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**Article:**

Wan, Zhonghao, Sun, Yuqing, Tsang, Daniel C.W. et al. (7 more authors) (2019) A sustainable biochar catalyst synergized with copper heteroatoms and CO<sub>2</sub> for singlet oxygenation and electron transfer routes. *Green Chemistry*. pp. 4800-4814. ISSN 1463-9262

<https://doi.org/10.1039/c9gc01843c>

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1 **Sustainable biochar catalyst synergized with copper heteroatoms and CO<sub>2</sub> for singlet**  
2 **oxygenation and electron transfer routes**

3  
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17

18 **Abstract**

19 We have developed a wood waste-derived biochar as a sustainable graphitic carbon catalyst for  
20 environmental remediation through catalytic pyrolysis under the synergistic effects between Cu heteroatoms  
21 and CO<sub>2</sub>, which for the first time are found to significantly enhance the oxygen functionalities, defective  
22 sites, and highly ordered *sp*<sup>2</sup>-hybridized carbon matrix. The copper-doped graphitic biochars (Cu-GBCs)  
23 were further characterized by XRD, FTIR, Raman, XPS, *etc.*, revealing that the modified specific surface  
24 area, pore structure, graphitization, and active sites (*i.e.*, defective sites and ketonic group) on the Cu-GBCs  
25 corresponded to the synergistic Cu species loading and Cu-induced carbon-matrix reformation under CO<sub>2</sub>  
26 environment during pyrolysis. The catalytic ability of the Cu-GBCs was evaluated using the ubiquitous  
27 peroxydisulfate (PDS) activation system for the removal of various organic contaminants (*i.e.*, Rhodamine  
28 B, phenol, bisphenol A, and 4-chlorophenol), and gave the highest degradation rate of 0.0312 min<sup>-1</sup> in  
29 comparison with those of pristine GBCs and N<sub>2</sub>-pyrolyzed Cu-GBCs ranging from 0.0056 to 0.0094 min<sup>-1</sup>.  
30 The synergistic effects were attributed to the encapsulated Cu heteroatoms, evolved ketonic groups, and  
31 abundant unconfined  $\pi$  electrons within the carbon lattice. According to scavenger experiments, ESR  
32 analysis, and the two-chamber experiments, selective and sustainable non-radical pathways (*i.e.*, singlet  
33 oxygenation and electron transfer) mediated by Cu-induced metastable surface complex were achieved in  
34 the Cu-GBC/PDS system. This study offers the first insights into the efficacy, sustainability, and mechanistic  
35 roles of Cu-GBCs as an emerging carbon-based catalyst for green environmental remediation.

36

37 **Keywords:** engineered biochar; heteroatoms doping; metal-carbon composite; non-radical activation;  
38 sustainable waste management; green and sustainable remediation.

## 39 1. Introduction

40 Biochar has been extensively explored in agricultural and environmental applications,<sup>1</sup> such as soil  
41 amendment and contaminant stabilization,<sup>2-5</sup> carbon sequestration,<sup>6-8</sup> water/wastewater treatment,<sup>9-14</sup> and  
42 catalytic biomass conversion.<sup>1,15-17</sup> It can be derived from various biomass wastes as renewable resources of  
43 high abundance, which favours the large-scale and economical production to satisfy sustainable  
44 development and circular bio-economy.<sup>17-19</sup> The versatile physicochemical properties of biochar are  
45 primarily determined by its intrinsic atomic arrangement of a carbon matrix, structural defective sites, pore  
46 structure, and surface functional groups.<sup>18,20,21</sup> To date, engineered metal-biochar composites with desirable  
47 physicochemical properties have been fabricated by introducing various multivalent transition metal  
48 components (Fe<sup>0</sup>,<sup>13,22,23</sup> Fe<sub>3</sub>O<sub>4</sub>,<sup>24-26</sup> and Co,<sup>27,28</sup> etc.) into the carbon lattice to evolve versatile active sites.  
49 Despite the high efficiency, the application of active multivalent transition metal-functionalized biochars  
50 unavoidably cause metal leaching into the environment, which is potentially hazardous to aquatic life and  
51 detrimental to clean water supply.<sup>29,30</sup> For green environmental remediation, it is imperative to devise a  
52 transition metal-biochar composite with low toxicity and exhibiting excellent adsorptive capability and  
53 potential catalytic activity.

54 In this study, Cu was employed as the metal heteroatom for its inherent catalytic capacity and low  
55 toxicity,<sup>31</sup> while the lignin-rich wood waste was adopted as the feedstock with macro-/meso-pores for  
56 housing Cu species. In contrast with the commonly used transition metal catalyst, such as Co and TiO<sub>2</sub> that  
57 are precious metal facing an increasing threat of depletion,<sup>27,28,32</sup> the use of the low-cost Cu in our study  
58 appears to be more sustainable. Recent studies have revealed that a CO<sub>2</sub> medium could create surface  
59 defects and oxygen-containing functional groups that significantly enhanced the catalytic performance of  
60 biochar-supported materials.<sup>24, 27, 28, 33, 34</sup> The catalytic reforming of carbon matrix and the potential  
61 interactions with copper heteroatoms during CO<sub>2</sub> pyrolysis are yet to be revealed, particularly for the

62 physicochemical properties, surface structure, and interfacial chemical behaviour of the resulting Cu-biochar  
63 composites for catalytic applications.

64 The heterogeneous peroxydisulfate (PDS,  $S_2O_8^{2-}$ ) activation system has been widely employed on  
65 engineered biochar. As an emerging green oxyanion, PDS can be directly activated by external energy input  
66 (heat, ultraviolet light, **and** ultrasound, *etc.*) or various metal-based catalysts to generate robust **sulfate**  
67 radicals ( $SO_4^{\bullet-}$ ), **which** exhibit higher redox potential ( $E^0 = 2.5\text{--}3.1$  V) and longer half-life period ( $t_{1/2} = 30\text{--}$   
68  $40$   $\mu\text{s}$ ) than  $\cdot\text{OH}$  ( $E^0 = 1.9\text{--}2.7$  V,  $t_{1/2} = 3\text{--}10$   $\mu\text{s}$ ) over a wide range of pH values (pH = 2–8).<sup>35,36</sup> Organics  
69 degradation *via* radical pathways often requires intensive energy or chemical input that would limit its **field**  
70 application, and the generated radicals would demonstrate non-selective oxidation capability (*e.g.*,  
71 self-scavenging effects **and** highly chlorinated byproducts),<sup>31,37</sup> wherein the induced cannibalistic surface  
72 oxidation reaction would **irreversibly alter the framework of carbon supports**.<sup>38</sup> Thus, PDS activation *via* a  
73 more sustainable pathway is highly desirable. Zhang et al. reported that copper species could activate PDS  
74 to degrade chlorophenols *via* a non-radical pathway by forming a metastable complex on its surface.<sup>31</sup> Zhu  
75 et al. found that crystallographic manganese oxide could activate PDS to generate singlet oxygen ( $O_2^1$ ) other  
76 than commonly reported free radicals (*e.g.*,  $\cdot\text{OH}$ ,  $SO_4^{\bullet-}$ , and  $O_2^{\bullet-}$ ) for the degradation of aqueous  
77 contaminants.<sup>39</sup> In addition, various carbonaceous materials (*e.g.*, activated carbon, carbon nanotube, and  
78 graphene oxide (GO)) **are** capable of catalysing PDS for organic degradation *via* electron transition through  
79 graphitic matrix, which potentially are even more efficient than transition metal oxides (*e.g.*,  $Fe_3O_4$ ,  $Co_3O_4$ ,  
80 and  $\alpha\text{-MnO}_2$ ).<sup>40</sup> This superior performance could **be** ascribed to the well-defined  $sp^2$ -hybridized carbon  
81 matrix with versatile catalytic centre (*e.g.*, defects and ketonic groups) and abundant unconfined  
82  $\pi$ -electrons.<sup>20,41-43</sup> In a recent study, graphitic biochar (GBC, pyrolyzed over 700 °C) **with** large specific  
83 surface area (SSA), ordered  $sp^2$ -hybridized structure, and tuneable defect sites as redox centre **facilitated**  
84 catalytic degradation.<sup>44</sup> Thus, it is hypothesized and then proven in this study that the introduction of

