evaporation of interstitial water between 126 °C and 200 °C, and the decomposition of the PBA framework above 200 °C.

Based on the TG results, the CuFe-PBA precursor was calcined at 300, 350, 400, 450 and 500 °C to obtain a series of CuFe₂O₄/CuO/C composites. The XRD patterns are displayed in Fig.1c and 1d. As shown in Fig. 1c, calcination at 300°C causes the complete disappearance of the CuFe-PBA diffraction peaks and the appearance of new reflections, indicating a significant phase transformation from CuFe-PBA to metal oxides. The peaks at 18.3°, 30.1°, 42.9°, 56.8°, 62.6°, and 74.9° are attributed to the (111), (220), (400), (511), (440), and (533) plane of cubic CuFe₂O₄ phase (PDF#25-0283), while those at 32.5°, 38.7°, 48.7°, 53.5°, 58.3°, 61.5°, 66.2°, and 68.1° are assigned to the (110), (111), (20-2), (020), (202), (11-3), (31-1), and (113) planes of monoclinic CuO phase (PDF#48-1548). Notably, the strongest peak at around 35.5° arises from the overlapping contributions of the CuFe₂O₄ (311) and CuO (11-1) reflections, which is consistent with their closely positioned standard peaks. No peak corresponding to the (002) plane of graphitic carbon is detected at 26.5° [45], implying that the carbon species are either poorly crystallized or present in an amount below XRD detection limit. Nevertheless, the presence of carbon was confirmed by subsequent EDS and XPS analyses. As the calcination temperature increases from 300 to 500 °C, the diffraction peaks of both CuFe₂O₄ and CuO gradually sharpen and intensify (Fig. 1d), reflecting the enhanced crystallinity of the composites, which is generally considered beneficial for photocatalytic performance. Overall, these results confirm the coexistence of CuFe₂O₄ and CuO in the prepared composites.

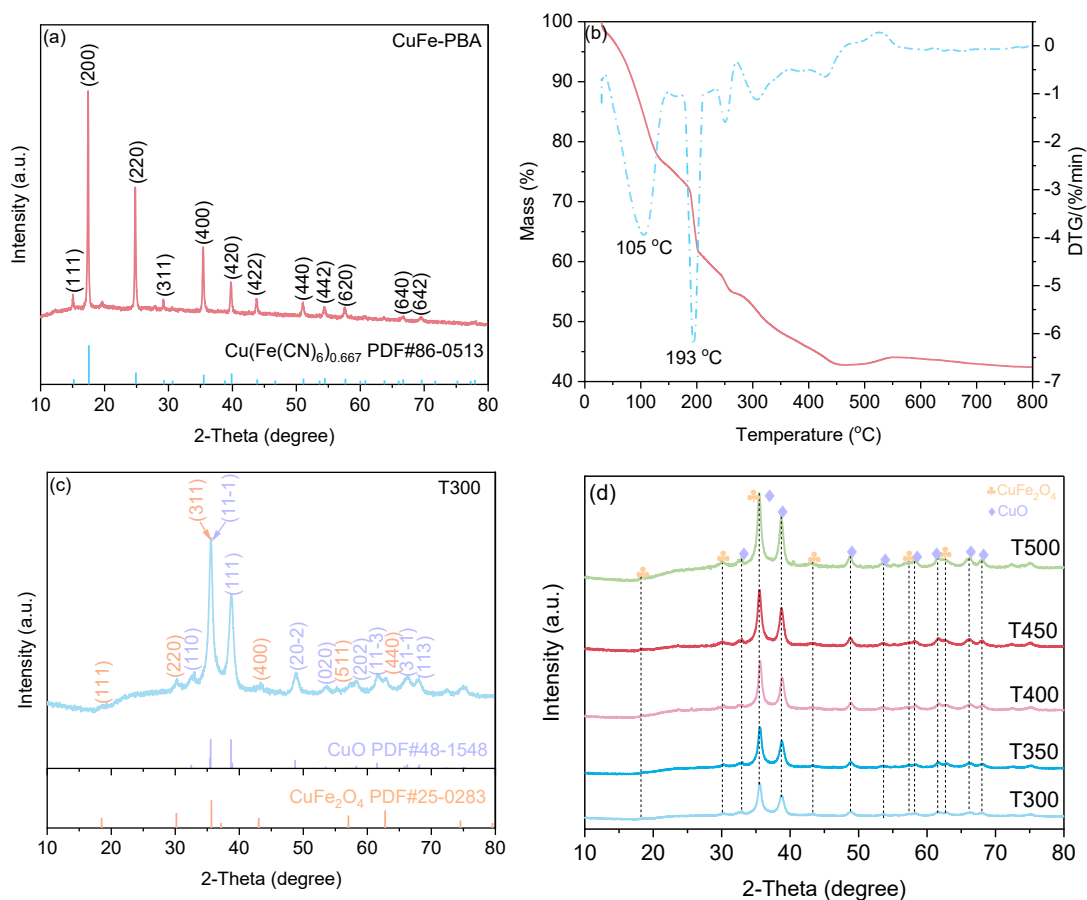


Fig. 1 (a) XRD pattern, (b) TG-DTG curves of CuFe-PBA, and (c,d) XRD patterns of CuFe₂O₄/CuO/C

composites

Next, SEM measurements were performed to trace the morphological evolution from the CuFe-PBA precursor to the CuFe₂O₄/CuO/C composites, and the resulting SEM images are shown in Fig. 2 and Fig. S1-S3. As presented in Fig. 2a and 2b, the precursor exhibits regular a cubic nanocrystal morphology with smooth surfaces and particle sizes ranging from 80 to 150 nm. EDS elemental mapping (Fig. S1) reveals a homogeneous distribution of Fe, Cu, C, and N throughout the particles, confirming the uniform elemental composition of the CuFe-PBA framework. After calcination, the original cubic structure of CuFe-PBA completely collapses, accompanied by the decomposition of cyanide ligands and the *in situ* generation of tiny CuFe₂O₄/CuO/C nanoparticles (Fig. 2c, 2d, and S2). The final product displays a rough granular morphology.

The T400 composite was further analyzed by TEM and HRTEM to gain insight into its interior microstructure. As shown in Fig.3a-3c, the TEM images reveal that the rough particles consists of densely assembled CuFe₂O₄/CuO nanocrystals with intimate interfacial contact. The HRTEM image (Fig. 3d) presents well-resolved lattice fringes with interplanar spacings of 282 pm and 239 pm, corresponding to the (220) plane of cubic CuFe₂O₄ and the (111) plane of monoclinic CuO, respectively. These lattice fingerprints are consistent with XRD observations and provide direct evidence for the successful formation of CuFe₂O₄/CuO heterostructure. EDS mapping results (Fig.4 and Fig. S3) confirm the coexistence and uniform dispersion of Cu, Fe, O, and C elements within the particles, demonstrating excellent compositional homogeneity of the CuFe₂O₄/CuO/C composite. Notably, the carbon content (Table S1) gradually decreases with increasing calcination temperature, consistent with the thermal decomposition of the cyanide ligands during calcination.

