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1 **Nanocellulose-derived carbon/g-C₃N₄ heterojunction with a**
2 **hybrid electron transfer pathway for highly photocatalytic**
3 **hydrogen peroxide production**

4
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14
15 **Abstract**

16 Using oxygen reduction for the photocatalytic production of hydrogen peroxide (H₂O₂)
17 has been considered a green and sustainable route. In the present study, to achieve
18 high efficiency, graphitic carbon nitride (g-C₃N₄) was obtained using thermal
19 polymerization from a bi-component precursor and was then assembled with cellulose
20 nanofibers. It was found that a small quantity of cellulose nanofibers that generates
21 carbon fibers upon pyrolysis greatly improves the photocatalytic activity compared
22 with that of g-C₃N₄ alone. The well-defined carbon/g-C₃N₄ heterojunction-type
23 material exhibits as high as 1.10 mmol L⁻¹ h⁻¹ of photo-production of H₂O₂ under
24 visible light, which is 4.2 times higher than that yielded by pristine g-C₃N₄ from a
25 single precursor. A comprehensive characterization of the photocatalyst enables us to
26 delineate the effect of the carbon nanofiber with respect to porosity, electron-hole
27 separation, band gap regulation, and especially the electron transfer pathway. Our

28 results demonstrate that nanocellulose-derived carbon, when precisely assembled with
29 other functional material such as a photocatalyst, is a promising promoter of their
30 activity.

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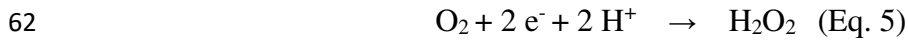
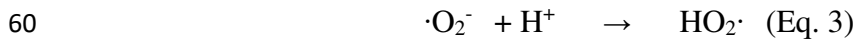
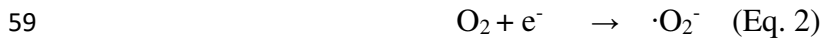
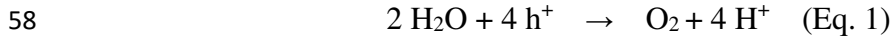
32 **Keywords:** Cellulose nanofibers; Photocatalysis; Carbon nitride; Hydrogen peroxide
33 production; Carbon fibers

34

35 **1. Introduction**

36 Hydrogen peroxide (H_2O_2) is a promising energy storage product widely used
37 both as an oxidant and reductant in chemical synthesis, industrial bleaching, and
38 medical sterilization [1, 2]. Moreover, in line with the need for new answers to the
39 increase in energy demand, H_2O_2 has been proposed as the oxidizing agent at the
40 cathode of fuel cells with environmentally acceptable by-products, H_2O and O_2 [3].
41 Presently, the methods adopted to produce H_2O_2 on a large scale are anthraquinone
42 autoxidation [4] and electrochemical synthesis [5]. These methods consume a large
43 amount of energy and organic solvents; in addition, contamination by various organic
44 impurities can occur and result in increased difficulties of purification [6, 7].
45 Consequently, new production processes must succeed in satisfying the demand for
46 H_2O_2 , resolve and eliminate the shortcomings of traditional production methods, be
47 efficient, and above all be sustainable and environmentally friendly with respect to the
48 principles of green chemistry.

49 In recent decades, photocatalysis has been employed in light-driven production
50 of H_2O_2 through photoreduction of O_2 in H_2O [8], a process governed by the basic
51 photochemical reaction resulting from light–semiconductor interaction in the presence
52 of water. In this approach, the semiconductor generates holes (h^+) in the valence band
53 (VB) that oxidize H_2O near the surface and release protons (H^+ ; Eq. 1).
54 Simultaneously, the electrons (e^-) promoted in the conduction band (CB) can reduce
55 O_2 to generate different species, including superoxide radicals ($\cdot\text{O}_2^-$) and, subsequently,
56 H_2O_2 by either a (i) single-electron indirect reduction and protonation (Eq. 2–4) or (ii)
57 one-step two-electron direct O_2 reduction (Eq. 5).



63 ZnO [9] and TiO₂ [10-14] are the two major classical inorganic semiconductors
64 used as photocatalysts [15, 16], among many others. Recently, carbon nitride with
65 graphitic structure (g-C₃N₄) has emerged as a highly promising photocatalyst.
66 Compared with classical metal-based semiconductors, it has a high efficiency and
67 several advantages [17-20], the most attractive one being the absence of metal species
68 known to decompose H₂O₂ via MOOH formation. Additionally, g-C₃N₄-based
69 catalysts exhibit good photostability and photocatalytic activity under visible light.
70 Finally, g-C₃N₄ can be prepared by the polycondensation and pyrolysis (500–600°C)
71 of nitrogen- and carbon-containing precursors such as melamine and urea, both being
72 cheap, abundant, and non-toxic in comparison with ZnO and TiO₂ [21]. However,
73 pure carbon nitride has some bottlenecks limiting its photocatalytic efficiency, such as
74 a fast electron–hole recombination of photogenerated species, insufficient absorption
75 in visible light, a relatively large band gap (~2.7 eV), and a low specific surface area
76 that limits the number of active sites for interfacial photoreactions. To address these
77 issues, different strategies have been employed to enhance the photocatalytic activity,
78 including non-metal doping (e.g., O [22, 23], P [24], N [25], and S [26]), metal ion
79 doping (K [7], Cu [27]), forming heterojunctions with other semiconductors (e.g.,
80 ZnO [28], MnO₂ [29], and CeO₂ [30]), composites with metal nanoparticles (e.g., Au
81 [20] and Ag [31]), and composites with carbonaceous materials (e.g., carbon dots [32],
82 graphene [33], and carbon nanotubes [34]). The carbonaceous materials are selected
83 as an electron transfer agent and photosensitizer in the photocatalysis field to reduce
84 the electron–hole (e⁻/h⁺) recombination and to increase the absorption of incident light,
85 respectively. Nowadays, the production of such functional carbon should avoid the
86 use of non-renewable and fossil fuel-derived carbon precursors (e.g., polyacrylonitrile
87 [PAN]), and instead use biosourced carbon. Cellulose nanofibers (CNF) are one

88 example, with 1–3 μm length and 5–10 nm width. They not only have the advantage
89 of size but also possess adequate surface functional groups such as -OH and -COOH,
90 facilitating regulation of the growth and chemical anchoring of chemical species such
91 as precursors of inorganic photocatalysts [35]. Therefore, anchoring graphitic-like
92 materials should be possible if they possess compatible functional groups. This
93 implies the necessity of edge functional groups in g-C₃N₄ that possess H-bonding
94 donor or acceptor ability.

95 Various research groups have already demonstrated the synergy of
96 nanocellulose/g-C₃N₄ composites, with or without pyrolysis of the cellulose. It has led
97 to the development of adsorbents or photocatalysts for the oxidation of dyes
98 (methylene blue [36-39] or rhodamine [40, 41]), formaldehyde [42], Cr(IV) [43, 44],
99 oil/water emulsion [45] or bacteria [46] and also the preparation of thermal insulator
100 materials [47, 48]. These are promising routes especially for pollutant remediation;
101 however, the future of photocatalysis also involves the production of chemicals by
102 clean and low-energy processes. To the best of our knowledge, only one previous
103 study used g-C₃N₄ and nanocellulose to produce an efficient photocatalyst to produce
104 chemicals, H₂ in that case. However, nanocellulose was used only as a template to
105 generate a chiral nematic structure in addition to the use of silica, with nanocellulose
106 subsequently eliminated by calcination [49]. In our study, we used nanocellulose as
107 both a template and a C-precursor to prepare a C/g-C₃N₄ composite by the simplest
108 possible process. It is also worth mentioning the work by Jin et al., who used soluble
109 cellulose acetate in combination with melamine as a g-C₃N₄ precursor to produce a
110 C/g-C₃N₄ photocatalyst for the production of hydrogen [50].

111 In the present study, g-C₃N₄ nanosheets (CN2) were fabricated for the first time
112 using a mixture of melamine and urea and a two-step calcination method, to generate
113 a higher proportion of amino groups (-NH_x) than that in g-C₃N₄ prepared with only
114 melamine (CN1); see Scheme 1 for the summary of the general strategy. We found
115 that the as-prepared g-C₃N₄ nanosheets can easily and strongly bind the CNF, possibly
116 by hydrogen or even covalent bonds. The cellulose nanofiber/g-C₃N₄ composite is
117 then transformed by pyrolysis into a covalent heterojunction C/g-C₃N₄ (CNCF1 or

118 CNCF2) with consequences on the band structure and electron transfer process and an
119 important improvement in the photocatalytic activity. As usual when designing a
120 nanocomposite, apart from the nature of the interaction between the components, their
121 mass ratio is an important factor. Prior experiments demonstrated that the optimum
122 mass ratio of the cellulose nanofiber/g-C₃N₄ is ~3–4 %; therefore, this ratio was
123 implemented throughout this study.

