

**This is the preprint of the contribution published as:**

Shi, Z., He, C., Huang, H., Huang, X., Hu, T., He, Y., Yang, D., Xia, S., **Zhang, H.**, Deng, L. (2025):

A novel polydopamine-loaded copper sulfide (CuS@PDA) for activating H<sub>2</sub>O<sub>2</sub> to eliminate tetracycline via <sup>1</sup>O<sub>2</sub> dominated oxidation pathway

*J. Water Process Eng.* **71** , art. 107223

**The publisher's version is available at:**

<https://doi.org/10.1016/j.jwpe.2025.107223>

1

2 A novel polydopamine-loaded copper sulfide (CuS@PDA) for  
3 activating H<sub>2</sub>O<sub>2</sub> to eliminate tetracycline via <sup>1</sup>O<sub>2</sub> dominated  
4 oxidation pathway

5

6 Zhou Shi<sup>a</sup>, Chenxi He<sup>a</sup>, Hao Huang<sup>a</sup>, Xile Huang<sup>a</sup>, Tong Hu<sup>a</sup>, Yijia He<sup>a</sup>, Dazhi Yang<sup>a</sup>,  
7 Simeng Xia<sup>a,\*</sup>, Haojie Zhang<sup>a,b,\*</sup>, Lin Deng<sup>a,\*</sup>

8

9

10 a. Hunan Engineering Research Center of Water Security Technology and Application,  
11 College of Civil Engineering, Hunan University, Changsha 410082, China

12 b. Helmholtz Centre for Environmental Research-UFZ, Department of Technical  
13 Biogeochemistry, Leipzig 04318, Germany

14

15

16 \*Corresponding authors.

17 *E-mail addresses:* sytheon@hnu.edu.cn (S. Xia); haojie.zhang@ufz.de (H. Zhang);

18 lindeng@hnu.edu.cn (L. Deng)

## Abstract

The frequently detected antibiotics in aquatic environments can induce antibiotic-resistance genes, thereby posing significant risks to both ecosystems and human health. Thus, it is imperative to remove antibiotics from water environments. We constructed a novel polydopamine-loaded copper sulfide (CuS@PDA) through a simple hydrothermal method to activate H<sub>2</sub>O<sub>2</sub> to degrade tetracycline (TC). Compared to CuS/H<sub>2</sub>O<sub>2</sub>, the CuS@PDA/H<sub>2</sub>O<sub>2</sub> system not only achieved efficient TC removal with kinetic rate constant of 0.20 min<sup>-1</sup>, but also showed much lower Cu<sup>2+</sup> ions leaching (3.81 mg/L from CuS vs. 0.21 mg/L from CuS@PDA). Besides, CuS@PDA exhibited remarkable recyclability with 93% removal in the fifth consecutive cycle. Mechanisms analysis revealed that Cu and S contributed to the H<sub>2</sub>O<sub>2</sub> activation and S promoted the conversion of Cu(II) to Cu(I), beneficial for the production of reactive oxygen species. <sup>1</sup>O<sub>2</sub> was found to play the dominant role in the degradation of TC on the basis of quenching tests and electron paramagnetic resonance (EPR) analysis. PDA in CuS@PDA composites facilitated easier complexation with H<sub>2</sub>O<sub>2</sub> and conferred stronger oxidation capability. Lastly, the TC degradation pathway by CuS@PDA/H<sub>2</sub>O<sub>2</sub> was proposed, and the ecotoxicity of its degradation intermediates was estimated. In conclusion, this work presents an approach for synthesizing high efficient and recyclable CuS-based catalysts that activate H<sub>2</sub>O<sub>2</sub> to efficiently degrade organic pollutants through a nonradical pathway predominantly mediated by <sup>1</sup>O<sub>2</sub>.

**Keywords:** CuS; Polydopamine; H<sub>2</sub>O<sub>2</sub> activation; Tetracycline degradation; <sup>1</sup>O<sub>2</sub> dominated

## 43 **1. Introduction**

44 The presence of pharmaceutical and personal care products in aquatic environment  
45 leads to severe ecological risks such as endocrine disruption and bioaccumulation [1].  
46 Tetracyclines (TC), extensively used in aquaculture and veterinary medicine [2], has  
47 been frequently detected in surface water, groundwater, and municipal wastewater due  
48 to its hydrophilicity, weak volatility, and high adsorptive capacity [3]. This poses  
49 serious threat to human health, induces bacteria resistance, and endangers the ecological  
50 environment [4]. Conventional water and wastewater treatment methods such as  
51 flocculation, precipitation, adsorption, and activated sludge process fail to efficiently  
52 remove TC from aqueous solutions [5]. Thus, it's urgent to find effective and  
53 environmental-friendly strategies to deal with the intractable problems of antibiotic  
54 pollution.

55 In recent years, advanced oxidation processes (AOPs) that can generate reactive  
56 oxygen species (ROS, such as  $\bullet\text{OH}$ ,  $\text{SO}_4^{\bullet-}$ , etc.) have been considered as one of the  
57 most promising techniques to eliminate refractory organic pollutants [6]. The high  
58 oxidation ability of ROS can decompose the targeted pollutants into small molecules  
59 with low-toxicity, and even mineralize them into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [7]. The Fenton/Fenton-  
60 like processes, based on  $\text{H}_2\text{O}_2$  activation, has garnered increasing attention due to their  
61 advantages of simplicity in operation, high effectiveness, mild reaction conditions, and  
62 environmental friendliness [8]. The commonly employed activation approaches  
63 encompass photocatalysis [9,10], electrocatalysis [11], transition metals (i.e. Fe [12],  
64 Co [13], Cu [14], Mn [15], etc), carbon [16] and bimetallic metals catalysts activation  
65 [17].

66 Due to the significantly higher reaction rate constant of Cu(I) with  $\text{H}_2\text{O}_2$  ( $10^4 \text{ M}^{-1}$   
67  $\text{S}^{-1}$ ) compared to Fe(II) ( $76 \text{ M}^{-1} \text{ S}^{-1}$ ), various solid catalysts containing copper have

68 been employed as alternatives to iron-based catalysts [18], including zero valent copper  
69 [19], copper oxides [20], and copper-based composites [21]. Copper sulfide (CuS) has  
70 drawn considerable attention due to the weaker bonding energy between Cu and S  
71 compared to Cu and O, which can effectively improve the catalytic reaction rate [22].  
72 Additionally, sulfur species ( $S^{2-}$ ,  $S_n^{2-}$ ) present in CuS can facilitate the reduction of  
73 high-valence Cu to low-valence Cu, thereby significantly enhancing the catalytic  
74 activity as well [23]. However, the  $Cu^{2+}$  ions leakage from CuS during the catalytic  
75 reaction in pollutants removal greatly inhibits its practical application.

76 Dopamine (DA) is a molecule containing amine and catechol functional groups  
77 [24], which can undergo self-polymerization reaction in a simple environment to  
78 produce polydopamine (PDA) [25]. PDA possesses abundant functional groups such as  
79 carboxyl groups, amino groups, and  $\pi$ - $\pi$  bond. These functional groups make it an  
80 excellent in-situ reduction reagent for metal nanoparticles [26], as well as an anchorage  
81 point for metal-based materials to construct various secondary reaction platforms.  
82 Moreover, these groups can establish strong interactions including hydrogen bonding,  
83 electrostatic interactions, and  $\pi$ - $\pi$  interactions to enhance the adsorption properties of  
84 carriers for catalysts and pollutants [27]. Besides, the  $\pi$ - $\pi$  stacked PDA coating exhibits  
85 favorable electrochemical property that significantly accelerate the electron transfer  
86 rate [24,25]. Utilizing PDA as a modification carrier enables uniform distribution of  
87 metal particles, increased surface area, and generation of nanostructured catalysts with  
88 enhanced stability and catalytic efficiency [28].

89 Considering all the above-mentioned points, we speculated that the introduction  
90 of PDA onto CuS to synthesize CuS@PDA composite could prevent the copper ions  
91 leaching, making it a high-effective, structure stable and recyclable  $H_2O_2$  activator.  
92 Nevertheless, to the best of our knowledge, the application of CuS@PDA in  $H_2O_2$

93 activation for refractory organic pollutants degradation has rarely been reported. Herein,  
94 spherical CuS@PDA composites were synthesized via a hydrothermal method. The  
95 morphology, crystal structure, and chemical composition of CuS@PDA were  
96 systematically characterized. The catalytic activity of CuS@PDA in activating H<sub>2</sub>O<sub>2</sub>  
97 for TC degradation was investigated with respect to several key parameters, including  
98 initial pH, H<sub>2</sub>O<sub>2</sub> concentration, CuS@PDA dosage, and co-existing inorganic anions.  
99 Besides, electron paramagnetic resonance (EPR) analysis and quenching experiments  
100 were performed to elucidate the production and contribution ratios of ROS to the  
101 degradation. The mechanisms underlying TC degradation by CuS@PDA/H<sub>2</sub>O<sub>2</sub> were  
102 proposed, and the degradation intermediates and pathways were identified as well.

## 103 **2. Experimental methods**

### 104 2.1. Chemicals

105 Tetracycline (TC), Sulfadiazine (SDZ), carbamazepine (CBZ), Tris  
106 (hydroxymethyl) aminomethane Hydrochloride (Tris-HCl), tert-butanol (TBA), L-  
107 histidine (l-his), NaF, furfuryl alcohol (FFA) were provided by Macklin Biochemical  
108 Technology Co. Ltd. (Shanghai, China). Sulfamethoxazole (SMX), coumarin (CM),  
109 hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), ethyl alcohol (EtOH), methanol (MeOH), 1,4-benzo-  
110 quinone (BQ), 5,5-Dimethyl-1-pyrroline N-oxide (DMPO), 2,2,6,6-tetra-methyl-4-  
111 piperidone (TEMP) were obtained from Sigma-Aldrich Chemical Co. Ltd. (China).  
112 Dopamine hydrochloride (DA) and CuCl<sub>2</sub>•2H<sub>2</sub>O were supplied by Aladdin Biological  
113 Technology Co. Ltd. (Shanghai, China). Thiourea (CH<sub>4</sub>N<sub>2</sub>S), Potassiumperiodate  
114 (KIO<sub>4</sub>), NaOH, HCl, NaCl, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaHCO<sub>3</sub>, NaH<sub>2</sub>PO<sub>4</sub> were purchased from  
115 Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All chemicals were of at  
116 least analytical grade and used without further purification. Ultrapure water (18.2 MΩ  
117 ·cm) used throughout the study was prepared using a Millipore system (Bedford, USA).

## 118 2.2. Catalysts synthesis and characterization

119 The CuS@PDA composite was synthesized via a facile hydrothermal method, as  
120 illustrated in [Figure 1a](#). Initially, a precise amount of Tris-HCl (10 mM) weighing 145  
121 mg was dissolved in 80 mL of ultrapure water to prepare solution A. Subsequently,  
122 solution B was prepared by dissolving 204 mg of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  accurately weighed in  
123 40 mL of ultrapure water. Then, under magnetic stirring and pH adjustment to 8.5,  
124 solution A was supplemented with 232 mg of DA while simultaneously introducing  
125  $\text{CH}_4\text{N}_2\text{S}$  weighing 91 mg into solution B with continuous stirring. After a reaction time  
126 of 30 min, solution B was poured into solution A and the resulting mixture was stirred  
127 for an additional duration of 24 h until it attained a grayish white coloration. The  
128 reaction mixture was transferred to an autoclave and maintained at a temperature of  
129  $120^\circ\text{C}$  for a period of 12 h. Upon cooling to room temperature, the solids were collected  
130 by filtration and thoroughly rinsed multiple times with deionized water. Finally, the  
131 solids were vacuum dried at  $60^\circ\text{C}$  for 12 h to obtain CuS@PDA composites. PDA and  
132 CuS were prepared following the identical procedure as CuS@PDA but without adding  
133  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and DA, respectively.

134 The analytical and characterization methods are described in [Text S1](#).

## 135 2.3. Degradation tests of TC

136 The degradation experiments were conducted in a series of 100 mL glass beakers.  
137 Typically, 5 mg of catalyst was mixed with 50 mL of a  $40\ \mu\text{M}$  TC solution and dispersed  
138 ultrasonically for 1 min. Subsequently, 5 mM  $\text{H}_2\text{O}_2$  was added to initiate the  
139 degradation process. At predetermined time intervals, 0.5 mL of the solution was  
140 withdrawn, followed by filtration through a  $0.22\ \mu\text{m}$  membrane filter and immediate  
141 quenching with methanol (0.2 mL). The residual TC concentration in the solution was  
142 analyzed using high-performance liquid chromatography (HPLC). The initial pH of the

143 TC solution was adjusted using HCl or NaOH if necessary. To ensure experimental  
144 accuracy, all experiments were performed in triplicate and the results were reported as  
145 mean values with standard deviations.