85 low-toxicity copper heteroatoms into the graphitic biochar matrix can enable the complimentary coupling of  
86 the catalytic centre and graphitic matrix of carbonaceous materials. This technique is more economic,  
87 scalable, and sustainable for green remediation applications *via* the non-radical PDS activation route.

88 In this study, Cu-doped GBC composites were synthesized through a one-step pyrolysis of  
89 CuCl<sub>2</sub>-pretreated wood waste at 900 °C with continuous CO<sub>2</sub> purging as the reactive medium (in  
90 comparison to N<sub>2</sub> purging). The objectives of this research were to: (i) articulate the interactions of CO<sub>2</sub>  
91 medium and doped copper heteroatoms for tailoring the physicochemical properties, surface structure, and  
92 interfacial chemical behaviour of the resultant Cu-GBC composites, and (ii) capitalize on the evolution of  
93 sustainable pathways for non-radical PDS activation and catalytic degradation of various organic  
94 contaminants (*i.e.*, Rhodamine B (RB), phenol (PN), bisphenol A (BPA), and 4-chlorophenol (4-CH)). The  
95 results of this study are conducive to improving the future design of high-efficiency, engineered  
96 metal-biochar composites as green catalysts.

97

## 98 **2. Experimental**

### 99 *2.1. Materials and chemical reagents*

100 Apple-tree wood waste (collected from **Guiyang city, Guizhou province**, China) was selected as the  
101 feedstock of waste biomass. All the chemicals were of analytical reagent grade and solvents were of  
102 high-performance liquid chromatography (HPLC) grade. Ultrapure water (UW, 18.2 MΩ cm<sup>-1</sup>) obtained  
103 from a Millipore Milli-Q Water Purification System (Milford, USA) was used for all experimental solutions.

### 104 *2.2. Preparation of Cu-GBC composites*

105 Before use, wood waste was cut into small pieces (< 5 cm), washed with ultrapure water (UW) for  
106 several times, oven dried at 80 °C overnight, then crushed by a high-speed rotary pulverizer, and finally  
107 sieved through a 120-mesh (particle size < 0.125 mm). The suspension of biomass with Cu<sup>2+</sup> was prepared

108 by mixing 20 g wood with predetermined amounts of  $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$  in 1 L UW in a glass beaker, which was  
109 then agitated at 350 rpm for 24 h with a magnetic stirrer to maintain a uniform concentration. After **water**  
110 **removal** under continuous stirring at 80 °C for 12 h in a thermostat water **bath**, the **slurry** was completely  
111 dried **in an oven** at 80 °C for 24 h **and then was sieved again for homogeneity**. Next, the samples were  
112 placed in a tubular furnace with a medium heating rate of 5 °C  $\text{min}^{-1}$  to reach desired 900 °C, and the **peak**  
113 temperature was maintained for 2 h under  $\text{CO}_2$  or  $\text{N}_2$  purging at 500  $\text{mL min}^{-1}$ .<sup>44</sup> **After** cooling down to  
114 room temperature inside the furnace, the stabilized samples were collected **and rinsed with UW and alcohol**  
115 **for three times, respectively. After oven-drying overnight, the samples were** ground and passed through a  
116 200-mesh **sieve (particle size < 0.075 mm). This particle size was smaller than the 120-mesh sieve used for**  
117 **biomass before pyrolysis, for the purpose of preparing biochars with reproducible quality and homogeneity,**  
118 ***i.e.*, uniform chemical impregnation and even heat distribution. For comparison, the pristine biochar was**  
119 **prepared following the above procedure, except for the use of  $\text{CuCl}_2$ -free UW for the suspension of wood**  
120 **waste. All prepared samples were** stored in an airtight container for further use. The obtained products are  
121 denoted as Cu-GBCXC or Cu-GBCXN, where the X (5, 10, and 20%) and C/N represent the copper  
122 calculated mass ratio after wet digestion (Cu/BC, wt.%) and the **selected** purging gas (*i.e.*,  $\text{CO}_2$  or  $\text{N}_2$ ) during  
123 pyrolysis, respectively. **Concerns over the toxicity of  $\text{CuCl}_2$  are mitigated as the chloride ions evaporate**  
124 **during pyrolysis at 900 °C followed by absorption in NaOH solution (5 wt.%), while copper is retained on**  
125 **the carbon support. Nevertheless, life-cycle assessment is needed in the future to validate the net**  
126 **environmental benefits of Cu-GBC compared to conventional options.**

### 127 *2.3. Microscopic characterization of Cu-GBC composites*

128 The characteristics of the GBC and Cu-GBC composites were determined *via* employing the  
129 Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) porosity, **high resolution**  
130 **transmission electron microscopy (HRTEM)**, scanning electron microscopy-energy dispersive X-ray

131 spectroscopy (SEM-EDX), X-ray diffraction (XRD), Raman spectroscopy, Fourier-transform infrared  
132 spectroscopy (FTIR), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS).  
133 Detailed information on the characterization methods is available in the Supporting Information.