124

125 **2. Experimental**

126 *2.1 Materials and reagents*

127 Melamine (C₃H₆N₆; 99%), urea (CH₄N₂O; 99.5%), potassium dihydrogen
128 phosphate (KH₂PO₄; 99.5%), potassium hydrogen phosphate (K₂HPO₄; 99%),
129 N,N-Diethyl-p-phenylenediamine sulfate (DPD; 98%), horseradish peroxidase (POD;
130 enzymatic activity >160 units/mg), anhydrous ethanol (AR), 5,5-dimethyl-1-pyrroline
131 N-oxide (DMPO, 97%) were obtained from Aladdin Industrial Co., Ltd, China.
132 Cellulose nanofibers (1 wt% aqueous solution; average length: 1–3 μm, average width:
133 5–10 nm) was purchased from Guilin Qihong Technology Co., Ltd., China.
134 Polyethersulfone (PES) membrane (Ø 13 mm × 0.22 μm) was obtained from Jin Teng
135 Experimental Equipment Co., Ltd., Tianjin, China. All the chemical reagents
136 mentioned above were of analytical grade and were utilized without further
137 purification.

138

139 *2.2 Preparation of photocatalysts*

140 The g-C₃N₄ nanosheets were synthesized by a two-step pyrolysis treatment of
141 melamine and urea [51]. First, melamine (3.2 g) and urea (0.8 g) were uniformly
142 mixed and thoroughly ground in an agate mortar. The samples were placed into a
143 muffle furnace and heated to 500°C with a heating rate of 2°C min⁻¹ in static air and
144 left for 2 h; then, the temperature was risen to 520°C for 2 h at the heating rate of 2°C
145 min⁻¹. The residual yellow solids were ground into powder and calcined at 520°C for
146 4.5 h in air. Finally, the resultant light-yellow products with a productivity of 30%
147 were denoted as CN2. For comparison, g-C₃N₄ nanosheets from a single precursor

148 was also synthesized by calcining pure melamine through the same thermal treatment
149 and denoted as CN1, with a productivity of 36%.

150 The g-C₃N₄ composited with nanocarbon fibers was prepared by a one-step
151 thermal treatment of the compound of g-C₃N₄ and CNF. In brief, g-C₃N₄ nanosheets
152 (CN1 or CN2; 0.10 g) was added into 10 mL of deionized water containing a
153 suspension of CNF (0.33 g; CNF concentration 1 wt%) and ultrasonicated for 30 min,
154 as shown in Figure S1. Subsequently, the mixtures were vacuum-dried at 60°C for 12
155 h. Then, the residual white yellow solids were directly pyrolyzed at 500°C for 1 h at
156 the heating rate of 5°C min⁻¹ in argon atmosphere, marked as CNCF_x (x = 1, 2). The
157 final products (CNCF1 and CNCF2) obtained also retained the productivity of 80%
158 and 70%, respectively. The pure CNF were carbonized into cellulosic carbon fibers,
159 denoted as CF, under the same calcination conditions.

160

161 2.3 Characterization

162 The crystal structures of as-prepared samples were characterized using an X-ray
163 diffractometer (Rigaku, Ultima IV, Japan) with Cu K α radiation in the range between
164 5° and 80°. Fourier transform infrared (FTIR) spectra were recorded on a Bruker
165 VERTEX 70 spectrophotometer at the wavelength ranging from 400 to 4000 cm⁻¹.
166 The porosimetry measurements and BET-specific surface area of the samples was
167 detected by nitrogen adsorption/desorption on an adsorption apparatus (Micromeritics,
168 ASAP 2020, USA). The morphologies of the samples were observed using a scanning
169 electron microscope (Hitachi, SU8010, Japan) and transmission electron microscope
170 (JEOL, JEM-2100, Japan). The X-ray photoelectron spectrometer (XPS, ESCALAB
171 250, Thermo Scientific, USA) equipped with Al K α radiation monochromatic source
172 was used to detect chemical composition and elemental states. The ultraviolet
173 (UV)-vis diffuse reflectance spectra (UV-vis DRS) were obtained using a UV-vis
174 spectrophotometer (Cary 500, Varian, USA) in the range of 300–800 nm with BaSO₄
175 as a reflectance standard. Photoluminescence spectra were recorded on a LS55
176 spectrophotometer (Perkin-Elmer, USA) under the excitation wavelength of 365 nm at
177 room temperature. Time-resolved photoluminescence (TRPL) spectra were obtained
178 on a fluorescence spectrophotometer (FLS980, Edinburgh Instruments, UK).
179 Photo-generated ·O₂⁻ radical species in the photocatalytic process were detected with
180 DMPO as a trapping agent. The absorbance of hydrogen peroxide solution was

181 determined by UV–visible spectrophotometer (US-Vis, Agilent 8453, USA) at the
182 wavelength 551 nm.

183 *2.4 Photoelectrochemical and electrochemical measurement*

184 The transient photocurrent curves and electrochemical impedance spectroscopy
185 were obtained on CHI660-E electrochemical workstation (Chenhua Instrument
186 Company, Shanghai, China) based on a three-electrode cell composed of Pt wire as
187 the counter electrode, Ag/AgCl electrode as the reference electrode, and
188 fluorine-doped tin oxide (FTO) glass ($1 \times 1 \text{ cm}^2$) as the working electrode. Na_2SO_4
189 aqueous solution (0.2 mol/L) was used as the electrolyte. Five milligrams of the
190 sample (CNx or CNCFx) was added to 1 mL of Nafion solution (0.5%) under
191 ultrasonication for 30 min, and then deposited onto the FTO glass. The as-prepared
192 working electrode was dried at 80°C for 3 h. The photoelectrochemical measurement
193 was performed under visible light irradiation (Xe arc lamp: 300 W, the distance
194 between the surface of the solution and light filter: 10 cm, filter wavelength: $\lambda > 420$
195 nm). The transient photocurrent was collected with the light on and off. The
196 electrochemical impedance spectroscopy (EIS) was tested at the frequency of 0.01
197 and 10^6 Hz with the alternating current amplitude of 5 mV.

198 Rotating disk electrode (RDE) tests were also taken on a CHI660-E
199 electrochemical workstation with a modulated speed rotator and a glassy carbon disk
200 electrode (working electrode). The Ag/AgCl electrode and Pt wire electrode were
201 used as the reference electrode and counter electrode, respectively. Two milligrams of
202 the photocatalyst was dispersed into 1 mL of Nafion solution (10%) under
203 ultrasonication for 30 min. Then, 10 μL of the suspension was dropped on a glassy
204 carbon electrode with a diameter of 5 mm and air-dried at room temperature as the
205 working electrode. The linear sweep voltammetry (LSV) curves were obtained using a
206 phosphate buffer solution (0.1 mmol/L; pH 7) with O_2 -saturated purging at a scanning
207 rate of 10 mV/s and the rotating speed between 0 and 2500 rpm.

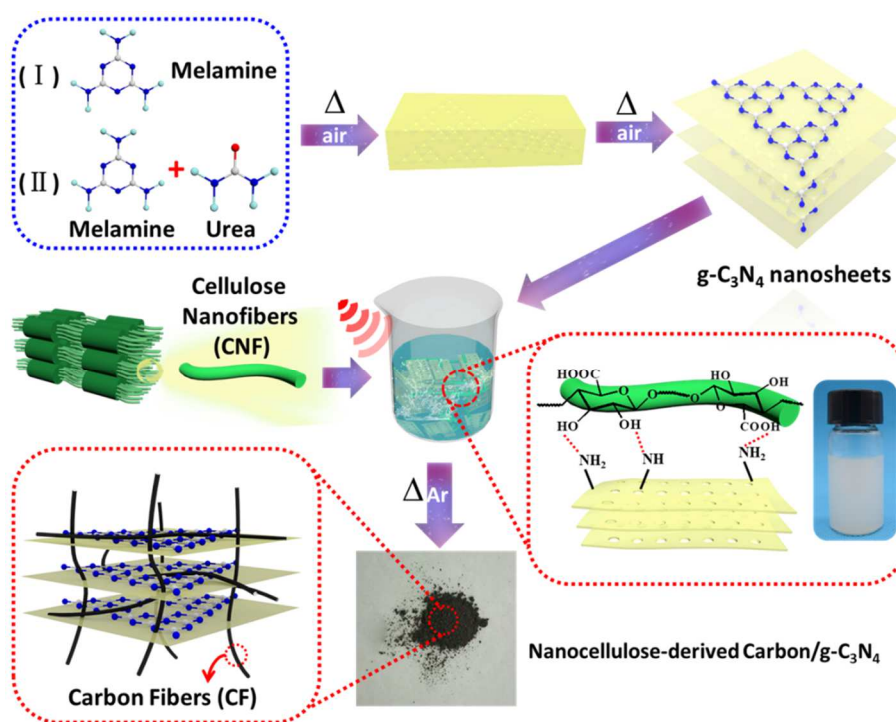
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209 *2.5 Photocatalytic activity measurements*

210 For evaluating the photocatalytic H_2O_2 generation, the catalyst powder (50 mg)
211 was dispersed in a solution of deionized water (45 mL) and ethanol (5 mL). Then, the
212 suspension was ultrasonicated for 5 min and purged with O_2 gas for 30 min prior to
213 visible irradiation. Then, the photocatalytic performance was examined under visible

214 light irradiation (Xe arc lamp: 300 W, the distance between surface of the solution and
215 light filter: 10 cm, filter wavelength: $\lambda > 420$ nm) with continuous O₂ purging and
216 stirring for 6 h. Every hour, an aliquot of the suspension (4 mL) was taken and filtered
217 to remove the catalysts. The concentration of H₂O₂ was measured by a colorimetric
218 method. To this end, 5 mL of the filtered solution was immediately mixed with 0.5
219 mL of phosphate buffer (0.5 M K₂HPO₄ and 0.5 M KH₂PO₄), DPD solution (50 μ L),
220 and peroxidase (50 μ L), with vigorous shaking for 30 s. Then, the absorbance of the
221 aqueous solution was measured at 551 nm using a UV-visible spectrophotometer
222 [52].