### 146 **3. Results and discussion**

#### 147 3.1. Characterization

148 The microstructure and surface morphology of CuS, PDA, and CuS@PDA were  
149 characterized using SEM and TEM images. As shown in [Figure 1b](#) and [e](#), CuS exhibits  
150 a tubular flower-like morphology composed of nanosheets. On the other hand, PDA  
151 possesses a uniform nanospherical structure with a smooth surface, having an average  
152 diameter of approximately 200-500 nm ([Figure 1c](#) and [f](#)). In contrast, CuS@PDA  
153 maintains its spherical structure but displays a rougher morphology with smaller  
154 particle size and more pronounced agglomeration ([Figure 1d](#)). The TEM image in  
155 [Figure 1g](#) clearly reveals that the prepared CuS@PDA consists of randomly assembled  
156 nanorods. Additionally, the HRTEM image of CuS@PDA in [Figure 2h](#) exhibits  
157 uniformly distributed lattice fringes measuring at 0.305, 0.190, and 0.281 nm,  
158 corresponding to the (102), (110), and (103) crystal faces of the CuS nanocrystals  
159 respectively [[29,30](#)]. EDS elemental mapping also confirms that both Cu and S are  
160 evenly distributed throughout the material as shown in [Figure 1i](#).

161 XRD patterns were utilized to analyze the crystalline structure of CuS, PDA, and  
162 CuS@PDA as depicted in [Figure 2a](#). The characteristic peaks of CuS@PDA observed  
163 at  $2\theta$  of  $27.7^\circ$ ,  $29.3^\circ$ ,  $31.8^\circ$ ,  $32.9^\circ$ ,  $48.0^\circ$ ,  $52.7^\circ$ , and  $59.3^\circ$  can be indexed to the (101),  
164 (102), (103), (006), (110), (108) and (116) planes of CuS (JCPDS 20-0534),  
165 respectively. This indicates a well-defined crystalline structure of CuS grown on the  
166 PDA matrix [[31,32](#)]. The intensity of overlapped peaks for both (103) and (006) is much  
167 weaker than that for (110), which suggests preferential growth along the direction (110)

168 and polysulfide formation in CuS [33]. Compared to the pure CuS, the intensity of some  
169 diffraction peaks in CuS@PDA is slightly reduced, and this can be related to the surface  
170 modification by PDA on specific crystalline surfaces of CuS [34]. The Brunauer-  
171 Emmett-Teller (BET) and specific surface areas ( $S_{\text{BET}}$ ) of CuS@PDA were examined  
172 by  $\text{N}_2$  adsorption/desorption isotherms. As shown in Figure 2b, CuS@PDA displays a  
173 typical IV-type isotherm accompanied by a H3 hysteresis loop, indicating the presence  
174 of mesoporous structure. The  $S_{\text{BET}}$  of CuS@PDA was calculated to be  $55.67 \text{ m}^2/\text{g}$ , with  
175 a total pore volume of  $0.21 \text{ cm}^3/\text{g}$  and average pore diameter of  $\sim 15 \text{ nm}$  (Figure 2c).  
176 The surface functional groups of CuS, PDA, and CuS@PDA were analyzed by FTIR.  
177 As depicted in Figure 2d, the pure PDA exhibits several characteristic absorption peaks  
178 at 1290, 1512, 1618, and  $3100\text{-}3600 \text{ cm}^{-1}$ , corresponding to the C–O stretching  
179 vibration, N–H shear vibration, N–H bending vibration [35], and O–H stretching  
180 vibration of surface hydroxyl groups, respectively [36]. In the FTIR spectrum of CuS,  
181 the absorption peak at  $612 \text{ cm}^{-1}$  can be assigned to the Cu–S stretching vibration [37],  
182 and the peak centered at  $1109 \text{ cm}^{-1}$  is related to the S–O stretching vibration [38].  
183 Obviously, the as-synthesized CuS@PDA possesses the characteristic peaks of both  
184 CuS and PDA. Due to the encapsulation of PDA, the Cu–S bond weakens, and the S–O  
185 bond disappears. The results indicate that CuS@PDA was successfully prepared. These  
186 results demonstrate the successful synthesis of CuS@PDA.

### 187 3.2. Catalytic activity tests

188 The catalytic activity of CuS@PDA in activating  $\text{H}_2\text{O}_2$  for TC degradation is  
189 demonstrated in Figure 3. As shown in Figure 3a, the individual utilization of  $\text{H}_2\text{O}_2$  or  
190 PDA exhibited negligible TC removal within a 30 min timeframe, indicating that the  
191 direct oxidation failed to achieve satisfactory TC removal and the adsorption capacity  
192 of PDA was insignificant. The removal efficiency achieved by CuS reached 37.2%, and

193 it increased to 58.4% when using CuS@PDA as the adsorbent. As expected,  
194 simultaneous addition of H<sub>2</sub>O<sub>2</sub> (5 mM) and CuS@PDA (0.1 g/L) resulted in accelerated  
195 TC removal. As shown in Figure 3b, the pseudo-first-order kinetic rate constant (*k*)  
196 obtained by CuS@PDA/H<sub>2</sub>O<sub>2</sub> was determined to be 0.20 min<sup>-1</sup>, higher than that  
197 obtained by CuS/H<sub>2</sub>O<sub>2</sub> (0.12 min<sup>-1</sup>). Further, the presence of 0.1 g/L PDA in CuS/H<sub>2</sub>O<sub>2</sub>  
198 system improved the *k* value from 0.12 to 0.15 min<sup>-1</sup>, indicating its promotion effect to  
199 degrade TC. Overall, the as-synthesized CuS@PDA exhibited the highest catalytic  
200 activity while effectively mitigating Cu ions leaching compared to other catalysts tested  
201 as illustrated in Figure 3c. It's worth noting that the leaching concentrations of Cu<sup>2+</sup>  
202 ions in the CuS@PDA/H<sub>2</sub>O<sub>2</sub> system was only 0.2 mg/L, significantly lower than the  
203 integrated tap-water standard of U.S. Environmental Protection Agency (1.3 mg/L).  
204 While the leaching concentration of Cu<sup>2+</sup> ions in the CuS/H<sub>2</sub>O<sub>2</sub> system was 3.81 mg/L.  
205 Obviously, the incorporation of PDA effectively alleviated the release of Cu<sup>2+</sup> from CuS,  
206 which is advantageous for practical application. Table S2 compares the kinetic rate  
207 constants of TC degradation by different catalysts in H<sub>2</sub>O<sub>2</sub>-based AOPs. As observed,  
208 CuS@PDA demonstrates a much higher *k* value compared to the reported catalysts.

209 The recyclability of solid catalysts are crucial characteristics for their practical  
210 application. In this study, five consecutive cycling tests were conducted to compare the  
211 recyclability of CuS@PDA and CuS. After each cycle, the solid catalyst was collected,  
212 washed with ethanol and ultrapure water, vacuum dried, and subsequently reused. As  
213 shown in Figure 3d, the degradation of TC reduced to 73% in the fifth run when using  
214 CuS as the catalyst due to the reduced active sites caused by copper ions leakage from  
215 CuS. In contrast, CuS@PDA consistently maintained a removal efficiency 93% after  
216 five repeated cycles.

217 These findings demonstrated that CuS@PDA exhibited high efficiency,

218 exceptional recyclability and structural stability, thereby potentially reducing  
219 environmental organic pollutants.

### 220 **3.3. Influencing factors on TC degradation**

221 The influences of operational parameters (i.e., CuS@PDA dosage, H<sub>2</sub>O<sub>2</sub>  
222 concentration, initial pH, and coexisting anions) on TC removal by the CuS@PDA  
223 activated H<sub>2</sub>O<sub>2</sub> system are discussed in the following section. [Figure 4a](#) illustrates the  
224 impact of catalyst dosage (0, 5, 8, 10, and 13 mg). It is evident that different catalyst  
225 dosages have varying effects on the removal efficiency of TC. In the absence of  
226 CuS@PDA in the solution, the removal was minimal, indicating that the self-  
227 decomposition of H<sub>2</sub>O<sub>2</sub> was ineffective. Conversely, when 5 mg of CuS@PDA  
228 presented, 94.46% of TC was removed in 30 min. This was related to the surface active  
229 sites on the catalyst that could rapidly activate H<sub>2</sub>O<sub>2</sub> to produce high-effective active  
230 substances to degrade TC [\[39\]](#). Yet, further increase in catalyst dosage from 10 to 13  
231 mg led to a declined degradation rate, which was related to the self-quenching effect  
232 caused by excess radicals and diffusion limitation caused by excess catalyst [\[40\]](#).  
233 Considering the removal efficiency and cost control, the optimum dosage of 5 mg  
234 CuS@PDA was selected in the subsequent tests. The H<sub>2</sub>O<sub>2</sub> concentration also played a  
235 pivotal role in the degradation of TC by CuS@PDA/H<sub>2</sub>O<sub>2</sub>. As shown in [Figure 4b](#), the  
236 removal efficiency was limited to approximately 58.4% in the absence of H<sub>2</sub>O<sub>2</sub>.  
237 However, with the addition of 1 mM H<sub>2</sub>O<sub>2</sub>, the degradation rapidly improved to 86.5%.  
238 Furthermore, a gradual enhancement in degradation was observed as the H<sub>2</sub>O<sub>2</sub>  
239 concentration increased from 1 to 10 mM. Ultimately, an optimum H<sub>2</sub>O<sub>2</sub> concentration  
240 of 5 mM was selected.

241 The initial solution pH also impacts the performance heterogeneous catalysis in  
242 the degradation of organic pollutants. As shown in [Figure 4c](#), an extremely acidic

243 condition (pH=3) was found to be unfavorable for TC degradation. Nevertheless, a high  
244 removal efficiency above 90% was maintained across a wide pH range of 5–11,  
245 indicating that CuS@PDA can be practically utilized without requiring pH adjustment.  
246 At low pH,  $H^+$  can serve as a scavenger for  $\bullet OH$  via equation of  $H^+ + \bullet OH + e^+ \rightarrow$   
247  $H_2O$  [41]. Additionally, literature reports suggest that the increasing electron density in  
248 the  $TC^-$  and  $TC^{2-}$  ring systems with rising pH promotes direct decomposition of TC  
249 molecules through the direct attack of  $H_2O_2$  and free radicals [42]. To gain a deeper  
250 understanding of the influence of initial pH on TC removal, the zeta potential of  
251 CuS@PDA at various pH levels was recorded as depicted in Figure S1. The surface  
252 charge of CuS@PDA was negative within the tested pH range, which was primarily  
253 induced by imine, quinone, and catechol groups on PDA [43]. Besides, the  
254 deprotonation/protonation and reversible dissociation of catechol groups and amines  
255 also contributed to the negative charge on CuS@PDA as reported previously [44].  
256 These findings suggest that the electrostatic force might played a minor role in the  
257 degradation of TC.

258 Considering the presence of various inorganic anions ( $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $H_2PO_4^-$ ,  
259 and  $HCO_3^-$ ) in natural water, their impact on TC degradation was investigated as shown  
260 in Figure 4d. The degradation was inhibited by 9% when 20 mM  $Cl^-$  was present due  
261 to the generation of less reactive  $ClOH^{\bullet-}$  ( $\bullet OH + Cl^- \rightarrow ClOH^{\bullet-}$ ) [45]. The inhibiting  
262 effect of 20 mM  $NO_3^-$  could be attributed to the competition between  $NO_3^-$  and TC for  
263 adsorption sites on CuS@PDA.  $SO_4^{2-}$  can be adsorbed on the catalyst surface and  
264 compete with TC molecules for active site, thereby hindering TC degradation [39,46].  
265  $H_2PO_4^-$  exhibits a quenching effect on  $\bullet OH$  through the formation of low-active  
266  $H_2PO_4^{\bullet-}$ , consequently impeding the degradation. Although  $HCO_3^-$  is considered as a  
267 scavenger of  $\bullet OH$  ( $k = 8.5 \times 10^6 M^{-1}s^{-1}$ ) [39,47], it actually promoted the degradation

268 in this study due to the production of  $\bullet\text{OH}$  and  $^1\text{O}_2$  from  $\text{HCO}_3^-$  [48]. Nevertheless,  
269 even in the presence of excessive inorganic anions the CuS@PDA/ $\text{H}_2\text{O}_2$  system still  
270 achieved ~80% TC removal, suggesting its robustness and suitability for actual  
271 application.