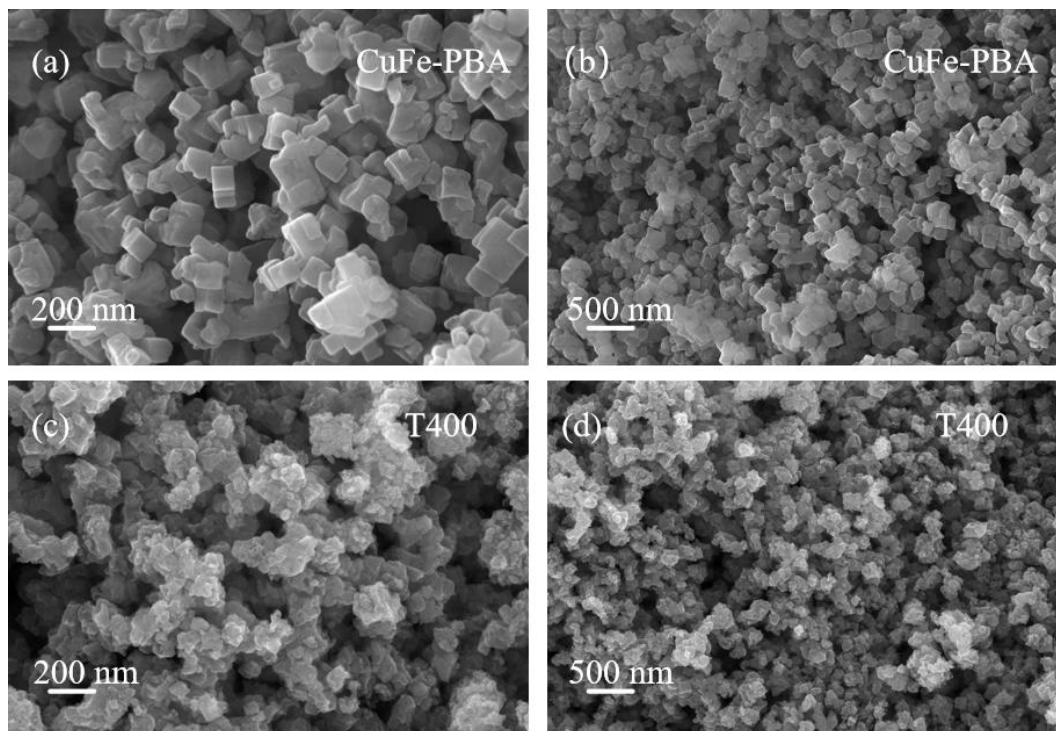


Fig. 2 SEM images of (a,b) CuFe-PBA and (c,d) T400

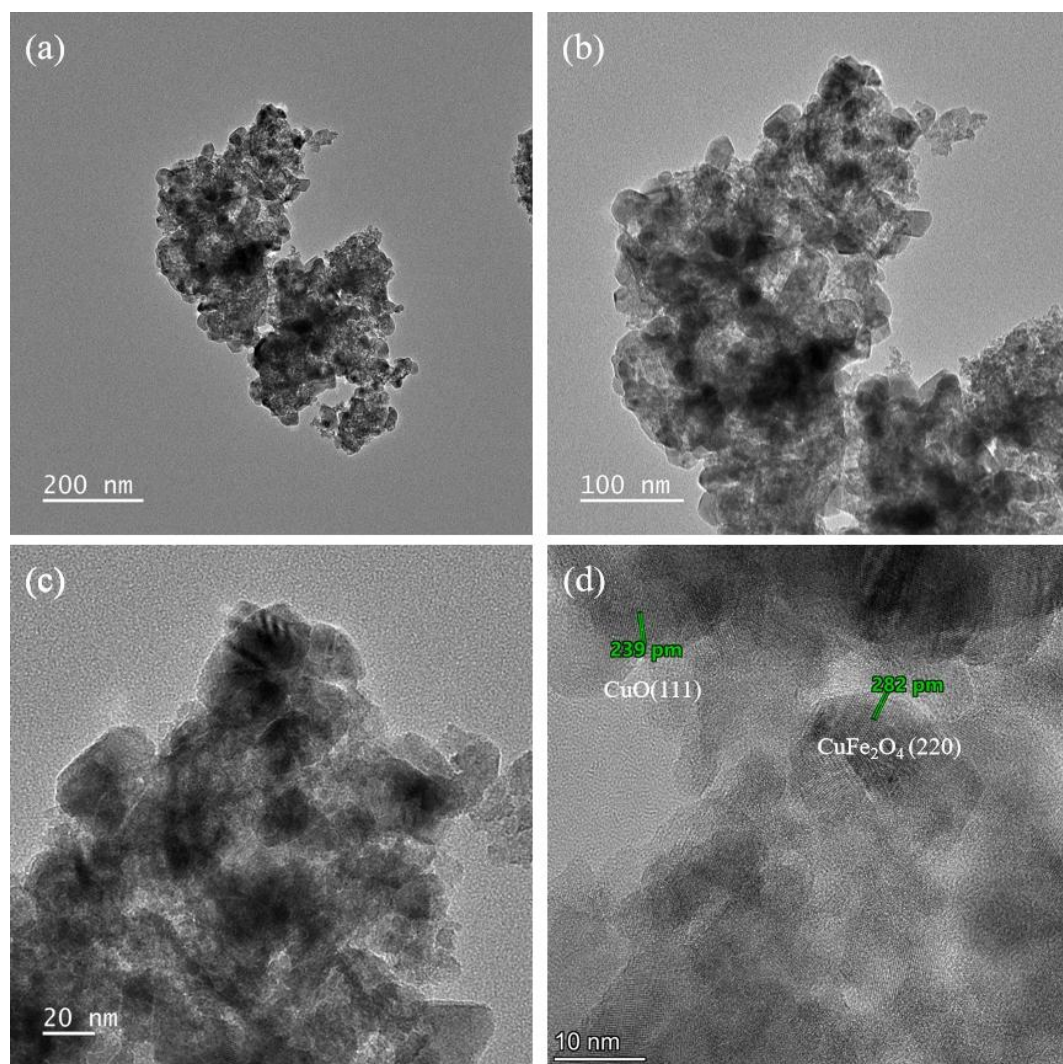


Fig. 3 (a,b,c)TEM images, (d) HRTEM image of CuFe₂O₄/CuO/C synthesized at 400 °C

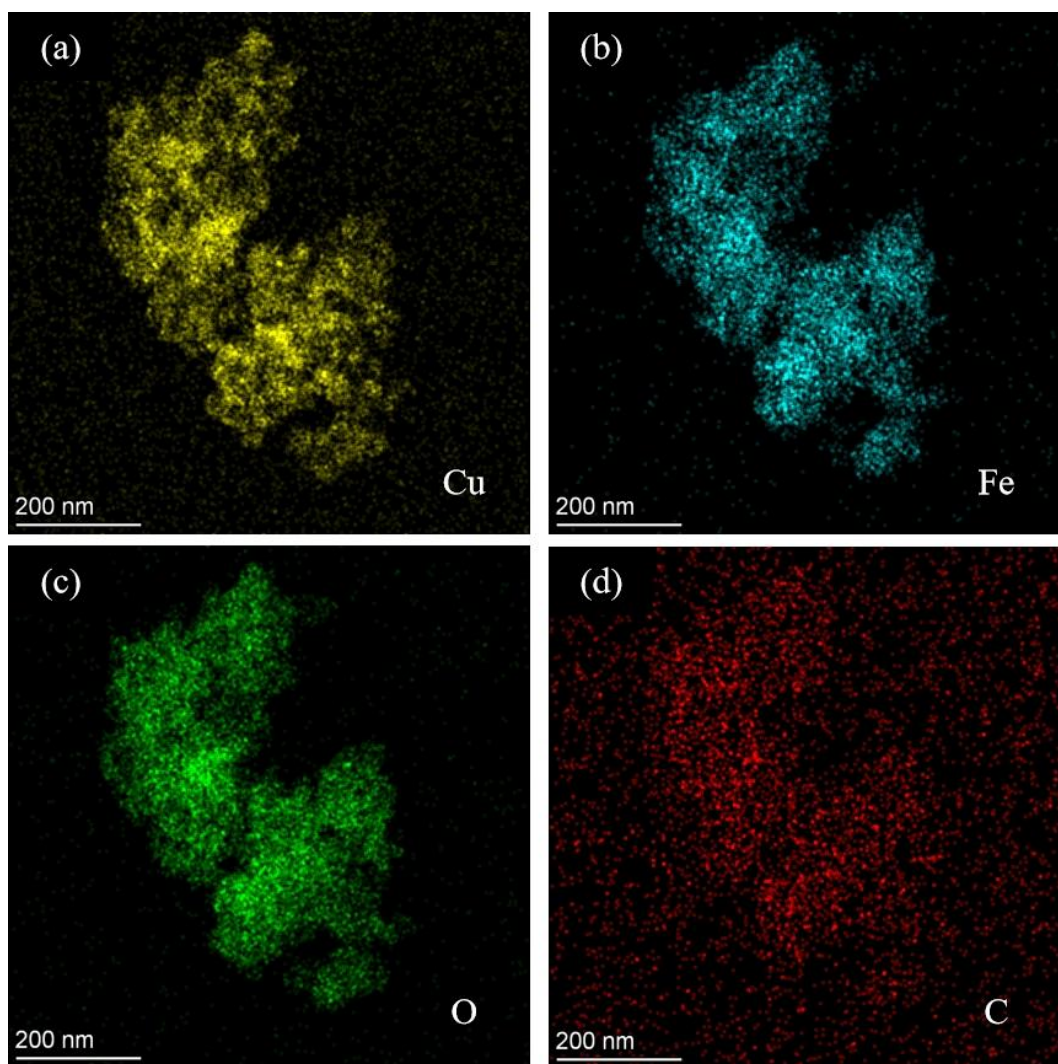


Fig. 4 Elemental mapping images of CuFe₂O₄/CuO/C synthesized at 400 °C

Furthermore, XPS analysis was conducted on the T400 composite to confirm the chemical states and surface composition of the constituent elements. The survey spectrum (Fig. 5a) suggests that the sample contains Cu, Fe, O, and C with no detectable impurities, fully consistent with the EDS results. High-resolution Cu 2p, Fe 2p, O 1s, and C 1s spectra were subsequently deconvoluted to investigate the detailed chemical environments of each element.

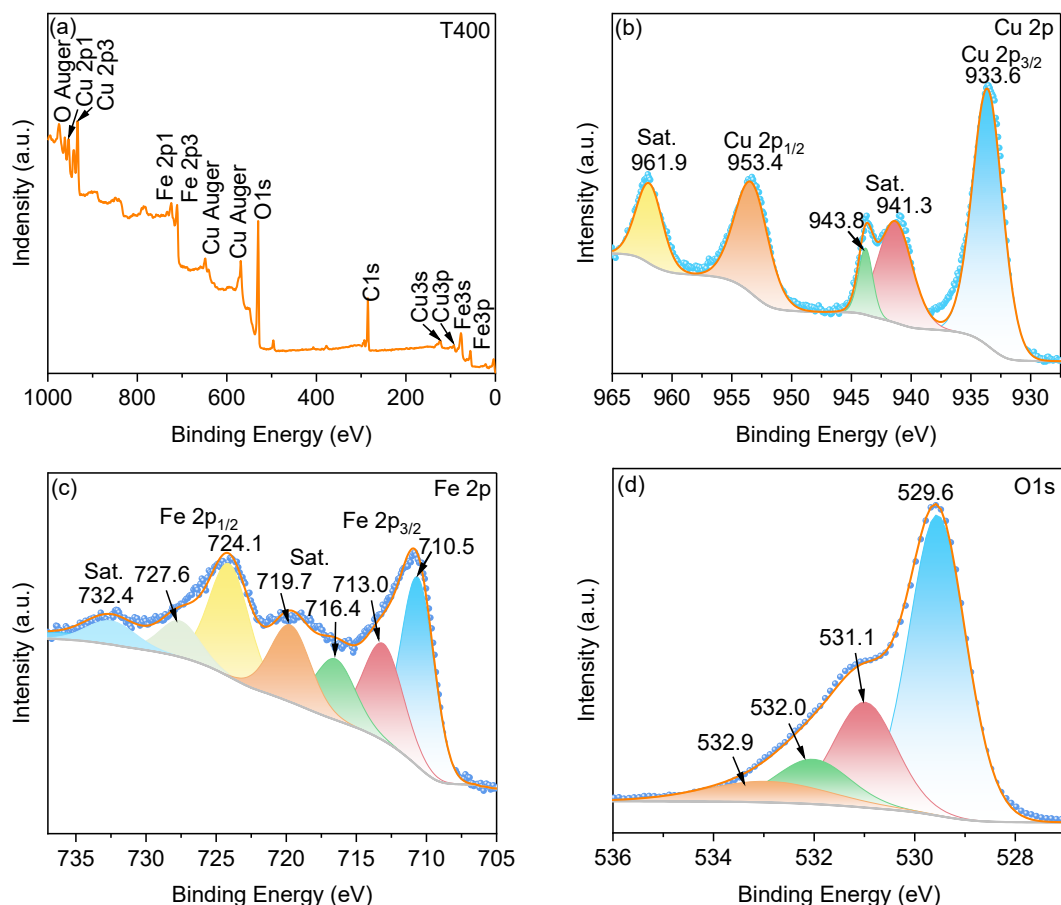
The high-resolution Cu 2p spectrum is illustrated in Fig. 5b. The two main peaks at 933.6 and 953.4 eV are attributable to Cu 2p_{3/2} and Cu 2p_{1/2} of Cu²⁺, respectively [46]. In the Cu 2p_{3/2} region, a multiplet-split subpeak appears at 941.3 eV, arising from the unpaired 3d electrons of Cu²⁺ species. This feature is absent for Cu⁺ or Cu⁰ species due to their fully filled 3d¹⁰ configurations [47]. A shake-up satellite at 943.8 eV, along with the Cu 2p_{1/2} satellite at 961.9 eV, further confirms the dominance of Cu²⁺. No signals attributable to Cu⁺ or Cu⁰ are observed in the 932–933 eV range, indicating that copper in the composite exists predominantly in the +2 oxidation state, originating from both CuO and CuFe₂O₄ phases.

Fig. 5c displays the high-resolution Fe 2p spectrum. The peaks at 710.5 eV (Fe 2p_{3/2}) and 724.1 eV (Fe 2p_{1/2}) are assigned to octahedrally coordinated Fe³⁺ species in the spinel lattice, while the peaks at 713.0 (Fe 2p_{3/2}) and 727.6 eV (Fe 2p_{1/2}) correspond to tetrahedrally coordinated Fe³⁺ [48]. A multiple-split subpeak at 716.4 eV in the Fe 2p_{3/2} region arises from the unpaired 3d electrons of

high-spin Fe^{3+} . Shake-up satellite peaks at 719.7 eV [49] and 732.4 eV [50] in the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ regions, respectively, provides strong evidence for the Fe^{3+} oxidation state. No signals attributable to Fe^{2+} (at ~ 709.5 eV for Fe $2p_{3/2}$) [51] or metallic Fe^0 (~ 706.8 eV) [52] are detected, confirming that iron exists exclusively as Fe^{3+} in the spinel CuFe_2O_4 phase.

The high-resolution O 1s spectrum is presented in Fig. 5d. The spectrum can be deconvoluted to four peaks located at 529.6, 531.0, 532.0 and 532.9 eV. The dominant peak at 529.6 eV is attributed to lattice oxygen from Cu-O and Fe-O bonds in CuFe_2O_4 and CuO phases [53]. The peak at 531.0 eV is assigned to multiple oxygen species on the composite surface, including oxygen vacancies [54], hydroxyl groups, and adsorbed oxygen species [55]. The peaks at 532.0 eV [56] and 532.9 eV [57] are correlated with C=O and C-O-C bonds, respectively.

The high-resolution C 1s spectrum (Fig. 5e) indicates well-resolved components at 284.8 eV, 286.5 eV, 288.5 eV, 292.7 eV and 295.5 eV. The intense peak at 284.8 eV is attributed to sp^2 hybridized graphitic carbon in C=C/C-C [58]. The peaks at 286.5 eV and 288.5 eV are assigned to C-OH and C=O groups [59], respectively. The peaks at 292.7 [60] and 295.5 eV [61] correspond to the π - π^* shake-up satellite features of conjugated sp^2 carbon species. The coexistence of these diverse carbon species may provide a multifunctional carbon matrix that facilitates electron transport, modulates surface hydrophilic wettability, and strengthens interfacial interactions between CuFe_2O_4 and CuO.