223 The decomposition behavior of H₂O₂ with photocatalysts was investigated by
224 adding 50 mg of the samples to 50 mL of H₂O₂ solution (1 mmol/L) with continuous
225 stirring under visible light irradiation for 1 h. The stability of the as-prepared samples
226 was evaluated by performing three consecutive tests. When finishing each run, the
227 photocatalyst was collected using membrane filtration and washed with deionized
228 water, then vacuum-dried at 50°C overnight, finally reused in the next cycle under the
229 same conditions. Photocatalytic H₂O₂ concentration was also investigated by
230 measuring the absorbance of the filtrate according to the Beer-Lambert law [52].



231

232

Scheme 1. Procedures for sample synthesis

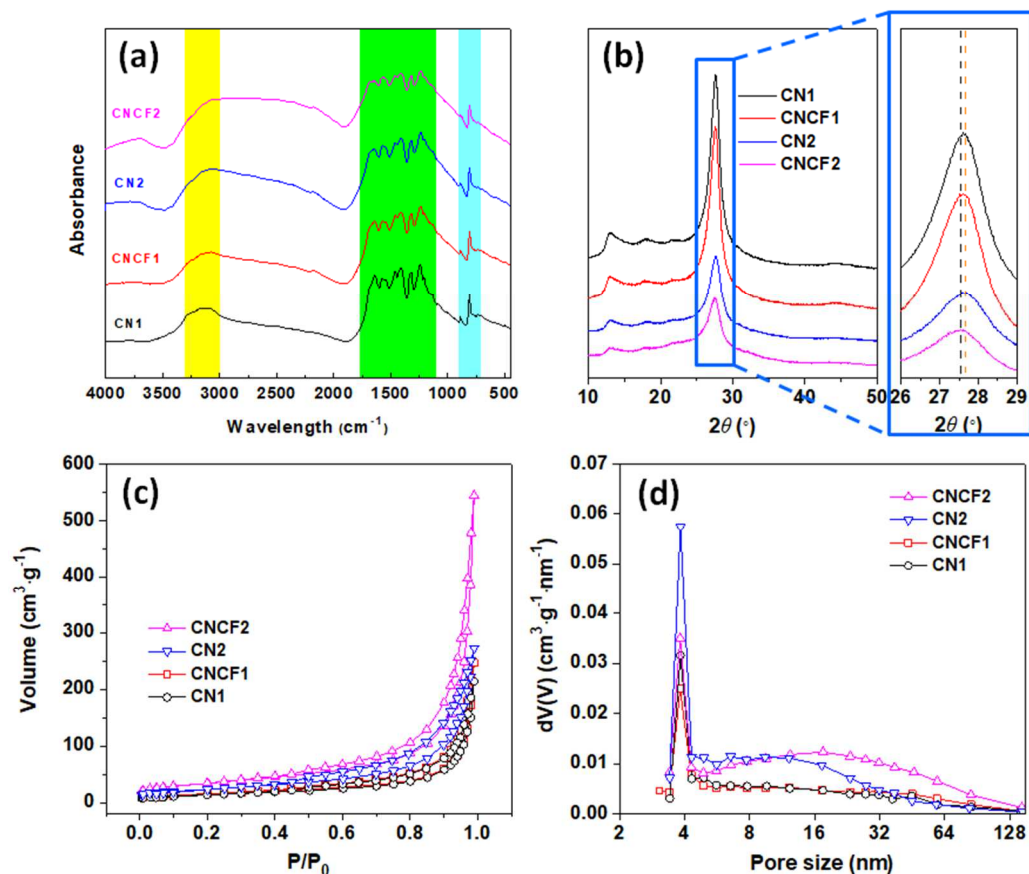
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234 **3. Results and discussion**

235 **3.1 Photocatalyst preparation and characterization**

236 Specific surface area is important for the activity of a photocatalyst; therefore, a
237 bi-component approach was selected to prepare g-C₃N₄ with the highest possible
238 surface area [53, 54]. Urea was used as an additive to melamine owing to the release
239 of large quantities of volatile gas during thermal treatment, resulting in high porosity
240 [55, 56]. It also can generate a high quantity of residual amino groups, generally on
241 the edges of the nanosheets. Because CNF have surface -OH and -COOH groups,
242 H-bonding and formation of amide or ester groups can occur through reactions with
243 amino-rich carbon nitride. For comparison, a g-C₃N₄ was prepared by the
244 mono-component approach using only melamine, which is referred to as CN1. A
245 comparison between the dispersal behaviors of CN1 and CN2 with CNF in aqueous
246 phase is shown in Figure S1, suggesting a higher stabilization of the suspension in the
247 case of CNF/CN2 mixture.

248 Carbonization at 500°C of the CNF/CN1 and CNF/CN2 mixtures transforms
249 their CNF into carbon, generating porosity throughout the materials and modifying
250 the hydrophilic/hydrophobic balance of the surface in the corresponding CNCF1 and
251 CNCF2, as shown in Figure S2. The results show that the CN2 (from dual precursors)
252 was more hydrophilic than CN1 (from single precursor) owing to the presence of
253 more hydrophilic groups (amino groups) in CN2. Moreover, the contact angles of
254 CN1 (24.5°) and CN2 (20.5°) respectively decreased to 17.6° (CNCF1) and 11°
255 (CNCF2) when g-C₃N₄ assembled with the carbon nanofibers pyrolyzed from
256 nanocellulose was used, because of the increase in the stacking distance in g-C₃N₄.
257 The optimized mass ratio of CNF/g-C₃N₄ is ~3.3 wt%, which is a miniscule quantity
258 of CNF, but as shown below, it has a substantial effect on the photocatalytic
259 performance compared with pure carbon nitride. Moreover, the sample yield is ~70–
260 80% and with cheap and renewable products. This weight loss is attributed to the
261 decomposition of cellulose and also the condensation reaction between the surface
262 functional groups of cellulose and g-C₃N₄.



263

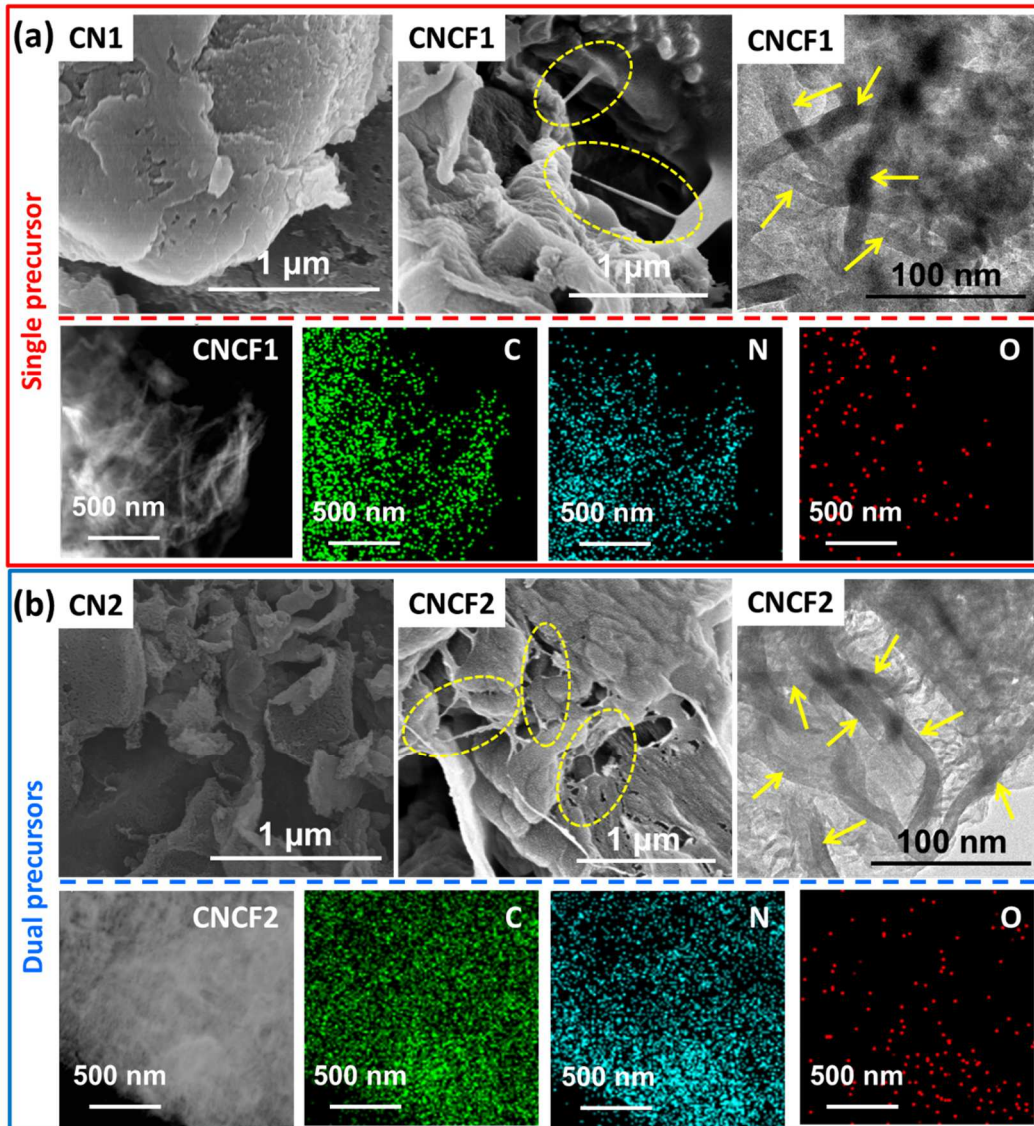
264 **Figure 1.** Fourier transform infrared spectroscopy curves (a), X-ray diffraction patterns (b), N_2
 265 adsorption-desorption isotherms (c) and pore size distribution derived from desorption isotherm (d)
 266 of CN1, CN2, CNCF1, and CNCF2.