### 272 **3.5. Mechanisms understanding of TC degradation by CuS@PDA/ $\text{H}_2\text{O}_2$**

#### 273 3.5.1. Identification of possible reactive species

274 Quenching tests and electron paramagnetic resonance (EPR) were applied to  
275 uncover the reactive oxygen species (ROS) responsible for TC degradation in the  
276 CuS@PDA/ $\text{H}_2\text{O}_2$  system. Tert-butanol (TBA) is an effective scavenger of  $\bullet\text{OH}$  with  
277 quenching rate of  $(3.8\text{--}7.6)\times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , while *p*-benzoquinone (BQ) and L-histidine  
278 (L-his) can act as quenchers of  $\text{O}_2^{\bullet-}$  [ $(0.9\text{--}1.9)\times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ] and  $^1\text{O}_2$  ( $3.2\times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ),  
279 respectively [49,50]. NaF is a typical quenching agent for surface bound free radicals  
280 on the catalyst surface in heterogeneous catalysis [49]. As shown in Figure 5a, in  
281 contrast to the control group without scavengers addition, the presence of 200 mM TBA  
282 inhibited a slightly inhibitory effect on the degradation. Even with an increased TBA  
283 concentration of 1 M, TC removal only dropped to 77.4%, indicating that  $\bullet\text{OH}$  played  
284 a minor role in TC oxidation. Furthermore, instead of inhibition, the inclusion of 20  
285 mM BQ demonstrated a promotional effect, suggesting that  $\text{O}_2^{\bullet-}$  might not serve as the  
286 primary active species for the degradation either. As illustrated in Figure 5b, the  
287 introduction of 10 mM NaF had no impact on the degradation, implying that surface-  
288 bound free radicals had negligible influence on the degradation of TC [51]. In  
289 comparison, the addition of 100 mM L-his suppressed the degradation to 60%. Yet, the  
290 inhibitory effect of L-his does not provide direct evidence for the involvement of  $^1\text{O}_2$   
291 as the main reactive species since L-his can readily form a complex with Cu(II), thereby  
292 obstructing ROS formation [52]. A pronounced quenching effect was also observed for

293 furfuryl alcohol (FFA). This tentatively indicated that the degradation of TC did not  
294 rely on free radicals, with  $^1\text{O}_2$  being the major contributor.

295 To ascertain the production of Cu(III) in the CuS@PDA/H<sub>2</sub>O<sub>2</sub> system, periodate  
296 was used as a chemical probe for Cu(III) [40,53]. Surprisingly, the presence of 1 mM  
297 periodate sharply expedited the degradation (Figure 5b). This observation suggested  
298 that periodate did not complex with Cu(III), but rather functioned as an oxidizing agent  
299 to facilitate the degradation. The formation of Cu(III) was excluded.

300 To further validate the quenching tests results, EPR analysis using DMPO and  
301 TEMP as spin trapping agents were further conducted to identify the formed ROS in  
302 the CuS@PDA/H<sub>2</sub>O<sub>2</sub> system. As depicted in Figure 5c, d, and e, no signal was found  
303 in the absence of H<sub>2</sub>O<sub>2</sub>, demonstrating that CuS@PDA itself can not produce ROS. In  
304 contrast, characteristic peaks of DMPO-•OH (1:2:2:1), DMPO-O<sub>2</sub><sup>•-</sup> (1:2:2:1), and  
305 TEMP-<sup>1</sup>O<sub>2</sub> (1:1:1) appeared with the coexistence of CuS@PDA and H<sub>2</sub>O<sub>2</sub>, further  
306 validating the generation of •OH, O<sub>2</sub><sup>•-</sup>, and <sup>1</sup>O<sub>2</sub>. As the reaction time prolonged, the  
307 peak intensity enhanced gradually, verifying the continuously production of ROS by  
308 CuS@PDA/H<sub>2</sub>O<sub>2</sub>. Thus, the above results conclusively indicated that <sup>1</sup>O<sub>2</sub> plays a major  
309 role in the degradation.

310 Further investigations into the generation of <sup>1</sup>O<sub>2</sub> in the CuS@PDA/H<sub>2</sub>O<sub>2</sub> system  
311 was performed to understand the underlying processes as dissolved oxygen [54], light  
312 irradiation [55] and O<sub>2</sub><sup>•-</sup> reorganization [40] have been reported to be responsible for  
313 <sup>1</sup>O<sub>2</sub> production. As shown in Figure S2, the degradation was barely influenced under  
314 continuous N<sub>2</sub> pumping and dark conditions, which ruled out dissolved oxygen as a  
315 precursor of <sup>1</sup>O<sub>2</sub>. Combining with the result in Figure 5a that O<sub>2</sub><sup>•-</sup> did not contribute to  
316 the degradation, it was concluded that <sup>1</sup>O<sub>2</sub> mainly originated from H<sub>2</sub>O<sub>2</sub> and rather than  
317 the recombination of O<sub>2</sub><sup>•-</sup>.

### 318 3.5.2. The role of PDA

319 To examine the role of PDA on the enhanced catalytic activity of CuS@PDA, the  
320 electrochemical responses of PDA, CuS, and CuS@PDA towards H<sub>2</sub>O<sub>2</sub> and TC were  
321 recorded by determining the open-circuit potential (OCP), as shown in [Figure 5f](#). The  
322 OCP values exhibited by PDA, CuS, and CuS@PDA were found to be 0.088, 0.26, and  
323 0.24 V, respectively. The enhanced content of pyridine and pyrrolic N in CuS@PDA  
324 resulting from the introduction of PDA facilitated easier complexation with H<sub>2</sub>O<sub>2</sub> and  
325 conferred stronger oxidation capability [\[56\]](#). Thus, upon addition of H<sub>2</sub>O<sub>2</sub>, the OCP of  
326 CuS@PDA abruptly improved from 0.24 to 0.43 V owing to the elevated potential  
327 associated with formed H<sub>2</sub>O<sub>2</sub> complexes. While, regarding to CuS, it only increased by  
328 0.1 V (from 0.26 to 0.36 V). Subsequently, the OCP value gradually decreased by 0.016  
329 V following TC injection due to the decomposition of surface complexes. The  
330 CuS@PDA displayed a more pronounced decline in OCP, indicating that active  
331 complexes formed on its surface possessed superior oxidation ability towards TC  
332 compared to those formed on CuS.

333 Furthermore, the FTIR spectrum of the fresh and used CuS@PDA was recorded  
334 to determine the change in surface functional groups. As shown in [Figure 6a](#), after the  
335 catalytic reaction, the absorption peak corresponding to N–H bending vibration shifted  
336 from 1618 to 1579 cm<sup>-1</sup>, and the peak belonging to N–H scissoring vibration at 1439  
337 cm<sup>-1</sup> enhanced significantly, suggesting the participation of N–H in the catalytic  
338 degradation of TC in the studied CuS@PDA/H<sub>2</sub>O<sub>2</sub> system. The peak related to Cu–S  
339 bond also shifted from 612 to 608 cm<sup>-1</sup>, which evidenced the involvement Cu–S.

### 340 3.5.3. Mechanism investigation of TC degradation by CuS@PDA/H<sub>2</sub>O<sub>2</sub>

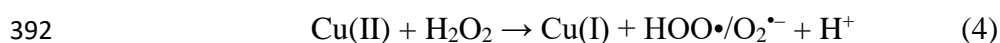
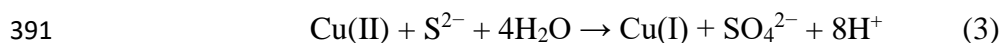
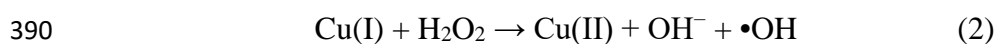
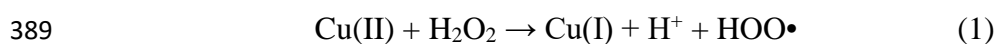
341 To further elucidate the mechanisms underlying TC degradation by  
342 CuS@PDA/H<sub>2</sub>O<sub>2</sub>, XPS analysis was conducted to determine the chemical composition

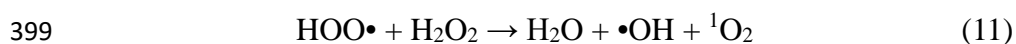
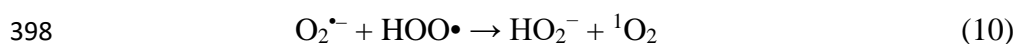
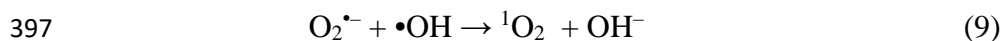
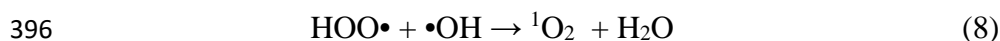
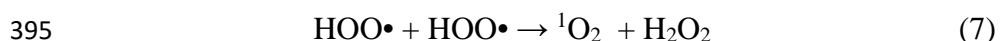
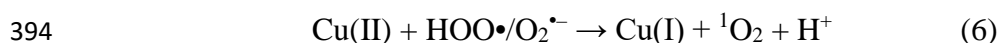
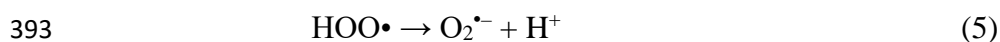
343 and valence states of both fresh and used CuS@PDA. Figure 6b presents the full-scale  
344 XPS spectra, which clearly indicates the presence of Cu, O, N, C, and S elements in the  
345 as-synthesized CuS@PDA. The high-resolution N 1s spectrum (Figure 6c) was  
346 deconvoluted into three distinct peaks corresponding to imino groups, substituted  
347 amines, and amine groups at binding energies of 398.8, 399.8, and 400.7 eV,  
348 respectively [31]. These peaks primarily originate from the indole or indoline structure  
349 in PDA [57]. XPS analysis of Cu displays two main peaks at binding energies of 932.6  
350 eV and 952.6 eV (Figure 6d), belonging to Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> spin orbitals,  
351 respectively [58]. The Cu 2p<sub>3/2</sub> spectrum is further resolved into two individual peaks,  
352 with Cu(I) appearing at 932.2 eV and Cu(II) at 933.2 eV. As seen, the Cu 2p XPS  
353 spectrum of CuS@PDA exhibits remarkable similarity to that of CuS, indicating the  
354 relatively stability of copper element in CuS during the complexation process with DA.  
355 Regarding the high-resolution S 2p spectrum (Figure 6e), the peaks observed at 161.5  
356 eV and 163.4 eV can be assigned to sulfide ions (S<sup>2-</sup>) and polysulfide (S<sub>n</sub><sup>2-</sup>),  
357 respectively [39,59]. The peaks centered at 164.4 eV and 168.6 eV correspond to  
358 elemental sulfur (S<sup>0</sup>) and sulfate ions, respectively [39,59,60]. In contrast with CuS, the  
359 absence of S<sup>0</sup> peak and presence of sulfate ions peak in CuS@PDA may be attributed  
360 to the oxidation of CuS during the self-polymerization process of DA [60].

361 Obviously, after activating H<sub>2</sub>O<sub>2</sub> for TC degradation, the relative proportion of  
362 Cu(II) in CuS@PDA reduced from 50.37% to 37.41%, accompanied by an increase in  
363 the proportion of Cu(I) from 49.63% to 62.59%. This shift indicated a transition in  
364 oxidation state from Cu(II) to Cu(I), providing evidence for the involvement of Cu(II)  
365 in the catalytic process. On the other hand, there was a significant decline in the relative  
366 proportion of S<sup>2-</sup> from 84.46% to 19.82%, while varying degrees of increases were  
367 observed in the S<sub>n</sub><sup>2-</sup>, S<sup>0</sup>, and sulfate content, suggesting the participation of S<sup>2-</sup> in the

368 catalytic process. The XPS analysis revealed the involvement of both Cu and S, with S  
369 exhibiting an accelerating effect on the conversion of Cu(II) to Cu(I) [61].

370 Based on the preceding discussion, a possible mechanism of TC degradation by  
371 the CuS@PDA activated H<sub>2</sub>O<sub>2</sub> system was proposed as schematically in Figure 7. As  
372 H<sub>2</sub>O<sub>2</sub> molecule reached the surface of CuS@PDA, the exposed Cu active site on which  
373 underwent redox cycle with H<sub>2</sub>O<sub>2</sub> according to Eqs. 1 and 2 [62,63]. However, the slow  
374 reaction rate between Cu(II) and H<sub>2</sub>O<sub>2</sub> greatly affected the regeneration of Cu(I) [64].  
375 Fortunately, the presence of sulfur in CuS@PDA expedited the conversion of Cu(II) to  
376 Cu(I) according to Eq. 3, thereby accelerating the production of •OH (Eq. 2) [62]. <sup>1</sup>O<sub>2</sub>  
377 was considered as the predominant ROS contributing to the degradation of TC. The  
378 generation of <sup>1</sup>O<sub>2</sub> from H<sub>2</sub>O<sub>2</sub> can occur via either a one-step two-electron or a two-step  
379 one-electron transfer pathway [65]. Based on quenching tests and the Haber-Weiss  
380 cycle theory, two-step one-electron transfer was supposed to be a reliable pathway for  
381 <sup>1</sup>O<sub>2</sub> production [66]. The first one-electron pathway yielded HOO•/O<sub>2</sub><sup>•-</sup> via Eq. 4, where  
382 an electron was transferred from H<sub>2</sub>O<sub>2</sub> to Cu(II) (Eq. 1). Subsequently, O<sub>2</sub><sup>•-</sup> was  
383 produced from HOO• through Eq. 5 [66]. The second one-electron pathway entailed  
384 <sup>1</sup>O<sub>2</sub> generation from HOO•/O<sub>2</sub><sup>•-</sup> and encompassed three possible routes: rapid oxidation  
385 of spin-state Cu(II) by the generated HOO•/O<sub>2</sub><sup>•-</sup> (Eq. 6), reactive species reactions  
386 involving recombination of HOO• and reactions between HOO•, O<sub>2</sub><sup>•-</sup>, and •OH  
387 according to Eqs. 7-10 [65,67], and reactions between H<sub>2</sub>O<sub>2</sub> with HOO•/O<sub>2</sub><sup>•-</sup> (Eqs. 11  
388 and 12) [68].





