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1 **Photoelectrocatalysis of paracetamol on Pd-ZnO/ N- doped Carbon nanofibers electrode**

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22 **Abstract**

23 The presence of pharmaceuticals in water bodies has become a major concern in recent years. An
24 efficient and innovative way of eliminating these pollutants is through photoelectrocatalytic (PEC)
25 degradation owing to its environmental sustainability and its ability to remove recalcitrant
26 pollutants. In this study, palladium loaded zinc oxide/carbon nanofibers (CZnO-Pd) were
27 employed as a novel photoanode for PEC degradation of paracetamol. The CZnO-Pd composite
28 was prepared through electrospinning and atomic layer deposition (ALD). The obtained materials
29 were characterized. Photoelectrochemical studies were carried out with linear sweep voltammetry
30 and chronoamperometry. The removal efficiency was recorded using high-performance liquid
31 chromatography coupled to a mass spectrometer detector (HPLC-MS), while the mineralization
32 was assessed through total organic carbon (TOC) removal. The composite electrode of CZnO-Pd
33 nanofiber showed higher photoelectrochemical activity than ZnO carbon nanofiber, which was
34 evident in the higher photocurrent response recorded. Upon application of the material in
35 photoelectrocatalysis, the total removal of paracetamol was achieved within 3 h with an applied
36 current density of 10 mAcm^{-2} . The percentage of TOC removal was $71.20 \pm 0.31\%$ after 4 h, which
37 indicated significant mineralization. The results obtained in the present work reveal that Pd-ZnO/C
38 has great potential for photoelectrocatalytic removal of organic micropollutants.

39

40 **Keywords:** Photoelectrocatalysis; zinc oxide; carbon nanofibers; paracetamol; water treatment

41

42 **1.0 Introduction**

43 There is a growing need for clean and safe water for industrial and domestic use. The major threat
44 to the availability of clean water over the years is the prevalent of water pollution. Rapid
45 urbanization and industrialization contribute largely to the rise in water pollution [1–6]. Recently,
46 it has been identified that the complexity and the diversity of the nature of organic pollutants is a
47 major contributing factor to the effect of water pollution. The class of water pollutants refers to as
48 emerging contaminants that have been the focus of many research works in recent times due to the
49 recalcitrant or persistent nature and adverse effect of these pollutants [7–10]. The most common
50 examples of these emerging contaminants are pharmaceuticals. The contamination of water bodies
51 by pharmaceuticals is majorly due to improper disposal of effluents from pharmaceutical industries
52 and hospitals [11]. Additionally, effluents from households have been reported found to contain
53 pharmaceuticals due to the improper disposal of unused or expired drugs as well as human
54 excretion (urine) containing unmetabolized drugs [12,13]. Exposure to water contaminated with
55 pharmaceutical residues can result in several health problems in humans depending on the nature
56 of concentration and type of pharmaceutical as well as the duration of exposure [14]. Aquatic
57 organisms are, however, more susceptible to hazards of pharmaceutical polluted water [15,16].

58 Unfortunately, traditional/conventional water treatment methods such as filtration, coagulation
59 and adsorption have been inadequate for the complete removal of pharmaceutical pollutants from
60 water [17,18]. This has led to the development of advanced oxidation processes (AOPs). In AOPs,
61 complete mineralization of organics to carbon dioxide and water is achieved by the actions of *in*
62 *situ* generated hydroxyl radicals (strong oxidants) [19]. Common examples of AOPs for water
63 treatment are heterogenous photocatalysis, Fenton processes, ozonation and anodic oxidation
64 [18,20–22]. A recent form of AOP is photoelectrochemical oxidation (PEC). In PEC, the
65 synergistic effect of the combination of electrochemical oxidation and photocatalysis results in

66 enhanced mineralization efficiency of the AOP [23,24]. Similar to typical photocatalysis, a
67 semiconducting metal oxide is often used in PEC and irradiation of the semiconductor with the
68 light of sufficient energy results to photogeneration electron-hole pairs. The holes then react with
69 water to produce hydroxyl radicals that oxidize organic molecules. However, unlike
70 photocatalysis, the problem of rapid recombination of photogenerated electron-hole pairs is
71 reduced by the application of bias potential, which helps in driving the photogenerated electrons
72 away from the semiconducting anode [23,25–27]. Additionally, PEC offers better reusability of
73 material since the metal oxides semiconductors are used as compact and stable electrode [28].
74 Examples of commonly used metal oxides include TiO_2 [29,30], BiVO_4 [31], MoS_2 [32], Cu_2O
75 [33], Fe_2O_3 [34] and WO_3 [35].

76 Zinc oxide has been widely studied for its application as photocatalyst for water treatment
77 applications [36]. The wide use of ZnO can be rightly attributed to its fascinating properties such
78 as ease of synthesis, non-toxicity, abundance in nature, good photocatalytic properties, large
79 surface area, high electron mobility, remarkable thermal and chemical stability [37,38]. However,
80 due to the large band gap of ZnO (3.37 eV), it performs better with ultraviolet light irradiation. In
81 order to enhance its performance under visible light radiation, several strategies have been
82 employed, such as doping with metals, metal loading, morphological control and formation of
83 heterojunction with visible light active semiconductors [36]. ZnO nanoparticles have been
84 employed to improve the electron-mobility in perovskite solar cells [39,40]. ZnO photoanodes
85 have also found extensive applications in PEC water splitting [41–43]. Several interesting reported
86 works are also available on the use of ZnO as photoanode for PEC water treatment applications.
87 For instance, 53% removal of methylene blue dye has been recorded with the use of ZnO prepared
88 through chemical bath deposition on silicon substrates as photoanode [44]. In another study by

89 Hosseini *et al.*, enhanced PEC degradation efficiency of ZnO was achieved by doping with nickel
90 [45]. The Ni-doped ZnO achieved total removal of ciprofloxacin within 90 min with using UV
91 light irradiation when 1.87 mA cm^{-2} current density was applied. Similarly, Feng *et al.*, reported
92 87.5% PEC removal tetracycline after 3 h on Ni-doped ZnO anodes with an applied potential of
93 0.8 V [46]. The PEC performance of Ni-doped ZnO was found to be 17% higher than the undoped.
94 The increased performance of ZnO has also been reported in its heterostructures. For example,
95 100% removal of Acid Red 1 has been achieved with the use of ZnO/MoS₂ photoanode, which
96 was higher than 53% removal recorded on pristine ZnO anode [47]. ZnO/BiVO₄ photoanodes
97 have also been successfully applied for the removal of organics [48,49]. On the other hand, Carbon
98 nanofibers (CNFs) incorporating with metal oxide nanoparticles (NPs) are interesting materials
99 for water treatment via photo-electrocatalysis technique because of their high dimensional
100 stability, large specific surface, good electrical conductivity, high electrocatalytic activity as well
101 as the ability to minimize electrode surface fouling [50–52]. CNF-based electrodes are among the
102 most interesting electrode materials for water treatment [53], electrochemical water splitting
103 [54,55] and fuel cells [56]. In addition, the CNF has many active sites, good electrical conductivity,
104 mechanical stability and electrolyte diffusion [57].

105 In this present study, palladium loaded zinc oxide/carbon nanofibers are used as suitable
106 photoanode for the removal of paracetamol as a model pollutant. The composite materials were
107 prepared through the combination of atomic layer deposition and electrospinning. ZnO/CNFs
108 materials were firstly prepared through electrospinning. This is because of the advantages of
109 electrospinning, such as being a low-cost method and the ease of controlling the size, porosity and
110 morphology of nanofibers [58–60]. Moreover, carbon nanofibers have proven to possess attractive
111 attributes, including high electrical conductivity and excellent mechanical stability. ALD was

112 subsequently used to deposit palladium on the ZnO/CNFs because, with ALD, the nanoscale
113 dimensions of nanoparticle thin films can easily be controlled [61–63]. The extent of PEC removal
114 and mineralization of paracetamol molecules using the fabricated electrode was studied in detail
115 using chromatographic technique and total organic carbon evaluation. From the results obtained,
116 the prepared anode has great potential for the removal of organics from wastewater through PEC
117 applications.

118

119 **2. Experimental**

120 **2.1 Materials and chemicals**

121 Polyacrylonitrile (PAN, Mwt ~150000, CAS 25014-41-9, Sigma-Aldrich), Zinc (II) acetate
122 dihydrate ($\text{Ni}(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$, 99.9%, CAS No. 5970-45-6, Sigma-Aldrich), N,N-
123 Dimethylformamide (DMF, 98%, CAS No. 68-12-2, Sigma-Aldrich) and ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99%,
124 CAS No. 64-17-5, Sigma-Aldrich) were used for electrospinning of CNFs decorated with ZnO
125 NPs. Palladium (II) hexafluoroacetylacetonate ($\text{Pd}(\text{C}_5\text{HF}_6\text{O}_2)_2$, CAS 64916-48-9, 99%, Sigma-
126 Aldrich) was used as Pd precursor and formaldehyde (HCHO , CAS No. 50-00-0, 37%, Sigma-
127 Aldrich) used as co-reactant for ALD deposition of Pd NPs. Milli-Q water was used without further
128 purification. Paracetamol (CAS number: 103-90-2), sodium sulphate (anhydrous, $\geq 99\%$; CAS
129 number: 7757-82-6), absolute acetone (99%; CAS number: 67-64-1), formic acid (CAS number:
130 64-18-6), acetonitrile (HPLC grade; CAS number: 75-05-8), isopropanol ($\geq 99.5\%$; CAS number:
131 67-63-0), sodium ethylenediaminetetraacetate ($\geq 98\%$; CAS number: 6381-92-6) and p-
132 benzoquinone ($\geq 98\%$; CAS number: 106-51-4) were obtained from Sigma-Aldrich (Germany).