267

268 The generation of carbon results in an important modification of the color of the
 269 material from slightly yellow for pure carbon nitride (CN1 and CN2) to gray for
 270 CNCF1 and CNCF2, as shown in Figure S3. Analyzed by FT-IR (Figure 1a), all
 271 spectra of CN_x and $CNCF_x$ ($x = 1, 2$) are dominated by the signals related to the
 272 presence of $g-C_3N_4$. Several strong bands in the $1200\text{--}1600\text{ cm}^{-1}$ region were typical
 273 for the stretching modes of the CN heterocycles [57]. The sharp peak at 810 cm^{-1}
 274 corresponds to the characteristic breathing vibration of tri-s-triazine units [58]. The
 275 broad bands ranging from 3000 cm^{-1} to 3300 cm^{-1} correspond to the NH and OH
 276 stretching vibrations [59]. The peak intensity of $-NH_x$ between 3000 cm^{-1} and 3300
 277 cm^{-1} in CNCF1 and CNCF2 is slightly lower than that of CN1 and CN2, respectively;
 278 it implies a decrease in the number of amino groups [60].

279 The presence of g-C₃N₄ was also clearly detected in the signals observed in the
280 X-ray diffraction powder patterns of the CN_x and CNCF_x samples, as shown in
281 Figure 1b. The two characteristic peaks at $2\theta = 12.9^\circ$ and 27.5° are ascribed to the
282 (100) and (002) diffraction planes of the in-plane repeat tri-s-triazine units and the
283 interlayer stacking reflection of conjugated aromatic segments, respectively [61-63].
284 A slight downshift in the position of the (002) crystal plane was detected when
285 comparing CN1 and CN2 and CNCF_x. It corresponds to a very small increase in the
286 stacking distance in g-C₃N₄ when assembled with the carbon nanofibers [64], possibly
287 owing to the intercalation of organic species during pyrolysis. A weaker peak intensity
288 of (002) was noted for CN2 and CNCF2 than for CN1 and CNCF1, respectively,
289 which may be ascribed to the effective exfoliation of g-C₃N₄ into sheet-like structures
290 by overcoming the weak van der Waals forces between layers in the calcination
291 process; this finding is consistent with other reports on g-C₃N₄ [65].

292 Porosity of the materials was determined by N₂ adsorption-desorption with the
293 isotherms shown in Figure 1c. All samples exhibited typical type IV isotherms with
294 H3 type hysteresis loops, indicating that the samples were micro-, meso-, and slightly
295 macroporous with a specific surface area of 50 m² g⁻¹ (CN1), 55 m² g⁻¹ (CNCF1), 83
296 m² g⁻¹ (CN2), and 120 m² g⁻¹ (CNCF2). The data emphasize the effect of CNF in
297 addition to the preparation method of g-C₃N₄. CN2 and CNCF2 exhibited 1.5–2.4
298 times higher BET SSA than CN1 and CNCF1 (Table S1). An increase was also
299 observed for the average pore volume, calculated to be 0.34 m³ g⁻¹ (CN1), 0.39 m³ g⁻¹
300 (CNCF1), 0.44 m³ g⁻¹ (CN2), and 0.85 m³ g⁻¹ (CNCF2; Table S1). Clearly, the
301 bi-component route results in materials with enhanced porosity that is ascribed to a
302 higher proportion of CO₂ and NH₃ release during calcination [66]. Notably, the
303 assembly of CNF with CN1 or CN2 leads to a decrease in the number of small
304 mesopores and an increase in the number of large mesopores increased, which is
305 expected when considering the formation of carbonaceous residue upon pyrolysis of
306 CNF (Figure 1d).



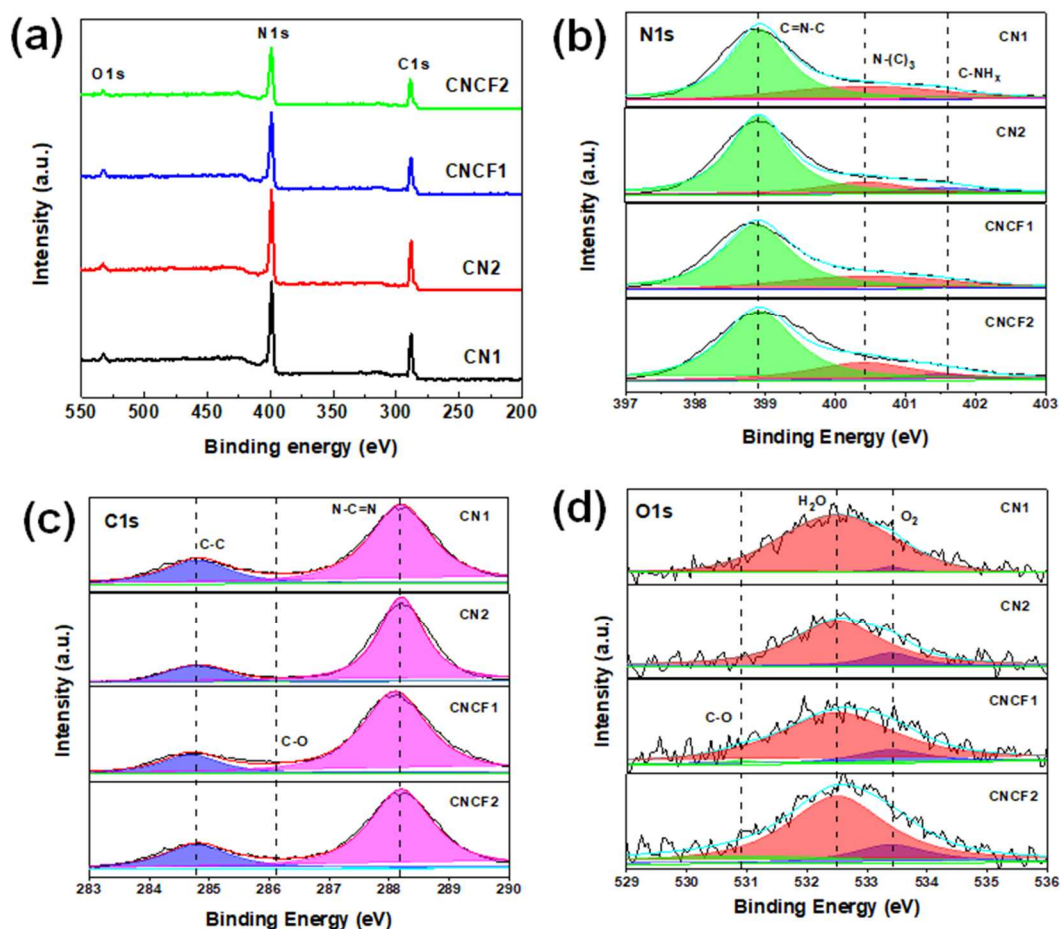
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308 **Figure 2.** Scanning electron microscopy (SEM) images of CN1 and CNCF1; transmission
 309 electron microscopy (TEM) and TEM mapping of CNCF1 (a), SEM images of CN2 and CNCF2;
 310 TEM and TEM mapping of CNCF2 (b).