### 401 3.6. Degradation pathways and toxicity analysis of intermediates

402 A total of eighteen intermediates of TC degradation by CuS@PDA/H<sub>2</sub>O<sub>2</sub> were  
 403 identified as shown in Figure S3 and Table S3. Three potential degradation pathways  
 404 including terminal oxidation, dealkylation, deamination and ring-opening reactions  
 405 were proposed in Figure 8 [69]. In pathway 1, TC underwent terminal oxidation to  
 406 generate the intermediate P7 (m/z=475), which was subsequently degraded into p9  
 407 (m/z=360) through dealkylation and disruption of the benzene ring [70]. The ring  
 408 cleavage under <sup>1</sup>O<sub>2</sub> attack led to the formation of P10, P11, and P12 [71]. In pathway  
 409 2, nucleophilic reactions occurred to produce P1 (m/z=461) and P2 (m/z=477),  
 410 followed by dehydrogenation under O<sub>2</sub><sup>·-</sup> attack to form a downstream intermediate P3  
 411 (m/z=459) [72]. In pathway 3, TC was attacked by ROS to produce P4 (m/z=417) via  
 412 an N-demethylation process [73], which further underwent amide group destruction,  
 413 demethylation, and dehydroxylation to produce P5 (m/z=339) and P6 (m/z=325).  
 414 Thereafter, a ring-opening reaction occurred yielding P7 (m/z=171) [74]. Additionally,  
 415 several small molecules including P13 (m/z=262), P14 (m/z=223) [72], P15 (m/z=132)  
 416 [74], P16 (m/z=118) [75], P17 (m/z=90) and P18 (m/z=60) [73] were detected as well.  
 417 All intermediates could be further decomposed into low molecular compounds such as

418 H<sub>2</sub>O, CO<sub>2</sub>, and NO<sub>3</sub><sup>-</sup> via subsequent reactions with <sup>1</sup>O<sub>2</sub>, •OH and O<sub>2</sub><sup>•-</sup> [69,76,77].

419 The developmental toxicity and mutagenic toxicity of TC and main degradation  
420 intermediates were predicted and assessed through Toxicity Estimation Software  
421 (T.E.S.T.) based on quantitative structure-activity relationship (QSAQ) as shown in  
422 [Figure S4](#). TC has significant developmental toxicity (0.86) and positive mutagenic  
423 toxicity (0.6). Compared to the parent TC, the toxicity of most intermediates declined.  
424 As shown in [Figure S4a](#), apart from P4 and P6, the developmental toxicity of other  
425 intermediates was reduced. Similarly, most intermediates exhibited a reduction in  
426 mutagenicity ([Figure S4b](#)). Thus, it could be deduced that the CuS@PDA/H<sub>2</sub>O<sub>2</sub> system  
427 not only efficiently eliminated TC, but also mitigated the toxicity of degradation  
428 intermediates during the degradation. This was of great significance for the safety of  
429 water environment.

#### 430 **4. Conclusions**

431 In this study, CuS@PDA composite was synthesized via a simple hydrothermal  
432 method using DA and CuS, aiming for activating H<sub>2</sub>O<sub>2</sub> to remove TC from aqueous  
433 solutions. The degradation tests results showed that a removal efficiency of 94.9% was  
434 achieved within 30 min in the presence of 0.1 g/L CuS@PDA and 5 mM H<sub>2</sub>O<sub>2</sub>. The as-  
435 synthesized CuS@PDA not only exhibited excellent catalytic activity within a wide pH  
436 range from 5 to 11, but also showed remarkable recyclability with 93% removal in the  
437 fifth consecutive cycle. Quenching experiments and EPR analysis confirmed that <sup>1</sup>O<sub>2</sub>  
438 played a crucial role in the degradation of TC. Mechanistic analysis revealed that S in  
439 CuS@PDA facilitated the Cu(II)/Cu(I) redox cycle, with H<sub>2</sub>O<sub>2</sub> serving as the main  
440 source for generating <sup>1</sup>O<sub>2</sub>. Further, the degradation pathways and intermediate toxicity  
441 of TC were also studied. In conclusion, this study presents an efficient and recyclable  
442 CuS@PDA composite to activate H<sub>2</sub>O<sub>2</sub> for refractory organic pollutants removal in

443 water and wastewater treatments.

444

445 **Acknowledgments**

446 This work was financially supported by National Natural Science Foundation of China

447 (52270004).

448

## 449 Reference

- 450 [1] Current research trends on emerging contaminants pharmaceutical and personal care products  
451 (PPCPs): A comprehensive review, *Sci. Total Environ.* 859 (2023) 160031.  
452 <https://doi.org/10.1016/j.scitotenv.2022.160031>.
- 453 [2] J.J. López Peñalver, C.V. Gómez Pacheco, M. Sánchez Polo, J. Rivera Utrilla, Degradation of  
454 tetracyclines in different water matrices by advanced oxidation/reduction processes based on gamma  
455 radiation, *J. Chem. Technol. Biotechnol.* 88 (2013) 1096–1108. <https://doi.org/10.1002/jctb.3946>.
- 456 [3] R. Daghrir, P. Drogui, Tetracycline antibiotics in the environment: a review, *Environ. Chem. Lett.*  
457 11 (2013) 209–227. <https://doi.org/10.1007/s10311-013-0404-8>.
- 458 [4] Y. Amangelsin, Y. Semenova, M. Dadar, M. Aljofan, G. Björklund, The Impact of Tetracycline  
459 Pollution on the Aquatic Environment and Removal Strategies, *Antibiotics* 12 (2023) 440.  
460 <https://doi.org/10.3390/antibiotics12030440>.
- 461 [5] K. Ming, F. Chen, L. Zhu, S. Xia, L. Yang, Z. Shi, L. Deng, H. Zhang, Perborate accelerated copper-  
462 immobilized carbon nanofibers activating peroxymonosulfate process for sulfadiazine degradation:  
463 Performance and mechanisms understanding, *Sep. Purif. Technol.* 324 (2023) 124587.  
464 <https://doi.org/10.1016/j.seppur.2023.124587>.
- 465 [6] Z. Cheng, L. Ling, Z. Wu, J. Fang, P. Westerhoff, C. Shang, Novel Visible Light-Driven  
466 Photocatalytic Chlorine Activation Process for Carbamazepine Degradation in Drinking Water, *Environ.*  
467 *Sci. Technol.* 54 (2020) 11584–11593. <https://doi.org/10.1021/acs.est.0c03170>.
- 468 [7] F. Ahmad, D. Zhu, J. Sun, Environmental fate of tetracycline antibiotics: degradation pathway  
469 mechanisms, challenges, and perspectives, *Environ. Sci. Eur.* 33 (2021) 64.  
470 <https://doi.org/10.1186/s12302-021-00505-y>.
- 471 [8] Y. Liu, Y. Zhao, J. Wang, Fenton/Fenton-like processes with in-situ production of hydrogen  
472 peroxide/hydroxyl radical for degradation of emerging contaminants: Advances and prospects, *J. Hazard.*  
473 *Mater.* 404 (2021) 124191. <https://doi.org/10.1016/j.jhazmat.2020.124191>.
- 474 [9] Y. Huang, M. Kong, S. Coffin, K.H. Cochran, D.C. Westerman, D. Schlenk, S.D. Richardson, L.  
475 Lei, D.D. Dionysiou, Degradation of contaminants of emerging concern by UV/H<sub>2</sub>O<sub>2</sub> for water reuse:  
476 Kinetics, mechanisms, and cytotoxicity analysis, *Water Res.* 174 (2020) 115587.  
477 <https://doi.org/10.1016/j.watres.2020.115587>.
- 478 [10] IJERPH | Free Full-Text | Removal of Sulfamethoxazole, Sulfathiazole and Sulfamethazine in their  
479 Mixed Solution by UV/H<sub>2</sub>O<sub>2</sub> Process, (n.d.). <https://www.mdpi.com/1660-4601/16/10/1797> (accessed  
480 June 17, 2024).
- 481 [11] Y. Zhu, F. Deng, S. Qiu, F. Ma, Y. Zheng, R. Lian, Enhanced electro-Fenton degradation of  
482 sulfonamides using the N, S co-doped cathode: Mechanism for H<sub>2</sub>O<sub>2</sub> formation and pollutants decay, *J.*  
483 *Hazard. Mater.* 403 (2021) 123950. <https://doi.org/10.1016/j.jhazmat.2020.123950>.
- 484 [12] Y. Qu, Z. Chen, Y. Duan, L. Liu, H<sub>2</sub>O<sub>2</sub> assisted photocatalysis over Fe-MOF modified BiOBr for  
485 degradation of RhB, *J. Chem. Technol. Biotechnol.* 97 (2022) 2881–2888.  
486 <https://doi.org/10.1002/jctb.7199>.
- 487 [13] X. Long, Z. Yang, H. Wang, M. Chen, K. Peng, Q. Zeng, A. Xu, Selective Degradation of Orange  
488 II with the Cobalt(II)–Bicarbonate–Hydrogen Peroxide System, *Ind. Eng. Chem. Res.* 51 (2012) 11998–  
489 12003. <https://doi.org/10.1021/ie3013924>.
- 490 [14] C. Meng, Z. Wang, W. Zhang, L. Cui, B. Yang, H. Xie, Z. Zhang, Lamina membranes assembled  
491 by ultrathin cobalt-copper oxide nanosheets for nanoconfined catalytic degradation of contaminants,

492 Chem. Eng. J. 449 (2022) 137811. <https://doi.org/10.1016/j.cej.2022.137811>.

493 [15] L. Chen, T. Maqbool, C. Hou, W. Fu, X. Zhang, Mechanistic study of oxidative removal of  
494 bisphenol A by pristine nanocatalyst MnO/peroxymonosulfate<sup>34</sup>, Sep. Purif. Technol. 281 (2022)  
495 119882. <https://doi.org/10.1016/j.seppur.2021.119882>.

496 [16] X. Zhang, P. Sun, K. Wei, X. Huang, X. Zhang, Enhanced H<sub>2</sub>O<sub>2</sub> activation and sulfamethoxazole  
497 degradation by Fe-impregnated biochar, Chem. Eng. J. 385 (2020) 123921.  
498 <https://doi.org/10.1016/j.cej.2019.123921>.

499 [17] N. Li, X. He, J. Ye, H. Dai, W. Peng, Z. Cheng, B. Yan, G. Chen, S. Wang, H<sub>2</sub>O<sub>2</sub> activation and  
500 contaminants removal in heterogeneous Fenton-like systems, J. Hazard. Mater. 458 (2023) 131926.  
501 <https://doi.org/10.1016/j.jhazmat.2023.131926>.

502 [18] J. Li, A.N. Pham, R. Dai, Z. Wang, T.D. Waite, Recent advances in Cu-Fenton systems for the  
503 treatment of industrial wastewaters: Role of Cu complexes and Cu composites, J. Hazard. Mater. 392  
504 (2020) 122261. <https://doi.org/10.1016/j.jhazmat.2020.122261>.

505 [19] S. Guo, M. Chen, L. You, Y. Wei, C. Cai, Q. Wei, H. Zhang, K. Zhou, 3D printed hierarchically  
506 porous zero-valent copper for efficient pollutant degradation through peroxymonosulfate activation, Sep.  
507 Purif. Technol. 305 (2023) 122437. <https://doi.org/10.1016/j.seppur.2022.122437>.

508 [20] Y. Li, J. Wang, Z. Wei, W. Li, W. Duan, X. Feng, Q. Ma, Q. Zhang, H. Chen, X. Wu, Effective  
509 periodate activation by peculiar Cu<sub>2</sub>O nanocrystal for antibiotics degradation: The critical role of  
510 structure and underlying mechanism study, Appl. Catal. B Environ. 341 (2024) 123351.  
511 <https://doi.org/10.1016/j.apcatb.2023.123351>.

512 [21] A. Fiorentino, R. Cucciniello, A. Di Cesare, D. Fontaneto, P. Prete, L. Rizzo, G. Corno, A. Proto,  
513 Disinfection of urban wastewater by a new photo-Fenton like process using Cu-iminodisuccinic acid  
514 complex as catalyst at neutral pH, Water Res. 146 (2018) 206–215.  
515 <https://doi.org/10.1016/j.watres.2018.08.024>.

