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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  $10 \text{ mAcm}^{-2}$ . 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  $\text{TiO}_2$  [29,30],  $\text{BiVO}_4$  [31],  $\text{MoS}_2$  [32],  $\text{Cu}_2\text{O}$   
75 [33],  $\text{Fe}_2\text{O}_3$  [34] and  $\text{WO}_3$  [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  $1.87 \text{ mA cm}^{-2}$  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/MoS<sub>2</sub> photoanode, which  
96 was higher than 53% removal recorded on pristine ZnO anode [47]. ZnO/BiVO<sub>4</sub> 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 ( $\text{HCHO}$ , 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 N<sub>2</sub> 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)<sub>2</sub> 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)<sub>2</sub>, 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 $\alpha$ 1 radiation wavelength 0.1540598 nm and CuK $\alpha$ 2 radiation  
158 wavelength 0.1544426 nm). Raman spectra were measured on a Senterra Bruker using a doubled  
159 Nd:YAG laser ( $\lambda$ = 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  $\mu$ 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) ( $\lambda$ =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 cm<sup>2</sup>  
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 Na<sub>2</sub>SO<sub>4</sub> (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.

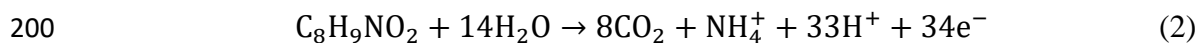
## 183 **2.5 Analytical Procedures**

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<sup>-1</sup>), V<sub>s</sub> is the solution volume (L),  
195 Δ(TOC)<sub>exp</sub> is the experimental TOC decay (mg L<sup>-1</sup>), 4.32×10<sup>7</sup> is a conversion factor (3600 s  
196 h<sup>-1</sup>×12000 mg carbon mol<sup>-1</sup>), 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  $\mu\text{L}$  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  $\text{mL min}^{-1}$ , 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  $\text{L h}^{-1}$ , and desolvation  
213 gas flow 450  $\text{L h}^{-1}$ . Nitrogen (99.5% purity) was the nebulizer gas.

214

## 215 **Results and discussion**

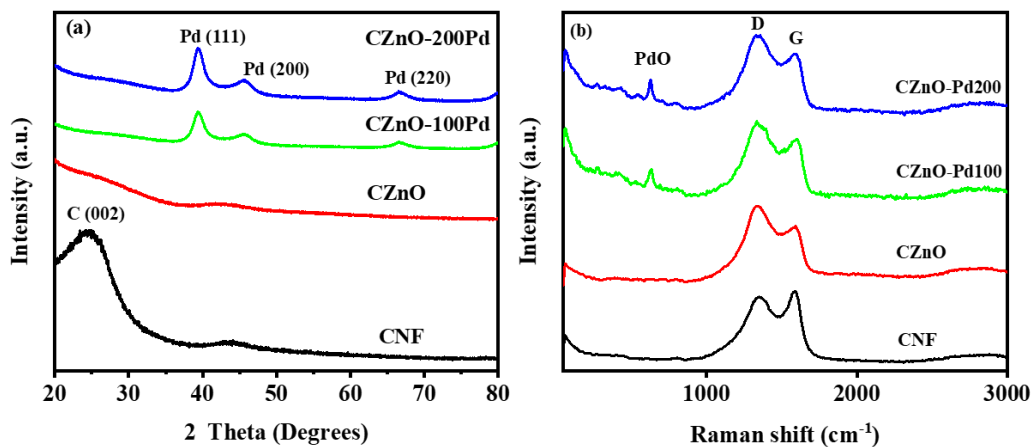
### 216 **3.1 Characterisation results**

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  $\text{N}_2$ . 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  $1354\text{ cm}^{-1}$  and graphite peak  
243 (G-band) at  $1591\text{ cm}^{-1}$ . 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  $sp^2$  -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.