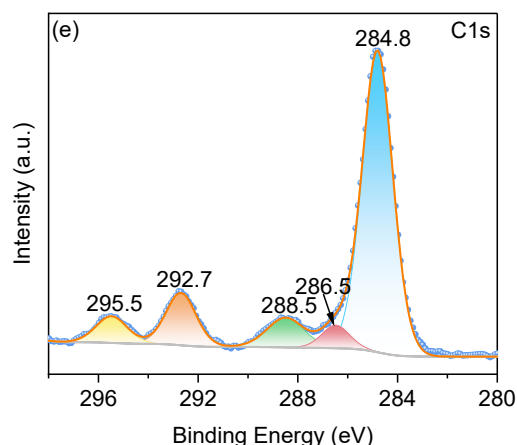


Fig. 5 (a) Survey XPS spectrum, high-resolution XPS spectra of (b) Cu 2p, (c) Fe 2p, (d) O 1 s, and (e) C 1 s of T400

3.2 Optical properties

Light harvesting capacity of a photocatalyst determines its utilization efficiency of incident photons and governs the intrinsic photocatalytic activity. UV-vis DRS was thus employed to investigate the optical absorption characteristics of the $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ composites calcined at different temperatures (300, 350, 400, 450 and 500 °C), and the corresponding spectra are presented in Fig. 6a. All five samples exhibit broad absorption spanning the 200–800 nm range, covering ultraviolet, visible and partial near-infrared regions, which demonstrates their capability to harvest incident photons and generate more photogenerated carriers, which lays a favorable foundation for improved photocatalytic performance. Notably, T300 shows the strongest light absorbance across the entire measured wavelength range, and the optical absorption intensity gradually declines as calcination temperature rises from 300 °C to 500 °C. This declining trend mainly originates from the improved crystallinity of CuFe_2O_4 and CuO phases and the reduced carbon content at higher temperatures. Enhanced crystallization reduces surface defective sites that contribute to sub-bandgap light absorption, thereby lowering the broadband absorbance [62]. In addition, the carbon component facilitates multiple internal light reflections that strengthen light trapping [63], so its gradual loss at higher temperatures suppresses the light-absorbing performance.

Tauc plots converted from UV-vis DRS data were constructed to determine the band gaps of the samples. A segmented Tauc plot method [64] was applied to separately extract the band gap values of CuFe_2O_4 and CuO from the composite spectra. Fig. 6b displays the Tauc curve of the T400 sample, while the curves for T300, T350, T450 and T500 are presented in Fig. S4. Two independent linear segments can be identified on the Tauc curves of all samples, in line with the coexistence of CuFe_2O_4 and CuO in the composites. The band gaps of both components exhibit a slight widening trend with increasing calcination temperature, which matches well with the blue shift of the absorption edges observed in UV-vis DRS spectra. For instance, the band gaps of CuFe_2O_4 and CuO for T300 are approximately 1.45 eV and 1.23 eV, respectively, increasing to 1.47 eV and 1.27 eV for T500, with intermediate values for the other temperatures. Despite such minor variation, all samples retain narrow band gaps, endowing the heterostructures with prominent photoresponse across visible and near-infrared regions. Mulliken's electronegativity theory [65] was employed to calculate the conduction band (CB) and valence band (VB) potentials of CuFe_2O_4 and CuO. Fig. 6c presents the band alignment diagram of T400, while the calculated VB and CB potential values for the remaining samples are summarized in Table S2. Combined with the intimate interfacial contact verified by

HRTEM characterization, the staggered band alignment between CuFe_2O_4 and CuO establishes a solid band-structure foundation for formation of type-II or S-scheme charge transfer pathways, which facilitates the spatial separation of photogenerated electrons and holes.

Fig. 6d displays the PL spectra of $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ composites. Generally, a lower fluorescence intensity indicates more efficient separation of photogenerated electron-hole pairs [66]. As shown in Fig. 6d, the PL peak intensities follows the order of $\text{T500} > \text{T450} > \text{T300} > \text{T350} > \text{T400}$. Significantly, T400 exhibits the weakest PL emission signal among all the composites, suggesting that it has the most efficient inhibition of photogenerated carrier recombination. This outstanding carrier separation performance originates from synergistic effects of moderate crystallinity, intimate heterointerface between CuFe_2O_4 and CuO , as well as staggered band alignment that enables rapid interfacial charge migration.

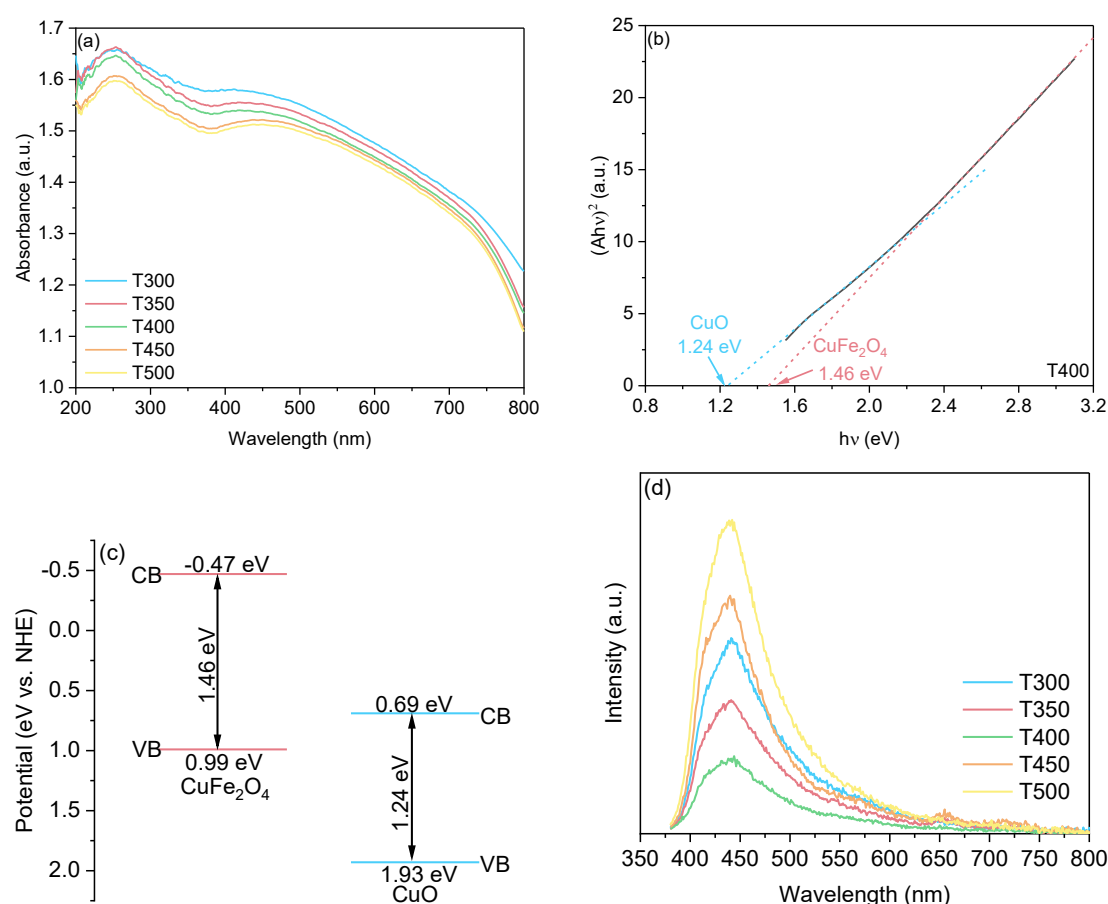


Fig.6 (a) UV-vis DRS spectra, (b) Tuac plot, (c) band alignment diagram, and (f) PL spectra of $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ composites

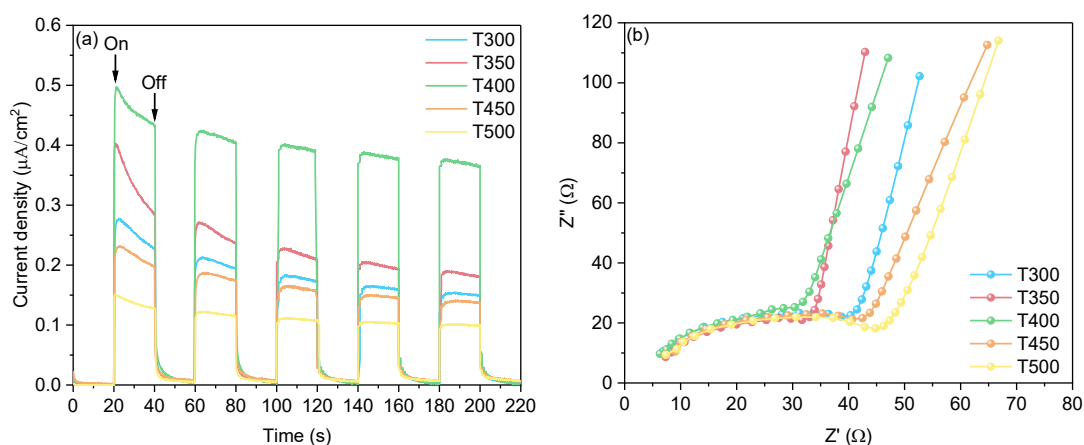
3.3 Electrochemical properties

Photoelectrochemical characteristics largely determine the performance of photocatalysts. Accordingly, transient photocurrent response, EIS and CV measurements were thus conducted to investigate the charge separation and interfacial transfer kinetics. Transient photocurrent and CV tests were performed in a standard three-electrode cell with 0.5 M Na_2SO_4 electrolyte. For EIS measurements, the same configuration was adopted except that the electrolyte was changed to 0.2 M Na_2SO_4 and the working and electrodes were replaced by a GCE.

Fig. 7a illustrates the transient photocurrent responses under periodic on/off light irradiation. Upon illumination, all samples generate rapid and reproducible photocurrent signals, which rapidly decay

to near zero once the light is switched off, confirming that the photocurrent originates from photoexcited electron-hole pairs. After five consecutive on/off cycles, each sample maintains stable and repeatable photocurrent output without noticeable attenuation, indicating satisfactory photochemical stability of the as-prepared composites. The photocurrent densities follow the descending order of $T400 > T350 > T300 > T450 > T500$. The photocurrent density reflects the efficiency of photogenerated carrier separation and migration [67]. Remarkably, T400 delivers the strongest photocurrent signal among all samples, consistent with its lowest PL emission intensity. This superior photocurrent performance stems from the intimate $\text{CuFe}_2\text{O}_4/\text{CuO}$ heterointerface and the staggered band alignment, which synergistically inhibit charge recombination and promote interfacial charge transfer. Fig. 7b presents the Nyquist plots, whose arc radii follow the sequence of $T400 < T350 < T300 < T450 < T500$. Typically, a smaller arc radius corresponds to lower charge transfer resistance and faster interfacial electron transfer kinetics [68]. Evidently, T400 exhibits the smallest semicircle, suggesting that it possesses the most efficient separation and transport of photogenerated carriers. This finding is fully consistent with the transient photocurrent and PL results.