133

134 **2.2 Synthesis of ZnO-Carbon Nanofibers composites**

135 Zn@CNF was prepared by electrospinning followed by thermal preoxidation and then
136 thermal treatment (CZnO). First, 2 g PAN powder was dissolved in 20 mL DMF under vigorous
137 magnetic stirring until obtaining a uniform PAN precursor solution. Then, 1 g zinc acetate powder
138 was added. The mixture solution was lifted under stirring overnight to the obtained Zn- PAN
139 precursor solution. The electrospinning process was performed at a distance of 15 cm (solution
140 syringe tip to collector), a voltage of 15 kV, a feeding rate of 0.5 ml/min, and a drum rotation speed
141 of 300 rpm. The as-prepared Zn-PAN nanofibers first underwent peroxidation step at 250 °C for
142 2 h in an air atmosphere and then a thermal carbonation step at 800 °C for 1 h in N₂ atmosphere.
143 The heating and cooling rates were kept constant at 1 °C/min. For comparison CNFs were prepared
144 as the prewise method without Zn precursor (CNF sample).

145

146 **2.2 Deposition of Pd@ ZnO-Carbon Nanofibers composites**

147 The ALD deposition of Pd was carried out in a low-pressure thermal (home-built) ALD reactor. A
148 detailed description of this reactor can be found in a previous study [54]. The precursors, consisting
149 of Pd(hfac)₂ and reducing agent formalin, were contained in stainless steel cylinders whose lines
150 were heated at 70 °C and 100 °C, while the deposition chamber was pre-heated at 220 °C. The
151 ALD cycle used for this study was consisted of 5 s pulse of Pd(hfac)₂, 15 s exposure, and 10 s
152 purge, while the formalin had 1 s pulse, 15 s exposure, and 60 s purge. The ALD cycles were
153 repeated 100 and 200 times to get CZnO-Pd100 and CZnO-Pd200, respectively.

154 **2.3 Characterisation of materials**

155 The crystallinity of the prepared materials was analysed using X-ray diffraction (XRD) with a
156 PANalytical Xpert-PRO diffractometer equipped with an Xcelerator detector and using a Ni-
157 filtered Cu-radiation (CuK α 1 radiation wavelength 0.1540598 nm and CuK α 2 radiation
158 wavelength 0.1544426 nm). Raman spectra were measured on a Senterra Bruker using a doubled
159 Nd:YAG laser (λ = 532 nm) at a power of 10 W and an objective microscope lens of 100x. The
160 elemental composition on the surface of the grown thin films was determined by X-ray
161 photoelectron spectroscopy (XPS) on an Escalab 250 (Thermo Fisher Scientific, USA) using a
162 monochromatic Al K Alpha (1486.6 eV) at 2kV and 1 μ A. The morphology of nanofibers was put
163 in evidence by using a Hitachi S4800 (Japan) scanning electron microscope (SEM). The fiber
164 morphology was also examined using high-resolution transmission electron microscopy (HRTEM,
165 JEOL JEM 2100, Japan) working at 200kV equipped with energy-dispersive X-ray (EDX)
166 spectroscopy. Diffuse reflectance was measured by using HR2000+ Ocean Optics spectrometer
167 (USA), integration sphere and Deuterium-Tungsten Halogen light source DH-2000.
168 Photoluminescence (PL) spectra of samples were measured in the range of 350-850 nm using
169 HR2000+ Ocean Optics spectrometer (USA). Excitation of photoluminescence was performed by
170 Nd:YAG laser (China) (λ =266 nm, output power 29 mW).

171

172 **2.4 PEC degradation experiments**

173 The prepared materials were deposited onto FTO glass with a coverage of approximately 1 cm²
174 and were used as electrodes (photoanodes). The experiments were carried out in a 100 mL capacity
175 undivided two-electrodes cell and a power source (CNB Electronique, EU) was used to control the
176 applied current within the cell. Platinum mesh was used as the cathode and its distance from the
177 anode was kept constant at 3 cm. A 150 W linear halogen lamp (in the range of 420-600 nm) was

178 used as the light source and the photoanode was irradiated from the rear with a distance of 20 cm
179 from the lamp. The working solution consisted of 50 mL 0.1 mM paracetamol prepared in a
180 solution of 50 mM Na₂SO₄ (supporting electrolyte). All the experiments were performed at neutral
181 pH. Sample aliquots were taken at specified time intervals (20, 40, 60, 90, 120, 150, 180 min) for
182 paracetamol concentration and total organic carbon contents.

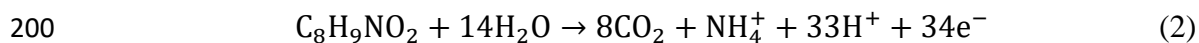
183 **2.5 Analytical Procedures**

184 Decrease in the total organic carbon (TOC) was used to assess the extent of mineralization of the
185 paracetamol molecules by measuring the TOC contents of the initial and aliquots solutions on a
186 TOC-L CSH/CSN Shimadzu (Japan) analyzer. Calibration curves for total carbon (TC) and
187 inorganic carbon (IC) analysis were built up by automatic dilution of standards solutions of TOC
188 (potassium hydrogen phthalate) and IC (sodium hydrogen carbonate). The TOC data obtained were
189 then used to estimate the mineralization current efficiency (MCE, %) of the solutions over a
190 specified time t (h) using equation 1 [64].

$$191 \quad \text{MCE}(\%) = \frac{nFV_s\Delta(\text{TOC})_{\text{exp}}}{4.32 \times 10^7 \text{ mIt}} \cdot 100 \quad (1)$$

192

193 The number of electrons consumed in the mineralization of each paracetamol molecule is
194 represented by n, F is the Faraday constant (96485 C mol⁻¹), V_s is the solution volume (L),
195 Δ(TOC)_{exp} is the experimental TOC decay (mg L⁻¹), 4.32×10⁷ is a conversion factor (3600 s
196 h⁻¹×12000 mg carbon mol⁻¹), m is the number of carbon atoms in each paracetamol molecule (8
197 atoms), the current passing through the system in time t is denoted as I. The number of electrons
198 (n) consumed for complete mineralization was 34 for the paracetamol molecule, according to the
199 stoichiometry of the reaction in equation 2 [65]:



201 The concentration decay of paracetamol molecules was estimated through high performance liquid
202 chromatography – mass spectrometry (HPLC-MS). HPLC-MS was carried out with a Waters 2695
203 pump, an auto sampler with 20 μL loop, a Waters 2695 separation module (HPLC), and a Waters
204 Micromass (Wythenshawe, Manchester, UK) Quattro Micro mass spectrometer equipped with ESI
205 (Electrospray Ionization). HPLC was performed on a Waters – Xselect HSS T3 column at a column
206 temperature of 25 $^\circ\text{C}$. The mobile phase was a Buffer A (HPLC grade water + 0.1% formic acid)
207 and Buffer B (HPLC grade acetonitrile + 0.05% formic acid). The flow-rate was constant at 0.25
208 mL min^{-1} , with a split of 20% to the mass spectrometer. The triple quadrupole MS was operated
209 in selected-ion-recording (SIR) mode with compounds being ionized in the negative electrospray
210 ionization mode. To achieve the best sensitivity, the MS was adjusted to facilitate the ionization
211 process. The detection conditions were: capillary potential 3.5 kV, cone potential 30 V, source
212 temperature 120 $^\circ\text{C}$, desolvation temperature 450 $^\circ\text{C}$, cone gas flow 50 L h^{-1} , and desolvation
213 gas flow 450 L h^{-1} . Nitrogen (99.5% purity) was the nebulizer gas.

214

215 **Results and discussion**

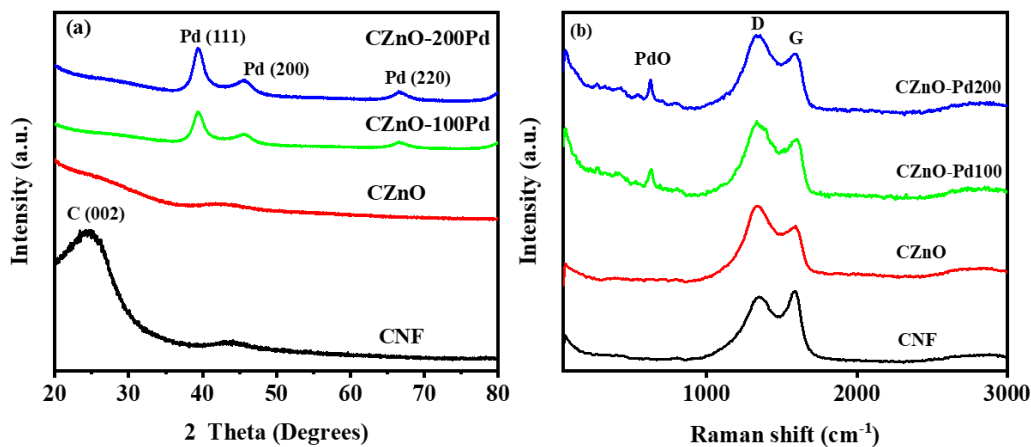
216 **3.1 Characterisation results**

217 The CNF and CZnO were elaborated via electrospinning of polymeric solution containing PAN
218 and zinc acetate as precursors, followed by pyrolysis under nitrogen at 800 $^\circ\text{C}$ for 1 h in N_2 . CZnO-
219 Pd100 and CZnO-Pd200 samples were prepared on CZnO as a substrate by the deposition of
220 metallic Pd by ALD using 100 and 200 cycles, respectively. As shown in Figure 1a, two broad
221 reflections, which correspond to the (002) and (101) reflections of a turbostratic structure of carbon

222 [66], are observed in the XRD pattern of CNF sample. The crystallite size of the turbostratic carbon
223 along the c-axis (L_c) in CNF is found to be 0.8 nm, as revealed by Rietveld refinement of XRD
224 data. Moreover, the average number of graphite stacking layers (N_c), which is estimated from the
225 interlayer spacing d_{002} and crystallite size along the c-axis (L_c) [67], is found to be 2.5. The
226 intensities of these XRD reflections in the XRD pattern of CZnO are vanished, indicating that the
227 structure of carbon becomes highly disordered by introducing ZnO to the surface of the nanofibers.
228 Moreover, no XRD reflections corresponding to any of crystalline Zn or ZnO are observed in the
229 XRD pattern of CZnO, CZnO-Pd100 and CZnO-Pd200 samples, which can be explained by the
230 amorphous structure or small weight fractions of ZnO in these samples in order to be detected by
231 XRD measurements. However, XPS analysis (Table S1) shows that the CZnO sample contains a
232 high amount of elemental Zn (6.7 wt%, which corresponds to 8.3 wt% of ZnO) on the surface of
233 carbon nanofibers, suggesting the amorphous structure of ZnO in the sample. In contrast, Pd
234 crystallized in metallic form in CZnO-Pd100 and CZnO-Pd200 samples during ALD deposition.
235 All the peaks appearing on the XRD patterns can be indexed to the cubic structure of metallic Pd
236 (PDF No. #00-065-6174). A similar crystallite size of 3.7 nm is determined by Rietveld refinement
237 for metallic Pd in both samples, which suggests that the increase in the deposition time might
238 increase the number of deposited Pd particles on the surface of carbon nanofibers, but without
239 altering their crystallinity.