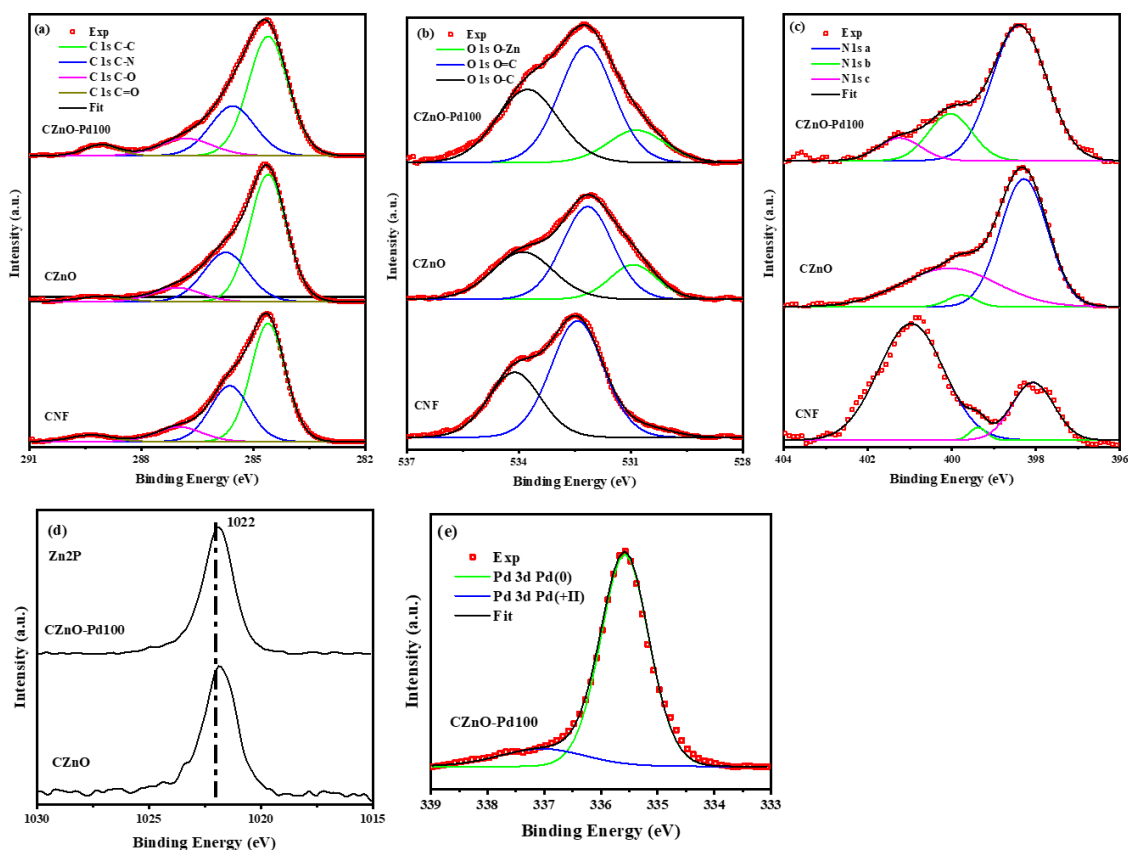


257  
 258 **Figure 1:** (a) XRD patterns of prepared CNF, CZnO, CZnO-Pd100, CZnO-Pd200 nanofibers. (b)  
 259 Raman spectra of prepared nanofibers.

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 N<sub>2</sub> 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 sp<sup>2</sup> 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<sub>3/2</sub> 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 Pd<sup>0</sup> and Pd<sup>+2</sup> species, respectively. The Pd<sup>+2</sup>/Pd<sup>0</sup> ratio is found to be 0.15, suggesting the small  
 288 mass fraction of oxidized Pd<sup>+2</sup> species in the samples, which agrees with the results of Raman  
 289 characterizations.