#### 134 2.4. Catalytic degradation of various organic contaminants by Cu-GBC composites

135 The organic removal experiments were performed at  $25 \pm 1$  °C under intensive mixing by a thermostatic  
136 oscillator (180 rpm). The solution pH was adjusted to  $5.8 \pm 0.2$  using 0.1 M NaOH or HNO<sub>3</sub>. To investigate  
137 the removal kinetics of various organic contaminants (*i.e.*, RB, PH, BPA, and 4-CH) by Cu-GBC  
138 composites, 0.3 g L<sup>-1</sup> suspensions of Cu-GBC composites and 2 mM PDS (determined according to  
139 preliminary results) were added into 100 mL UW containing 0.1 mM organic contaminants in 250-mL  
140 conical flasks, while a similar reaction with GBC was also conducted for comparison. The commercial  
141 metal and metal-free catalysts (Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, zero valent iron (ZVI), CuO, CoO, MnO<sub>2</sub>, ZnO, and GO)  
142 were also evaluated for PDS activation. At predetermined time interval for sampling, aliquot sample of 1  
143 mL was extracted from the conical flask to a glass vial and ethyl alcohol (EtOH) was added in excess for  
144 quenching. Same batch experiments quenching with sodium nitrite (NaNO<sub>2</sub>) were also conducted to  
145 differentiate the contribution of adsorption and catalytic degradation. Then, the sample was filtered through  
146 a 0.45- $\mu$ m pore-size polytetrafluoroethylene (PTFE) membrane (Millipore, USA) and analysed for the  
147 organic concentration. After the reaction, the Cu-GBC suspension was centrifuged, and the catalyst was  
148 collected and recovered by acetone (solid/acetone, 1:158, wt.%), which can effectively remove residual  
149 organics from the catalyst surface without altering its properties, according to our preliminary experiments  
150 (Supporting Information).

151 The scavenging experiments were performed to illustrate the contribution of different reactive oxygen  
152 species (*i.e.*,  $\cdot$ OH, SO<sub>4</sub><sup>-</sup>, O<sub>2</sub><sup>-</sup>, and O<sub>2</sub><sup>1</sup>) by using 4 M EtOH (for  $\cdot$ OH and SO<sub>4</sub><sup>-</sup>), 0.5 M tert-butanol (TBA)  
153 (for  $\cdot$ OH), 0.05 M chloroform (CF) (for O<sub>2</sub><sup>-</sup>), and 0.01 M furfuryl alcohol (FFA) (for O<sub>2</sub><sup>1</sup>), respectively.<sup>29</sup>



154 Potassium iodide (KI, 10 mM) and pure acetone were chosen as inhibitors of non-radical pathway to  
155 suppress the surface-bound reactive species formation and direct contact between organic contaminants and  
156 carbon matrix, respectively.<sup>44</sup> Similar experiments (without the PDS addition) using the composites  
157 pre-treated by excess PDS (1 M) were performed to identify the contribution of organic removal *via*  
158 metastable complex.<sup>45</sup> The metal-free GBC (treated with ethylene-diamine-tetraacetic acid (EDTA)) and  
159 phenol-free GBC (treated with glycerol) were also employed (Supporting Information).<sup>26</sup> To identify the  
160 direct electron-transfer process during PDS activation, a two-chamber reactor separated by proton exchange  
161 membrane (PEM), equipped with carbon fibre electrodes, connected *via* electric wire, and loaded with  
162 Cu-GBC composite as an activator was prepared to separate organic contaminants from PDS (Supporting  
163 Information).

#### 164 2.5. Analytical methods

165 The concentrations of organic pollutants were analysed by an UV-Vis spectrophotometer at a wavelength  
166 of 554 nm (UV-1100, China, limit of detection (LOD) of 0.1 mg L<sup>-1</sup>) or a high-performance liquid  
167 chromatography (HPLC, Hitachi, Japan, LOD of 0.1 mg L<sup>-1</sup>). The total organic carbon (TOC) was  
168 measured with a TOC analyser (SSM-5000A, Japan, LOD of 0.1 mg L<sup>-1</sup>). The PDS concentration was  
169 determined by another UV-Vis spectrophotometer coupled with a computational platform (Optizen Pop,  
170 South Korea, LOD of 0.1 mg L<sup>-1</sup>). The metal concentration was quantified by inductively coupled plasma  
171 atomic emission spectroscopy (ICP-AES, Thermo Scientific, USA, LOD of 0.1 µg L<sup>-1</sup>). The electron spin  
172 resonance (ESR) spectra were obtained using an EMX10/12 spectrometer (Bruker, Germany). The solution  
173 pH was measured by a digital pH meter (Thermo 911600, USA). Detailed information on the analytical  
174 methods is available in the Supporting Information. Calibration of standard organic/inorganic concentrations  
175 was carried out prior to each analysis. Standards were analysed every 10 samples for quality assurance and

176 quality control. All experiments were performed in triplicate, and the results are presented as mean  $\pm$   
177 standard deviations.

178

179

### 180 3. Results and discussion

#### 181 3.1. Physiochemical properties and crystalline structure of Cu-GBC composites

182 Selected physiochemical properties of GBC and the synthesized Cu-GBC composites with different Cu  
183 loadings (5–20 wt.%) under N<sub>2</sub> or CO<sub>2</sub> environment are summarized in Table 1. After wet digestion, the  
184 total Cu content in the Cu-GBC composites was shown to range from  $3.8 \pm 1.1$  to  $23.2 \pm 5.5$  wt.%. The  
185 HR-TEM images are shown in Fig. 1a-f. Homogeneous distribution of copper nanoparticles can be  
186 observed (Fig. 1b) with a lattice spacing of 0.223 nm assigned to the (111) plane of metal copper (Fig. 1d).  
187 These results suggest that copper was successfully reduced and loaded within the biochar framework after  
188 impregnation and pyrolysis processes. The specific surface area (SSA) and total pore volume of metal-free  
189 GBC fabricated in a CO<sub>2</sub> environment ( $358 \text{ m}^2 \text{ g}^{-1}$  and  $0.323 \text{ cm}^3 \text{ g}^{-1}$ ) were significantly higher than that  
190 generated in a N<sub>2</sub> environment ( $68.3 \text{ m}^2 \text{ g}^{-1}$  and  $0.0516 \text{ cm}^3 \text{ g}^{-1}$ ). The CO<sub>2</sub> medium promoted the formation  
191 of both micropores ( $219 \text{ m}^2 \text{ g}^{-1}$ ) and meso/macro-pores ( $139 \text{ m}^2 \text{ g}^{-1}$ ), as a result of intensive carbon  
192 reforming via Boudouard reaction ( $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$ ) taking place at  $\geq 710 \text{ }^\circ\text{C}$ .<sup>24,33,34</sup> The use of CO<sub>2</sub> may  
193 also react with the pore-blocking condensable hydrocarbons (e.g., volatile organic compounds and tars),  
194 which could be converted into gaseous products to free the blocked pores and/or create new ones.<sup>30,46</sup> The  
195 SSA increased from  $358 \text{ m}^2 \text{ g}^{-1}$  for the control CO<sub>2</sub>-GBC to  $388 \text{ m}^2 \text{ g}^{-1}$  and  $468 \text{ m}^2 \text{ g}^{-1}$  for the Cu-GBC5C  
196 and Cu-GBC10C, respectively, indicating that CuCl<sub>2</sub> acted as a pore-forming agent. The external surface  
197 area and micropore volume also increased from 139 to  $175 \text{ m}^2 \text{ g}^{-1}$  and 0.121 to  $0.156 \text{ cm}^3 \text{ g}^{-1}$  (i.e.  
198 39.2–53.1% of total pore volume), respectively, suggesting the more significant formation of both