240 The incorporation and structure of ZnO and Pd on the surface of carbon nanofibers were further
241 investigated by Raman spectroscopy (Figure 1-b). All the prepared nanofibers displayed the
242 fingerprint bands of carbon, such as the disorder peak (D-band) at 1354 cm^{-1} and graphite peak
243 (G-band) at 1591 cm^{-1} . The presence of D band, which is characteristic of the disordered sp^2 -
244 hybridized modes in the rings, confirms the turbostratic structure of carbon in the samples as

245 revealed by XRD. In contrast, the G-band corresponds to the vibrational stretching mode of in-
 246 plane sp²-hybridized C atoms [68]. The relative intensities ($R = I_D/I_G$ value) of D and G bands
 247 could be used to evaluate the degree of structurally ordered graphite crystallites in carbon
 248 materials.[53] The R value of CNF was 0.93, and it increased to 1.18, 1.14 and 1.15 for CZnO,
 249 CZnO-Pd100 and CZnO-Pd200, respectively, indicating the increase in the degree of disordered
 250 carbon structures with introducing ZnO into the carbon nanofibers, which is in good agreement
 251 with XRD results. Moreover, no Raman modes were observed for ZnO in the spectra of CZnO,
 252 CZnO-Pd100 and CZnO-Pd200 samples, confirming the amorphous structure of ZnO as revealed
 253 by XRD analysis. In addition, strong bands are detected at 633 and 629 cm⁻¹ in the Raman spectra
 254 of CZnO-Pd100 and CZnO-Pd200, respectively, which can be attributed to the active B_{1g} vibration
 255 modes of PdO [69]. The presence of PdO in the CZnO-Pd100 sample is also confirmed by XPS
 256 characterization, as discussed below.

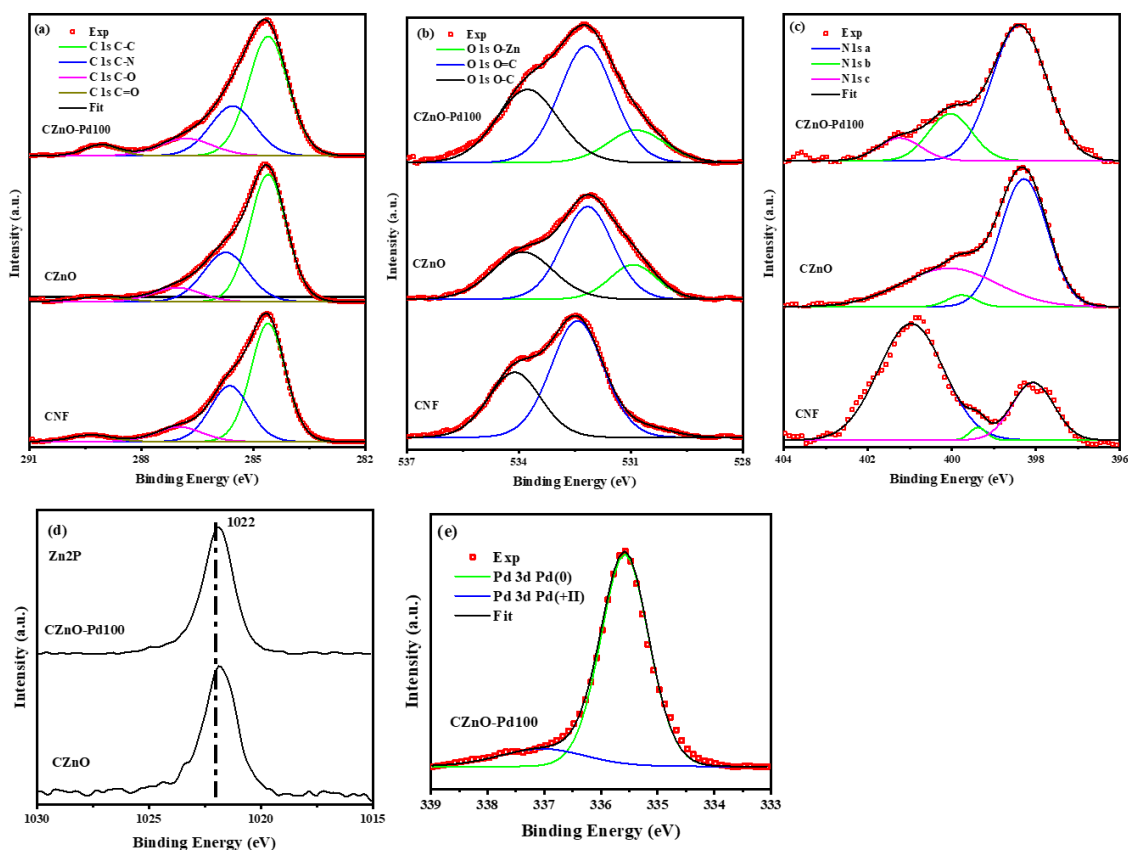


257
 258 **Figure 1:** (a) XRD patterns of prepared CNF, CZnO, CZnO-Pd100, CZnO-Pd200 nanofibers. (b)
 259 Raman spectra of prepared nanofibers.

260

261 The elemental compositions as well as the coordination and the oxidation states of different
262 elements in the obtained samples were characterized by XPS measurements. As shown in Figure
263 S1 and Table S1, the survey XPS spectra confirm the successful incorporation of elemental Zn and
264 Pd at the surface of the carbon nanofibers. The mass fraction of elemental Zn on the surface of
265 CZnO sample is found to be 6.7 wt% and decreased to 4.1 wt% on the surface of CZnO-Pd100
266 due to the successful deposition of Pd (i.e., 33 wt% of the sample). Additionally, remarkable
267 amounts of nitrogen are detected in all the samples, suggesting the nitrogen doping of the carbon
268 nanofibers. The N-doping of carbon nanofibers can be explained by the high content of N in PAN
269 polymer and the pyrolysis of the polymeric precursors under N₂ atmosphere. As shown in Table
270 S1, the mass fraction of N in CZnO sample is four times higher than that in the CNF samples,
271 which indicates that zinc salt might stabilize the nitrile group in the polymer during the
272 electrospinning process, and thus, it enhanced the N-doping of carbon nanofibers. The high-
273 resolution XPS spectra of C 1s, O 1s, N 1s, Zn 2p, and Pd 3d orbitals are shown in Figure 2 a-e.
274 The spectrum of C 1s (Figure 2-a) could be deconvoluted into four peaks located at about 284.6,
275 285.6, 287 and 289 eV, corresponding to sp² hybridized graphitic carbon C-C bond, C-N bond, C-
276 O bond, and C=O bond, respectively [70]. As shown in Figure 2-b, O 1s spectrum of CNF sample
277 can be fitted with two peaks at 532.2 and 534 eV, which can be attributed to C=O and C-O bond,
278 respectively. An additional peak is observed at about 530.5 eV in the O 1s spectra of CZnO and
279 CZnO-Pd100 samples, which can be assigned to the lattice oxygen of ZnO. As displayed in Figure
280 2c, the N 1s spectra can be fitted with three peaks a ~ 398, 399.4 and 400.9 eV, which can be
281 assigned to pyridinic N, pyrrolic N and graphitic N, respectively. The pyridinic N and pyrrolic N
282 species become the dominant nitrogen species in CZnO and CZnO-Pd100 samples, suggesting the
283 improvement of the electrochemical performance of these samples [70]. The incorporation of ZnO

284 in CZnO and CZnO-Pd100 samples is further confirmed by detecting the peak at 1022 eV
 285 corresponding to Zn 2p_{3/2} in ZnO (Figure 2d) [71]. The Pd 3d spectrum of In CZnO-Pd100
 286 nanofiber (Figure 2-e) can be deconvoluted into two peaks at ~ 335.6 and 337 eV, corresponding
 287 to Pd⁰ and Pd⁺² species, respectively. The Pd⁺²/Pd⁰ ratio is found to be 0.15, suggesting the small
 288 mass fraction of oxidized Pd⁺² species in the samples, which agrees with the results of Raman
 289 characterizations.