The electrochemical double-layer capacitance (C_{dl}) serves as an important parameter for quantifying the number of electrochemically active sites on photocatalyst surfaces. A higher C_{dl} value implies a larger electrochemically active surface area, more exposed active sites, and faster interfacial charge transfer kinetics [69]. Fig. 7c-7g shows the CV curves recorded at scan rates from 20 to 120 mV/s. The linear fitting plots of current density versus scan rate are presented in Fig. 7h, from which the C_{dl} values are derived as 73.5, 73.2, 61.9, 56.5 and 52.8 $\mu\text{F}/\text{cm}^2$ for T400, T350, T300, T450 and T500, respectively. Obviously, T400 possesses the largest C_{dl} , revealing that it exposes abundant active sites for photocatalytic redox reactions. The relatively low C_{dl} values of T450 and T500 originate from the substantial decomposition of the carbon matrix at elevated temperatures, which reduces surface conductivity and accessible active sites. Combined with the photocurrent and EIS results, the optimal C_{dl} of T400 contributes to its superior photocatalytic performance by simultaneously enhancing light harvesting, charge separation, and surface redox reaction kinetics.



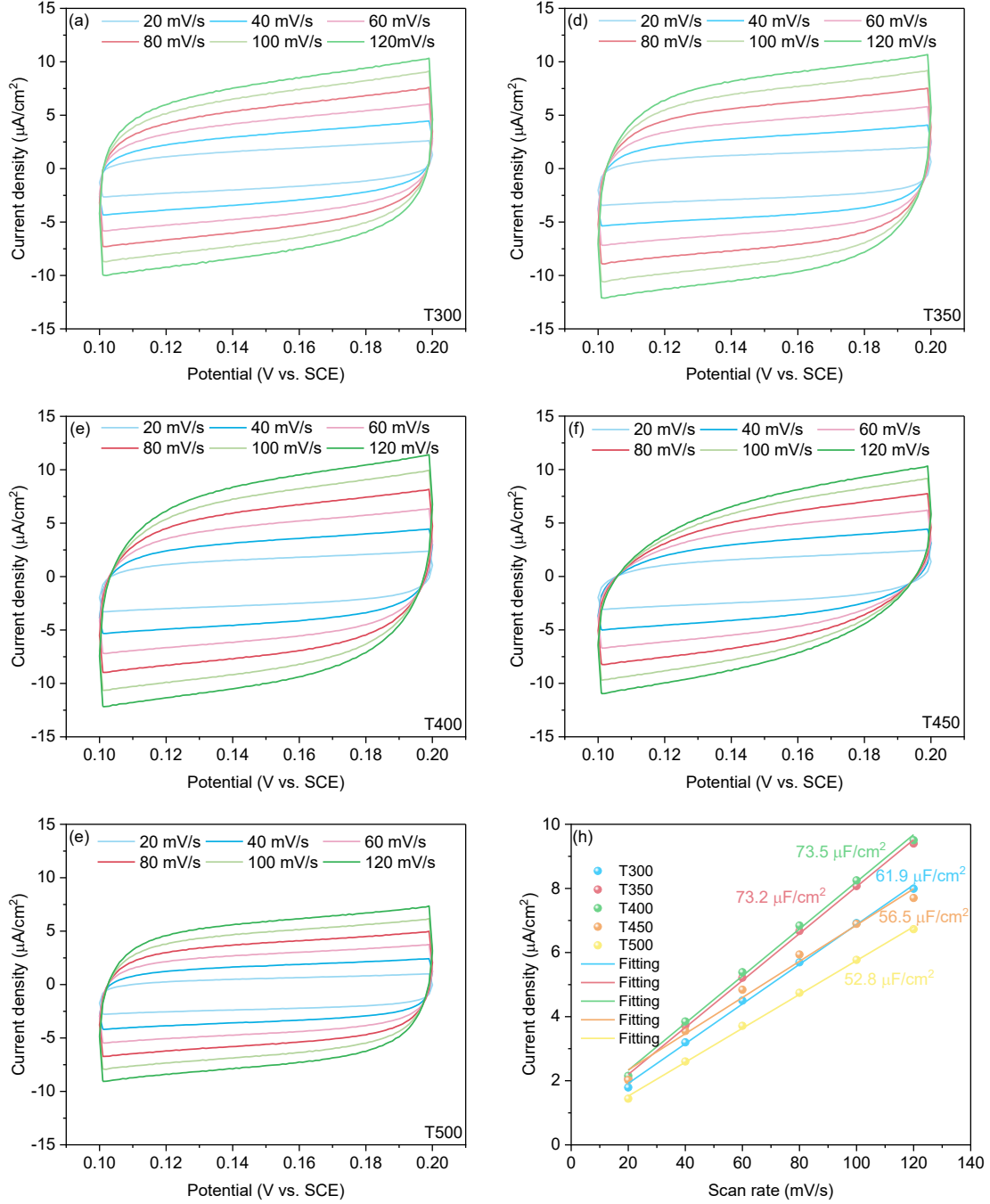


Fig. 7 (a) I-t curves, (b) EIS plots, (c-g) CV curves at different scan rates, and (h) linear relationship curves between current density and scan rate of $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ composites

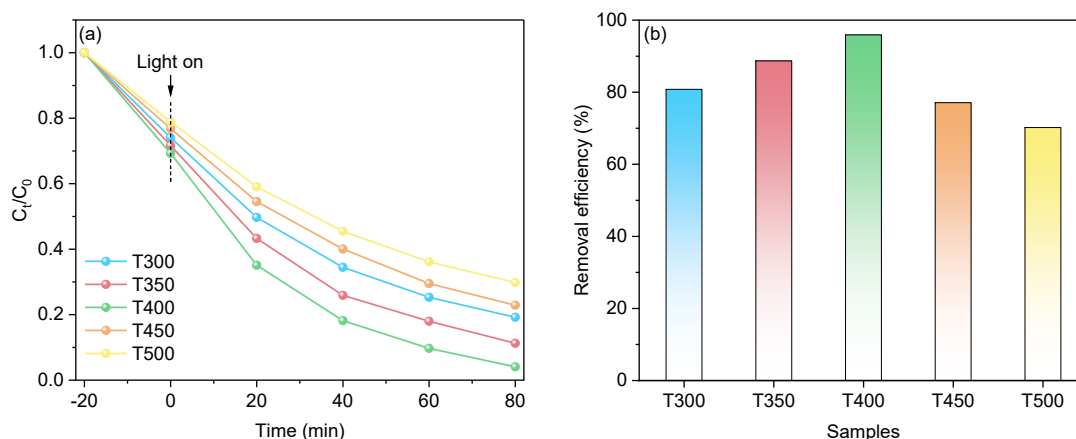
3.4 Photocatalytic degradation performance evaluation

3.4.1 Influence of calcination temperature

The photocatalytic TC degradation tests were carried out using the $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ composites synthesized at various calcination temperatures, and the corresponding time-dependent C_t/C_0 curves are presented in Fig. 8a. For all samples, the C_t/C_0 ratio progressively decreases with increasing irradiation time. Notably, the degradation kinetics exhibit a strong dependence on the calcination temperature. Among the tested samples, T400 shows the most rapid decrease, whereas T500 shows the slowest decay. With increasing calcination temperature from 300 °C to 400 °C, the removal efficiency increases from 80.7% to 95.9% (Fig. 8b). However, further increasing the temperature to 450 °C and

500 °C causes a dramatic decline in the removal efficiency. Obviously, T400 achieves the highest removal efficiency, followed by T350, T300, T450, and T500 in descending order, confirming that the calcination temperature significantly influences the photocatalytic activities of the CuFe₂O₄/CuO/C composites. The pseudo-first-order kinetic model was adopted to compare the degradation kinetics, and the linear fitting plots are presented in Fig. 8c. All samples exhibit good linear fitting ($R^2 > 0.99$), indicating that the degradation process follows pseudo-first-order reaction kinetics. The rate constants (k) obtained from the slopes are 0.0343, 0.0235, 0.0176, 0.0156, and 0.0127 min⁻¹ for T400, T350, T300, T450, and T500, respectively. Notably, T400 exhibits the highest k value among the five samples, which is in good agreement with the optical and electrochemical characterization results.

For T300, despite its the strongest light absorption, XRD analysis reveals poor crystallinity with abundant defects, which serve as charge recombination centers, as evidenced by its higher PL emission intensity and moderate photocurrent response, ultimately limiting its degradation efficiency to 80.7%. Compared with T300, T350 exhibits improved crystallinity, resulting in a lower PL intensity and a higher photocurrent. However, its C_{dl} value (73.2 $\mu\text{F}/\text{cm}^2$) is slightly lower than that of T400, hindering it from reaching the performance level of T400. In contrast, T400 achieves an optimal balance among crystallinity, carbon content, and defect density, as confirmed by XRD and EDS, while HRTEM further demonstrates intimate interfacial contact between CuFe₂O₄ and CuO that aligns well with the staggered band alignment derived from Mulliken's electronegativity theory. These favorable features lead to the lowest PL intensity, the highest transient photocurrent density, the smallest EIS arc radius, and the largest double-layer capacitance (73.5 $\mu\text{F}/\text{cm}^2$) among all samples, all of which synergistically promote charge separation and surface reactions, resulting in the highest removal efficiency (95.9%) and rate constant (0.0343 min⁻¹). For T450 and T500, however, the higher calcination temperature leads to notable enhanced crystallinity and carbon loss, as verified by XRD and EDS. Such adverse effect weakens the light-harvesting capability and the conductive network. As a result, both samples exhibit reduced photocurrent responses, enlarged EIS arcs, and decreased C_{dl} values (56.5 and 52.8 $\mu\text{F}/\text{cm}^2$, respectively), leading to markedly lower removal efficiencies of 77.1% and 70.2%. In addition, WCA measurements were performed to evaluate surface wettability. Generally, a higher WCA indicates lower surface hydrophilicity and stronger hydrophobicity [70]. As shown in Fig. 8d-8h, the WCA values for T300, T350, T400, T450, and T500 are 21.42°, 18.46°, 14.31°, 22.15°, and 28.96°, respectively. Notably, T400 exhibits the lowest WCA, indicating its superior hydrophilicity, which facilitates water adsorption and subsequent surface reactions. Such a favorable surface environment promotes the interfacial redox reactions essential for photocatalytic TC degradation.