311

312 Scanning electron microscopy (SEM) and transmission electron microscopy
 313 (TEM) revealed the morphology and microstructure of CN_x and CNCF_x (x = 1 or 2).
 314 As shown in Figure 2, CN1 and CN2 are mainly composed of stacked irregular
 315 nanosheets. Compared with CN1, a thinner sheet-like structure was obtained for CN2
 316 upon calcination. For samples after pyrolysis (CNCF1 and CNCF2), carbon
 317 nanofibers with an average length of 0.1–1 μm were identified on top of or between
 318 micron-sized layers of carbon nitride. Sheet-like carbon nitride particles of 8–12 μm

319 width were observed by TEM (Figure 2), suggesting that the assembly also occurs at
 320 the nanometer scale because isolated carbon nanofibers $\varnothing \approx 10\text{--}20$ nm were identified.
 321 This clearly showcases the integration of the CNF within the $g\text{-C}_3\text{N}_4$ during the
 322 assembly prior to pyrolysis. Elemental mapping by TEM shows that C and N, the two
 323 main elements of carbon nitride, are uniformly spread in CNCF1 and CNCF2, and
 324 only traces of oxygen are likewise distributed (Figure 2).



325
 326 **Figure 3.** X-ray photoelectron spectroscopy data of CN1, CN2, CNCF1, and CNCF2 samples:
 327 survey scan (a), core spectra with deconvolution for N1s (b), C1s (c), and O1s (d).

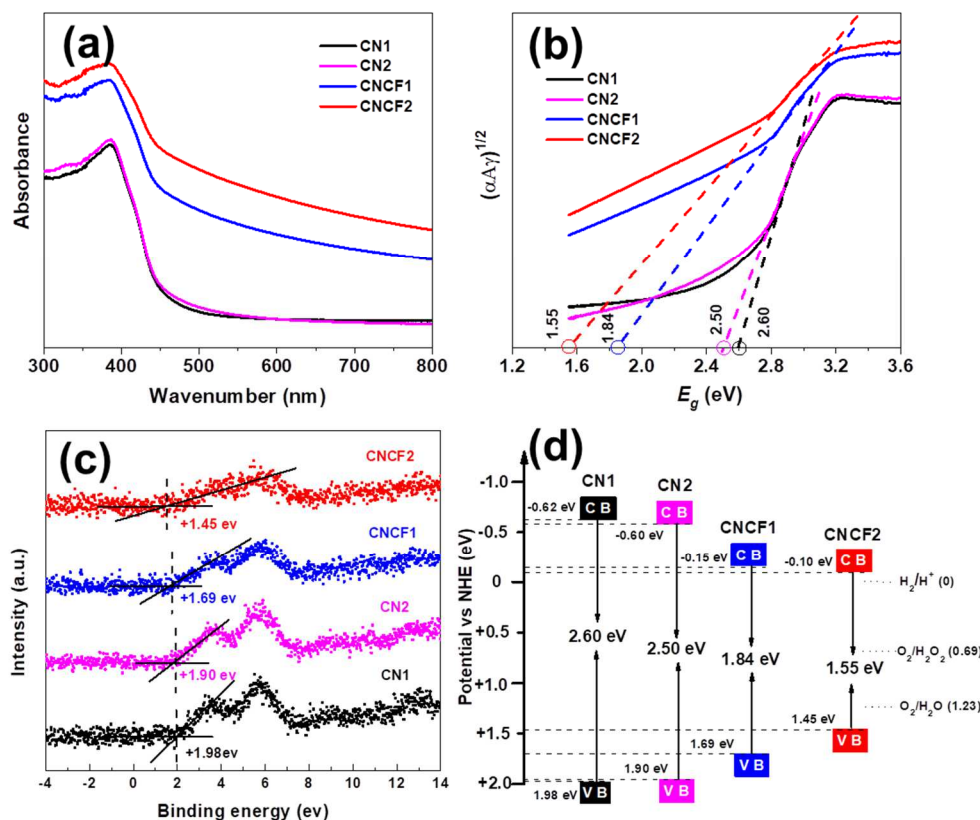
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329 X-ray photoelectron spectroscopy (XPS) allowed us to identify the composition
 330 and chemical status of the main elements in the samples (Figure 3). As shown in
 331 Figure 3a, similar X-ray photoelectron spectra were recorded for the four samples
 332 exhibiting the two peaks expected for $g\text{-C}_3\text{N}_4$, namely N 1s and C 1s and a weak
 333 signal of O 1s [67]. For N 1s spectra in Figure 3b, the three peaks at 398.9, 400.4, and

334 401.5 eV are assigned to sp^2 -hybridized nitrogen (C=N-C), tertiary nitrogen (N-(C_x)₃)
335 and C-NH_x, respectively [41]. An estimate of the relative proportion of the different
336 species was obtained by deconvolution (Table S2). It appears that the percentage of
337 C-NH_x either in CN2 or CNCF2 prepared by the bi-component route is considerably
338 higher than that for the materials prepared by the mono-component route (CN1 and
339 CNCF1). This is an additional indication of the effect of the urea precursor during the
340 formation of the materials, and it is consistent with the FT-IR data [68] (Figure 1a).
341 Moreover, the content of C-NH_x decreased after g-C₃N₄ was assembled and pyrolyzed
342 with CNF, a possible explanation being the reaction of this amino group with the
343 functional groups of cellulose (hydroxyl and carboxylic group) during assembly or
344 with gaseous products issued from the decomposition of cellulose during pyrolysis.

345 In Figure 3c, C 1s spectrum could be deconvoluted into two peaks at 284.8 and
346 288.2 eV. The peak at 288.2 eV represents by far the highest proportion of C species
347 and was attributed to sp^2 -hybridized carbon covalently bound by N atom (N=C-N), as
348 expected for g-C₃N₄. The peak at 284.8 eV was assigned to C-C carbon species [69],
349 both routes of preparation led to a similar quantity of this species, indicating the
350 presence of carbonaceous residue. With the assembly and pyrolysis of CNF, the
351 content of N-C=N decreased by a few percent and that of C-C increased by 10% for
352 CNCF1, which is expected because the pyrolysis of CNF leads to the formation of
353 carbonaceous char that can adsorb on the surface of g-C₃N₄. However, this increase
354 was not observed when comparing CN2 and CNCF2 and is attributable to a higher
355 integration of the carbon fiber into the sheet-like structure of g-C₃N₄. C 1s XPS data
356 also revealed a peak at 286.1 eV for CNCF1 and CNCF2, which was ascribed to C-O
357 [70] that likely results from the assembly and pyrolysis with CNF, which generates
358 O-containing carbon as observed in carbon-derived polysaccharides [71]. However,
359 different routes of preparation resulted in different C-O content: 1–2% in CNCF1
360 versus 4–5 % for CNCF2. Concerning oxygen, the high-resolution O 1s spectra was
361 fitted based on two reference peaks centered at binding energies of 533.4 eV and
362 532.5 eV for adsorbed O₂ and adsorbed H₂O, respectively [72]. Compared with the
363 as-prepared g-C₃N₄ samples CN1 and CN2, the new peak at 530.9 eV in

364 CNF-modified g-C₃N₄ samples (CNCF1 and CNCF2) was ascribed to C-O [73].
 365 These data are consistent with the C-O content observed on the C1 XPS spectra, the
 366 proportion of O in C-O species being 1–2% in CNCF1 and 3–4 % in CNCF2.