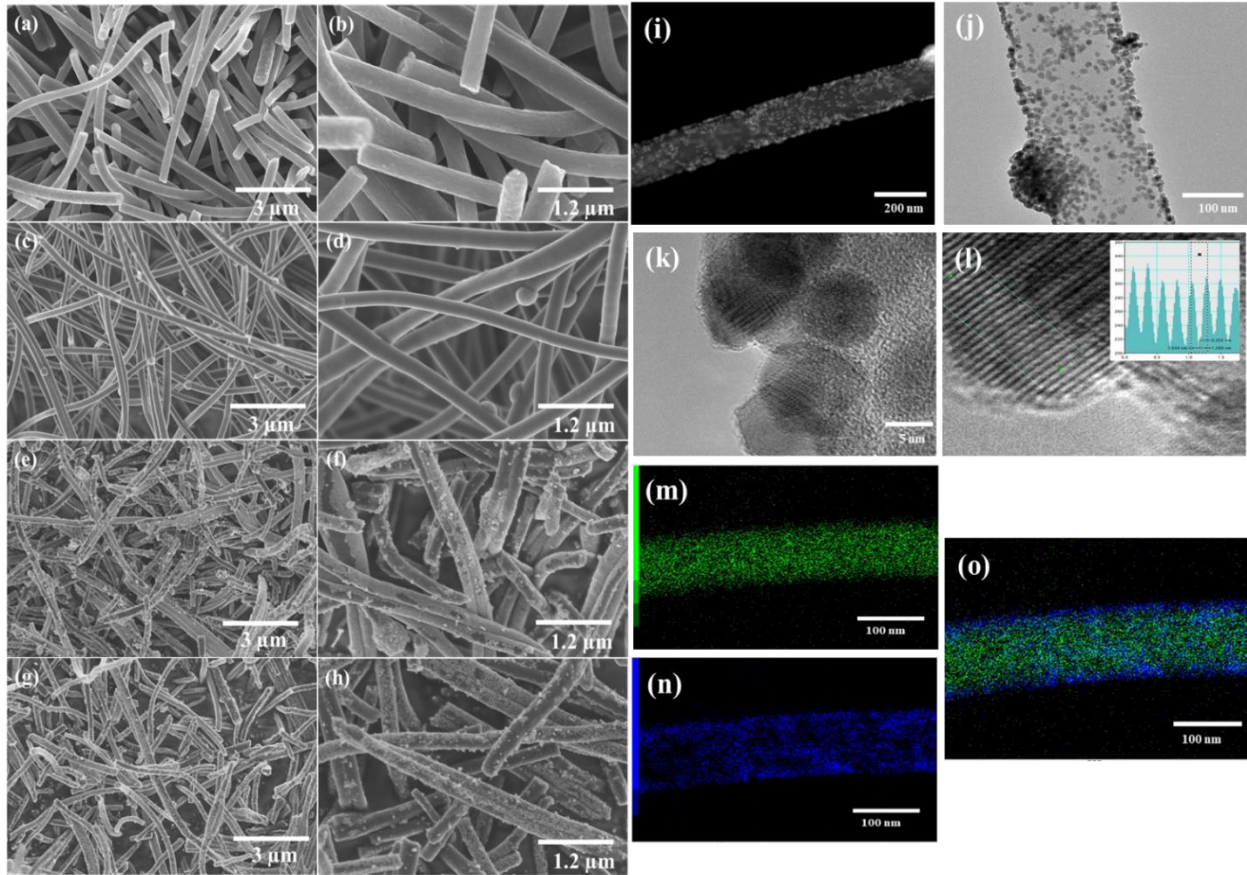


290
 291 **Figure 2:** (a) High-resolution XPS spectra of C 1s (a), O 1s (b), N 1s (c), Zn 2p (d), and Pd 3d (e)
 292 for CNF, CZnO and CZnO-Pd100.

293

294 The morphology of the elaborated nanofibers was investigated by SEM characterization, as
295 illustrated in Fig. 2(a-h). The CZnO, CZnO-Pd100 and CZnO-Pd200 samples consist of carbon
296 fibers with an average diameter of $0.25 \pm 0.02 \mu\text{m}$, which is smaller than that of CNF sample (0.45
297 $\pm 0.02 \mu\text{m}$). This result suggests that the addition of zinc salt during the electrospinning process
298 hinders the growth of the carbon nanofibers during the pyrolysis. As shown in Figure 3e-h, the
299 metallic Pd are uniformly deposited as spherical particles with an average diameter of $5.6 \pm 1 \text{nm}$ on
300 the surface of the carbon nanofibers in the CZnO-Pd100 and CZnO-Pd200 samples. Although the
301 particle size of metallic Pd does not change with increasing the deposition time, the number of
302 metallic Pd increases, which agrees with XRD results. The homogeneous distribution of Zn on the
303 entire surface of carbon nanofibers is confirmed by TEM, STEM, and EDX mapping, as presented
304 in Figure S2. In contrast, the metallic Pd nanoparticles are deposited on the edge/shell of the
305 nanofibers to form coaxial or core/shell structure, as revealed by HRTEM (Figure 3i-l) and EDX
306 mapping (Figure 3m-o). The fast Fourier transform (FFT) pattern of CZnO-Pd100 nanofibers for
307 a square box (inset Fig. 3l) confirmed the cubic structure of metallic Pd nanoparticles by detecting
308 the d spacing 0.23nm corresponding to the (111) planes of metallic Pd.

309



310

311 **Figure 3:** Field emission SEM images of the prepared nanofibers; CNF (a,b), CZnO (c,d), CZnO-
 312 Pd100 (e,f), and CZnO-Pd200 (g,h). High-resolution transition microscope of CZnO-Pd100 (i - l)
 313 and the fast Fourier transform (FFT) pattern of the area marked by the blue square box of CZnO-
 314 Pd100 and the corresponding intensity profiles in inset (l), with EDX elemental mapping of CZnO-
 315 Pd100 the zinc (m), palladium (n) and Zn overlap Pd (o).

316

317 In the next step, the optical properties influence of Pd on CZnO nanofibers were detected by the
 318 optical band gap by UV-vis. in addition, the generation and stability of e^-/h^+ were detected by PL
 319 side by side of determine the optical band gap. The measured reflectance spectra were converted
 320 into absorption spectra according to equation 1 [72].

321
$$F = \frac{(I - R)^2}{2 \cdot R} (*) \quad \text{equation 1}$$

322 where the parameters F and R refer to the absorption coefficient and diffuse reflectance of the
323 sample, respectively. The obtained spectra are shown in Figure 4a. All samples show low
324 absorbance in the UV range and high absorbance in the visible range. Although no absorption edge
325 is observed for ZnO-based samples, absorbance value is increased in the visible range by adding
326 ZnO and Pd on the surface of carbon nanofibers. This finding will be explained further.

327 PL spectra of the samples are shown in Figure 4b. Weak characteristic PL peak is observed at 3.25
328 eV in the spectrum of CNF sample, which could be related to delocalized π electrons available at
329 the surface of carbon nanofibers [73]. The successful addition of ZnO on the surface of carbon
330 nanofibers is confirmed by the strong PL peak at 3.24 eV observed in the spectrum of CZnO
331 sample that corresponds to ZnO excitonic emission [72]. The deposition of metallic Pd on the
332 surface of ZnO/CNF had different effects on ZnO emission: enhancement of ZnO emission in
333 ZnO-PD100 samples and quenching for ZnO-PD200 samples. According to the literature [74–78],
334 Pd nanostructures have at least 2 absorption bands: in UV and visible ranges, related to localized
335 surface plasmon resonance (SPR) effect [74–78]. The position and FWHM of the bands depend
336 on the size and shape of Pd nanostructures [79]. It was shown that due to differences between ZnO
337 and Pd work functions, Schottky barrier is expected at ZnO/Pd interface, inducing electron flow
338 from conduction band (CB) of ZnO to Pd [79,80]. It results in increase of absorption and decrease
339 of ZnO emission. However, alternative mechanisms at ZnO/Pd interface are possible [69,71]. It
340 was reported that UV emission of ZnO can be increase due to passivation of surface states during
341 Pd deposition [79,81]. We suppose, that Pd morphology will define the ZnO/Pd optical properties.
342 Comparative analysis of absorption and photoluminescence spectra points to the fact, that the

343 absence of characteristic absorption edges of ZnO in ZnO/Pd nanostructures points to hot electron
344 effect (HEE) in Pd nanoparticles [82]. This effect is based on transition of excited SPR electrons
345 from Pd to CB of ZnO [82]. The hot electron effect is assisted with increase of visible absorption
346 and fading of UV absorption bands [82]. The HEE depends on morphology of ZnO/Pd interface.
347 At lower Pd concentrations, Pd layer is cluster-like and increase of PL can be observed. The
348 increase of Pd thickness might promote light scattering (no excitation light is absorbed by ZnO)
349 and, thus, diminishing ZnO emission.