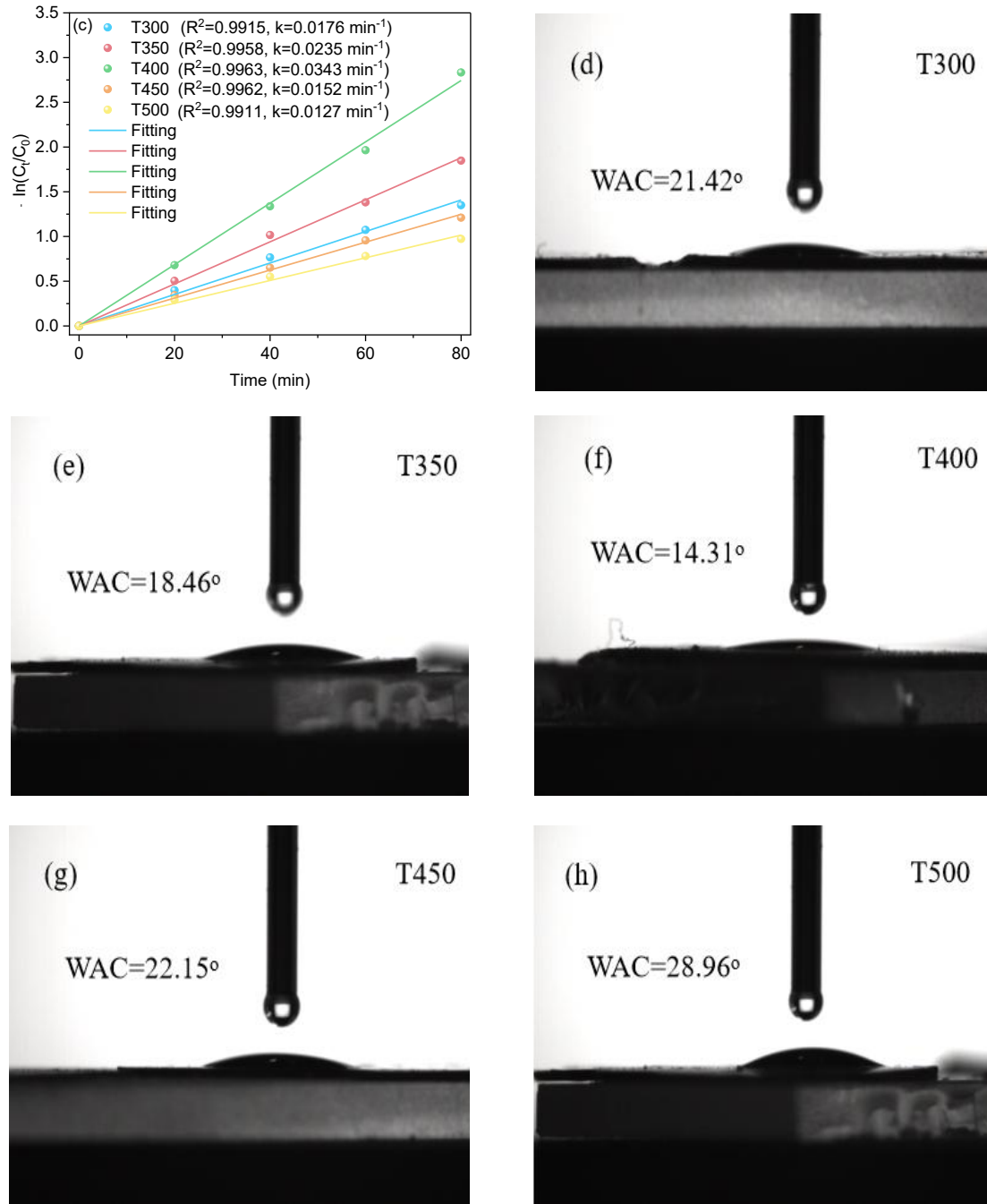


Fig. 8 (a) C_t/C_0 curves, (b) TC removal efficiencies, (c) rate constant curves, (d-h) WCAs of $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ composites

3.4.2 Influence of catalyst dosage

The influence of catalyst dosage on the degradation performance of the T400 composite was investigated with catalyst loadings ranging from 0.1 to 0.5 g/L, and the resulting C_t/C_0 curves are displayed in Fig. 9a. As the catalyst dosage increases from 0.1 to 0.4 g/L, the C_t/C_0 value declines significantly, indicating that a higher dosage provides more active sites and enhances light-harvesting capacity, thereby accelerating TC degradation. However, continuous increasing the catalyst loading to 0.5 g/L leads to a reduction in the removal efficiency, as illustrated in Fig. 9b. This phenomenon is attributable to the light-shielding effect, where excessive solid particles scatter and block the light, thereby reducing the photon utilization efficiency in the reaction system [71]. The pseudo-first-order

kinetic model was further adopted to analyze the effect of catalyst dosage on the photocatalytic performance of the T400 composite. The linear fitting results are presented in Fig. 9c. Remarkably, all fitting curves exhibit outstanding linear correlations ($R^2 > 0.99$), confirming that pseudo-first-order kinetic behavior governs TC degradation across the entire dosage range. The rate constants for 0.1, 0.2, 0.3, 0.4, and 0.5 g/L are determined as 0.0131, 0.0165, 0.0209, 0.0343, and 0.0257 min^{-1} , respectively, with the maximum value achieved at 0.4 g/L. At lower dosages, insufficient active sites limit the generation of photogenerated carriers and reactive radicals, while increasing the dosage to 0.4 g/L enhances the availability of active sites and thus promotes the degradation. However, a further increase to 0.5 g/L introduces severe light scattering that reduces the effective light absorption, thereby retarding the reaction. Based on these results, 0.4 g/L is selected as the optimal dosage.

3.4.3 Influence of initial TC concentration

The influence of initial TC concentration on the degradation performance of the T400 composite was explored with TC concentrations varying from 10 to 50 mg/L, and the corresponding C_t/C_0 curves are presented in Fig. 9d. At same irradiation time, the C_t/C_0 value increases steadily as the initial TC concentration rises, indicating that higher initial TC loading suppresses the removal performance. After 80 min of irradiation, the removal efficiencies (Fig. 9e) are 95.9%, 93.7%, 90.4%, 77.7%, and 65.9% for initial TC concentrations of 10, 20, 30, 40, and 50 mg/L, respectively. Notably, the $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ heterostructure exhibits excellent photocatalytic performance when the initial TC concentration does not exceed 30 mg/L. The pseudo-first-order kinetic model was also adopted to quantitatively compare the reaction kinetics under different initial TC concentrations, and the fitting kinetic plots are displayed in Fig. 9f. All samples exhibit favorable linear correlation coefficients ($R^2 > 0.99$), verifying that TC degradation obeys pseudo-first-order kinetics across the tested concentration range. The rate constants for initial TC concentrations of 10, 20, 30, 40, and 50 mg/L are calculated as 0.0343, 0.0291, 0.0242, 0.0162, and 0.0114 min^{-1} , respectively. This decreasing trend can be attributed to two factors. On one hand, high-concentration TC molecules occupy most of the surface active sites of $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ heterostructure, thereby restricting the generation and transfer of photogenerated carriers and reactive radicals. On the other hand, abundant TC molecules absorb a large proportion of visible light, reducing the photon flux reaching the photocatalyst particles and suppressing the production of reactive oxidative species. In addition, the intermediate products generated during TC degradation accumulate more severely in high-concentration systems, competing with TC for reactive radicals and further slowing down the mineralization process.

3.4.4 Influence of initial solution pH

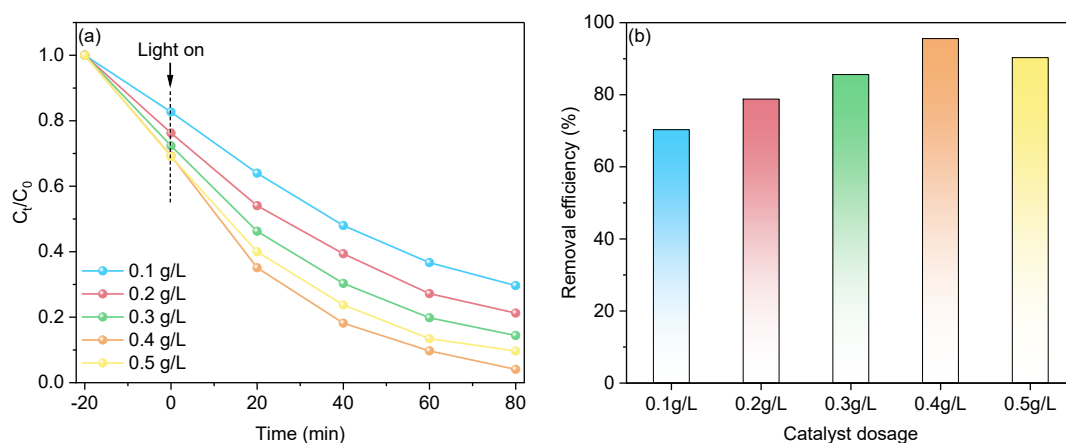
The influence of initial solution pH values on the TC removal efficiency over the T400 composite was investigated in the pH range of 3-11, and the relevant results are shown in Fig. 9g-9i. As displayed in Fig. 9g, the photocatalytic performance is strongly dependent on the solution pH. According to the Fig. 9h, the highest TC removal efficiency is obtained at pH 5, while satisfactory degradation is also achieved at pH 7 and 9. Both strongly acidic (pH 3) and alkaline conditions (pH 11) lead to deteriorated removal performance. Pseudo-first-order kinetic fitting (Fig. 9i) further quantifies this tendency. The largest rate constant $k = 0.0343 \text{ min}^{-1}$ is obtained at pH 5. The rate constants follow the order: pH 5 (0.0343 min^{-1}) > pH 7 (0.0326 min^{-1}) > pH 9 (0.0276 min^{-1}) > pH 3 (0.0219 min^{-1}) > pH 11 (0.0166 min^{-1}). Such pH-dependent behavior originates from the surface charge state of the photocatalyst and the existing species of TC molecules [30]. Under weakly acidic conditions around pH 5, the surface charge of the catalyst and the molecular form of TC are well-matched, which facilitates the adsorption of TC onto catalyst surface and accelerates the oxidation reaction [72]. Under strong-acid conditions

(pH 3), excessive H^+ competes for active sites and suppresses the generation of reactive oxygen species [73]. Under alkaline conditions (pH 9-11), high-concentration OH^- quenches photogenerated holes and $\cdot OH$ radicals. Meanwhile, surface-metal-site passivation may occur, which jointly suppresses the photodegradation of TC [74]. Overall, the $CuFe_2O_4/Cu/C$ composite exhibits optimal photocatalytic activity under weakly acidic conditions, and maintains acceptable degradation capacity within a broad pH window of 3-9, whereas extreme alkaline environment significantly deteriorates its performance.

3.4.5 Influence of common substances in water

Various inorganic anions and HA existing in actual water bodies can interfere with the photocatalytic degradation of TC. Therefore, five common coexisting anions ($H_2PO_4^-$, Cl^- , HCO_3^- , NO_3^- , SO_4^{2-}) and HA were introduced into the reaction system separately to evaluate the practical application potential of the $CuFe_2O_4/Cu/C$ composite, and the corresponding results is presented in Fig. 9i. As illustrated in Fig. 9i, NO_3^- and SO_4^{2-} exhibit negligible adverse impacts on TC elimination, and their removal efficiencies are close to the blank group. The introduction of Cl^- and HCO_3^- induces only slight reduction of degradation performance. In contrast, obvious inhibitory effects are observed for HA and especially $H_2PO_4^-$. Among all tested substances, $H_2PO_4^-$ displays the strongest suppression toward TC degradation.

The negligible interference of SO_4^{2-} arises from its chemical inertness toward photogenerated reactive oxygen species, only competing for limited surface adsorption sites weakly [38]. NO_3^- can capture partial photogenerated electrons, yet it hardly consumes h^+ and $\cdot OH$, leading to trivial performance reduction [75]. For Cl^- , it reacts with photogenerated holes to generate low-oxidability chlorine radicals, thus moderately weakening TC oxidation capacity [76]. As a typical radical scavenger, HCO_3^- reacts with $\cdot OH$ to produce carbonate radicals with weak oxidation ability, bringing about medium inhibitory effect on photocatalysis [77]. For HA, it competes with TC molecules for active adsorption sites on the composite surface, and reduces light transmittance of aqueous solution to cut down photon utilization efficiency [30]. The strongest suppression of $H_2PO_4^-$ is attributed to its complexation with Cu/Fe metal active sites on $CuFe_2O_4/Cu/C$ surface, which blocks reactive centers and restrains the generation of h^+ and $\cdot OH$ [78]. These results suggest that the as-prepared $CuFe_2O_4/Cu/C$ composite possesses favorable tolerance toward SO_4^{2-} , NO_3^- , Cl^- and HCO_3^- , while $H_2PO_4^-$ and HA would restrain its photocatalytic performance.