199 mesopores (2–50 nm) and micropores (< 2 nm) in Cu-GBC10C framework, which are also displayed in the  
200 HR-TEM image (Fig. 1e). Thus, the Cu-induced catalytic graphitization of carbon matrix during pyrolysis  
201 could possibly generate more zero-dimensional point defects (*i.e.*, vacancy and edge sites) and  
202 three-dimensional volume defects (*i.e.*, lattice disorder and void).<sup>46</sup> However, excessive Cu loading caused a  
203 sharp decrease in SSA ( $4.89 \text{ m}^2 \text{ g}^{-1}$ ) for the Cu-GBC20C, which might result from the pore blockage after  
204 Cu precipitation. As shown in Fig. 2a & S1, N<sub>2</sub> adsorption curves of all the composites exhibited the typical  
205 type-IV adsorption/desorption isotherms with H4-type hysteresis loop at medium relative pressure ( $P/P_0 =$   
206  $0.45\text{--}0.95$ ), which further demonstrated the existence of micropores and mesopores derived from capillary  
207 condensation,<sup>47</sup> corresponding to the average pore size data of GBC and Cu-GBC composites in Table 1.

208 Compared with the control CO<sub>2</sub>-GBC, the pH of the Cu-GBC composites decreased from 10.5 to 10.3–  
209 8.51, which is attributed to the hydrolysis of Cu<sup>2+</sup> and/or the generation of acidic functional groups (*e.g.*,  
210 phenolic and carboxylic groups).<sup>48</sup> The pH value at the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) increased after copper  
211 encapsulation (Fig. S2) owing to an increasing positive surface charge after the incorporation of copper  
212 atoms, which is expected to tailor the electronic states of the adjacent carbon *via* charge transport to  
213 modulate the electron density.<sup>40</sup> The SEM-EDX analysis of the GBC and Cu-GBC composites are  
214 presented in Figs. S3-S5. In contrast to the relative smooth surface with multilayer structure on the N<sub>2</sub>-GBC  
215 (Fig.S3a-b), porous channels and more mesopores were observed on the surface of CO<sub>2</sub>-GBC (Fig.S3c-d).  
216 With respect to Cu-GBC5C, Cu particles were mainly incorporated in the interior micropores of the flaky  
217 cracking GBC surface (Fig. S3e). As the Cu loading increased, *i.e.*, for Cu-GBC10C, Cu particles with  
218 diameters ranging from micro- to nano-scale became evident (Fig. S4c-d). These particles were evenly  
219 distributed in the pores and on the surfaces of bulkier dendritic flocs, up to a particle size of 400–500 nm. In  
220 contrast, obvious particle aggregation into discrete spheres of ~10  $\mu\text{m}$  was observed in the Cu-GBC20C  
221 (Fig. S3f). These findings are consistent with the variation in surface area and pore size distribution of the

222 Cu-GBC composites (Table 1). EDX analysis (Fig. S5) revealed the co-existence of Cu, O, C, Ca, Mg, and  
223 P elements on the Cu-GBC10C **surfaces**. The significantly higher oxygen content (21.1 wt.%) of  
224 Cu-GBC10C compared with that of the Cu-GBC10N (1.83 wt.%) indicated that more oxygen could be  
225 introduced into the carbon matrix under CO<sub>2</sub> medium. **Enriched** oxygen-containing functionalities **may act**  
226 as the anchoring sites **for** the impregnation of Cu species (Table 1).<sup>49</sup> Besides, the induced edges terminated  
227 with hydrogen and oxygen atoms on the *sp*<sup>2</sup>-hybridized carbon were reported to possess high affinity to  
228 adsorb oxyanions.<sup>20,50</sup>

229 The XRD patterns of the GBC and Cu-GBC composites are shown in Fig. 2b. In the case of the N<sub>2</sub>-GBC,  
230 the carbon matrix demonstrated a broad peak at 2θ value of 20–25°, which can be assigned to graphite  
231 corresponding to the amorphous plane of (002) in carbonaceous materials.<sup>51</sup> Nonetheless, the spectra of the  
232 CO<sub>2</sub>-GBC presented the characteristic peaks at 29.41°, 35.93°, 39.42°, 47.14°, and 47.42° corresponding to  
233 the (104), (110), (113), (024), and (018) planes of calcite, respectively, as typical ash component of wood  
234 waste.<sup>52, 53</sup> As for the Cu-GBC composites, the characteristic peaks at 35.04°, 38.48°, and 50.43° were  
235 assigned to the (002), (111), and (112) planes of CuO,<sup>54, 55</sup> while the peaks at 43.29° and 74.13°  
236 corresponded to the (111) and (220) planes of Cu<sup>0</sup>,<sup>56</sup> respectively. In particular, in contrast with the  
237 N<sub>2</sub>-pyrolysis, the CO<sub>2</sub> environment suppressed the crystalline sizes of CuO (0.61 vs. 0.89 nm) and Cu<sup>0</sup> (1.97  
238 vs. 2.28 nm) particles, based on the calculation using the Scherrer equation.<sup>45</sup> Thus, copper heteroatoms can  
239 be successfully grafted in the framework of **biochar**, and hence likely to significantly increase its catalytic  
240 reactivity by forming Lewis acid-**base adduct** (*i.e.*, **reversibly donate and accept electrons**)<sup>57,58</sup> or surface  
241 metastable complex (*i.e.*, non-radical pathway).<sup>31</sup> **The** absence of a calcite peak in the Cu-GBC XRD  
242 pattern suggests that the doped copper heteroatoms saturated the exchangeable sites that originally held  
243 Ca.<sup>13</sup>