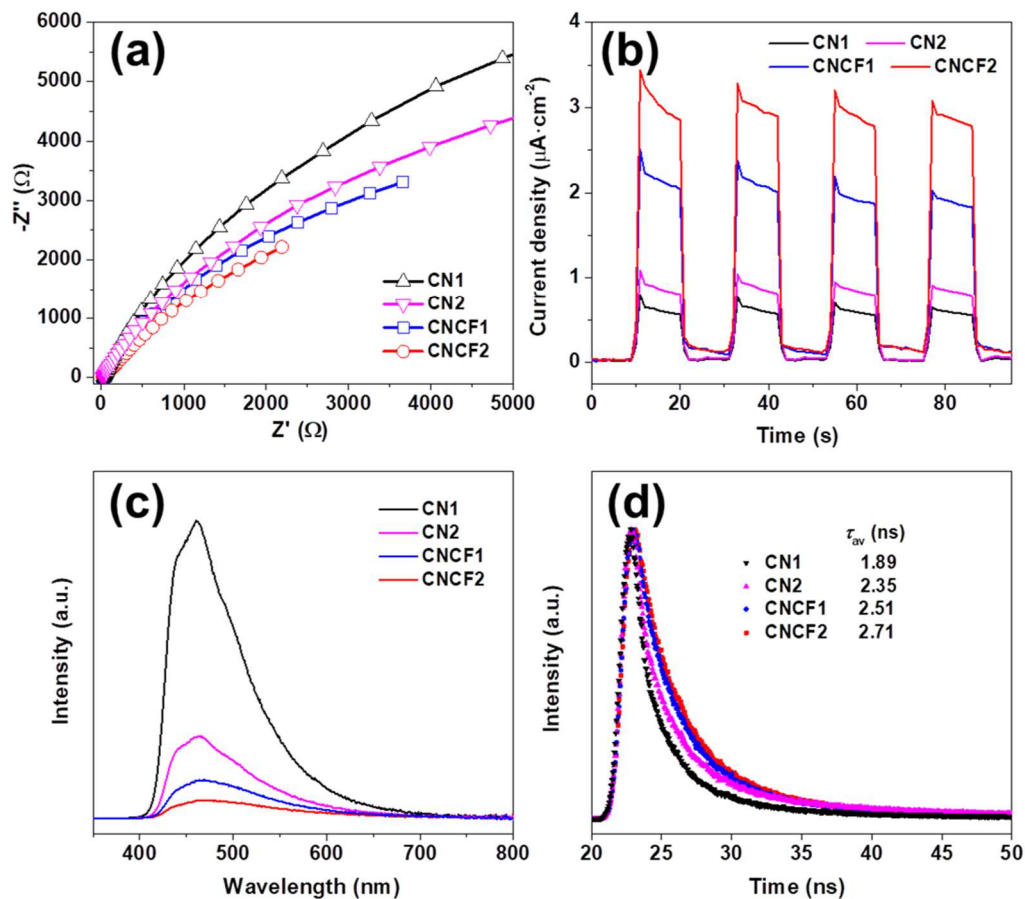


367
 368 **Figure 4.** For CN1, CN2, CNCF1, and CNCF2: characterization by UV-vis DRS spectra (a),
 369 determination of the band gaps (b), determination of VB XPS spectra (c), and energy band
 370 structures (d)

371

372 To investigate the optical absorption and band structures, UV–visible diffuse
 373 reflectance spectra (UV-vis DRS) of the samples were recorded (Figure 4a). All
 374 samples presented absorption in the blue region typical of the 2D structure of carbon
 375 nitride [74]. However, compared with CN1 and CN2, the absorption intensity of both
 376 CNCF1 and CNCF2 was significantly increased owing to the presence of carbon
 377 fibers and multiple reflection of incident ray light across porous structures and band
 378 structure regulation [75]. The corresponding band gaps determined from Tauc's plots
 379 were 2.60, 2.50, 1.84, and 1.55 eV for CN1, CN2, CNCF1, and CNCF2, respectively

380 (Figure 4b). Therefore, the CNCF1 and CNCF2 samples exhibited a narrower band
381 gap than other samples and consequently higher absorption of visible light useful in
382 photogenerating carriers. The band structures of different samples were further
383 investigated by VB XPS spectra as shown in Figure 4c. An additional effect of the
384 presence of carbon fibers is the variation of the VB potential; values for CN1 (1.98 eV)
385 and CN2 (1.90 eV) were decreased for CNCF1 (1.69 eV) and CNCF2 (1.45 eV). A
386 decrease in the VB potential is beneficial in narrowing the band gap and decreasing
387 the generation of $\cdot\text{OH}$ because of the decreased oxidation ability. Combining the VB
388 XPS spectra (Figure 4c), the location of VB and CB bands was determined using the
389 formula $E_g = E_{\text{VB}} - E_{\text{CB}}$ (where E_g : band gap, E_{VB} : VB value, E_{CB} : CB value; Figure
390 4d). The E_g of CNCF1 and CNCF2 was smaller than that of CN1 and CN2,
391 respectively. Importantly, the E_g is the smallest for CNCF2, which also has a more
392 positive CB level (-0.1 eV vs NHE) than other samples, which is 0.79 eV more
393 negative than the reduction potential of $\text{O}_2/\text{H}_2\text{O}_2$ (0.69 eV) and large enough to reduce
394 O_2 to H_2O_2 [76]. Moreover, the positive shift of CB could easily trigger
395 photogenerated electrons from CB, accepting electrons from carbon fibers and
396 enhancing the two-electron reduction of O_2 to H_2O_2 [77, 78].



397

398 **Figure 5.** Electrochemical impedance spectra: Nyquist plots (a), transient photocurrent response
 399 curves (b), photoluminescence spectra (c), time-resolved photoluminescence decay spectra (d) of
 400 the samples.

401

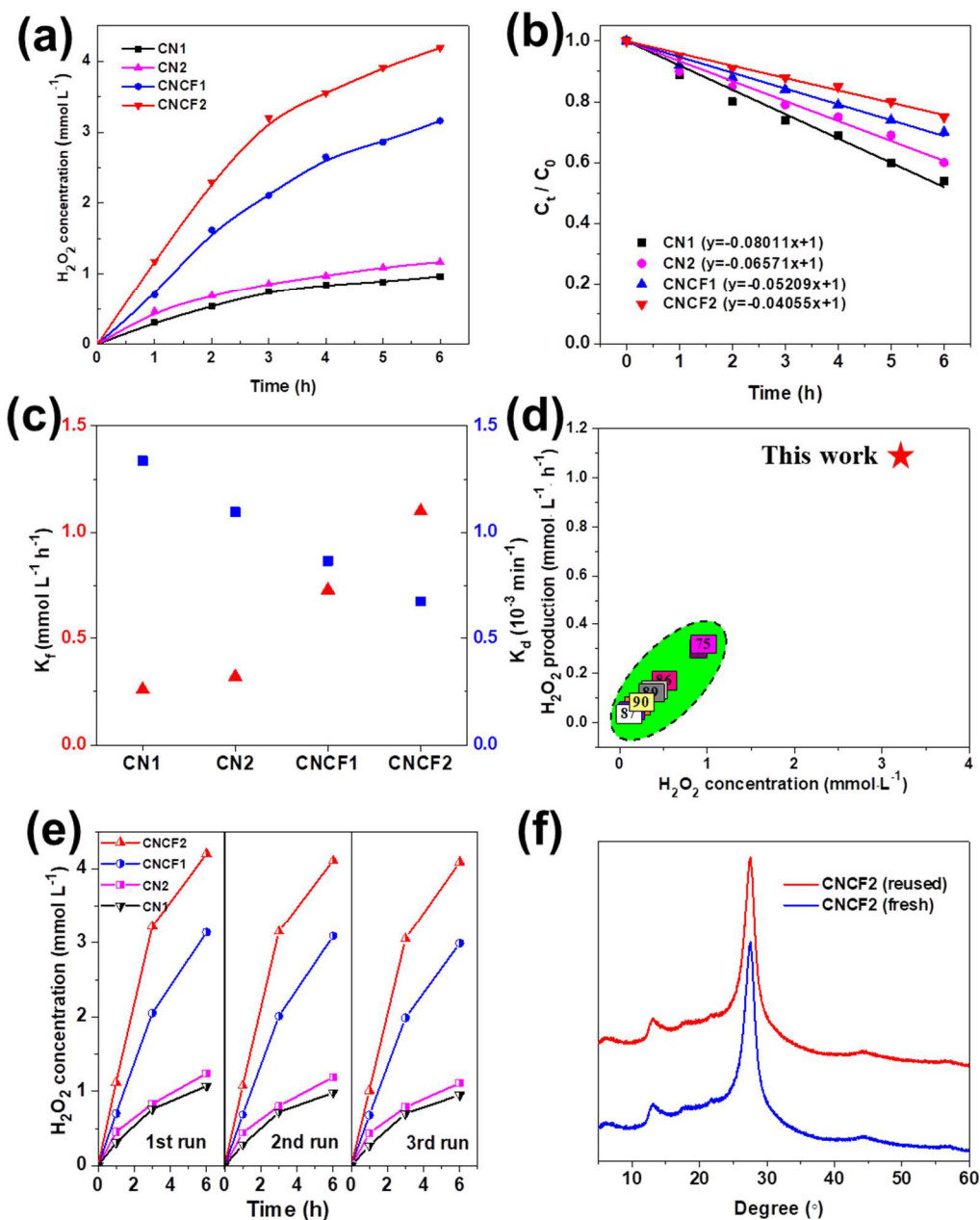
402 Electrochemical impedance spectroscopy (EIS) was further employed to
 403 understand the charge separation and their transfer. As shown in Figure 5a, the
 404 Nyquist plots revealed that under visible light irradiation, the observed arc radius of
 405 CNCF_x is smaller than the corresponding CN_x, which indicates that the charge
 406 transfer resistance of CNCF_x is significantly decreased. This is ascribed to the
 407 introduction of carbon nanofibers and carbonaceous residue that enhance electron
 408 transfer. The smaller arc radius of CNCF₂ than CNCF₁ indicates a faster charge
 409 transfer and a better efficiency of electron–hole separation. The transient photocurrent
 410 curves under visible light irradiation of the as-prepared samples are shown in Figure
 411 5b. CNCF₁ and CNCF₂ displayed much higher photocurrent than that of CN1 and
 412 CN2, confirming that carbon fibers derived from nanocellulose accelerate electron