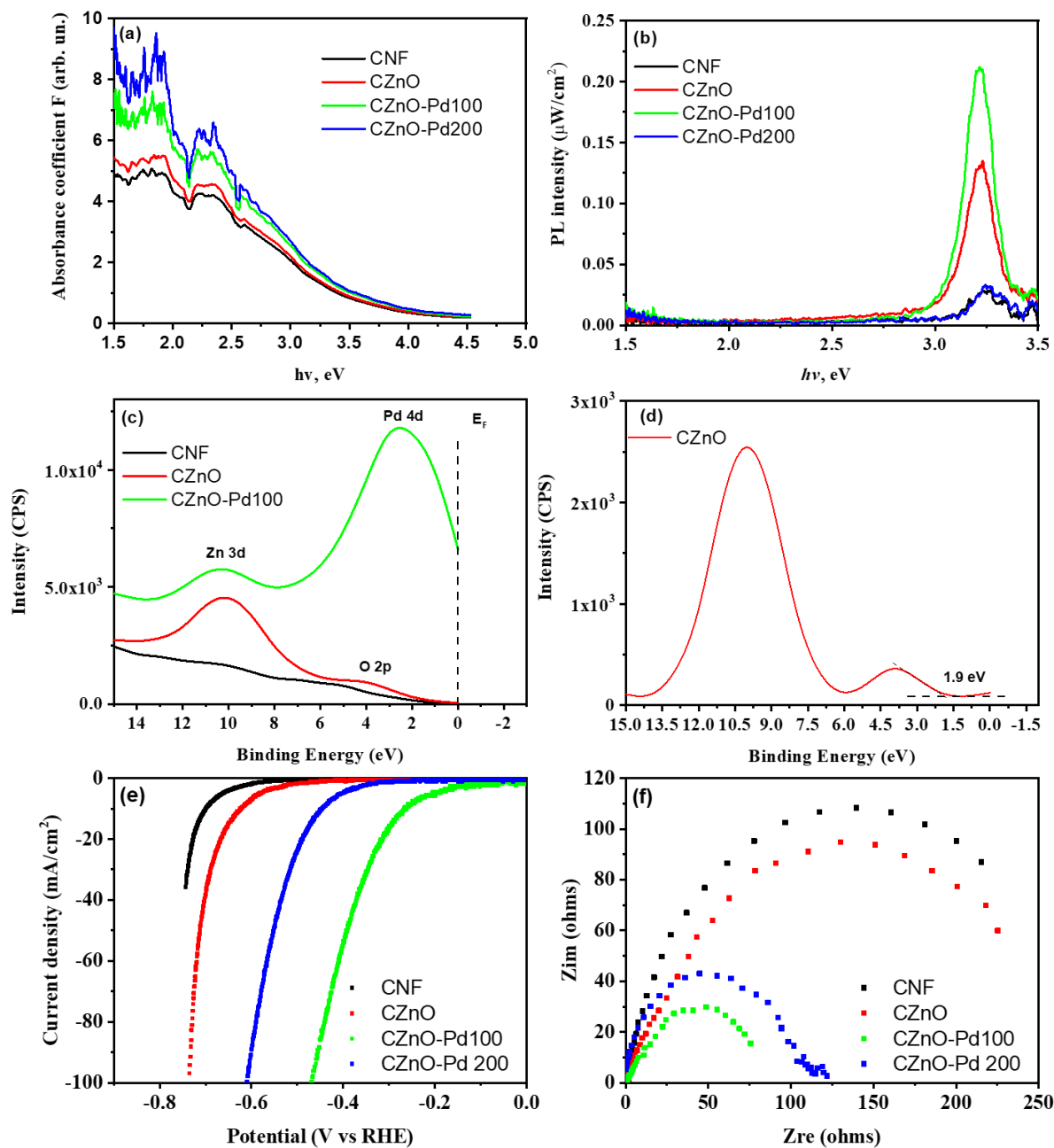
350 Moreover, the increase in the absorbance of carbon-based samples (Figure 4a) points to a wide
351 absorbance band of Pd nanostructures in the range of 1.5-3 eV. The absorption values increase
352 with increasing the amount of Pd on the surface of carbon nanofibers. Forming of carbon-ZnO and
353 Pd/ZnO interfaces makes impact on photoluminescence properties of the composite nanomaterial
354 [81,83–85]. The presence of carbon nanofibers with ZnO results in quenching of
355 photoluminescence due to charge transfer [83]. Deposition of Pd layer over ZnO could result in
356 quenching of visible PL [81,84] and/or quenching of PL in all measured spectra due to the
357 passivation of ZnO photoluminescence centers [85]. The common effect in Pd/ZnO nanostructures
358 was observed in blue shift of UV PL peak [81,84,85]. In the present work, no shift of PL was
359 observed for ZnO/Pd100 samples. The increase of Pd concentration resulted in almost complete
360 quenching of the PL. However, the UV peak in CZnO/Pd sample was similar to the PL peak in
361 untreated CNF.

362 It was shown that UV emission in carbon nanomaterials corresponds to π - π transition in C=O
363 bonds [86,87]. The observed emission could be explained from oxidized surface of CNF in case
364 of full passivation of ZnO emission centers.

365 In addition, the valence band (VB) XPS was studied for the extra analysis of electronic states
366 induced by defects above the valence band as presented in Figure 4c-d. It is clearly seen few XPS
367 features at 2.5 eV, 5 eV and 10 eV attributed to Pd 4d, O 2p and Zn 3p peaks, respectively.
368 Typically, the density of states of ZnO below Fermi level is consisted from two bands: the upper
369 peak at ~10 eV mainly derived from Zn 3d orbitals, and the lower band at ~5 eV arises from
370 almost O 2p hybridized with the Zn 4s and Zn 4p states [88]. We estimated the VB maximum
371 (VBM) using standard method as described elsewhere [89]. The VB spectrum for the CNF is in a
372 good agreement with those reported for carbon [90]. The VBM of Pd (estimated from the
373 extrapolation) was observed at around 2 eV above the Fermi level (EF) indicating the metallic
374 behavior, while the VBM for CZnO had a value around 1.9 eV below the EF. Typically, the values
375 of VBM for undoped crystalline ZnO are in the range of 2.54 eV to 2.11 eV. This shift of the VBM
376 might be associated with an increase in the concentration of defects and/or doping (carbon,
377 nitrogen etc.) of ZnO. Besides, we may observe the shift of Zn 3p maxima from 10.19 eV to 10.42
378 eV after the Pd deposition. This can be explained by the redistribution of electron density in the d-
379 orbitals of the Zn²⁺ and the Pd²⁺ which is believed to have produced additional energy levels near
380 the VB of the ZnO narrowing its band gap, what as a consequence may change photocatalytic
381 properties of produced nanocomposites [89].

382 Hydrogen Evolution Reaction (HER) of the prepared nanofibers has been studied to manifest the
383 role of palladium. The HER linear sweep voltammetry curves (LSV) of the prepared nanofibers
384 were presented in Figure 4e. From the data, the CZnO-Pd100 has better electrochemical activity
385 than other prepared nanofibers. It was shown lower overpotential than other nanofibers (250 mV)
386 at 10 mA/cm² of the current density. In contrast, the overpotential of CNF, CZnO and CZnO-
387 Pd200 are 695, 620 and 441 mV at 10 mA/cm² of the current density, respectively. CZnO-Pd100

388 recorded the best activity of HER due to the good distribution of Pd NPs on the nanofibers. We
389 note here that the CZnO-Pd200 has less activity than CZnO-Pd100 because of the Pd NPs
390 aggregation on the surface of the nanofibers as reported elsewhere [52,54,91]. Furthermore, the
391 electrochemical impedance has been measured as illustrated in Figure 4f. The charge transfers
392 resistance (R_{ct}) was calculated from the Nyquist plots in Figure 4f. The CZnO-Pd100 recorded
393 lower resistance (80Ω) than the other nanofibers CNF (275Ω), CZnO (240Ω) and CZnO-Pd200
394 (120Ω), in agreement with its HER activity results and lower overpotential.



395

396 **Figure 4:** Absorbance spectra of CNF, CZnO, CZnO-Pd100 and CZnO-Pd200 nanofibers (a); PL
 397 of CNF, CZnO, CZnO-Pd100 and CZnO-Pd200 nanofibers (b); VB-XPS of CNF, CZnO, CZnO-
 398 Pd100 (c); Zooming of VB-XPS of CZnO (d); HER of CNF, CZnO, CZnO-Pd100 and CZnO-
 399 Pd200 nanofibers (e); and EIS of CNF, CZnO, CZnO-Pd100 and CZnO-Pd200 nanofibers (f).

400

401 **3.2 PEC degradation of paracetamol**

402 The results for the PEC degradation of paracetamol using the prepared photoanode are presented
403 in Figures 5a-d. After 150 min, total removal (100%) of paracetamol was achieved using CZnO-
404 Pd100 anode (Fig 5a) with an applied current of 10 mA cm^{-2} (corresponding to 4.2 V). The
405 incorporation of Pd on the surface of ZnO/CNFs led to this impressive result because the CZnO
406 anode achieved just $56.40 \pm 2.10\%$ PEC removal of paracetamol after 150 min. This could be due
407 to the fact that transition metals improve the photocatalytic efficiencies of semiconductors by
408 increasing their light absorptivity and limiting spontaneous recombination. This is in line with
409 previous studies where doping ZnO with Pd has also been reported to increase the photocatalytic
410 efficiency of ZnO [92,93]. However, with CZnO-Pd200 photoanode, the percentage removal was
411 about $80.00 \pm 0.20\%$ after 150 min, and this revealed that the excessive amount of Pd in the
412 composite material could diminish its efficiency. The CZnO-Pd100 photoanode was subsequently
413 used to access the degradation of paracetamol through an electrochemical oxidation and
414 photocatalytic process in order to establish the superiority of PEC process. As shown in Figure 5b,
415 in the absence of light, the percentage removal of paracetamol decreased to about $82.20 \pm 0.14 \%$
416 after 3 h, and this revealed that irradiation greatly enhanced the efficiency of the electrode. On the
417 other hand, when the degradation experiment was performed without applying an external current
418 (photocatalysis), the percentage removal reduced drastically to $14.30 \pm 0.12\%$. The lower
419 efficiency of the electrode in photocatalysis further showed that the applied current in the PEC
420 process remarkably improve the performance of the electrode by promoting efficient charge
421 separation since it provides a driving force for the photogenerated electron to move away from the

422 anode surface. Additionally, anodic oxidation of the paracetamol was also possible with the
423 application of external current.

424 In order to confirm the dependence of the PEC degradation process on the applied current, the
425 experiments were also performed with the application of 5 mA cm^{-2} (3.3 V) and compared with
426 the results obtained with 10 mA cm^{-2} . As presented in Figure 5c, at lower applied current (5 mA
427 cm^{-2}), the percentage of paracetamol degradation was reduced to $78.11 \pm 0.20\%$ after 150 min.
428 This clearly showed that the magnitude of applied current also has an effect on the separation of
429 photogenerated electron-hole pairs within ZnO. The space charge region and Helmholtz layer on
430 the surface of the photoanode largely determine the mobility of photogenerated charge carriers.
431 Applied current increases the width of the charge region, and when this happens, the spontaneous
432 recombination of photogenerated carriers is reduced [45]. An increase in the magnitude of applied
433 current could increase the width of the space charge region, and this evidently led to an increase
434 in percentage removal of paracetamol when the current was increased from 5 mA cm^{-2} to 10 mA
435 cm^{-2} . However, too high applied current promotes oxygen generation, which decreases PEC
436 degradation performance and could also affect the integrity of the electrode.