516 [22] Y. Fang, D. Luan, X.W. (David) Lou, Recent Advances on Mixed Metal Sulfides for Advanced  
517 Sodium-Ion Batteries, Adv. Mater. 32 (2020) 2002976. <https://doi.org/10.1002/adma.202002976>.

518 [23] Y. Huang, L. Nengzi, X. Zhang, J. Gou, Y. Gao, G. Zhu, Q. Cheng, X. Cheng, Catalytic degradation  
519 of ciprofloxacin by magnetic CuS/Fe<sub>2</sub>O<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> nanocomposite activated peroxymonosulfate:  
520 Influence factors, degradation pathways and reaction mechanism, Chem. Eng. J. 388 (2020) 124274.  
521 <https://doi.org/10.1016/j.cej.2020.124274>.

522 [24] B. Mao, Q. An, B. Zhai, Z. Xiao, S. Zhai, Multifunctional hollow polydopamine-based composites  
523 (Fe<sub>3</sub>O<sub>4</sub>/PDA@Ag) for efficient degradation of organic dyes, RSC Adv. 6 (2016) 47761–47770.  
524 <https://doi.org/10.1039/C6RA05954F>.

525 [25] S. Cheng, X. Pan, C. Zhang, X. Lin, Q. Zhuang, Y. Jiao, W. Dong, X. Qi, UV-assisted ultrafast  
526 construction of robust Fe<sub>3</sub>O<sub>4</sub>/polydopamine/Ag Fenton-like catalysts for highly efficient micropollutant  
527 decomposition, Sci. Total Environ. 810 (2022) 151182. <https://doi.org/10.1016/j.scitotenv.2021.151182>.

528 [26] B. Jin, D. Zhao, H. Yu, W. Liu, C. Zhang, M. Wu, Rapid degradation of organic pollutants by  
529 Fe<sub>3</sub>O<sub>4</sub>@PDA/Ag catalyst in advanced oxidation process, Chemosphere 307 (2022) 135791.  
530 <https://doi.org/10.1016/j.chemosphere.2022.135791>.

531 [27] Q.U. Ain, U. Rasheed, M. Yaseen, H. Zhang, Z. Tong, Superior dye degradation and adsorption  
532 capability of polydopamine modified Fe<sub>3</sub>O<sub>4</sub>-pillared bentonite composite, J. Hazard. Mater. 397 (2020)  
533 122758. <https://doi.org/10.1016/j.jhazmat.2020.122758>.

534 [28] W. Chen, T. Zhou, D. Gu, Y. He, Z. Zhang, J. Tian, F. Fu, Polydopamine-coated carbonized cotton  
535 fabrics with β-FeOOH nanorods composites for highly efficient photo-Fenton degradation of organic

536 pollutants, *Appl. Surf. Sci.* 637 (2023) 157955. <https://doi.org/10.1016/j.apsusc.2023.157955>.

537 [29] Concerted catalytic and photocatalytic degradation of organic pollutants over CuS/g-C<sub>3</sub>N<sub>4</sub> catalysts  
538 under light and dark conditions, *J. Adv. Res.* 16 (2019) 135–143.  
539 <https://doi.org/10.1016/j.jare.2018.10.003>.

540 [30] Z. Huang, L. Wang, H. Wu, H. Hu, H. Lin, L. Qin, Q. Li, Shape-controlled synthesis of CuS as a  
541 Fenton-like photocatalyst with high catalytic performance and stability, *J. Alloys Compd.* 896 (2022)  
542 163045. <https://doi.org/10.1016/j.jallcom.2021.163045>.

543 [31] T. Zhang, Y. Xiang, Y. Su, Y. Zhang, X. Huang, X. Qian, Anchoring of copper sulfide on cellulose  
544 fibers with polydopamine for efficient and recyclable photocatalytic degradation of organic dyes, *Ind.*  
545 *Crops Prod.* 187 (2022) 115357. <https://doi.org/10.1016/j.indcrop.2022.115357>.

546 [32] M. Saranya, C. Santhosh, R. Ramachandran, P. Kollu, P. Saravanan, M. Vinoba, S.K. Jeong, A.N.  
547 Grace, Hydrothermal growth of CuS nanostructures and its photocatalytic properties, *Powder Technol.*  
548 252 (2014) 25–32. <https://doi.org/10.1016/j.powtec.2013.10.031>.

549 [33] H. Wu, V. W. Or, S. Gonzalez-Calzada, V. H. Grassian, CuS nanoparticles in humid environments:  
550 adsorbed water enhances the transformation of CuS to CuSO<sub>4</sub>, *Nanoscale* 12 (2020) 19350–19358.  
551 <https://doi.org/10.1039/D0NR05934J>.

552 [34] Fabrication of h-BN-rGO@PDA nanohybrids for composite coatings with enhanced anticorrosion  
553 performance, *Prog. Org. Coat.* 130 (2019) 124–131. <https://doi.org/10.1016/j.porgcoat.2019.01.059>.

554 [35] L. Shang, W. Li, X. Wang, L. Ma, L. Li, Q. Duan, Y. Li, Preparation of magnetic Fe<sub>3</sub>O<sub>4</sub>@PDA/CuS  
555 core-shell nanocomposite as a green photocatalyst, *Synth. Met.* 292 (2023) 117230.  
556 <https://doi.org/10.1016/j.synthmet.2022.117230>.

557 [36] X. Wang, C. Deng, Preparation of magnetic graphene @polydopamine @Zr-MOF material for the  
558 extraction and analysis of bisphenols in water samples, *Talanta* 144 (2015) 1329–1335.  
559 <https://doi.org/10.1016/j.talanta.2015.08.014>.

560 [37] K. Zhang, J. Zhang, A. Yang, Photoheating Effects of CuS@PEI\_GQDs Nanoshells under Near-  
561 Infrared Laser and Sunlight Irradiation, *Cryst. Growth Des.* 23 (2023) 1697–1708.  
562 <https://doi.org/10.1021/acs.cgd.2c01274>.

563 [38] Preparation of photothermal alginate/chitosan derivative/CuS@polydopamine composite fibers and  
564 application in desalination, *Int. J. Biol. Macromol.* 277 (2024) 134142.  
565 <https://doi.org/10.1016/j.ijbiomac.2024.134142>.

566 [39] H. Zhang, C. Zhou, H. Zeng, H. Wu, L. Yang, L. Deng, Z. Shi, ZIF-8 assisted synthesis of magnetic  
567 core-shell FeO@CuS nanoparticles for efficient sulfadiazine degradation via HO<sub>2</sub> activation:  
568 Performance and mechanism, *J. Colloid Interface Sci.* 594 (2021) 502–512.  
569 <https://doi.org/10.1016/j.jcis.2021.03.057>.

570 [40] J. Zhang, H. Zeng, L. Bu, S. Zhou, Z. Shi, L. Deng, Cu<sup>0</sup> incorporated cobalt/nitrogen doped  
571 carbonaceous frameworks derived from ZIF-67 (Cu@CoNC) as PMS activator for efficient degradation  
572 of naproxen: Direct electron transfer and <sup>1</sup>O<sub>2</sub> dominated nonradical mechanisms, *Chem. Eng. J.* 454  
573 (2023) 139989. <https://doi.org/10.1016/j.cej.2022.139989>.

574 [41] X. Xie, Y. Hu, H. Cheng, Rapid degradation of p-arsanilic acid with simultaneous arsenic removal  
575 from aqueous solution using Fenton process, *Water Res.* 89 (2016) 59–67.  
576 <https://doi.org/10.1016/j.watres.2015.11.037>.

577 [42] Y.-Y. Chen, Y.-L. Ma, J. Yang, L.-Q. Wang, J.-M. Lv, C.-J. Ren, Aqueous tetracycline degradation  
578 by H<sub>2</sub>O<sub>2</sub> alone: Removal and transformation pathway, *Chem. Eng. J.* 307 (2017) 15–23.  
579 <https://doi.org/10.1016/j.cej.2016.08.046>.

580 [43] F. Bernsmann, B. Frisch, C. Ringwald, V. Ball, Protein adsorption on dopamine–melanin films:  
581 Role of electrostatic interactions inferred from  $\zeta$ -potential measurements versus chemisorption, *J. Colloid*  
582 *Interface Sci.* 344 (2010) 54–60. <https://doi.org/10.1016/j.jcis.2009.12.052>.

583 [44] R. Tejido-Rastrilla, S. Ferraris, W.H. Goldmann, A. Grünewald, R. Detsch, G. Baldi, S. Spriano,  
584 A.R. Boccaccini, Studies on Cell Compatibility, Antibacterial Behavior, and Zeta Potential of Ag-  
585 Containing Polydopamine-Coated Bioactive Glass-Ceramic, *Materials* 12 (2019) 500.  
586 <https://doi.org/10.3390/ma12030500>.

587 [45] J.E. Grebel, J.J. Pignatello, W.A. Mitch, Effect of Halide Ions and Carbonates on Organic  
588 Contaminant Degradation by Hydroxyl Radical-Based Advanced Oxidation Processes in Saline Waters,  
589 *Environ. Sci. Technol.* 44 (2010) 6822–6828. <https://doi.org/10.1021/es1010225>.

590 [46] H. Liang, X. Li, Y. Yang, K. Sze, Effects of dissolved oxygen, pH, and anions on the 2,3-  
591 dichlorophenol degradation by photocatalytic reaction with anodic TiO<sub>2</sub> nanotube films, *Chemosphere*  
592 73 (2008) 805–812. <https://doi.org/10.1016/j.chemosphere.2008.06.007>.

593 [47] A. Jawad, X. Lu, Z. Chen, G. Yin, Degradation of Chlorophenols by Supported Co–Mg–Al Layered  
594 Double Hydrotalcite with Bicarbonate Activated Hydrogen Peroxide, *J. Phys. Chem. A* 118 (2014)  
595 10028–10035. <https://doi.org/10.1021/jp5085313>.

596 [48] Y. Zhang, J. Lou, L. Wu, M. Nie, C. Yan, M. Ding, P. Wang, H. Zhang, Minute Cu coupling with  
597 HCO for efficient degradation of acetaminophen via HO activation<sup>2+3–22</sup>, *Ecotoxicol. Environ. Saf.*  
598 221 (2021) 112422. <https://doi.org/10.1016/j.ecoenv.2021.112422>.

599 [49] H. Zeng, L. Deng, H. Zhang, C. Zhou, Z. Shi, Development of oxygen vacancies enriched CoAl  
600 hydroxide@hydroxysulfide hollow flowers for peroxymonosulfate activation: A highly efficient singlet  
601 oxygen-dominated oxidation process for sulfamethoxazole degradation, *J. Hazard. Mater.* 400 (2020)  
602 123297. <https://doi.org/10.1016/j.jhazmat.2020.123297>.

603 [50] T. Peng, H. Zhang, S. Xia, S. Zhou, Z. Shi, G. Li, L. Deng, MoS<sub>2</sub> Nanosheets Anchored onto MIL-  
604 100(Fe)-Derived FeS<sub>2</sub> as a Peroxymonosulfate Activator for Efficient Sulfamethoxazole Degradation:  
605 Insights into the Mechanism, *ACS EST Water* 3 (2023) 213–226.  
606 <https://doi.org/10.1021/acsestwater.2c00501>.

607 [51] X. Liu, P. Xu, Q. Fu, R. Li, C. He, W. Yao, L. Wang, S. Xie, Z. Xie, Q. He, J.C. Crittenden, Ferric  
608 ion promoted degradation of acetaminophen with zero – valent copper activated peroxymonosulfate  
609 process, *Chem. Eng. J.* 426 (2021) 131679. <https://doi.org/10.1016/j.cej.2021.131679>.

610 [52] F. Sun, T. Chen, Z. Chu, P. Zhai, H. Liu, Q. Wang, X. Zou, D. Chen, The synergistic effect of calcite  
611 and Cu<sup>2+</sup> on the degradation of sulfadiazine via PDS activation: A role of Cu(III), *Water Res.* 219 (2022)  
612 118529. <https://doi.org/10.1016/j.watres.2022.118529>.

613 [53] Y. Wei, J. Miao, J. Ge, J. Lang, C. Yu, L. Zhang, P.J.J. Alvarez, M. Long, Ultrahigh  
614 Peroxymonosulfate Utilization Efficiency over CuO Nanosheets via Heterogeneous Cu(III) Formation  
615 and Preferential Electron Transfer during Degradation of Phenols, *Environ. Sci. Technol.* 56 (2022)  
616 8984–8992. <https://doi.org/10.1021/acs.est.2c01968>.

617 [54] X. Liu, M. Li, Z. Xie, P. Li, C. Du, Y. Su, Oxygen vacancy-enriched kaolinite/WO<sub>3-x</sub>  
618 nanocomposites exhibiting enhanced photo-synergetic H<sub>2</sub>O<sub>2</sub> activation for tetracycline degradation  
619 boosted by hydroxyl groups and exciton, *Sep. Purif. Technol.* 347 (2024) 127675.  
620 <https://doi.org/10.1016/j.seppur.2024.127675>.