244 The Raman spectra of the GBC and Cu-GBC composites further elucidated the physical characteristics of  
245 the carbonaceous materials, as shown in Figs. 2c & S6. The two peaks at 1310 and 1590  $\text{cm}^{-1}$  correspond to  
246 the characteristic D and G bands of carbon, *i.e.*, defects of  $sp^3$  C and in-plane vibrations of  $sp^2$  C in curved  
247 graphitized carbon sheet.<sup>42,59</sup> In all samples, the Raman spectra were deconvoluted into eight characteristic  
248 peaks that were assigned to  $sp^2$  C–H of aromatic rings ( $S^1$ ) at 1060  $\text{cm}^{-1}$ ,  $C_{\text{aromatic}}\text{--}C_{\text{alkyl}}$  (S) at 1185  $\text{cm}^{-1}$ ,  
249 Aryl-alkyl ether ( $S^2$ ) at 1230  $\text{cm}^{-1}$ , defect bands and small ordered fused benzene rings (D) at 1310  $\text{cm}^{-1}$ ,  
250 methyl group and amorphous carbon ( $V^1$ ) at 1380  $\text{cm}^{-1}$ , semicircle ring breathing (V) at 1465  $\text{cm}^{-1}$ ,  
251 aromatics with 3–5 rings ( $G^1$ ) at 1540  $\text{cm}^{-1}$ , and highly ordered  $sp^2$  graphitic carbon (G) at 1590  $\text{cm}^{-1}$ .<sup>60,61</sup>  
252 The area ratios of the D peak to the G peak ( $A_D/A_G$ ) and the sum of G, V, and  $V^1$  peaks ( $A_D/A_{(G+V+V^1)}$ ) of the  
253  $\text{CO}_2$ -pyrolyzed composites are greater than that produced in  $\text{N}_2$ , suggesting that  $\text{CO}_2$  medium induced more  
254 fused aromatic rings and structural edge defects within the biochar matrix during pyrolysis.<sup>23,62,63</sup> This can  
255 be attributed to the enhanced dehydrogenation of organic matter (*viz.* Boudouard reaction:  $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$ ;  
256 biomass  $\rightarrow$  biochar + tar +  $\text{C}_n\text{H}_m$ ) at high temperature with  $\text{CO}_2$  purging, which could generate more  
257 vacancy and zigzag edges as structural-dimensional defects.<sup>46</sup> The ratios of  $A_D/A_G$  and  $A_D/A_{(G+V+V^1)}$  also  
258 increased with the increasing Cu loading (Fig. S6c-d), suggesting that  $\text{CuCl}_2$  may promote the catalytic  
259 graphitization of biochar during the synthesis of the Cu-GBC composites, which accounted for more newly  
260 formed volume defects (*e.g.*, void).<sup>64</sup> Intriguingly, the Cu-GBC10C composite exhibited both a higher level  
261 of graphitization and defects than the lab-synthesized GO (Fig. S7b) prepared in our recent study,<sup>49</sup> which  
262 possibly account for the improved performance in the catalytic activation of PDS for organics degradation  
263 with abundant free-flowing  $\pi$  electrons and defective sites. Graphitic carbon clusters with a crystalline  
264 spacing of 0.25 nm (assigned to graphite) can be observed in the HR-TEM images of Cu-GBC10C (Fig.  
265 1e-f), which further confirms the emergence of highly ordered graphitic nature after the introduction of  
266 copper heteroatoms.

267 3.2. Surface chemical behaviour and thermal stability of Cu-GBC composites

268 FTIR spectra helped to determine the functional groups on the surfaces of the GBC and Cu-GBC  
269 composites (Fig. 2d). In the case of the N<sub>2</sub>-pyrolyzed composites, the broad spectral band with a weak peak  
270 at 3429 cm<sup>-1</sup> was attributed to the presence of the O–H stretching vibration in alcoholic and phenolic –OH  
271 groups. The pyrolysis at 900 °C diminished most of the functional groups ubiquitously present in  
272 low-temperature biochars, because dehydration of cellulosic and ligneous components at high temperature  
273 (>700 °C) tend to decompose the majority of the aliphatic and phenolic organic compounds.<sup>1,48,65</sup> After Cu  
274 impregnation and pyrolysis in CO<sub>2</sub> environment, the band disappeared for –OH and C–H at 3429 and 835  
275 cm<sup>-1</sup>, respectively, whereas an aromatic C=O stretching vibration in conjugated ketones and quinones  
276 evolved at 1659 cm<sup>-1</sup>.<sup>66</sup> This was indicative of catalytic reformation and condensation of carbon matrix  
277 during the synthesis of the Cu-GBC composites,<sup>27,67</sup> which may account for the greater graphitic carbon  
278 observed in the Raman spectra (Figs. 2c & S6). It should be noted that the produced ketonic group (C=O) is  
279 indispensable for the activation of PDS and the generation of singlet oxygenation for organics degradation.<sup>20,</sup>  
280 41,44,68,69

281 TGA was employed to verify the generation of ketonic group (C=O) during the aforementioned catalytic  
282 reformation. As shown in Fig. S17, the mass decay (TG) of raw wood waste exceeded 80% and the broad  
283 peak (*peak 1*) at 345.5 °C in derivative thermogravimetry (DTG) was consistent with the dehydration of  
284 cellulosic or ligneous components and the lignin/cellulose-derived transformation at mid-level pyrolytic  
285 temperature (200-550 °C).<sup>48,65</sup> The CO<sub>2</sub>-pyrolyzed biochar composites exhibited greater mass decay than  
286 their N<sub>2</sub>-pyrolyzed counterparts, especially for Cu-GBC10C (30.1%, compared to 17.1% of Cu-GBC10N).  
287 Both apparent peaks at 643.6 °C (*peak 2*) and 634.8 °C (*peak 3*) in the DTG curves for CO<sub>2</sub>-GBC and  
288 Cu-GBC10C correspond to the decomposition of conjugated ketones (C=O),<sup>65</sup> suggesting that copper  
289 heteroatoms and CO<sub>2</sub> medium could synergistically increase the oxygen levels during the pyrolytic process.

290 The XPS data indicated that the GBC was composed of C 1s and O 1s, whereas the Cu-GBC composites  
291 **comprised** C 1s, O 1s, and Cu 2p. In all samples, the C 1s spectra **consisted** of five different peaks that were  
292 assigned to O=C–OH at 288.8 eV, C=O at 286.6 eV, C–O at 285.8 eV, C–C at 285.4 eV, and C=C at 284.8  
293 eV, while the three fitted peaks of O 1s could be assigned to O–C=O at 533.6 eV, O–C at 532.2 eV, and O=C  
294 at 530.8 eV, respectively.<sup>70</sup> As the Cu impregnated biomass was pyrolyzed under CO<sub>2</sub> purging, there was a  
295 significant increase in the content of O=C (from 17.7% to 41.1%) compared to CO<sub>2</sub>-GBC (Fig. 3b & S8).  
296 This observation corroborates the transformation of O–C (532.2 eV) into O=C (530.8 eV) *via* Cu-induced  
297 catalytic oxidation process.<sup>42</sup> Duan et al. reported that **oxygen functionalities can determine** the inherent  
298 catalytic capability of carbonaceous materials, and both oxygen contents and species of oxygen groups  
299 should be carefully optimized.<sup>20</sup> In this research, copper heteroatoms are favourable to tune the oxygen  
300 groups by transforming more oxygen functionalities into ketonic C=O, which would **contribute to** the better  
301 catalytic performance of Cu-GBC10C in the subsequent section.