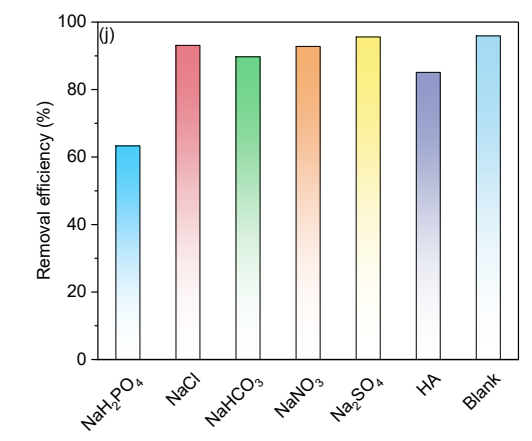
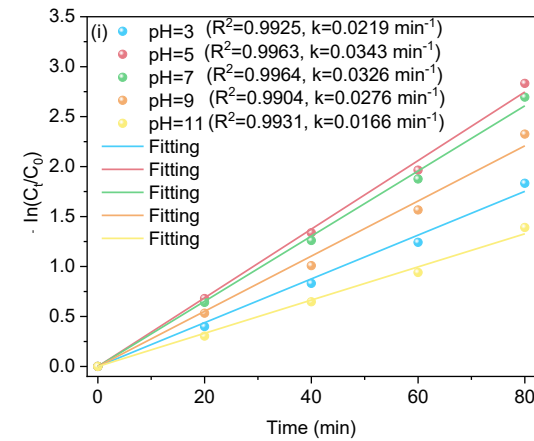
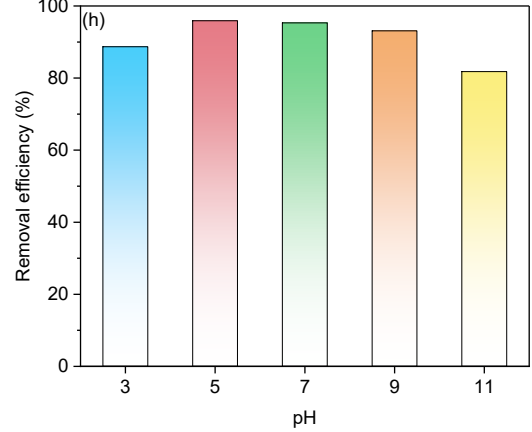
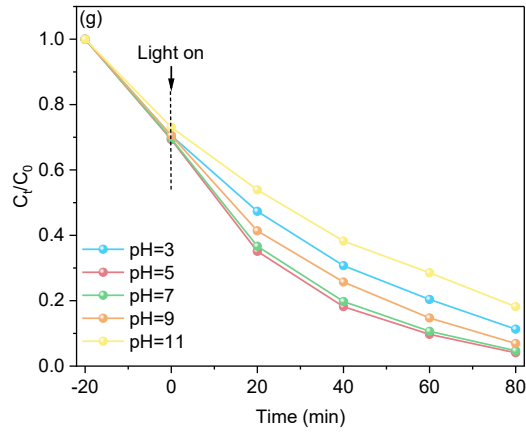
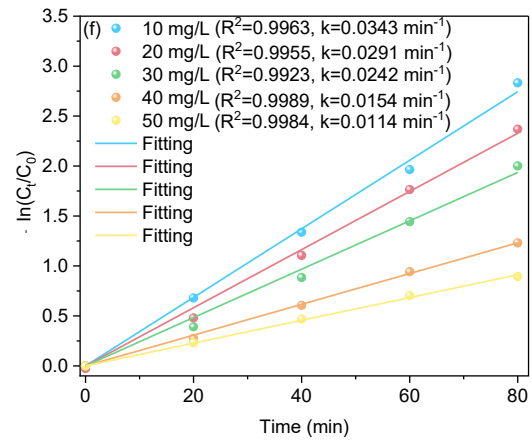
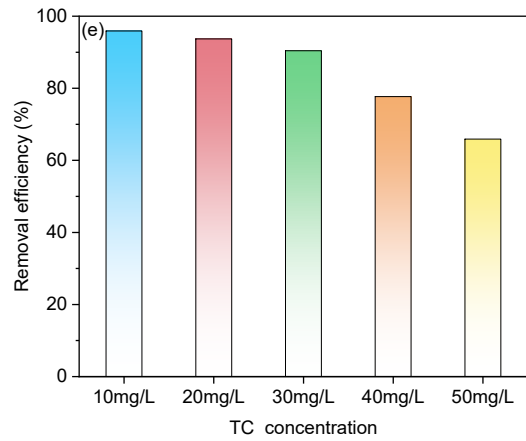
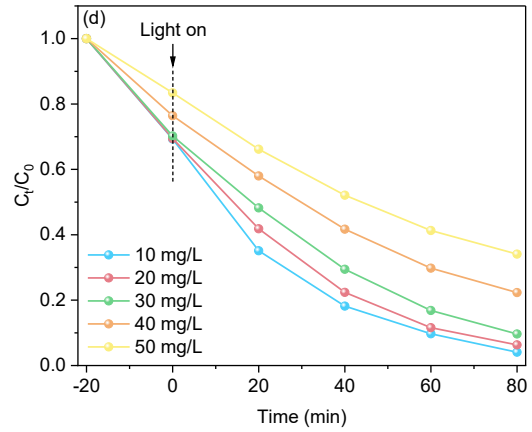
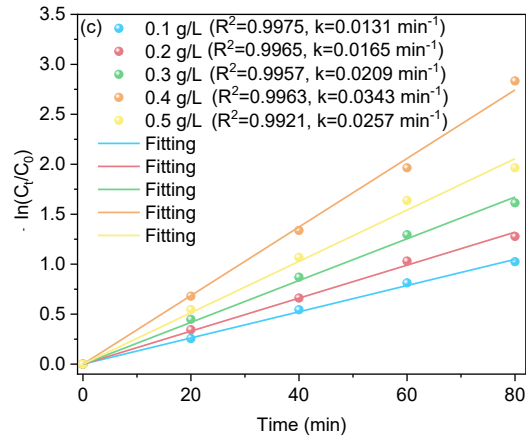


Fig. 9 Degradation of TC in different systems (a-c) catalyst dosages, (d-f) initial TC concentrations, (g-i) initial solution pH, and (j) coexistence of substances

3.4.6 Stability and reusability

Consecutive recycling photocatalytic degradation experiments were conducted to investigate the long-term stability of the $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ composite. As displayed in Fig. 10a, The results suggest that the photocatalytic activity remains essentially unchanged after ten consecutive runs, with TC removal efficiency consistently exceeding 90%. Post-reaction characterizations (Fig. 10c and 10d) further support this excellent stability, revealing no obvious changes in the crystal structure and morphology of the $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ composite, thus confirming the robust durability of the $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ heterostructure during photocatalytic TC degradation.

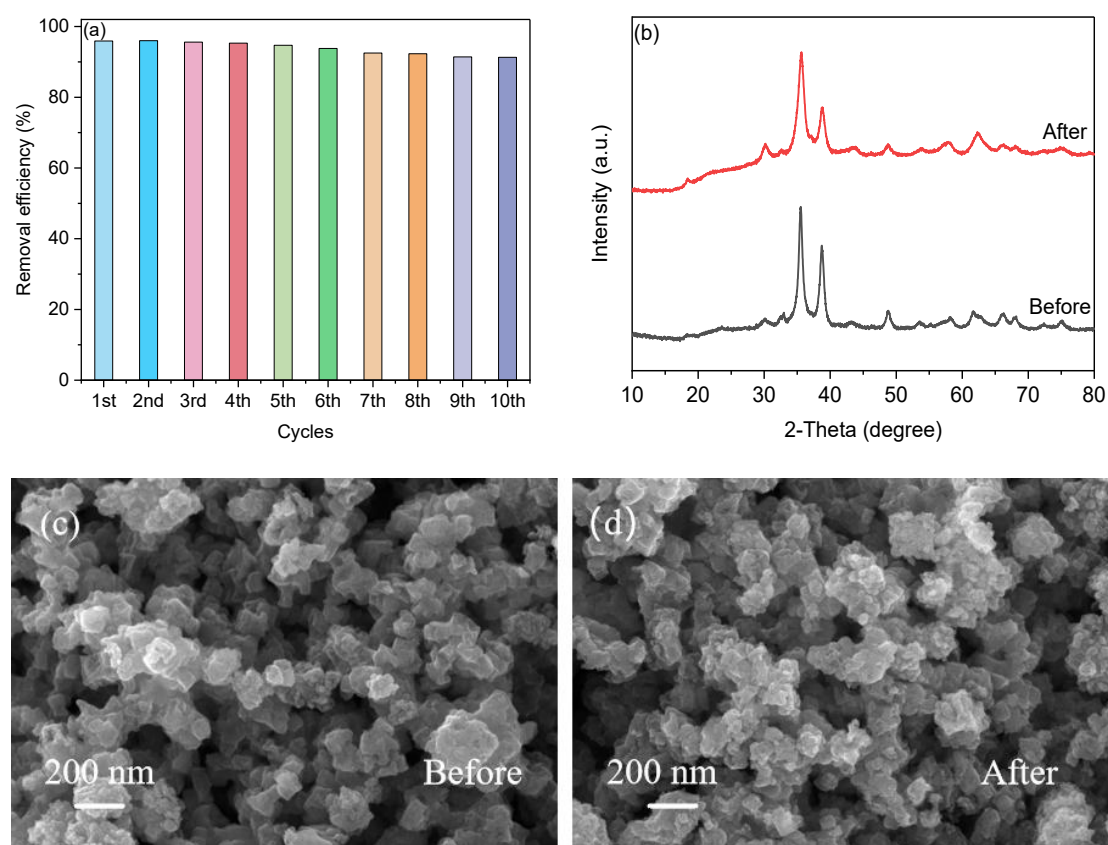


Fig. 10 (a) TC removal efficiencies, (b) XRD patterns, and (c-d) SEM images of T400 before and after use

3.4.7 Comparison with previously reported CuFe_2O_4 -based photocatalysts

The visible-light-driven TC degradation performance of the as-prepared $\text{CuO}/\text{CuFe}_2\text{O}_4/\text{C}$ composite was compared with a series of recently reported CuFe_2O_4 -based photocatalysts, as summarized in Table 1. As shown in Table 1, many reported CuFe_2O_4 -based composites (e.g., $\text{Cu}/\text{CuFe}_2\text{O}_4$, $\text{Ag}/\text{CuFe}_2\text{O}_4/\text{CQDs}$, $\text{CuO}/\text{CuFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$, $\text{CuFe}_2\text{O}_4\text{-MoS}_2@\text{BC}$, $\text{CuFe}_2\text{O}_4/\text{C}/\text{SiO}_2$, $\text{CuO}/\text{Fe}_2\text{O}_3/\text{CuFe}_2\text{O}_4$, and $\text{C-CuFe}_2\text{O}_4$) achieve high TC removal efficiency, yet these systems rely on additional oxidants, such as persulfate, peroxydisulfate, peracetic acid or H_2O_2 , which increases chemical consumption and restricts practical application cost. By contrast, the photocatalytic activity of our $\text{CuO}/\text{CuFe}_2\text{O}_4/\text{C}$ composite remains highly competitive without introducing extra chemical oxidants. More importantly, most reported CuFe_2O_4 -based photocatalysts maintain only 73.5 %-93.5 % removal after 3-6 cyclic runs. Notably, the $\text{CuO}/\text{CuFe}_2\text{O}_4/\text{C}$ in this work exhibits 91.2 % efficiency

even after 10 cycles, which outperforms most referenced CuFe₂O₄-based photocatalysts. This superior long-term reusability demonstrates that the *in situ* generation of carbon effectively suppresses metal ion leaching and structural deterioration during repeated photocatalytic reactions. Admittedly, the catalyst dosage (0.4 g/L) in this work is not the lowest among these references. Some heterojunction catalysts such as CuO/Fe₂O₃/CuFe₂O₄ work at lower catalyst loading (0.1 g/L). However, such materials generally suffer from poor cycling performance. Collectively, benefiting from its outstanding cyclic stability, oxidant-free reaction system, and facile one-step synthesis strategy, the PBA-derived CuO/Fe₂O₃/CuFe₂O₄ composite can serve as an efficient, durable, and cost-effective photocatalyst for the remediation of TC-contaminated wastewater.