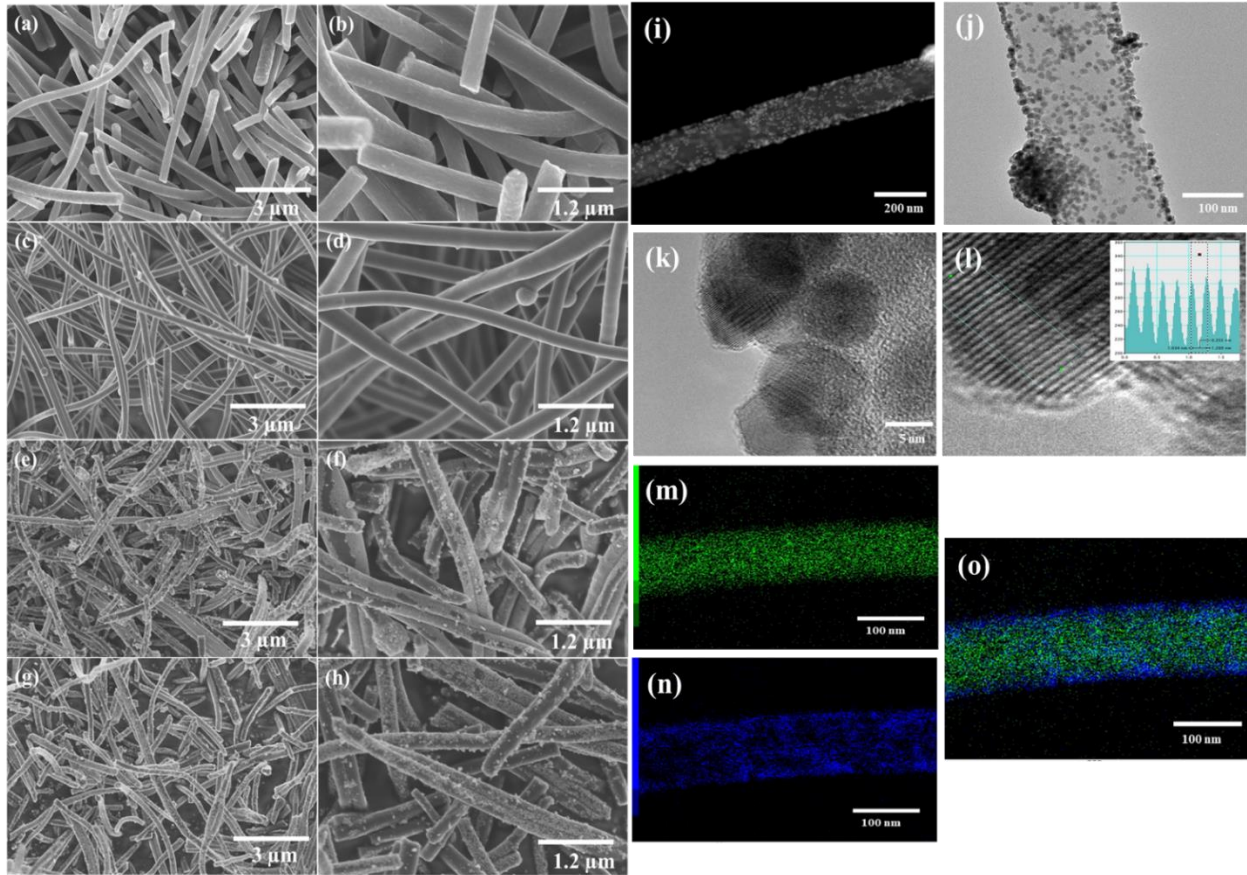
290  
 291 **Figure 2:** (a) High-resolution XPS spectra of C 1s (a), O 1s (b), N 1s (c), Zn 2p (d), and Pd 3d (e)  
 292 for CNF, CZnO and CZnO-Pd100.

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  $0.23 \text{nm}$  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  $\pi$  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.