302 In addition, as shown in Figs. 3c & S10, CuO shake-up (943.8 eV) accounted for only 19.9% and slight  
303 increases were observed after reaction (from 19.9% to 20.6% for CuO, 27.8% to 36.3% for Cu<sup>2+</sup>), which  
304 ruled out the electron donation or sole CuO-induced non-radical pathway as the primary reaction route. It  
305 has been reported that metal–O–C bond could give rise to denser local electronic states **forming** more  
306 reactive sites,<sup>40</sup> and similar synergy between Cu and graphitic carbon **may** explain the phenomenon in this  
307 work. **This should be further verified *via* density functional theory calculations and X-ray absorption**  
308 **spectroscopy in the future. The current study evidences that** the CO<sub>2</sub> environment and Cu doping promoted  
309 the formation of ketonic groups **during** pyrolysis,<sup>13,71,72</sup> and ultimately the *sp*<sup>2</sup>-hybridized carbon framework  
310 was converted into an active **state with the new** accommodated copper heteroatoms and tuned oxygen  
311 functionalities.

312 *3.3. Cu-GBC performance for PDS activation and catalytic degradation of organic contaminants*

313 A typical rhodamine dye of RB was chosen as the target organic pollutant to evaluate the catalytic  
314 performance of synthesized composites for PDS activation and the kinetic data were fitted using a  
315 pseudo-first-order kinetics model.<sup>31,39,73</sup> The raw wood waste (5 g) was combusted in air to obtain its ash  
316 (0.48 g), which was found to barely activate PDS for RB degradation, indicating that the metal residues in  
317 the biomass do not contribute to the catalytic oxidation on GBCs. The adsorptive removals of RB were  
318 insignificant on GBCs and Cu-GBC10N, while PDS alone could not oxidize the dye (< 5%) without the  
319 addition of catalysts (Fig. S11). In contrast, Cu-GBC10C showed notable RB adsorption (~ 40%), possibly  
320 due to **stronger interactions with the** enriched oxygen functionalities on the biochar surface. The larger SSA  
321 (468 m<sup>2</sup> g<sup>-1</sup>, Table 1) and higher graphitic level of Cu-GBC10C might also contribute to an improved  
322 adsorption capacity **with stronger pore-filling adsorption and  $\pi$ - $\pi$  interaction**. However, Cu-GBC5C and  
323 Cu-GBC20C demonstrated unfavourable adsorptive performance due to insufficient SSA and active sites  
324 (data not shown). An 86.4% degradation rate of RB was achieved in the Cu-GBC10C/PDS system in 30  
325 min, demonstrating a better degradation efficiency than most commercial heterogeneous catalysts  
326 (metal-based systems including CuO, ZVI, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, ZnO, CoO, and MnO<sub>2</sub>), while **an inferior**  
327 degradation rate of 22.3% was obtained by Cu-GBC10N (Fig. 4a). In Fig. S12, compared to the pristine  
328 **biochar** (N<sub>2</sub>-GBC, 0.0056 min<sup>-1</sup> with 7.8% degradation removal; CO<sub>2</sub>-GBC, 0.0071 min<sup>-1</sup> with 15.6%  
329 degradation removal) and Cu-GBC10N (0.0094 min<sup>-1</sup> with 22.3% degradation removal), Cu-GBC10C  
330 (0.03122 min<sup>-1</sup> with 86.4% degradation removal) gave rise to a **5.6-, 4.5-, and 3.3-**fold enhancement of the  
331 degradation rate as a result of the larger surface area, higher graphitization degree, and more active sites (*i.e.*,  
332 C=O in ketonic group). This **phenomenon also evidences** a synergism of the Cu catalytic reformation and  
333 CO<sub>2</sub> purging during biomass pyrolysis. **Cu-GBC10C** was chosen as the sustainable biochar catalyst for the  
334 subsequent comparative, kinetics, and mechanistic studies.



335 Fig. S13 shows that ~ 90% removals of RB, PN, and BPA at 0.1 mM could be rapidly achieved by  
336 Cu-GBC10C within 30 min. However, it was poor in 4-CH oxidation (39.8%). This lower performance  
337 probably indicates that organic pollutants (*e.g.*, RB, PN, and BPA) with lower ionization potential (IP) (IP =  
338 7.4–8.5) were more prone to be oxidized by mild reactive oxygen species (ROSS) (*e.g.*,  $^1\text{O}_2$ ) generated in  
339 Cu-GBC/PDS system *via* a non-radical pathway. Previous findings suggested that some highly-graphitic  
340 carbonaceous materials (CNTs and carbonized N-containing polymers, *etc.*) and metal oxides (CuO and  
341  $\beta\text{-MnO}_2$ , *etc.*) tended to exhibit a higher selectivity towards electron-rich phenolic compounds.<sup>31, 39, 41, 42</sup>  
342 When the concentration of organics increased to 0.5–0.6 mM, 40.3% and 79.7% removals of RB and PN  
343 were obtained in 30 min, possibly limited by the insufficient active sites on Cu-GBC10C.

344 To affirm the rate-determining step of the reaction (at  $\text{pH} = 5.8 \pm 0.2$ ), the pseudo-first-order kinetics was  
345 employed to calculate the observed rate constant ( $k_{obs}$ ) in the first 30 min at different catalyst loadings, PDS  
346 dosages, or organic concentrations. Increasing PDS concentration from 1 to 5 mM marginally improved  $k_{obs}$   
347 (Fig. 5b). Catalyst loading (0.1–0.5  $\text{g L}^{-1}$ ) and initial RB concentration (0.05–0.6 mM) posed more  
348 significant impact on the removal rate constants (Fig. 5a&c). The curves between logarithms of  $k_{obs}$  and  
349 dosages of Cu-GBC10C, PDS, and RB were plotted accordingly, showing good linearity between  $\ln(k_{obs})$   
350 with  $\ln(\text{Cu-GBC10C})$  ( $R^2 = 0.983$ ),  $\ln(\text{PDS})$  ( $R^2 = 0.821$ ), and  $\ln(\text{RB})$  ( $R^2 = 0.965$ ) (Fig. 5d). In addition,  
351 the positive correlation ( $R^2 = 0.999$ ) was established between the adsorbent dosage ( $\text{g L}^{-1}$ ) and adsorptive  
352 removal rate ( $k_{obs}$ ) (Fig. 5d). The slopes of  $\ln(k_{obs})$  against  $\ln(\text{Cu-GBC10C})$ ,  $\ln(\text{PDS})$ ,  $\ln(\text{RB})$ , and  
353  $\ln(\text{adsorbent})$  were estimated to be 0.968, 0.095, -0.653, and 0.860, respectively, which can be taken as the  
354 orders of reactivity in the overall organic removal rate. The lowest reaction order of PDS suggests that the  
355 active sites for PDS adsorption are limited, and self-scavenging effect or cannibalistic surface oxidation  
356 reaction could also be excluded accordingly, thus demonstrating the features of a typical non-radical  
357 activation.<sup>38, 74</sup> The higher reaction orders with respect to Cu-GBC10C, RB, and adsorbent concentrations

358 indicated that the adsorption of organic compounds on the Cu-doped GBC might be the rate-determining  
359 step for the non-radical oxidation.<sup>31,39,44,75</sup>

### 360 3.4. Contribution of radical and non-radical pathways to PDS activation and organics degradation

361 In previous studies, it has been discovered that the persistent free radicals (PFRs) were formed from the  
362 decomposition of organic structure (*i.e.*, hydroquinone) in **biochars** derived at moderate temperatures  
363 (300–500 °C),<sup>76</sup> which served as the redox centres to deliver electrons to PDS to evolve sulfate radicals.<sup>26</sup>  
364 However, Ruan et al. revealed that pyrolysis of different biomass (*e.g.*, pinewood, rice husk, and cow  
365 manure) at temperature above 700 °C generally removed all PFRs due to the elimination of oxygen  
366 functionalities and condensation/graphitization of carbon clusters.<sup>77</sup> In this work, the removal rate of  
367 phenol-free GBC (Supporting Information) was comparable to GBC, indicating that PDS activation by  
368 PFRs on highly graphitic **biochars** for catalytic degradation can be ruled out.