Table 1 Comparison of TC degradation over CuFe₂O₄-based photocatalysts under visible light

Catalyst	Dosage (g/L)	TC (mg/L)	Time (min)	η (%)	Cycles/ η (%)	Ref.
Cu/CuFe ₂ O ₄	0.3	50	120	76.7 ^a	3 / 73.5	[16]
CuFe ₂ O ₄ /ABC	0.2	30	180	94.9	5 / 88.0	[17]
Ag/CuFe ₂ O ₄ /CQDs	0.3	10	60	100.0 ^a	5 / 91.5	[18]
CuFe ₂ O ₄ /PANI	0.33	10	120	86.0	4 / 81.0	[20]
CuFe ₂ O ₄ /Bi ₂ MoO ₆	0.5	50	60	98.5	5 / 80.5	[22]
CuO/CuFe ₂ O ₄ /g-C ₃ N ₄	0.1	20	90	99.0 ^a	4 / 93.5	[23]
CuFe ₂ O ₄ /SnS ₂	0.2	20	90	98.0	6 / 93.0	[28]
BiOCl/BiOBr/CuFe ₂ O ₄	0.4	30	180	87.4	4 / 78.2	[29]
ZIF-8/g-C ₃ N ₄ /CuFe ₂ O ₄	0.75	15	95	99.2	4 / 84.2	[30]
FeOOH Ds/CuFe ₂ O ₄	0.3	10	180	92.1	5 / 90.4	[31]
CuFe ₂ O ₄ @NH ₂ -MIL-125(Ti)	0.075	15	150	89.0 ^b	-	[32]
CuFe ₂ O ₄ /AgBr	1.0	20	190	89.1	-	[33]
CuFe ₂ O ₄ -MoS ₂ @BC	0.5	50	60	93.9 ^b	3 / 70.0	[34]
CuFe ₂ O ₄ /C/SiO ₂	0.3	10	60	99.7 ^b	4 / 76.3	[38]
CuFe ₂ O ₄ @LBC	0.2	25	100	85.0 ^a	5 / 76.0	[39]
CuFe ₂ O ₄ @BC	0.3	50	60	85.0 ^c	5 / 80.0	[40]
CuO/Fe ₂ O ₃ /CuFe ₂ O ₄	0.1	20	30	97.8 ^b	4 / 85.1	[73]
C-CuFe ₂ O ₄	0.2	20	90	94.0 ^d	5 / 80.0	[79]
CuO/CuFe ₂ O ₄ /C	0.4	10	100	95.9	10 / 91.2	This work

^aOxidant: persulfate; ^bOxidant: peroxymonosulfate; ^cOxidant: peracetic acid; ^dOxidant: H₂O₂

3.5 Photocatalytic mechanism

Radical trapping experiments were performed to identify the dominant active species and degradation mechanism of TC over the CuFe₂O₄/CuO/C heterostructure. As shown in Fig. 11a and 11b, the introduction of different quenchers results in varying levels of photocatalytic activity inhibition. The TC removal efficiency reaches 95.9% in the absence of any scavenger. The addition of TBA causes only a slight decrease to 87.4%, indicating that $\cdot\text{OH}$ plays a negligible role in the degradation process. In contrast, the introduction of EDTA-2Na or BQ leads to remarkable inhibition, with the removal efficiencies dropping sharply to 31.1% and 49.7%, respectively. These results confirm that h^+ and $\cdot\text{O}_2^-$ are the dominant active species responsible for TC degradation, while $\cdot\text{OH}$ plays a minor role.

Futhermore, EPR measurements were performed to directly confirm the generation of these reactive species using DMPO for $\cdot\text{O}_2^-$ and $\cdot\text{OH}$, and TEMPO for h^+ as a spin-trapping agents. As displayed in Fig. 11c and 11d, the EPR spectra recorded in the dark exhibit no signals that could be assigned to

DMPO- $\cdot\text{O}_2^-$ or DMPO- $\cdot\text{OH}$ adducts. Upon irradiation, distinct peaks ascribable to DMPO- $\cdot\text{O}_2^-$ adducts are clearly observed, providing direct evidence for the abundant production of $\cdot\text{O}_2^-$ species. In contrast, only very weak DMPO- $\cdot\text{OH}$ signals are detected, demonstrating that the yield of $\cdot\text{OH}$ radicals is extremely low, which is consistent with the minor contribution of $\cdot\text{OH}$ revealed by the radical trapping experiments. Fig. 11e presents the EPR spectra recorded using TEMPO as the spin probe. In the dark, the strong characteristic triplet signal of pristine TEMPO is clearly detected. Under irradiation, however, the signal intensity decreases markedly, indicating the generation of abundant photogenerated holes in the system. This attenuation can be attributed to the scavenging of photogenerated electrons by TEMPO, which lowers the concentration of TEMPO radicals. As electrons and holes are generated in pairs upon photoexcitation, the consumption of TEMPO by electrons indirectly confirms the formation of h^+ .

These radical assignments are further rationalized by band structure analysis. The detected DMPO- $\cdot\text{O}_2^-$ signals arise from the photogenerated electrons accumulated in the CB of CuFe_2O_4 (-0.47 eV vs. NHE), which possess a sufficiently negative potential to reduce adsorbed O_2 to $\cdot\text{O}_2^-$ ($E(\text{O}_2/\cdot\text{O}_2^-) = -0.33$ eV vs. NHE). In contrast, the CB of CuO (0.69 eV vs. NHE) lacks the thermodynamic driving force for this oxygen reduction. Simultaneously, the observed decrease in TEMPO signal intensity originates from the highly oxidative holes accumulated in the VB of CuO . The weak DMPO- $\cdot\text{OH}$ signal can be rationalized by the VB edge potentials. The VB potential of CuO is 1.93 eV vs. NHE, which lies below the redox potential required for oxidizing $\text{H}_2\text{O}/\text{OH}^\cdot$ to $\cdot\text{OH}$ (1.99 eV vs. NHE). Therefore, the photogenerated holes in CuO lacks sufficient thermodynamic driving force to produce $\cdot\text{OH}$, which is in full agreement with the negligible $\cdot\text{OH}$ signal observed in both trapping and EPR experiments. The radical contribution and band alignment between CuFe_2O_4 and CuO strongly support the S-scheme charge transfer pathway, wherein the photogenerated electrons with the strongest reducing power and the holes with the highest oxidizing ability are retained at spatially separated sites, thereby preserving their respective redox potentials. Importantly, the combined EPR and trapping data rule out a conventional type-II heterojunction. Instead, the experimental data support an efficient S-scheme charge transfer mechanism in the $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ heterostructure.

In addition, *in situ* irradiated XPS was employed to probe the charge transfer behavior in the $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ heterostructure. As displayed in Fig. 11f, the Cu 2p peaks located at 933.6 eV, 941.3 eV, 943.8 eV, 953.4 eV, and 961.9 eV in the dark shift positively to 933.8 eV, 941.4 eV, 943.9 eV, 953.6 eV, and 962.0 eV under irradiation, indicating decreased electron density around Cu species and confirming CuO as the oxidative catalyst with electron depletion. In contrast, the Fe 2p peaks (at 710.6 eV, 713.1 eV, 716.4 eV, 719.7 eV, 724.1 eV, 727.6 eV, and 723. eV in the dark, Fig. 8h) shift negatively to 710.4 eV, 712.8 eV, 716.1 eV, 719.5 eV, 723.8 eV, 727.4 eV, and 723.2 eV upon illumination, reflecting increased electron density around Fe species and verifying CuFe_2O_4 as the reductive catalyst with electron accumulation. These shifts directly suggest that under illumination, photogenerated electrons migrate from CuO to CuFe_2O_4 , while holes are retained in CuO .

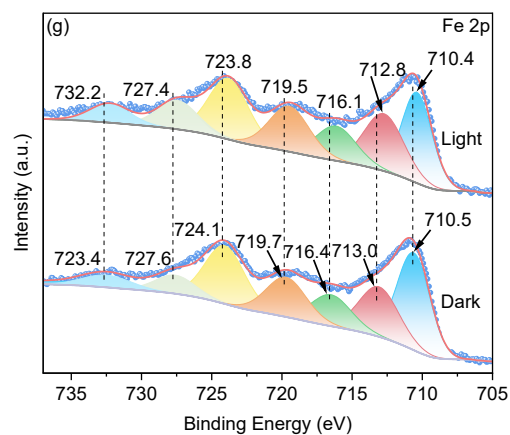
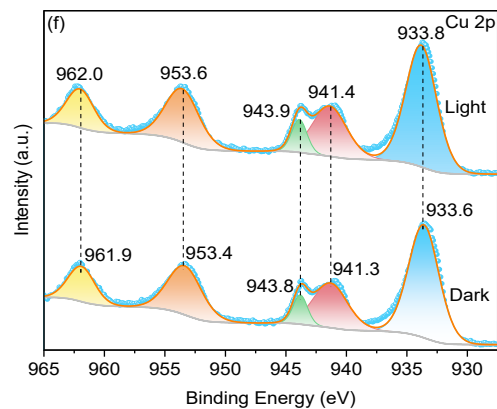
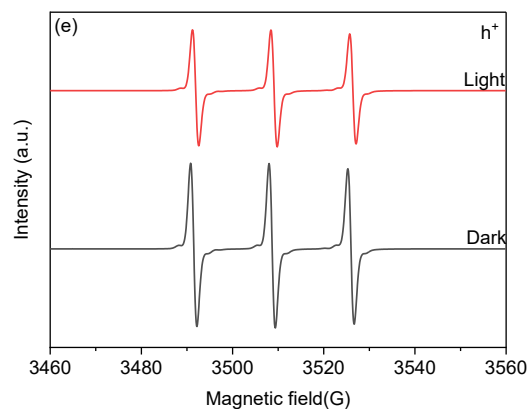
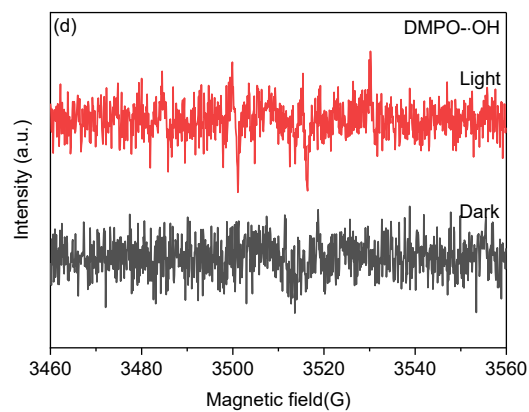
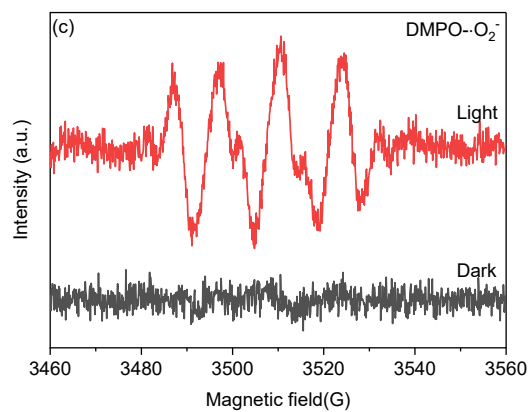
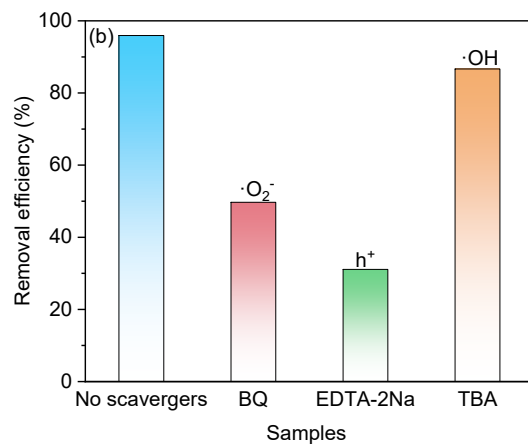
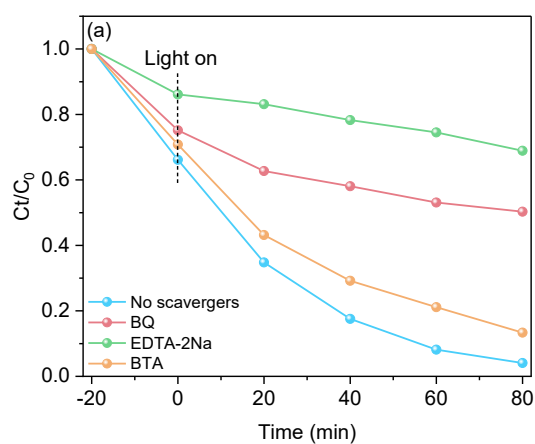