621 [55] X. Zhang, B. Yang, H. Quan, H. Pei, S.-Q. Guo, Surface methyl/methylene regulates WO  
622 directional activation of molecular oxygen into singlet oxygen for the removal of organic pollutants in

623 water3, Sep. Purif. Technol. 346 (2024) 127559. <https://doi.org/10.1016/j.seppur.2024.127559>.

624 [56] J. Miao, W. Geng, P.J.J. Alvarez, M. Long, 2D N-Doped Porous Carbon Derived from  
625 Polydopamine-Coated Graphitic Carbon Nitride for Efficient Nonradical Activation of  
626 Peroxymonosulfate, Environ. Sci. Technol. 54 (2020) 8473–8481.  
627 <https://doi.org/10.1021/acs.est.0c03207>.

628 [57] Y. Yu, J.G. Shapter, R. Popelka-Filcoff, J.W. Bennett, A.V. Ellis, Copper removal using bio-inspired  
629 polydopamine coated natural zeolites, J. Hazard. Mater. 273 (2014) 174–182.  
630 <https://doi.org/10.1016/j.jhazmat.2014.03.048>.

631 [58] M. Cheng, Y. Liu, D. Huang, C. Lai, G. Zeng, J. Huang, Z. Liu, C. Zhang, C. Zhou, L. Qin, W.  
632 Xiong, H. Yi, Y. Yang, Prussian blue analogue derived magnetic Cu-Fe oxide as a recyclable photo-  
633 Fenton catalyst for the efficient removal of sulfamethazine at near neutral pH values, Chem. Eng. J. 362  
634 (2019) 865–876. <https://doi.org/10.1016/j.cej.2019.01.101>.

635 [59] J. Peng, X. Lu, X. Jiang, Y. Zhang, Q. Chen, B. Lai, G. Yao, Degradation of atrazine by persulfate  
636 activation with copper sulfide (CuS): Kinetics study, degradation pathways and mechanism, Chem. Eng.  
637 J. 354 (2018) 740–752. <https://doi.org/10.1016/j.cej.2018.08.038>.

638 [60] S.-Q. Zhang, X. Liu, Q.-X. Sun, O. Johnson, T. Yang, M.-L. Chen, J.-H. Wang, W. Chen,  
639 CuS@PDA-FA nanocomposites: a dual stimuli-responsive DOX delivery vehicle with ultrahigh loading  
640 level for synergistic photothermal-chemotherapies on breast cancer, J. Mater. Chem. B 8 (2020) 1396–  
641 1404. <https://doi.org/10.1039/C9TB02440A>.

642 [61] Can Cu<sub>2</sub>ZnSnS<sub>4</sub> nanoparticles be used as heterogeneous catalysts for sulfadiazine degradation?, J.  
643 Hazard. Mater. 395 (2020) 122613. <https://doi.org/10.1016/j.jhazmat.2020.122613>.

644 [62] H. Zhang, L. Deng, J. Chen, Y. Zhang, M. Liu, Y. Han, Y. Chen, H. Zeng, Z. Shi, How MoS<sub>2</sub>  
645 assisted sulfur vacancies featured Cu<sub>2</sub>S in hollow Cu<sub>2</sub>S@MoS<sub>2</sub> nanoboxes to activate H<sub>2</sub>O<sub>2</sub> for efficient  
646 sulfadiazine degradation?, Chem. Eng. J. 446 (2022) 137364. <https://doi.org/10.1016/j.cej.2022.137364>.

647 [63] S. Dolai, R. Dey, S. Das, S. Hussain, R. Bhar, A.K. Pal, Cupric oxide (CuO) thin films prepared by  
648 reactive d.c. magnetron sputtering technique for photovoltaic application, J. Alloys Compd. 724 (2017)  
649 456–464. <https://doi.org/10.1016/j.jallcom.2017.07.061>.

650 [64] M. Cheng, Y. Liu, D. Huang, C. Lai, G. Zeng, J. Huang, Z. Liu, C. Zhang, C. Zhou, L. Qin, W.  
651 Xiong, H. Yi, Y. Yang, Prussian blue analogue derived magnetic Cu-Fe oxide as a recyclable photo-  
652 Fenton catalyst for the efficient removal of sulfamethazine at near neutral pH values, Chem. Eng. J. 362  
653 (2019) 865–876. <https://doi.org/10.1016/j.cej.2019.01.101>.

654 [65] Z. Yang, J. Qian, A. Yu, B. Pan, Singlet oxygen mediated iron-based Fenton-like catalysis under  
655 nanoconfinement, Proc. Natl. Acad. Sci. 116 (2019) 6659–6664.  
656 <https://doi.org/10.1073/pnas.1819382116>.

657 [66] A.U. Khan, M. Kasha, Singlet molecular oxygen in the Haber-Weiss reaction., Proc. Natl. Acad.  
658 Sci. 91 (1994) 12365–12367. <https://doi.org/10.1073/pnas.91.26.12365>.

659 [67] B. Sheng, C. Deng, Y. Li, S. Xie, Z. Wang, H. Sheng, J. Zhao, In Situ Hydroxylation of a Single-  
660 Atom Iron Catalyst for Preferential 1O<sub>2</sub> Production from H<sub>2</sub>O<sub>2</sub>, ACS Catal. 12 (2022) 14679–14688.  
661 <https://doi.org/10.1021/acscatal.2c04484>.

662 [68] F. Xu, C. Lai, M. Zhang, B. Li, L. Li, S. Liu, D. Ma, X. Zhou, H. Yan, X. Huo, B. Wang, H. Yi, L.  
663 Qin, L. Tang, High-loaded single-atom Cu-N<sub>3</sub> sites catalyze hydrogen peroxide decomposition to  
664 selectively induce singlet oxygen production for wastewater purification, Appl. Catal. B Environ. 339  
665 (2023) 123075. <https://doi.org/10.1016/j.apcatb.2023.123075>.

666 [69] Efficient degradation of tetracycline by heterogeneous electro-Fenton process using Cu-doped

667 Fe@Fe<sub>2</sub>O<sub>3</sub>: Mechanism and degradation pathway, *Chem. Eng. J.* 382 (2020) 122970.  
668 <https://doi.org/10.1016/j.cej.2019.122970>.

669 [70] Z. Yin, Y. Liu, S. Zhou, Z. Yang, W. Yang, Constructing zirconium based metal–organic frameworks  
670 based electrically-driven self-cleaning membrane for removal of tetracycline: Effect of ligand  
671 substitution, *Chem. Eng. J.* 450 (2022) 138100. <https://doi.org/10.1016/j.cej.2022.138100>.

672 [71] X. Li, T. Hou, L. Yan, L. Shan, X. Meng, Y. Zhao, Efficient degradation of tetracycline by CoFeLa-  
673 layered double hydroxides catalyzed peroxymonosulfate: Synergistic effect of radical and nonradical  
674 pathways, *J. Hazard. Mater.* 398 (2020) 122884. <https://doi.org/10.1016/j.jhazmat.2020.122884>.

675 [72] M. Jiang, X. Wang, R. Han, P. Ning, I. Lynch, J. Ma, Establishing photocatalysis-self-Fenton system  
676 over a S-scheme Fe/Fe<sub>2</sub>O<sub>3</sub>@CuBi<sub>2</sub>O<sub>4</sub> for enhancing TC removal via in-situ generating H<sub>2</sub>O<sub>2</sub> and Fe/Cu  
677 dual-metal electron cycle: Radical and non-radical pathways, *Sep. Purif. Technol.* 354 (2025) 128675.  
678 <https://doi.org/10.1016/j.seppur.2024.128675>.

679 [73] X. Li, Y. Jia, J. Zhang, Y. Qin, Y. Wu, M. Zhou, J. Sun, Efficient removal of tetracycline by H<sub>2</sub>O<sub>2</sub>  
680 activated with iron-doped biochar: Performance, mechanism, and degradation pathways, *Chin. Chem.*  
681 *Lett.* 33 (2022) 2105–2110. <https://doi.org/10.1016/j.cclet.2021.08.054>.

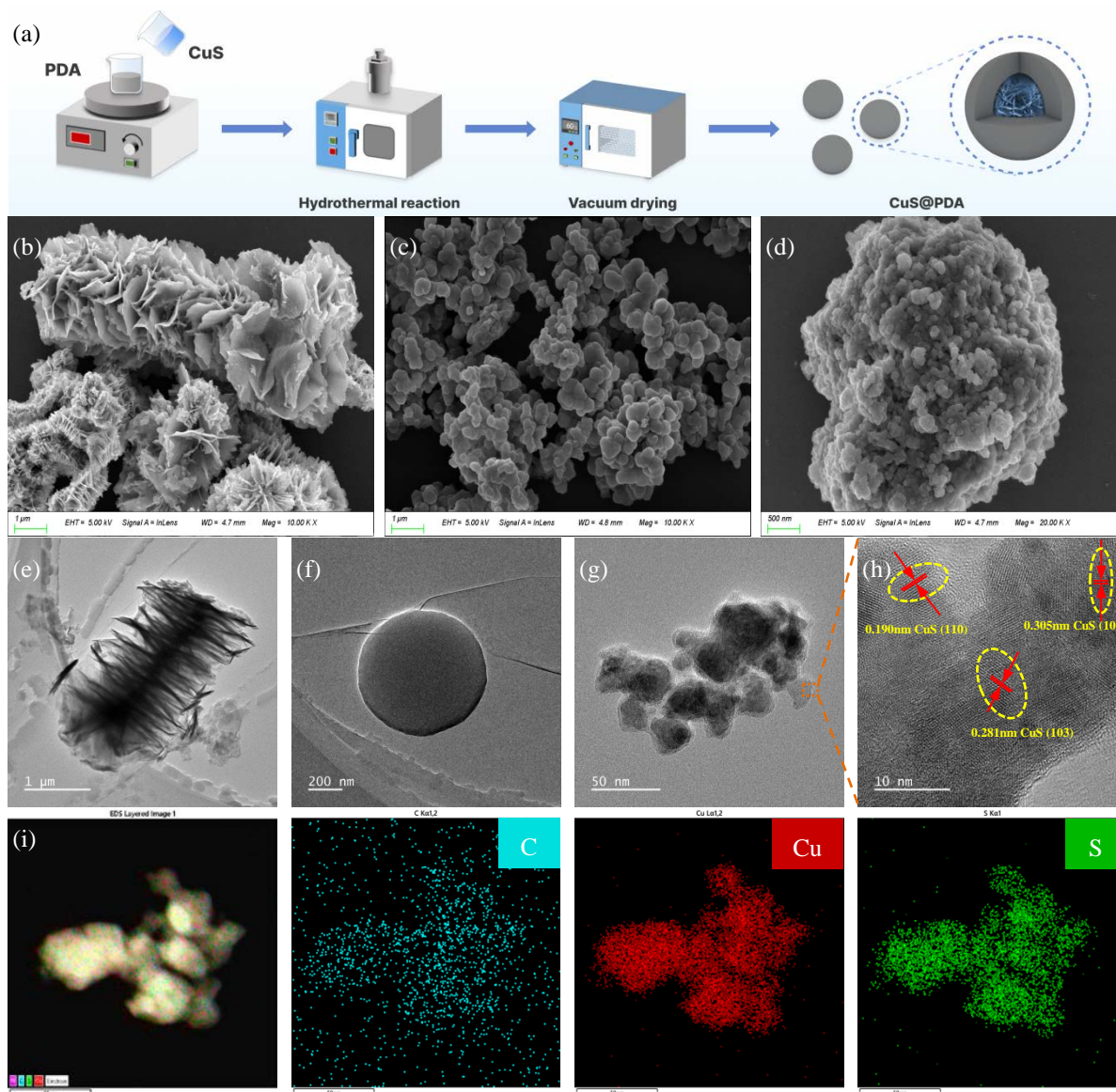
682 [74] M. Nie, Y. Li, L. Li, J. He, P. Hong, K. Zhang, X. Cai, L. Kong, J. Liu, Ultrathin iron-cobalt oxide  
683 nanosheets with enhanced H<sub>2</sub>O<sub>2</sub> activation performance for efficient degradation of tetracycline, *Appl.*  
684 *Surf. Sci.* 535 (2021) 147655. <https://doi.org/10.1016/j.apsusc.2020.147655>.

685 [75] S. Yang, Y. Feng, D. Gao, X. Wang, N. Suo, Y. Yu, S. Zhang, Electrocatalysis degradation of  
686 tetracycline in a three-dimensional aeration electrocatalysis reactor (3D-AER) with a flotation-tailings  
687 particle electrode (FPE): Physicochemical properties, influencing factors and the degradation mechanism,  
688 *J. Hazard. Mater.* 407 (2021) 124361. <https://doi.org/10.1016/j.jhazmat.2020.124361>.