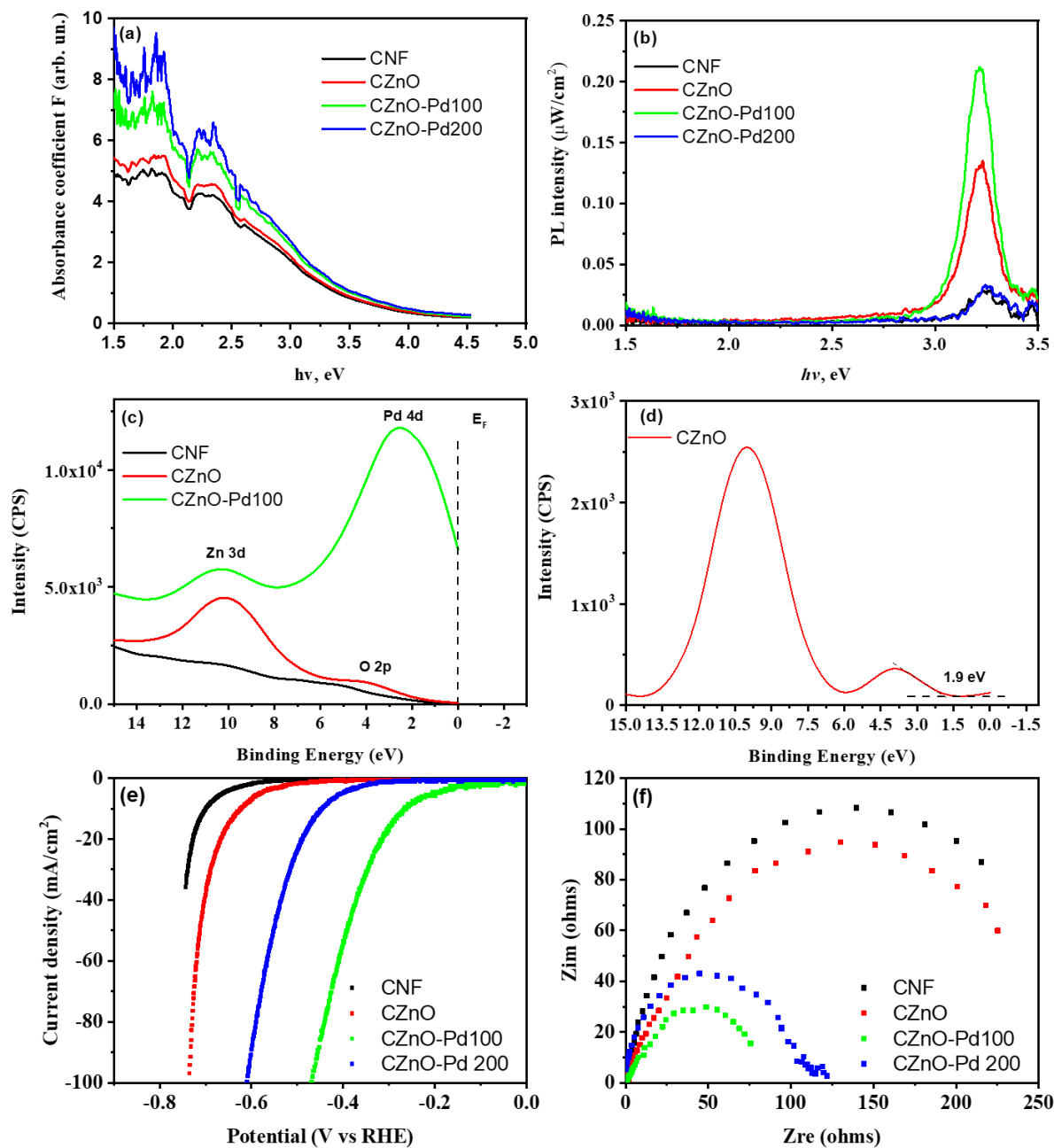
350 Moreover, the increase in the absorbance of carbon-based samples (Figure 4a) points to a wide  
351 absorbance band of Pd nanostructures in the range of 1.5-3 eV. The absorption values increase  
352 with increasing the amount of Pd on the surface of carbon nanofibers. Forming of carbon-ZnO and  
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  $\pi$ - $\pi$  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 Zn<sup>2+</sup> and the Pd<sup>2+</sup> 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/cm<sup>2</sup> of the current density. In contrast, the overpotential of CNF, CZnO and CZnO-  
387 Pd200 are 695, 620 and 441 mV at 10 mA/cm<sup>2</sup> 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 ( $80 \Omega$ ) than the other nanofibers CNF ( $275 \Omega$ ), CZnO ( $240 \Omega$ ) and CZnO-Pd200  
394 ( $120 \Omega$ ), 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  $10 \text{ mA cm}^{-2}$  (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  $5 \text{ mA cm}^{-2}$  (3.3 V) and compared with  
426 the results obtained with  $10 \text{ mA cm}^{-2}$ . As presented in Figure 5c, at lower applied current ( $5 \text{ mA}$   
427  $\text{cm}^{-2}$ ), 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  $5 \text{ mA cm}^{-2}$  to  $10 \text{ mA}$   
435  $\text{cm}^{-2}$ . 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].