Fig. 11 (a) Free radical trapping test, (b) TC removal efficiencies, (c) EPR spectrum of DMPO- $\cdot\text{O}_2^-$, (d) EPR spectrum of DMPO- $\cdot\text{OH}$, (e) EPR spectrum of h^+ , *in situ* irradiated XPS spectra of (f) Cu 2p, and (g) Fe 2p

The CB edge potentials (vs. NHE) were converted to the vacuum energy scale (E_{vac}) using the relation $E_{\text{vac}} = -4.5 - E_{\text{NHE}}$ to assess the interfacial energy alignment. CuFe_2O_4 and CuO are p-type semiconductors, whose Fermi level (E_f) lie close to their respective VB edges. For p-type semiconductors, E_f is generally located approximately 0.1-0.2 eV above the VB maximum [80]. The work function (Φ) was derived from $\Phi = E_{\text{vac}} - E_f$. As listed in Table S3 and S4, CuFe_2O_4 exhibits a lower Φ and a higher E_f than CuO . Therefore, upon interface formation in the dark, the E_f gradient drives electrons migration from CuFe_2O_4 to CuO until Fermi level equilibrium is reached (Fig. 12a). This charge redistribution generates a space-charge region, where negative charge accumulate on the CuO side and positive charge on the CuFe_2O_4 side, thereby producing a built-in electric field oriented from CuFe_2O_4 toward CuO (Fig. 12b). Under light irradiation, this interfacial configuration governs an S-scheme charge transfer route. The combined effect of band bending and the internal electric field facilitates the migration of photogenerated electrons from the CB of CuO to recombine with photogenerated holes from the VB of CuFe_2O_4 (Fig. 12c). Such a recombination pathway accomplishes effective carrier separation while concurrently retaining the high reducing capability of electrons in the CB of CuFe_2O_4 and the high oxidizing capability of holes in the VB of CuO . The resulting spatially separated redox centers offer ideal conditions for photocatalytic TC decomposition, where CuFe_2O_4 donates photogenerated electrons that reduce O_2 to $\cdot\text{O}_2^-$, and CuO supplies photogenerated holes for TC oxidation. Overall, the S-scheme configuration effectively suppresses photogenerated carries recombination, sustains robust redox potentials, and promotes the generation of $\cdot\text{O}_2^-$ and h^+ , thus accounting for the significantly enhanced photocatalytic performance of the $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ heterostructure.

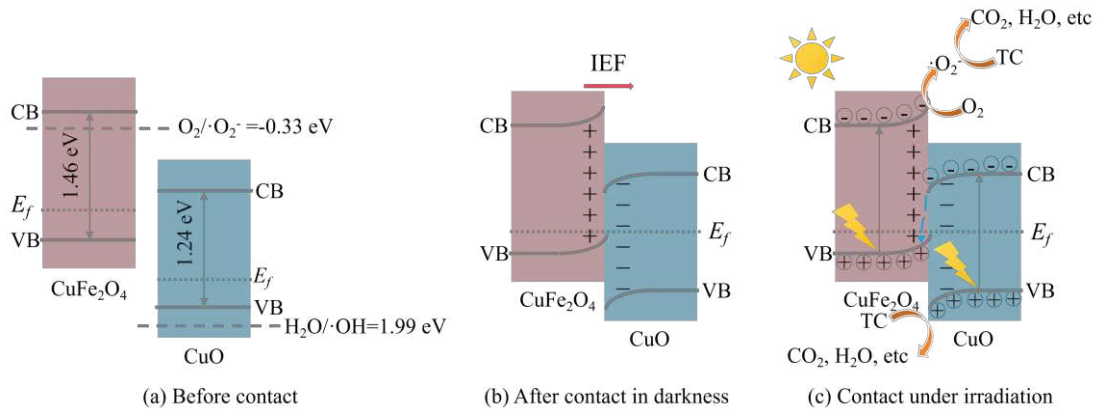


Fig.12 Schematic representation of charge transfer process in $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$

3.6 Proposed degradation pathways

LC-MS was employed to identify the intermediates formed during photocatalytic TC degradation. The parent TC molecule ionizes to yield a protonated molecular ion $[\text{M}+\text{H}]^+$ at $m/z=445$, and subsequent intermediates are detected as their corresponding protonated adducts. Based on the LC-MS results, the proposed degradation pathways of TC over the $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ heterostructure are illustrated in Fig. 13, with the detailed intermediate information summarized in Table S5 and the corresponding mass spectra presented in Fig. S5.

The TC degradation over the $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ heterostructure proceeds through four main pathways.

In pathway I, the C–N bond of the dimethylamino group is cleaved oxidatively by reactive oxygen species, followed by successive demethylation steps to yield P1 ($m/z=431$), which then dehydrates to form P2 ($m/z=413$) and P3 ($m/z=413$). In pathway II, photogenerated holes oxidize TC to generate a hydroxylated intermediate P4 ($m/z=461$), which subsequently undergoes C-ring opening to afford P5 ($m/z=463$). In pathway III, the D ring of TC is attacked by reactive oxygen species, triggering an oxidative ring-opening reaction that breaks the ring structure and yields P6 ($m/z=417$). This product then undergoes oxidative cleavage of the C–N bond and demethylation to generate P7 ($m/z=403$). In pathway IV, the C ring of TC is readily attacked by reactive oxygen species, leading to an oxidative ring-opening reaction that generates P8 ($m/z=461$). Under further attack by reactive species, this intermediate undergoes three parallel transformations. The A ring is hydroxylated to give P9 ($m/z=477$), while the D ring undergoes oxidative cleavage to form P10 ($m/z=479$), which subsequently eliminates formic acid to afford P11 ($m/z=433$). Meanwhile, P8 can also undergo decarboxylation to generate P12 ($m/z=417$), which is further converted by oxidative cleavage of the C–N bond in the dimethylamino group to yield P13 ($m/z=403$), and also by dehydration to give P14 ($m/z=399$). As the oxidation progresses, the continuous attack of reactive species gradually cleaves the ring structures of these intermediates, breaking them down into smaller organic acids and amines, and eventually achieving complete mineralization to H_2O , CO_2 , NO_3^- , and NH_4^+ .

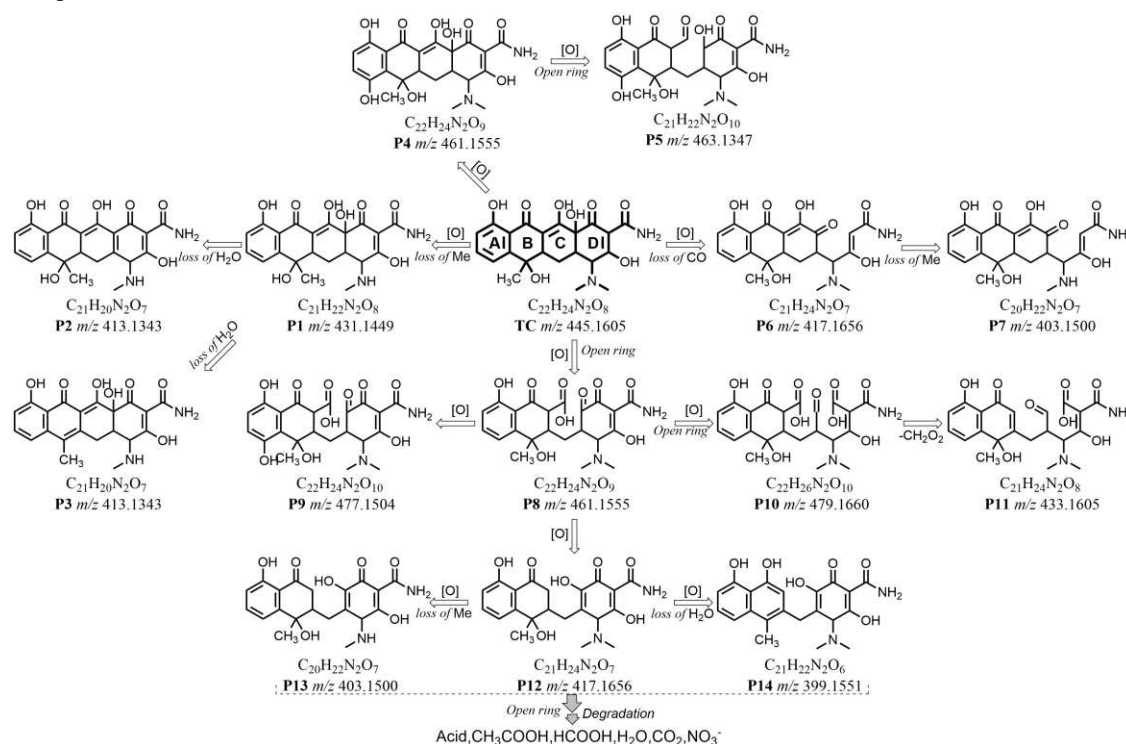


Fig. 13 Proposed degradation pathways of TC over the $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ heterostructure

4Conclusions

In summary, the $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ heterostructure with outstanding light-harvesting capacity and robust stability was successfully fabricated through a facile and scalable calcination method using CuFe-PBA as the self-sacrificial precursor. The heterostructure obtained at 400°C exhibits the best photocatalytic performance toward TC degradation, attaining 95.9% TC removal efficiency within 80 min under visible light irradiation, with a rate constant of 0.0343 min^{-1} . After 10 recycling tests, the catalyst still maintains more than 90% removal efficiency. Meanwhile, the composite maintains acceptable degradation capacity within a broad pH window of 3-9 and suffers negligible interference

from SO_4^{2-} , NO_3^- , Cl^- and HCO_3^- . This superior photocatalytic performance stems from the combined contribution of moderate crystallinity, proper residual carbon content, intimate interfacial contact, and abundant active sites. Particularly, the S-scheme charge transfer pathway preserves strong redox potentials while suppressing carrier recombination, as confirmed by radical trapping and EPR experiments, which identify $\cdot\text{O}_2^-$ and h^+ as the predominant active species, with $\cdot\text{OH}$ playing only a minor role. LC-MS analysis reveals that TC is decomposed through ring opening, demethylation, hydroxylation, and decarboxylation pathways, ultimately achieving mineralization to H_2O , CO_2 , NO_3^- , and NH_4^+ . These findings show that the $\text{CuFe}_2\text{O}_4/\text{CuO}/\text{C}$ heterostructure possesses scalable preparation routes, visible light responsive activity, and remarkable cycling durability, making it a promising candidate for practical antibiotic wastewater remediation. This work offers a feasible synthetic strategy for the rational design of high-performance heterojunction photocatalysts for water environmental purification.

Acknowledgements

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