437 Kinetics study was also performed by fitting the experimental data into the pseudo second order
438 reaction kinetics model. The apparent rate constants were obtained from the slope of the plots of
439 $\ln C_0/C_t$ versus time (Figure 5d). In the PEC degradation processes using different photoanodes,
440 the apparent rate constants were $7.88 \times 10^{-4} \text{ min}^{-1}$, $6.94 \times 10^{-3} \text{ min}^{-1}$ and $9.10 \times 10^{-3} \text{ min}^{-1}$ for CZnO,
441 CZnO-Pd200 and CZnO-Pd100 respectively. The highest rate constant obtained using CZnO-
442 Pd100 revealed that the PEC degradation is fastest using this electrode in addition to the highest
443 percentage removal obtained. Furthermore, the kinetics of photocatalytic, electrochemical (EC)
444 and PEC degradation were also studied using the CZnO-Pd100 electrode. It was found that the

445 order of increasing apparent rate constant was photocatalytic < electrochemical < PEC degradation
446 and this also showed that a combination of photocatalysis and electrochemical degradation in the
447 PEC process facilitated the fast rate at which paracetamol molecules were degraded. To further
448 justify the improved performance obtained through the incorporation of visible light irradiation
449 (photocatalysis) with applied external electric current, the degree of electrochemical enhancement
450 (E) and the degree of process synergy (S) were obtained using equations 3 and 4 respectively [94].

$$451 \quad E = (K_{PEC} - K_{PC})/K_{PEC} \quad (3)$$

$$452 \quad S = (K_{PEC} - (K_{PC} + K_{EC}))/K_{PEC} \quad (4)$$

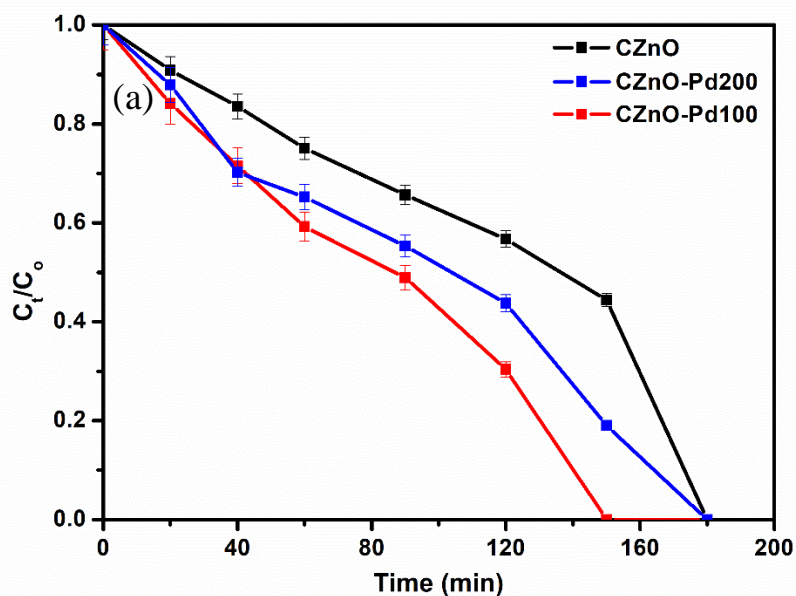
453 Where K_{PC} , K_{EC} , and K_{PEC} are apparent rate constants for photocatalytic ($7.883 \times 10^{-4} \text{ min}^{-1}$),
454 electrochemical ($5.37 \times 10^{-3} \text{ min}^{-1}$) and PEC degradation ($9.710 \times 10^{-3} \text{ min}^{-1}$) of paracetamol,
455 respectively. The degree of electrochemical enhancement was calculated to be 0.91 (91%), which
456 established that the application of electric current has a tremendous impact on the PEC process,
457 and the percentage removal obtained with electrochemical degradation likewise justify this. In line
458 with this, the degree of process synergy calculated (0.323) was obviously greater than zero, which
459 confirmed that the improved performance obtained with PEC degradation is more than the
460 summation of the individual electrochemical and photocatalytic degradation process, revealing
461 that the introduction of applied electric current with photocatalysis result in a synergistic effect
462 and not cumulative/summation effect [94,95].

463 The catalytic performance of ZnO/Pd depends on ratio between Pd thickness and concentration of
464 active sites at ZnO/Pd interface [82]. It was shown that catalytic performance as a function of Pd
465 concentration had maximum between 0% Pd and 18% Pd loading. Higher concentration of Pd
466 restricts the role of metal oxide component in photocatalysis and therefore reduces total

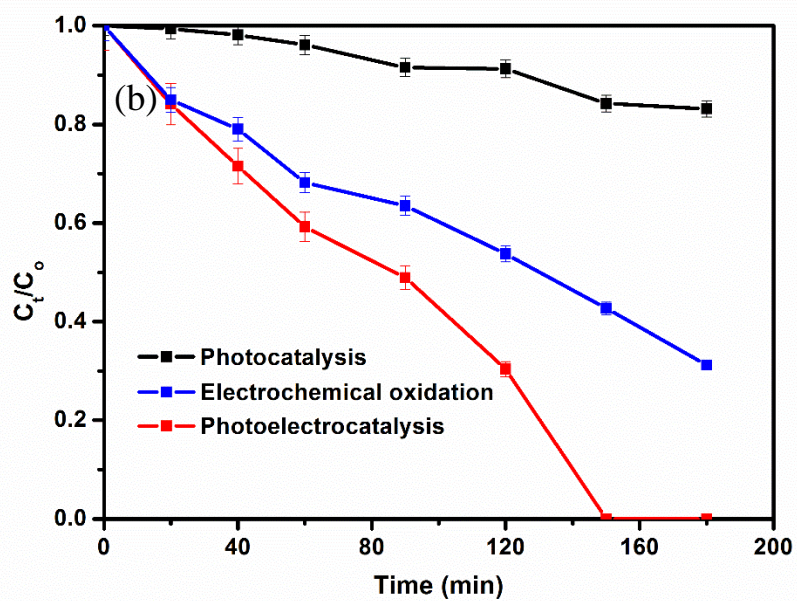
467 photocatalytic effectiveness. This was in agreement with the results obtained from the PL spectra
468 discussed earlier where increase in Pd loading resulted in light scattering effect on the surface of
469 the catalyst, thereby diminishing its photocatalytic activity.

470 In the present work, ZnO-Pd100 samples showed higher performance compared to ZnO-Pd200
471 due to higher concentration of active sites. This was confirmed by optical characterizations
472 (photoluminescence) where, we can get highly efficiency at the certain amount of Pd active sites
473 (CZnO-Pd100).

474

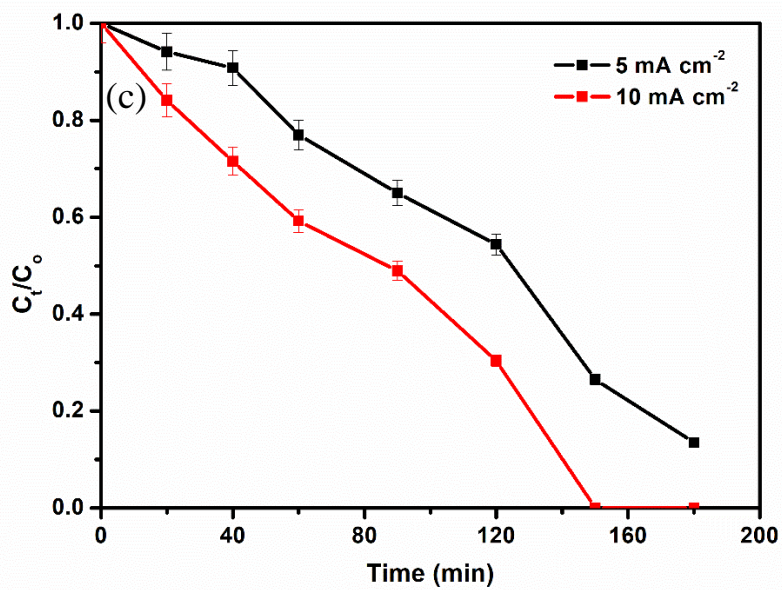


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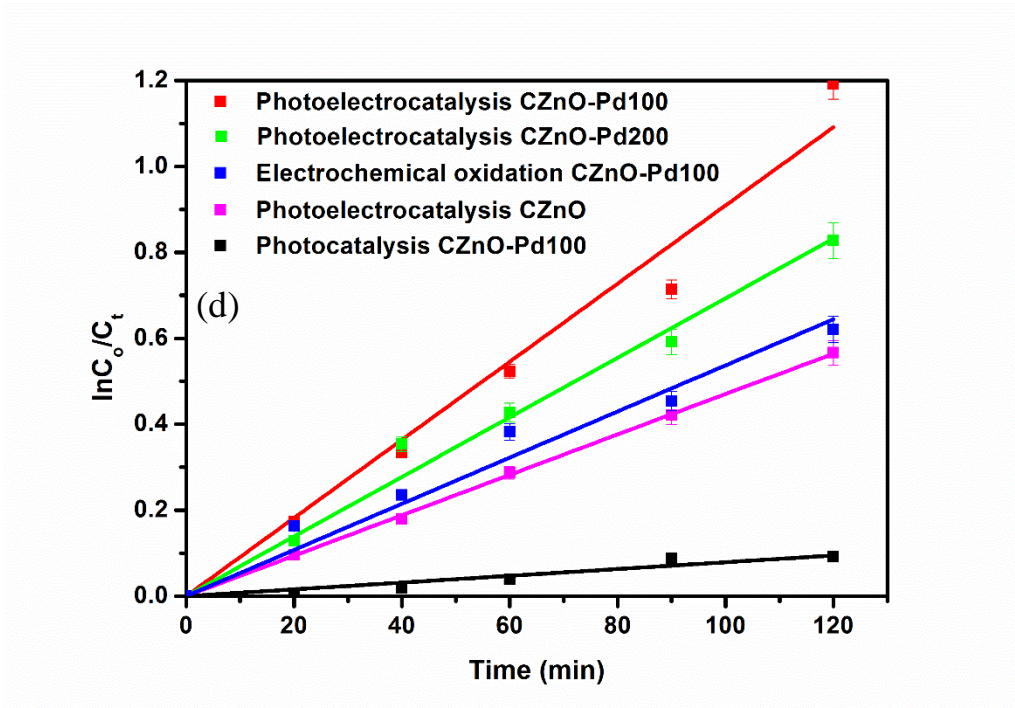
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480

481 **Figure 5:** Normalized concentration decay versus time plot for PEC degradation of paracetamol
 482 using (a) CZnO, CZnO-Pd100 and CZnO-Pd200; (b) Photocatalysis, electrochemical oxidation
 483 and photoelectrocatalysis using CZnO-Pd100; (c) Photoelectrocatalysis at different current
 484 densities using CZnO-Pd100; (d) Corresponding kinetics plot for the processes at 10 mAcm^{-2} (0.1
 485 mM paracetamol; pH 7; 50 mM Na_2SO_4)