369 More interestingly, the radical quenching tests (Fig. 6a and Table 2) indicate that the addition of free  
370 radical scavengers,<sup>44,57,78,79</sup> *i.e.*, EtOH ( $k_{\text{SO}_4^{\cdot-}} = (1.6\text{--}7.7) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\cdot\text{OH}} = (1.2\text{--}1.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ),  
371 TBA ( $k_{\text{SO}_4^{\cdot-}} = (4.0\text{--}9.5) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\cdot\text{OH}} = (3.2\text{--}7.6) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ), and CF ( $k_{\text{O}_2^{\cdot-}} = (1.1\text{--}3.2) \times 10^9 \text{ M}^{-1}$   
372  $\text{s}^{-1}$ ) had an insignificant impact on organics removal with only a 3.2, 0.19, and 9.4% decrease in the removal  
373 efficiency, respectively. This implies that Cu-GBC10C/PDS is an oxidative system not relying on free  
374 radicals but non-radical pathways due to the absence of DMPO–SO<sub>4</sub> characteristic signal peaks (1:1:1:1:1,  
375  $\alpha\text{N} = 13.2 \text{ G}$ ,  $\alpha\text{H} = 9.6 \text{ G}$ ,  $\alpha\text{H} = 1.48 \text{ G}$ ), although DMPO–OH characteristic signal peaks (1:2:2:1,  $\alpha\text{H} =$   
376  $\alpha\text{N} = 14.9 \text{ G}$ ) were observed in the ESR spectra (Fig. 4c). The generation of hydroxyl radicals might result  
377 from the oxidation of adsorbed water on the graphitic biochar surface, which has been reported in  
378 dimensional-structured nanocarbon system.<sup>20</sup> However, the impact of radical quenching on the reaction rate  
379 was moderate with 31.7%, 9.1%, and 39.1% decline, respectively, indicating that the scavengers with

380 nonpolar properties might suppress the adsorption of RB on the hydrophobic surface of Cu-GBC10C, and  
381 this phenomenon corresponds to the adsorption of organic compounds as the rate-limiting step.

382 To further investigate the interfacial reaction, KI and pure acetone were employed to quench the direct  
383 surface contact between PDS/RB and the carbon matrix, respectively.<sup>80,81</sup> The almost unaffected organic  
384 removal despite the excess KI (10 mM) addition suggests that the increase in ionic strength could not affect  
385 the strong interaction between Cu-GBC10C and PDS. The substantial inhibitory effect of pure acetone  
386 ( $0.00211 \text{ min}^{-1}$  with 18.9% removal) further indicates that the surface adsorption of organics could be vital  
387 for the total oxidation,<sup>44</sup> suggesting that the degradation occurred within the carbon matrix rather than the  
388 bulk solution corroborating the non-radical feature.

389 Recent studies have reported that ketonic- and quinone-like moieties on graphitic carbon with strong  
390 nucleophilic nature and high electron density can catalyze PDS to produce  $^1\text{O}_2$  under mild condition.<sup>41,44,80</sup>  
391 Thus, FFA ( $k_{^1\text{O}_2} = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) was used to scavenge  $^1\text{O}_2$  in the reaction. FFA (0.01 M) significantly  
392 reduced the RB removal efficiency to 50.0% ( $0.00593 \text{ min}^{-1}$ ) in 120 min, indicating that  $^1\text{O}_2$  contributed to  
393 a large portion (nearly half) of the catalytic oxidation. A trapping agent of TEMP was used to detect the  
394 production of  $^1\text{O}_2$  without light. A characteristic three-line signal of TEMPO adducts appeared (Fig. 4d,  
395 1:1:1,  $\alpha = 16.9 \text{ G}$ ), which can be assigned to the oxidation of TEMP by  $^1\text{O}_2$ . In contrast to other GBC  
396 composites, the intensities of TEMPO and DMPO-OH in Cu-GBC10C increased sharply, implying that  
397 Cu-GBC10C possessed the highest reactivity, which originated from the encapsulated copper heteroatoms  
398 and the evolved ketonic groups (C=O) on Cu-GBC10C, possibly at the edges of the carbon matrix.<sup>81</sup>  
399 Moreover, the PDS-pretreated Cu-GBC10C achieved an 8.15% RB degradation without the PDS addition,  
400 whereas those for the Cu-free  $\text{CO}_2$ -GBC and EDTA-pretreated Cu-GBC10C (2.12–2.31%) were negligible  
401 (Fig. S14). Thus, it can be inferred that C=O would induce the surface metastable complex between copper  
402 heteroatoms and PDS (*i.e.*,  $\equiv\text{Cu}-\text{O}_3\text{SOOSO}_3^-$  or  $\equiv\text{Cu}^{\text{II}}-\text{O}_3\text{SOOSO}_3^-$ ), which can readily accept electrons

403 from electron-rich phenolic compounds for  $^1\text{O}_2$  generation,<sup>68</sup> and correspond to a significant peak shift at  
404 531 nm in the UV-vis spectra of the Cu-GBC10C (Fig. 4b). This observation corroborates the C 1s spectra  
405 that depict a lower C=O ratio (from 41.1% to 17.4%) for the Cu-GBC10C after PDS activation.