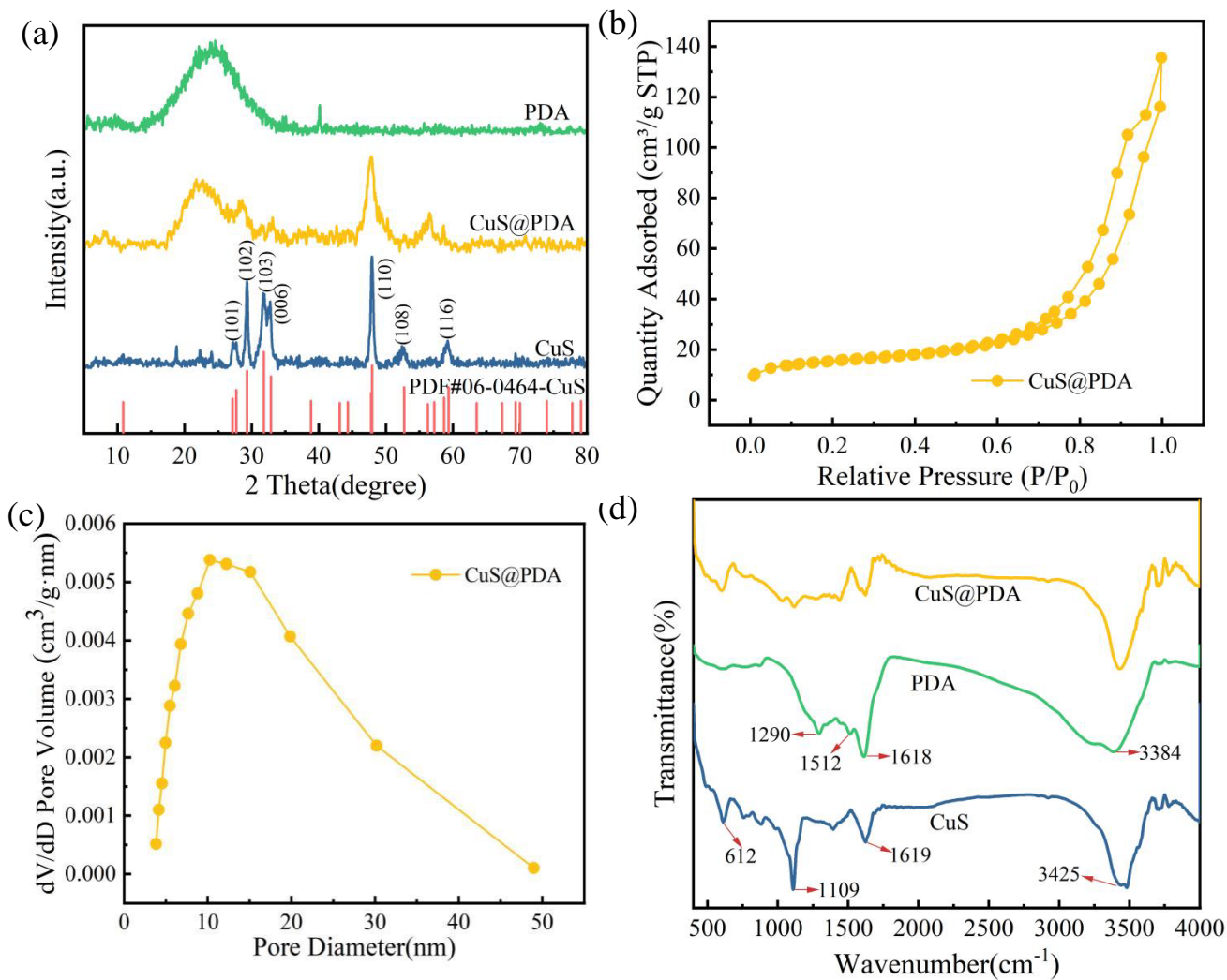
689 [76] Z. Li, C. Guo, J. Lyu, Z. Hu, M. Ge, Tetracycline degradation by persulfate activated with magnetic  
690 Cu/CuFe<sub>2</sub>O<sub>4</sub> composite: Efficiency, stability, mechanism and degradation pathway, *J. Hazard. Mater.*  
691 373 (2019) 85–96. <https://doi.org/10.1016/j.jhazmat.2019.03.075>.

692 [77] D. Chen, Q. Bai, T. Ma, X. Jing, Y. Tian, R. Zhao, G. Zhu, Stable metal–organic framework fixing  
693 within zeolite beads for effectively static and continuous flow degradation of tetracycline by  
694 peroxymonosulfate activation, *Chem. Eng. J.* 435 (2022) 134916.  
695 <https://doi.org/10.1016/j.cej.2022.134916>.

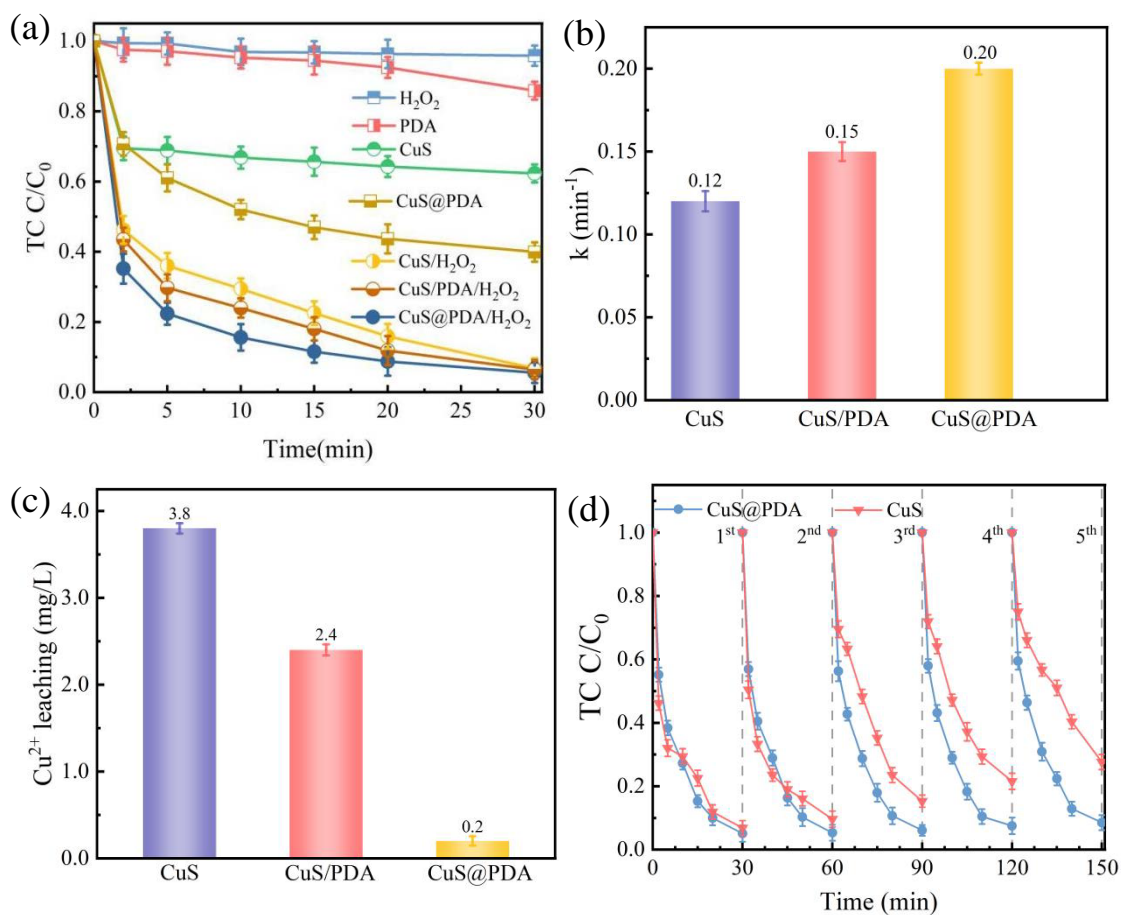
696



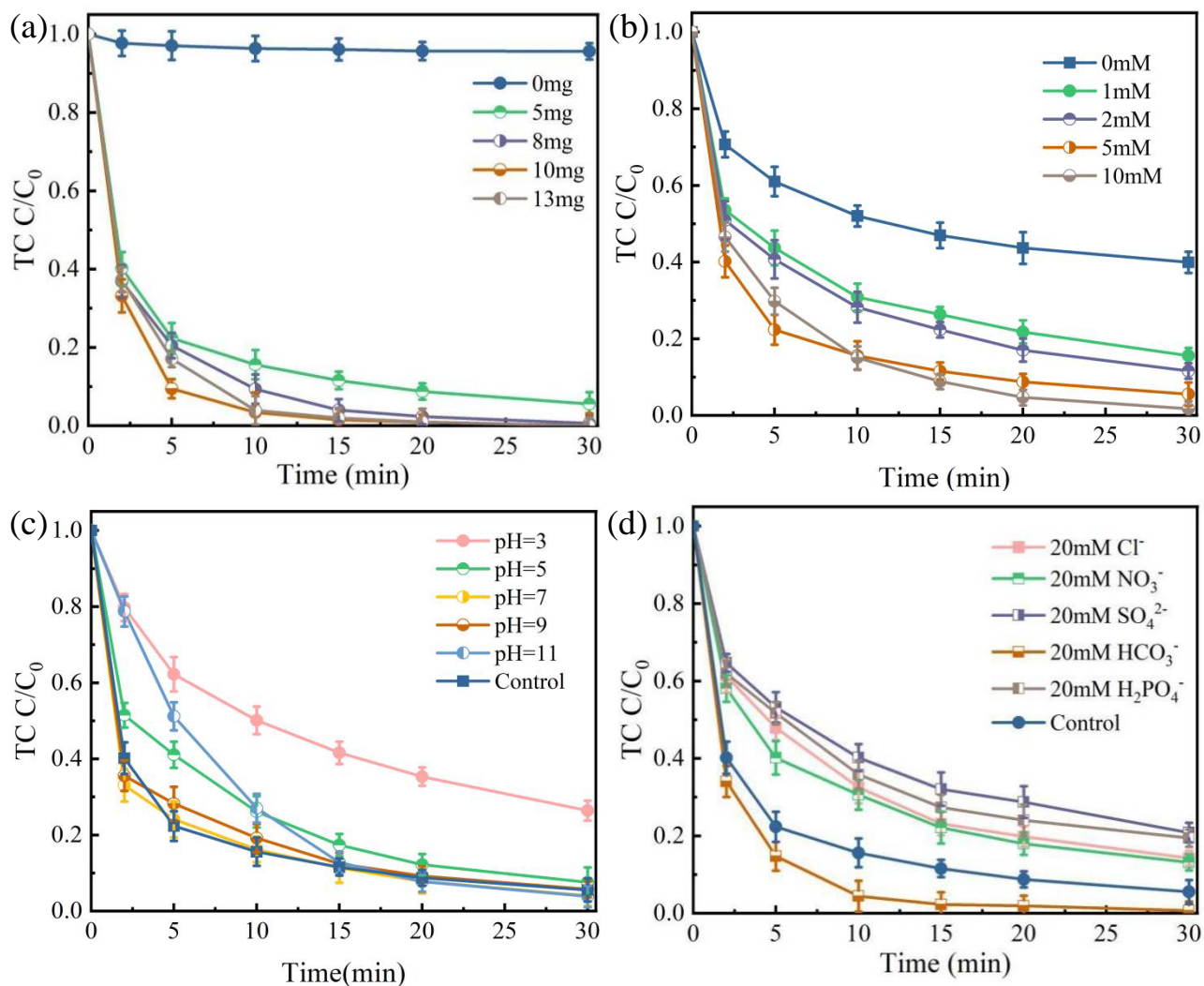
**Figure 1.** (a) The schematic synthesis route of CuS@PDA; SEM images of (b) CuS, (c) PDA and (d) CuS@PDA; TEM images of (e) CuS, (f) PDA and (g, h) CuS@PDA; (i) EDX elemental mapping images of CuS@PDA.