486

487 3.2.1 TOC removal and reusability of the electrode

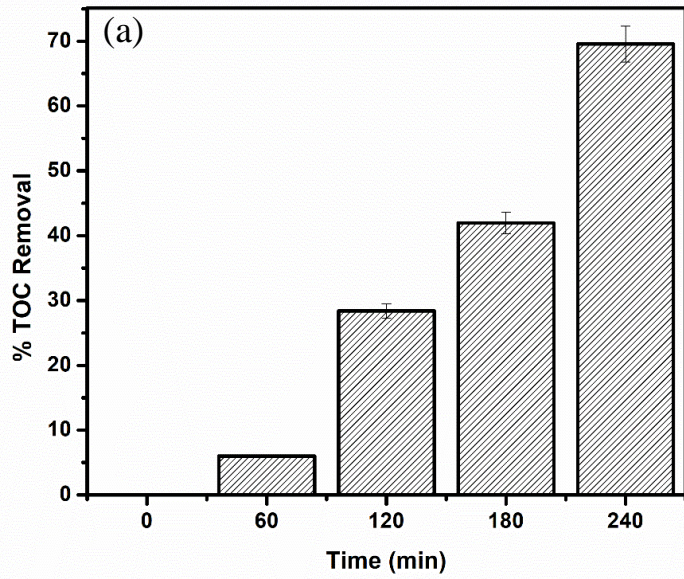
488 In PEC degradation of organics, similar to other advanced oxidation processes, it is envisaged that
 489 the total mineralization of organics to water and carbon dioxide would occur after some period of
 490 reaction. In order to quantify the extent of mineralization of paracetamol using the composite
 491 electrode of CZnO-Pd100, the total organic carbon (TOC) content was measured as the PEC
 492 process progressed. As shown in Figure 6a, the percentage of TOC removal was approximately

493 71.20 \pm 0.31% after 4 h. This clearly revealed that significant mineralization of paracetamol
494 molecules occurred in the PEC degradation. From the TOC results obtained, it became obvious
495 that the paracetamol was broken down totally to other smaller organics first, and this accounted
496 for the total removal of paracetamol achieved within 150 min. Since complete removal of TOC
497 was not recorded, smaller chain aliphatic organic acids such as fumaric, oxalic, acetic and maleic
498 acids, which are by products of paracetamol degradation, were still present in the solution [96,97].
499 Additionally, the corresponding calculated mineralization current efficiency (MCE%) was found
500 to decrease progressively with time from 15.10 \pm 0.23% at 1 h to about 6.34 \pm 0.03% after 4 h
501 (Figure 6b). This suggests a gradual reduction in the oxidation ability of the process, which could
502 be due to the generation of highly resistant short-chain hydrocarbon as by-products [98]. The
503 reduction in the organic content over a prolonged period could also limit the mass transport as well
504 as facilitating counterproductive reactions such as dimerization of hydroxyl radicals [99].

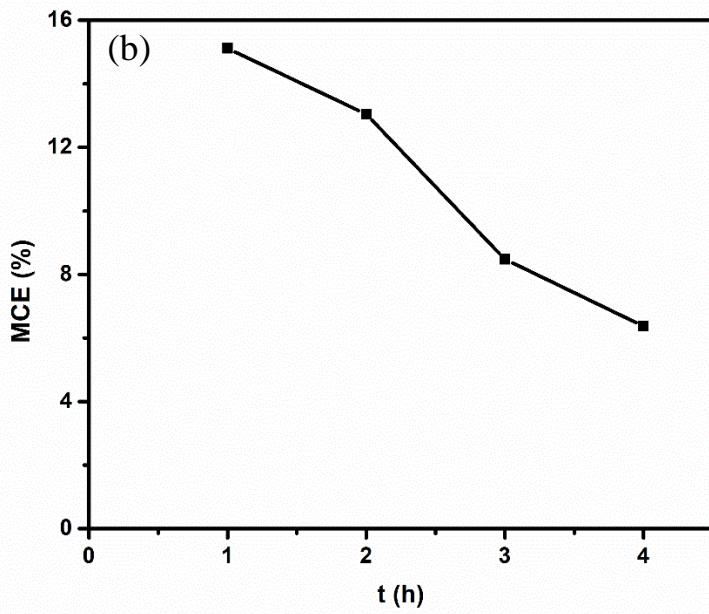
505 A desirable attribute of a potential photoanode for industrial water treatment applications is ease
506 of reusability. The reusability and stability of the CZnO-Pd100 anode were accessed by using the
507 electrode consecutively for eight times (8 runs or cycles) and recording the percentage removal
508 after 2 h (Figure 6c). After each run, the electrode was simply rinsed with deionized water and air-
509 dried overnight, unlike in some water treatment techniques where the recovery of the material is
510 often tedious and involves the use of strong chemicals [82,83]. After the eighth run, the difference
511 in the percentage removal was less than 4%, which confirmed the reusability of the anode. In
512 addition, we can note also that the crystallinity and the electronic state of CZnO-Pd100 nanofibers
513 (Figure S3) did not change after photoelectrocatalytic reaction as confirmed by XRD and XPS.

514

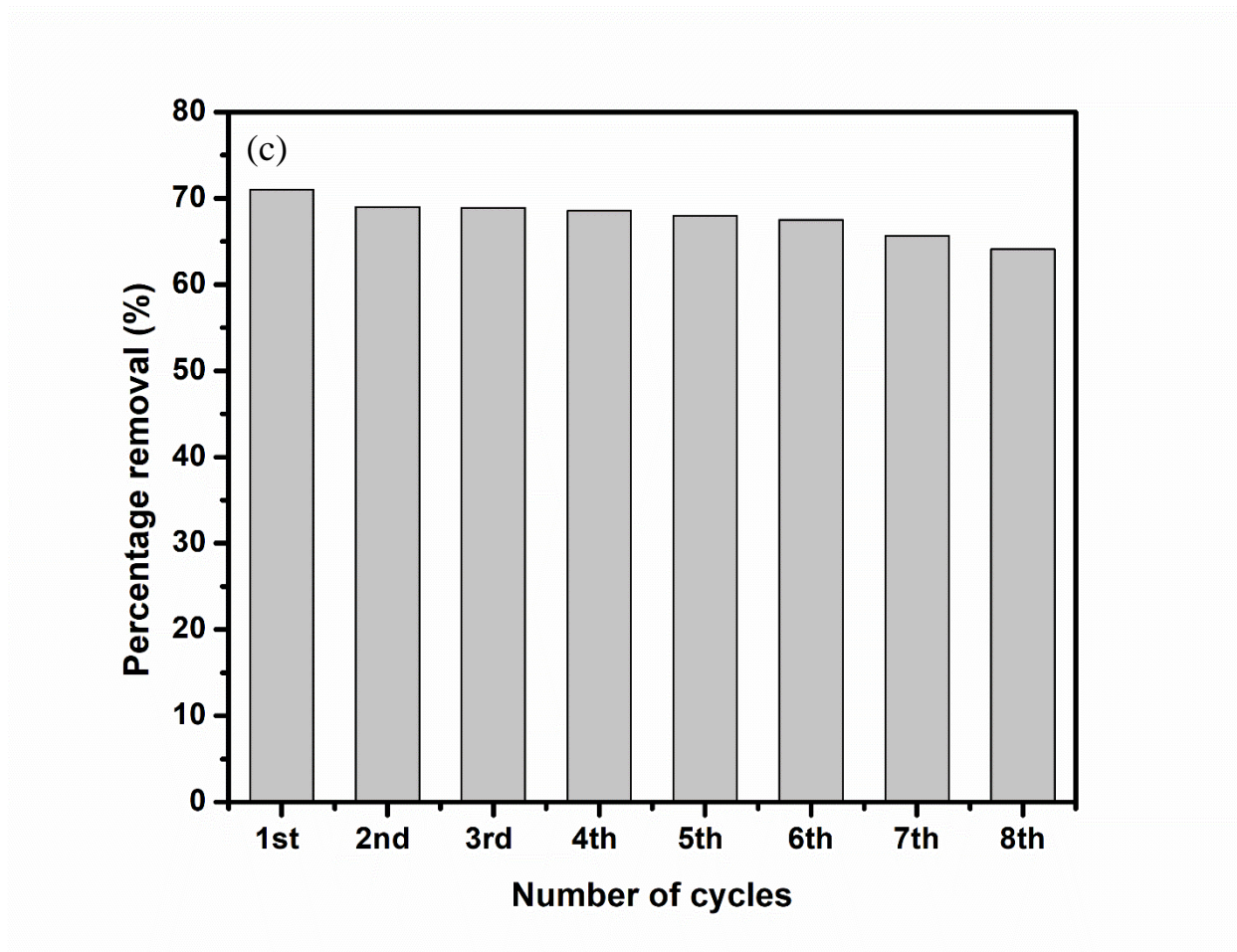
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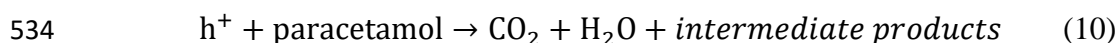
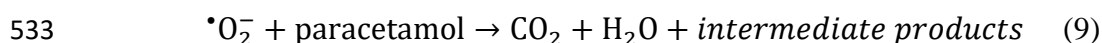
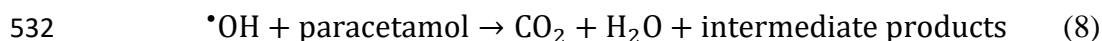
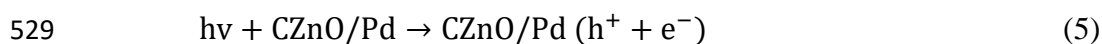
520 Figure 6: (a) Percentage total organic carbon removal in the PEC degradation of paracetamol; (b)
521 Corresponding percentage mineralization current efficiency with time; (c) Reusability tests (0.1
522 mM paracetamol; pH 7; CZnO-Pd100; 10 mA cm⁻²)