413 transfer. The recombination/separation of photogenerated species was investigated by
414 photoluminescence (PL) spectra of the samples (Figure 5c). As a general trend, the
415 lower the photoluminescence peak intensity, the higher the efficiency of
416 photogenerated electron-hole pairs. The strong fluorescence emission peaks of CN1
417 (462 nm) and CN2 (466 nm) were slightly red shifted to 470 nm and 469 nm for
418 CNCF1 and CNCF2, respectively, which further confirms the band gap decrease [79].
419 CNCF1 and CNCF2 samples had considerably lower photoluminescence intensities
420 than CN1 and CN2, respectively, suggesting better separation rate of electrons and
421 holes. Moreover, it is worth noting that the photoluminescence quenching efficiency
422 of CNCF2 was lower than CNCF1, suggesting more effective electron transfer from
423 photogenerated g-C₃N₄ to nanocarbon fibers [74]. To obtain the average radiative
424 lifetime of the recombining charge carriers, time-resolved photoluminescence (TRPL)
425 characterization was investigated (Figure 5d). The average radiative lifetime (τ_{ave}) was
426 further calculated according to the following equation: $\tau_{ave} = (B_1\tau_1^2 + B_2\tau_2^2)/(B_1\tau_1 +$
427 $B_2\tau_2)$. The value of τ_{ave} for CN1 and CN2 was 1.89 and 2.35 ns, respectively, whereas
428 that for CNCF1 and CNCF2 was 2.51 and 2.71 ns, respectively. This result indicated
429 that, with the addition of carbon fibers derived from nanocellulose, the markedly
430 extended lifetime of photogenerated charge carriers accelerates the charge separation
431 efficiency. In summary, the presence of cellulose-derived carbon fibers assembled
432 with g-C₃N₄ highly improved the efficiency of the photocatalysts in promoting charge
433 transfer and carrier separation in g-C₃N₄.

434

435

436 **3.2 Photocatalytic production of H₂O₂**



437

438 **Figure 6.** Photocatalytic production of H₂O₂ as a function of time under visible light with CN1,

439 CN2, CNCF1, and CNCF2 as photocatalysts (a); photocatalytic decomposition of H₂O₂ under

440 visible light irradiation (b); formation rate (K_f) and decomposition rate constant (K_d) for H₂O₂

441 photocatalytic production (c); comparison of reported photocatalytic performances (photocatalytic

442 production rate of H₂O₂ within 3h and H₂O₂ concentration after 3h reaction) (d); reusability

443 assessment of the different photocatalysts (e); X-ray diffraction patterns of CNCF2 before and

444 after photocatalytic H₂O₂ production (f)

445

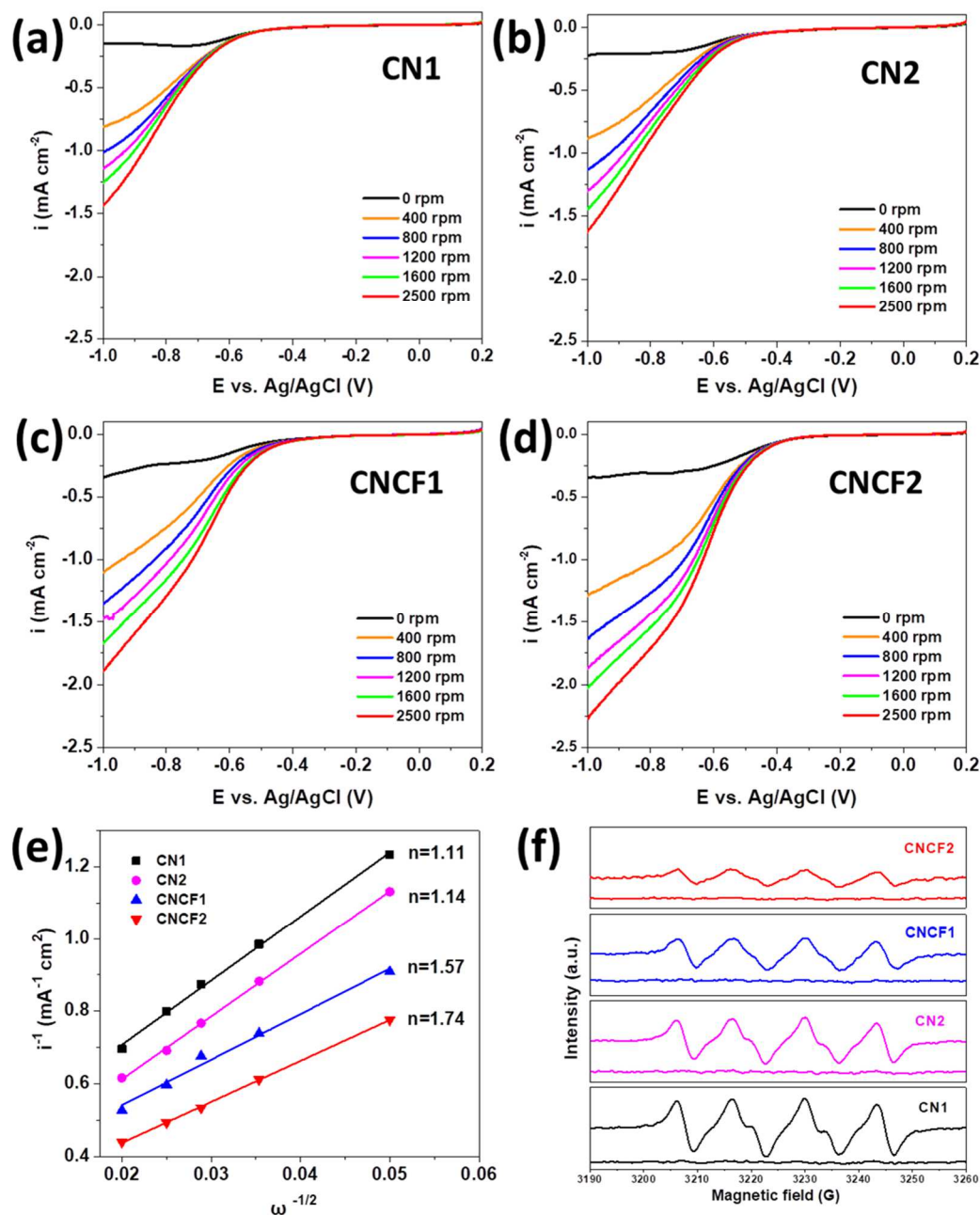
446 Photocatalytic production of H₂O₂ under visible light irradiation was evaluated
447 by measuring the quantity of H₂O₂ versus time of reaction under atmospheric pressure
448 at 25 ± 0.1°C using a catalyst concentration of 1.00 ± 0.01 g L⁻¹ (Figure 6a). Because
449 ethanol is known to have a good effect on photocatalytic H₂O₂ production when used
450 as a proton donor (Figure S4), 5 mL (85.9 mmol) ethanol was used in this
451 photocatalytic system with an ethanol-to-water ratio of 1: 9 (v/v). With CN1, only
452 0.31 mmol L⁻¹ of H₂O₂ is formed after 1 h. Although the productivity is improved
453 with CN2, it remains low: 0.47 mmol L⁻¹ of H₂O₂ after 1 h. CNCF1 and CNCF2
454 presented a considerably higher H₂O₂ productivity after 1 h, 0.7 mmol L⁻¹ and 1.18
455 mmol L⁻¹, respectively. Therefore, the kinetic study presented in Figure 6c suggests
456 that the order of photocatalytic efficiency is as follows: CNCF2 > CNCF1 > CN2 >
457 CN1.

458 The decomposition behavior of H₂O₂ was investigated under visible light
459 irradiation with photocatalysts and a H₂O₂ concentration = 1 mmol L⁻¹. As shown in
460 Figure 6b, the level of H₂O₂ decomposition was ~8% and ~5% with CNCF1 and
461 CNCF2, respectively, after 1 h of visible light irradiation, which was lower than that
462 with CN1 and CN2 (~10%). The H₂O₂ decomposition rate constant (K_d) was
463 calculated with the following equation: $K_d = -\ln(C_t/C_0)/t$, where C_t is the H₂O₂
464 concentration at time t , and C_0 is the initial concentration of H₂O₂ (1 mmol L⁻¹).
465 Figure 6c shows that the K_d of CN1 ($1.335 \times 10^{-3} \text{ min}^{-1}$) and CN2 ($1.095 \times 10^{-3} \text{ min}^{-1}$)
466 was higher than that of CNCF1 ($0.868 \times 10^{-3} \text{ min}^{-1}$) and CNCF2 ($0.676 \times 10^{-3} \text{ min}^{-1}$).
467 These results confirm that carbon fibers derived from nanocellulose effectively inhibit
468 the decomposition of H₂O₂ on carbon nitride.