### 406 3.5. PDS reduction and RB oxidation in two chambers separated by a proton exchange membrane

407 As above, the experimental results proved a significant role of  $^1\text{O}_2$  in PS activation *via* a non-radical  
408 reaction pathway, whereas the RB removal pathway was not completely terminated in the presence of  $^1\text{O}_2$   
409 quenchers. Moreover, in the Cu-GBC mediated non-radical pathway, an electron-transfer process from  
410 organics and donation of free-flowing  $\pi$  electrons by GBC to the activated surface metastable complexes *via*  
411 the conductive surface of carbonaceous materials was expected, in view of the differences of inherent redox  
412 potentials between organic pollutant and PDS molecules.<sup>23</sup> Thus, the electron-transfer non-radical pathway  
413 was further identified by examining Cu-GBC10C-mediated electron transfer from organic substrates to  
414 PDS using a PEM that physically partitioned the reaction system into two chambers containing PDS and  
415 RB (Fig. 7). In this system, free electrons were transported from the anode to the cathode through the  
416 connected wire. The Cu-GBC10C particles were homogeneously dispersed in the bulk solution under  
417 vigorous shaking to achieve sufficient contact with the electrodes, *i.e.*, carbon fibre brushes with high SSA.  
418 As a PEM with high water impermeability is likely to reject organic/inorganic impurities and ROSs (*e.g.*,  
419  $\cdot\text{OH}$  and  $^1\text{O}_2$ ), simultaneous RB oxidation and PDS reduction in the physically separated chambers (*i.e.*,  
420 anode and cathode) would be a strong evidence for the electron-transfer mechanism, in which Cu-GBC10C  
421 mediates electron transfer from organics to PDS.

422 As shown in Fig. 7, increased amounts of reactants (5-fold catalyst and oxidant addition) were added in  
423 the anode chamber (no oxidant) and cathode chamber (no pollutant), respectively. Control experiments were  
424 conducted detaching the linking wire between the two electrodes, and the results indicated that RB  
425 concentration in the cathode chamber declined to less than 5% in 360 min due to the adsorption by the

426 employed Cu-doped biochar, as approximately 10% PDS concentration decomposed simultaneously. The  
427 PDS-saturated state of the catalyst was reached after 360 min. A continuous PDS decrease to  $55.6 \pm 3.1\%$  in  
428 4320 min could be achieved in a wire-connected group compared with the wire-detached control ( $90.8 \pm 3.3\%$   
429 in 4320 min), which confirmed that the PDS was activated without direct contact with pollutant. Neither  
430 PDS nor RB was detected in the opposite side of PEM, thus the continuous PDS concentration decline in  
431 the separated chambers proved our hypothesis that electron transfer pathway does not rely on ROSs. The  
432 overall schematic diagram of the mechanistic routes (*i.e.*, singlet oxygenation and electron transfer) is  
433 presented in Fig. 8.

### 434 3.6. Effect of pH values and reusability/recyclability

435 Fig. S15 presents the influence of initial solution pH values on the organics degradation (*i.e.*, RB and PN)  
436 by the Cu-GBC10C. The performance of the Cu-GBC10C was highly pH-dependent and the degradation  
437 of PN steadily decreased with pH increasing from 3.0 to 9.0. In the case of RB, efficiency rose with  
438 increasing pH values from 3.0 to 5.8 followed by pronounced decrease in RB removal as the solution pH  
439 was further elevated to 9. Fig. S15 displays the highest degradation efficiency of PN and RB as 82.1% and  
440 86.4% at the solution pH values of 3.0 and 5.8, respectively. The obvious difference at various solution pH  
441 values can be ascribed to the composite surface charge, organic speciation, and Cu dissolution. As illustrated  
442 in Fig. S1, there was an obvious decrease in the zeta potential as the solution pH increased. At the solution  
443 pH above 2.08, the zeta potential was negative and undesirable for the removal of  
444 negatively-charged/deprotonated organics (RB- $pK_a = 3.5$  and PN- $pK_a = 9.8$ ).<sup>82,83</sup> Meanwhile, the surface of  
445 Cu-GBC10C became more negatively charged with the increase of solution pH, which was less conducive  
446 to anionic PDS ( $S_2O_8^{2-}$ ) forming a metastable complex.<sup>84</sup> In addition, an acidic environment at pH 3.0–6.0  
447 adversely affected the organics degradation due to inevitable Cu dissolution from the Cu-GBC10C  
448 ( $0.014\text{--}0.925\text{ mg L}^{-1}$ ).

449 Reusability/recyclability is an important indicator evaluating the sustainability of Cu-GBC10C. The  
450 removal efficiency decreased from 95.8% to 30.6% after four cycles (Fig. S16), probably because the Cu  
451 nanoparticles were exhausted by chemical reduction and/or the degradation intermediates/products covered  
452 the active sites, and changed the surface chemistry and electron transfer. Nevertheless, the Cu-GBC10C  
453 could maintain 73.2% of the RB removal efficiency after four cycles via facile acetone regeneration process,  
454 suggesting that the Cu-GBC10C had a good reusability/recyclability and stability when the degradation  
455 intermediates were removed. It is noted that the trivial amount of leached Cu (Fig. S15) in bulk solution  
456 could not catalyze the degradation, because adsorption of target contaminants on Cu-GBC composite  
457 surface was evidenced to be necessary (Section 3.4) and chemical desorption of organic  
458 intermediates/products in acetone was required to recover the catalytic activity (Fig. S16). We herein  
459 propose the Cu-based and ketonic active sites on GBC as a sustainable alternative to the consumable  
460 catalytic sites in the conventional carbocatalysts. By using persulfate activation as a model reaction, our  
461 findings can foster wider applications of Cu-GBC composites in sustainable biorefinery,<sup>85</sup> soil amendment,<sup>2,</sup>  
462 <sup>86</sup> stabilization/solidification,<sup>87</sup> etc., where electron transfer routes can potentially take place. Future studies  
463 may also investigate the production of Cu-GBC from wood waste contaminated by Cu-containing  
464 preservatives, which will further benefit sustainable development and zero waste principles.

465

#### 466 4. Conclusions

467 Through the integrated analysis of the surface characteristics and contaminant interactions, we  
468 demonstrated that the highly graphitic Cu-doped biochar fabricated in CO<sub>2</sub> environment manifested a  
469 superior catalytic performance of PDS activation for the degradation of various organic contaminants,  
470 out-performing most of popular and costly heterogeneous catalysts. Selective degradation routes via singlet  
471 oxygenation and mediated electron transfer were promoted by design and validated as the predominant

472 non-radical mechanisms. The organics adsorption was identified as the rate-determining step of the reaction.  
473 The scientific merits of this paper are highlighted as follows: (i) a new approach for utilizing waste biomass  
474 to synthesize value-added products with versatile metal-heteroatoms-induced active sites and high  
475 graphitization employing greenhouse gas CO<sub>2</sub>; (ii) a highly reactive, selective, green, and stable method for  
476 catalytic degradation of organic contaminants with cost-effective and environmentally benign biochar  
477 composites; (iii) advanced mechanistic insights into the synergistic effects of the copper heteroatoms and  
478 CO<sub>2</sub> environment during metal-impregnated biomass pyrolysis and catalytic degradation. Therefore, the  
479 Cu-biochar composites are easily prepared and low-cost carbon-based catalysts suitable for green and  
480 sustainable remediation.

481

#### 482 **Acknowledgement**

483 The authors appreciate the financial support from the Hong Kong Research Grants Council (PolyU  
484 15217818) and Hong Kong International Airport Environment Fund for this study. The support of the  
485 University Research Facility on Chemical and Environmental Analysis (URFCE) of PolyU is also  
486 acknowledged.

487

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