523

524 *3.2.2 Scavenger studies and proposed degradation mechanism*

525 In a typical PEC degradation process, in addition to hydroxyl radicals, other reactive species such
526 as photogenerated holes and superoxide radicals also contribute at different degrees to the

527 mineralization of organic molecules [98]. The stepwise formations of these reactive species and
528 their reaction with paracetamol molecules are presented in equations 5 – 10:

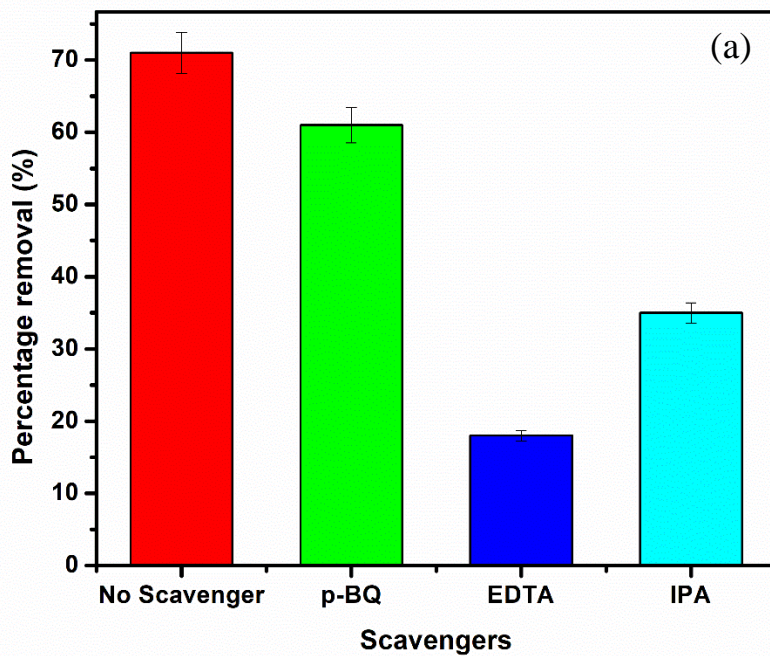


535

536 Trapping experiments were therefore conducted to understand the specific roles of hydroxyl
537 radicals, photogenerated holes and superoxide radicals in the PEC degradation of paracetamol by
538 the addition of 0.001 M Isopropanol (IPA), 0.02 M p-benzoquinone (p-BQ) and 0.01 M
539 ethylenediaminetetraacetate (EDTA) to the electrolytic solution to suppress the effect of hydroxyl
540 radicals, superoxide radicals and holes respectively [98,99]. As presented in Figure 7, upon the
541 addition of EDTA, the percentage removal of paracetamol dropped significantly to $18.70 \pm 0.20\%$
542 after 2 h. This revealed that separated photogenerated holes played a major role in the
543 mineralization of paracetamol. This is in agreement with literatures that photogenerated holes can
544 directly oxidize organics in solution rather than generating hydroxyl radicals first in PEC systems
545 [23]. Additionally, hydroxyl radicals also contributed to the total percentage removal obtained
546 because when the reaction was done in the presence of isopropanol, the percentage removal was
547 $35.10 \pm 1.40\%$. On the other hand, in the presence of p-BQ, substantial degradation percentage
548 was still recorded which clearly revealed that superoxide radicals played a far less role in the
549 degradation process. With these findings, it can be established that the degradation of paracetamol

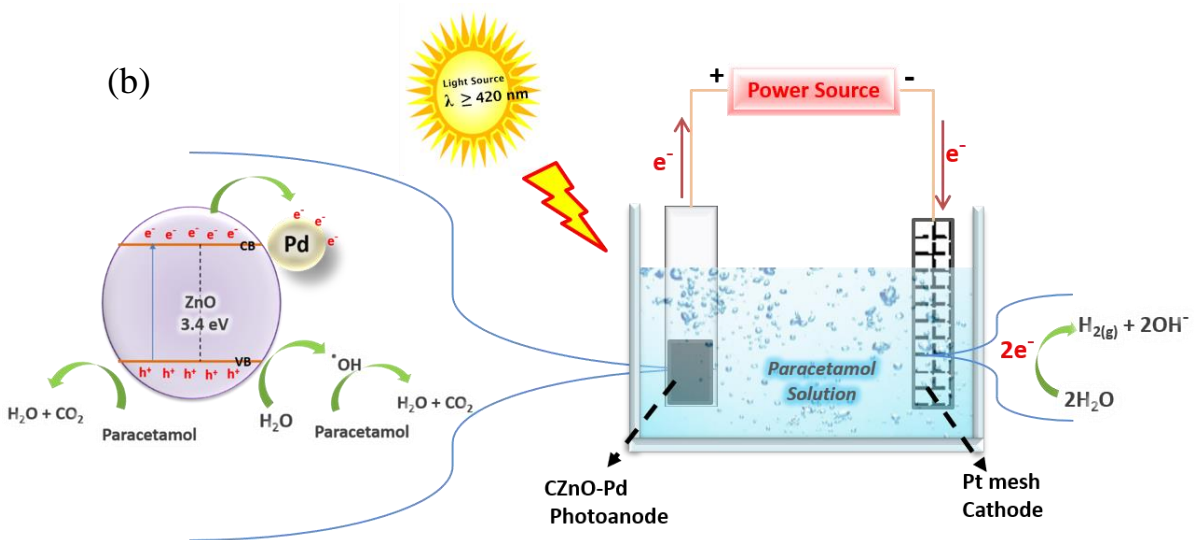
550 molecules using the CZnO-Pd photoanode depends largely on the photogenerated holes.
551 Generally, when a semiconductor is irradiated with light of appropriate energy, the photo excited
552 electrons transfer from the valence band to the conduction band while holes occupy the valence
553 band. However, the photogenerated electrons fall back within a short time to recombine with the
554 photogenerated holes and this prevents the photogenerated holes from reacting with water
555 molecules to produce hydroxyl radicals or directly oxidizing organic molecules present in the
556 solution. In the case of CZnO-Pd photoanode, the efficiency of ZnO is greatly enhanced through
557 improve charge carrier separation due to the presence of Pd. This is because when Pd is in contact
558 with ZnO, a Schottky barrier is created which facilitated the migration of photogenerated holes
559 from the conduction band of ZnO to Pd metal. Consequently, more photogenerated holes are
560 readily available in the valence band of ZnO which either react directly with the paracetamol
561 molecules or with water molecules to produce hydroxyl radicals which then oxidize the
562 paracetamol to water and carbon dioxide. It is also important to note that electrons migrate from
563 the photoanode to the cathode. These electrons could also produce superoxide radicals which can
564 contribute to the degradation of the paracetamol molecules, however, the trapping experiments
565 revealed that the contribution of superoxide radicals is negligible. There is also a possibility of the
566 generation of hydrogen molecules on the cathode by the reactions of electrons with water
567 molecules [100]. The proposed mechanism for the production of oxidants and degradation of
568 paracetamol molecules is illustrated in the schematic diagram presented in Figure 7b (Mechanism
569 PEC degradation process using CZnO-Pd100 photoanode).

570 .



571

572



573

574 **Figure 7:** (a) PEC degradation of paracetamol in the presence on scavengers; (b) Mechanism PEC

575 degradation process using CZnO-Pd100 photoanode (2 h; 0.1 mM paracetamol; 10 mA cm⁻²;

576 CZnO-Pd100)

577 3.2.3 Comparison with previous studies

578 Several kinds of semiconductor photoanodes have been explored for the PEC degradation of
579 pharmaceuticals. To clearly justify the performance of the CZnO-Pd photoanode, the results
580 obtained were compared with earlier literatures on PEC degradation of paracetamol. As presented
581 in Table 1, the percentage removal as well as TOC removal obtained with the present electrode
582 compares well with the previous studies and in fact, in some cases the electrode performed better
583 than other earlier reported electrodes. Therefore, CZnO-Pd can be a suitable photoanode for the
584 PEC removal of paracetamol molecules in wastewater.

585 **Table 1:** Comparison of electrode performance with previous studies

Photoanode	Paracetamol concentration (mgL ⁻¹)	Percentage Removal	%TOC removal	References
Au-TiO ₂	78.5	66% after 3 h	20% after 3 h	[101]
TiO ₂	60	100% after 70 min	-	[102]
BiVO ₄ /BiOI	10	68% after 2 h	59% after 2 h	[103]
TiO ₂	40	45% after 4 h	21% after 4 h	[104]
CZnO-Pd	151	100% after 150 min	71% after 4 h	Present study

586

587 Conclusion

588 In this work, successful preparation of Pd loaded zinc oxide carbon nanofibers (CZnO-Pd) was
589 achieved through electrospinning and atomic layer deposition. Results from the structural and
590 morphological characterization revealed that amorphous ZnO nanoparticles were homogenously
591 deposited on the surface of the carbon nanofibers while spherical metallic Pd nanoparticles were

592 deposited on the edge/shell of the nanofibers to form a coaxial or core/shell structure. The prepared
593 material (CZnO-Pd100) displayed good absorbance of photons in the visible light region due to
594 the presence of metallic Pd. However, the visible light absorption of the material decreased with
595 high content of Pd nanoparticles (ZCnO-Pd200). Similar trend was observed when the prepared
596 materials were applied for the photoelectrocatalytic removal of paracetamol. Total removal was
597 achieved in less than 3 h with $71.20 \pm 0.31\%$ TOC removal after 4 h with the use of CZnO-Pd100
598 while the percentage removal obtained with CZnO-Pd200 was lower due higher content of Pd
599 particles which decreased the photocatalytic active of the semiconductor. Additionally, the rate of
600 the PEC degradation process of paracetamol using the CZnO-Pd100 photoanode was fast and the
601 mechanism of the reaction suggests that both photogenerated holes and hydroxyl radicals played
602 substantial role in the degradation of the paracetamol molecules. Overall, the CZnO-Pd material
603 has a great potential as photoanode for the mineralization of organic pollutants in wastewater.

604

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613

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