469 Compared with previously reported values [7, 75, 80-86], the photocatalyst
470 CNCF2 presented a significantly improved activity (Figure 6d). To investigate the
471 recyclability of the as-prepared photocatalysts, after 6 h of reaction time, the catalyst
472 was separated and washed from the suspension by filtration and then used again in a
473 new batch of H₂O₂ production under the same conditions (Figure 6e). After three
474 cycles, the photocatalyst was almost unchanged and the photocatalytic activity was

475 maintained. The X-ray diffraction analysis showed that both the fresh and reused
476 CNCF2 catalysts exhibited almost the same typical peaks, as shown in Figure 6f.

477



478

479 **Figure 7.** Linear sweep voltammetry curves of CN1 (a), CN2 (b), CNCF1 (c) and CNCF2 (d)
480 measured on a rotating disk electrode at different rotating speeds; Koutecky-Levich plots of the
481 data obtained at a constant electrode potential (-1.0 V vs. Ag/AgCl) (e), Electron paramagnetic
482 resonance spectra of the DMPO- O_2^- adduct (f)

483

484 To further investigate the O₂ reduction pathway, a rotating disk electrode (RDE)
485 analysis of the O₂ reduction reaction (ORR) was performed. The linear sweep
486 voltammetry (LSV) curves in Figure 7a-d for the as-prepared samples were measured
487 by an RDE in phosphate buffer solution (0.1 mol L⁻¹, pH = 7) at different rotating
488 speeds. The Koutecky-Levich plots derived from the LSV data are presented in Figure
489 7e. The average number of transfer electrons was calculated using the following
490 equations:

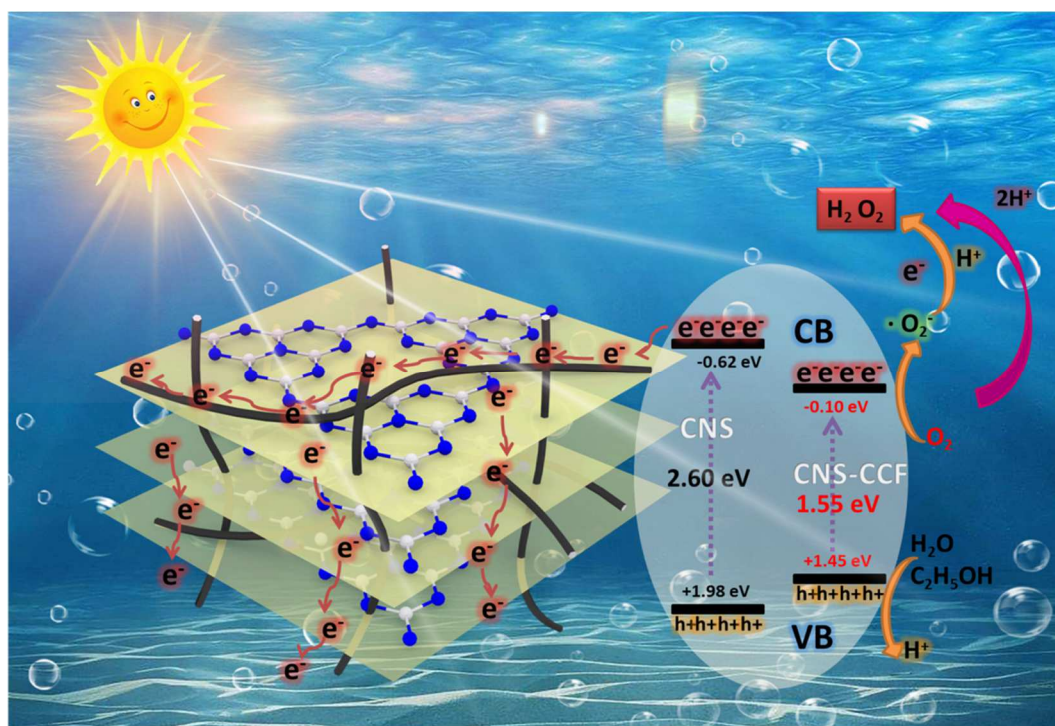
$$j^{-1} = j_k^{-1} + B^{-1}\omega^{-1/2}$$

$$B = 0.2nF\nu^{-1/6}CD^{2/3}$$

493 , where j is the current density, j_k is the kinetic current density, ω is the rotating speed,
494 F is the Faraday constant (96485 C mol⁻¹), ν is the kinetic viscosity of water (0.01 cm²
495 s⁻¹), and C is the O₂ concentration in water (1.26 × 10⁻⁵ mol cm⁻³). The average number
496 of electrons (n) was 1.11 and 1.14 for CN1 and CN2, respectively, and 1.57 and 1.74
497 for CNCF1 and CNCF2, respectively. These results suggest that single-electron O₂
498 reduction occurs on CN1 and CN2 because the n value of CN1 and CN2 was
499 approximately 1. In contrast, the average number of electrons is above 1.5 when
500 nanocellulose-derived carbon is present, especially for CNCF2, for which an O₂
501 reduction by two-electron process is likely. Thus, the ORR for CNCF1 and CNCF2
502 had a hybrid single/two-electron function, whereas that for CN1 and CN2 showed
503 only single-electron function.

504 Electron paramagnetic resonance (EPR) analysis with DMPO as a trapping agent
505 of ·O₂⁻ was performed to identify the pathway of conversion of molecular oxygen to
506 H₂O₂. As shown in Figure 7f, the characteristic peaks of DMPO·O₂⁻ were observed in
507 all samples, indicating that ·O₂⁻ was generated as an intermediate in the formation of
508 H₂O₂. As seen in Figure 7f, CN1 and CN2 both presented higher-intensity EPR
509 signals than CNCF1 and CNCF2, indicating that CN1 and CN2 generate more ·O₂⁻
510 than CNCF1 and CNCF2. The finding implies that reduction of O₂ into ·O₂⁻ occurs on
511 the four samples by a single-electron pathway leading to H₂O₂ formation. It is
512 interesting that, CNCF1 and CNCF2 present partial O₂ directly reduction into H₂O₂
513 by a two-electron pathway[87]. Scheme 2 illustrates photocatalytic H₂O₂ production

514 by nanocellulose-derived C/g-C₃N₄ nano-heterojunction. Cellulose nanofibers with
 515 -OH and -COOH groups can bind to carbon nitride with intrinsic amino groups (-NH,
 516 -NH₂) and thermally transform into an effective heterojunction, increasing the linking
 517 between g-C₃N₄ nanosheets and carbon fibers. Furthermore, the carbon fibers reduce
 518 the band gap and greatly increase the electron transfer during the photocatalytic
 519 reaction. The photocatalytic efficiency also depends on the capacity and strength of
 520 adsorption of molecular oxygen onto the surface of carbon nitride. By porosimetric,
 521 BET SSA of CN2 is 2.2 times higher than that of CN1 (Table S1), which provides
 522 more space and active sites to adsorb oxygen molecules [88]. The adsorption strength
 523 of molecular oxygen is also potentially reinforced by the presence of N atoms of
 524 amino groups in CN2, which are able to bind to oxygen as a Lewis acid [89]. As
 525 previously reported, such adsorption of oxygen on the surface of the photocatalyst
 526 catalyst is highly beneficial to the electron transfer [90]. An exciting point is to
 527 observe that with the presence of carbon nanofiber, the EPR intensity of $\cdot\text{O}_2^-$
 528 CNCF1 is higher than CNCF2. The data demonstrate the interest of the bi-component
 529 synthetic route chosen for the preparation of the g-C₃N₄. This is ascribed to both the
 530 larger BET specific surface area and the specific photophysical properties.



531

532 **Scheme 2.** Role of cellulosic carbon fibers for photocatalytic H₂O₂ production photocatalyzed by
533 a nanocellulose-derived carbon/g-C₃N₄ nanocomposite.

534

535 **4. Conclusions**

536 The high improvement of the photocatalytic production of hydrogen peroxide
537 (H₂O₂) over carbon nitride (g-C₃N₄) that we report is ascribable of main major
538 phenomenon. First, we show that the presence of a very low content of
539 nanocellulose-derived carbon deeply modify the photoactivity of the g-C₃N₄
540 assembled with it. The result is an outstanding photocatalytic H₂O₂ production of 1.10
541 mmol L⁻¹ h⁻¹ under visible light. The second critical point is to achieve a high level of
542 interaction between the g-C₃N₄ nanosheets and CNF when assembling these two
543 nanocomponents. Third, a high level of interaction can be achieved through the
544 preparation of amino-rich g-C₃N₄ using a bi-component mixture of melamine and
545 urea. When carbon fibers are closely incorporated into the stacked structure of g-C₃N₄,
546 the nanofibers not only improve the porosity of the materials but also have a strong
547 effect on the photophysical properties of the g-C₃N₄ in narrowing the band gap;
548 improving the visible light absorption; increasing the number of photogenerated
549 carriers, especially excitable electrons; and accelerating the electron transfer and
550 further promoting a direct two-electron O₂ reduction reaction to generate hydrogen
551 peroxide. In subsequent studies, this approach will be tested for other materials for the
552 photoproduction of other chemicals.

553

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561

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