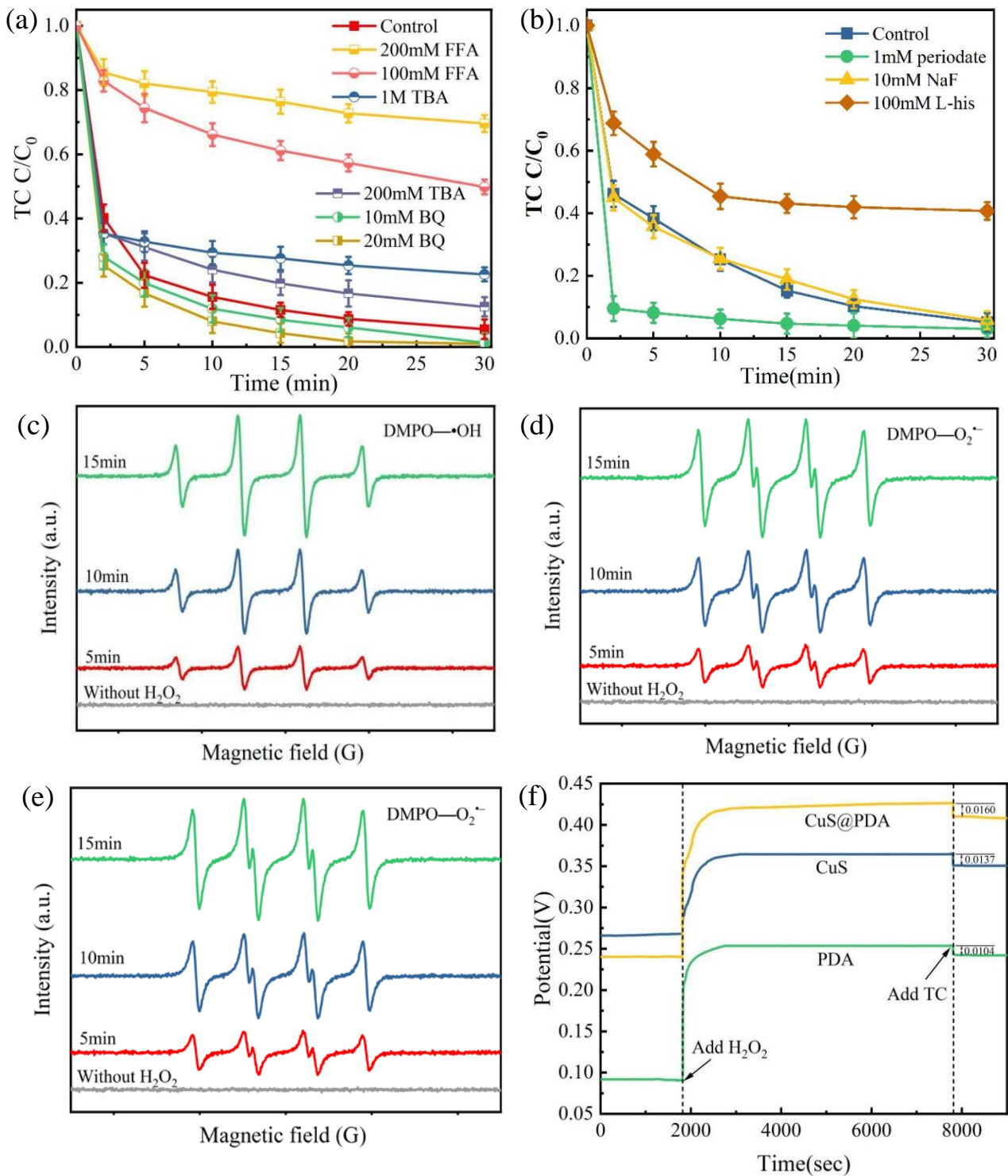
**Figure 2.** (a) XRD patterns of CuS, PDA and CuS@PDA; (b) N<sub>2</sub> adsorption/desorption isotherm and (c) pore size distribution of CuS@PDA; (d) FTIR spectra of CuS, PDA and CuS@PDA.



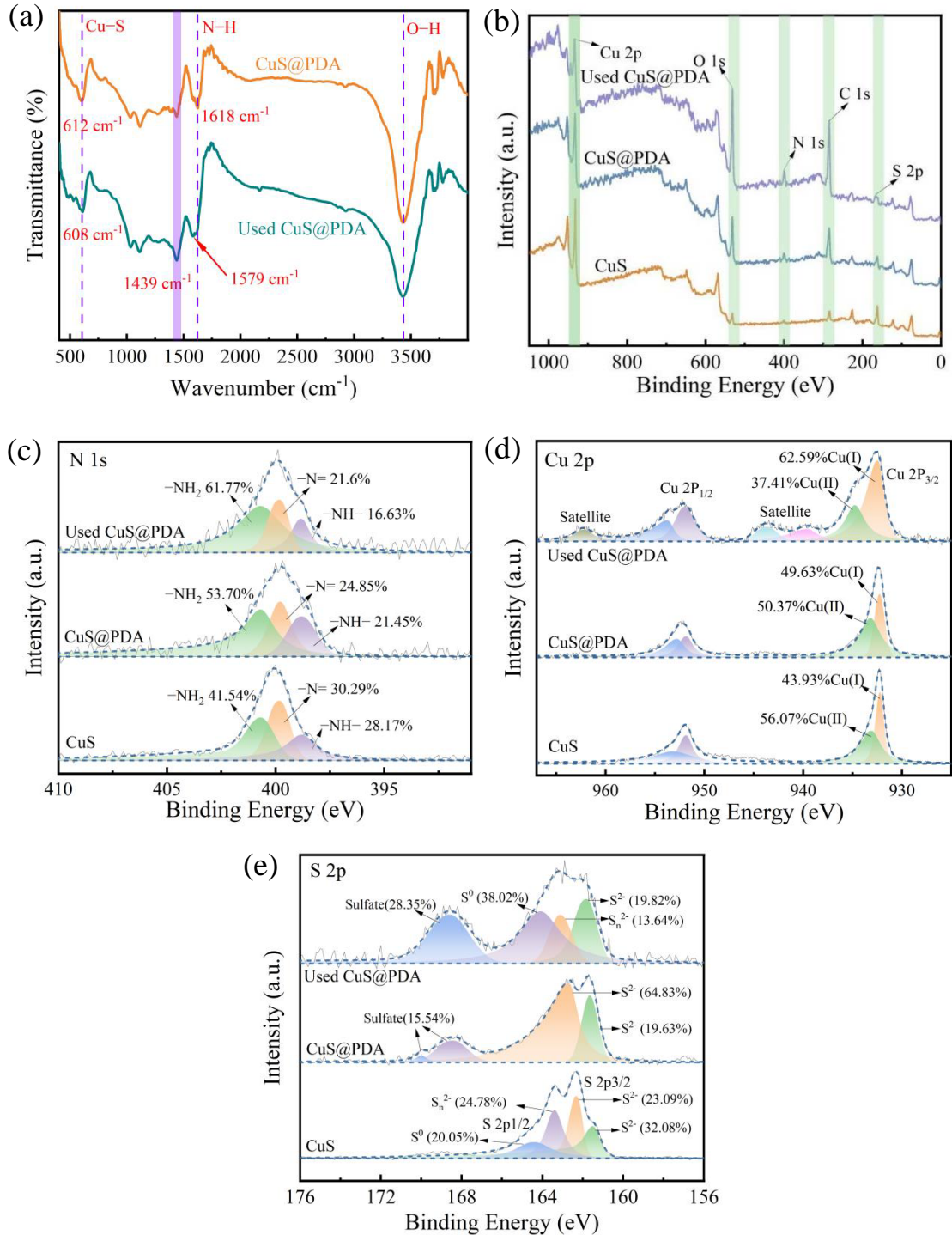
**Figure 3.** (a) TC removal in different systems; (b) the fitted kinetic rate constants of TC degradation by CuS, CuS/PDA, and CuS@PDA in the presence of  $H_2O_2$ ; (c)  $Cu^{2+}$  leakage from different catalysts; (d) recyclability of CuS and CuS@PDA for activating  $H_2O_2$  to degrade TC ( $[TC] = 40 \mu M$ ,  $[catalyst] = 0.1 g/L$ ,  $[H_2O_2] = 5 mM$ ).



**Figure 4.** Influences of (a) catalyst dosage, (b)  $H_2O_2$  concentration, (c) initial solution pH, and (d) coexisting ions on TC degradation ( $[catalyst] = 0.1\text{ g/L}$  (except a),  $[H_2O_2] = 5\text{ mM}$  (except b),  $[TC] = 40\ \mu\text{M}$ ).



**Figure 5.** Effect of different radical scavengers (a), periodate, NaF and L-his (b) on the degradation of TC; EPR spectroscopy of (c) DMPO-•OH, (d) DMPO- O<sub>2</sub><sup>•-</sup> and (e) TEMP-<sup>1</sup>O<sub>2</sub>; (f) open circuit potential contrast of working electrodes in different systems ([TC] = 40μM, [catalyst] = 0.1g/L, [H<sub>2</sub>O<sub>2</sub>] = 5 mM).



**Figure 6.** The FTIR spectrum of the fresh and used CuS@PDA; The XPS spectrum of CuS, CuS@PDA and used CuS@PDA: (a) survey, (b) N 1s, (c) Cu 2p, and (d) S 2p.

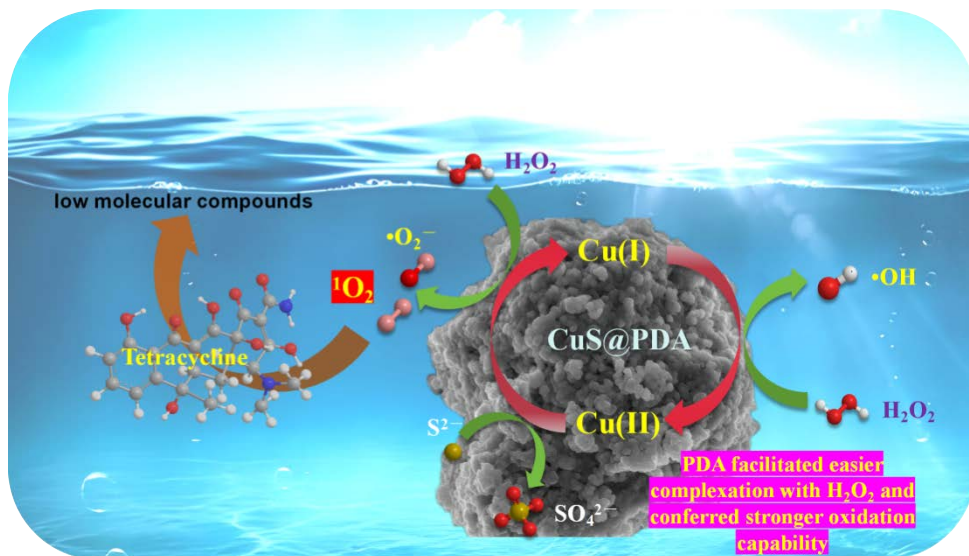


Figure 7. Schematically illustrating the degradation mechanisms of TC by CuS@PDA/H<sub>2</sub>O<sub>2</sub>.

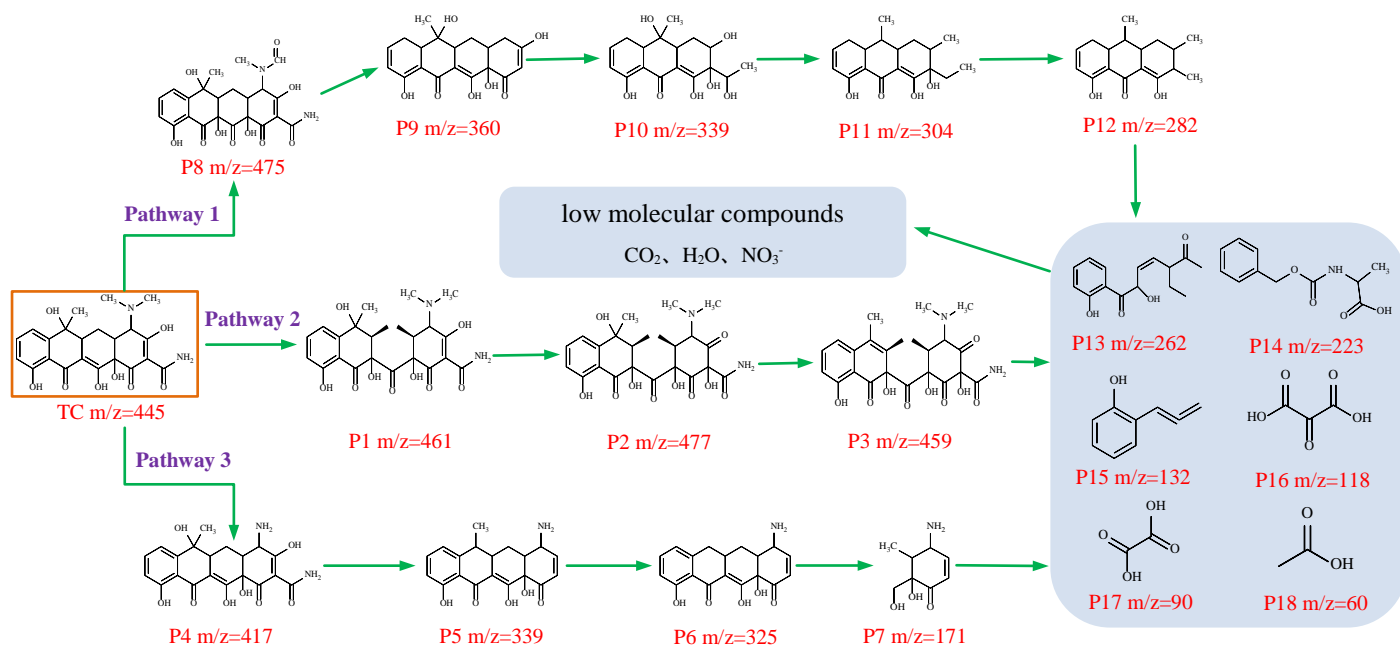


Figure 8. Possible degradation pathways of TC by CuS@PDA/H<sub>2</sub>O<sub>2</sub> system.