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

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

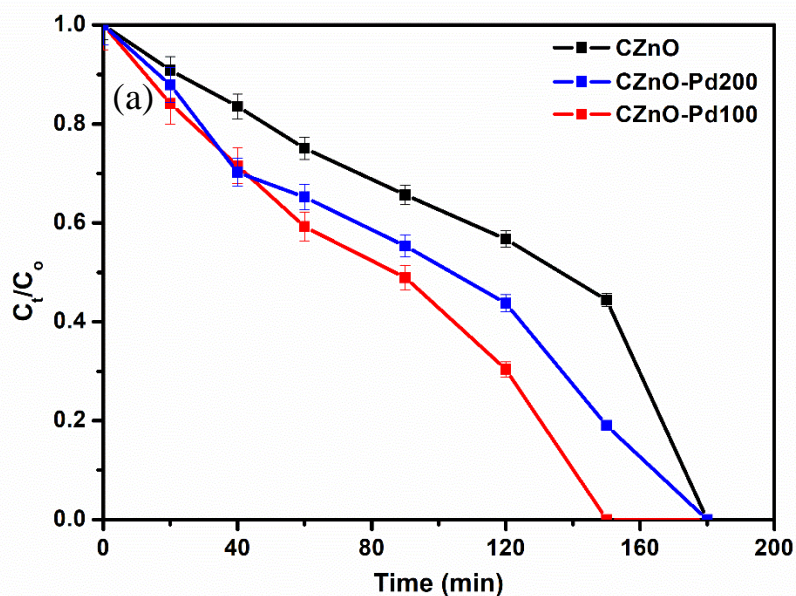
453 Where  $K_{PC}$ ,  $K_{EC}$ , and  $K_{PEC}$  are apparent rate constants for photocatalytic ( $7.883 \times 10^{-4} \text{ min}^{-1}$ ),  
454 electrochemical ( $5.37 \times 10^{-3} \text{ min}^{-1}$ ) and PEC degradation ( $9.710 \times 10^{-3} \text{ min}^{-1}$ ) of paracetamol,  
455 respectively. 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

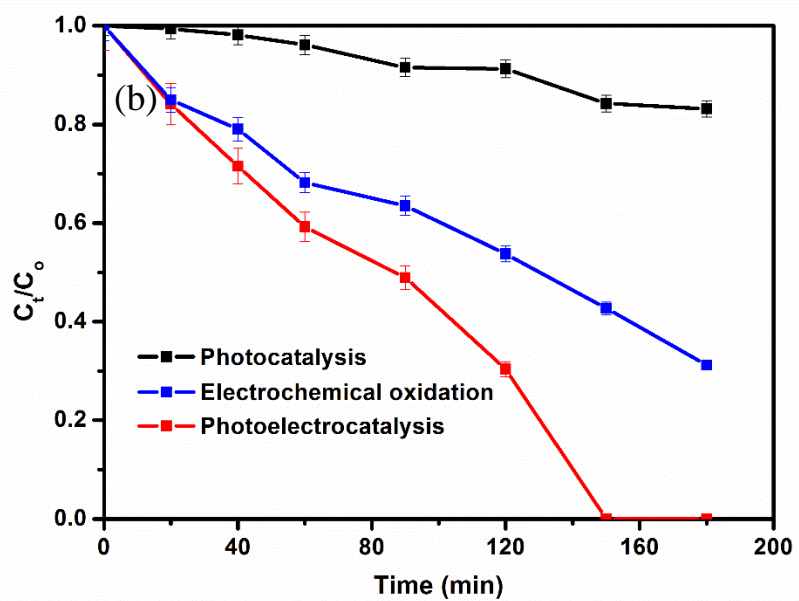
467 photocatalytic effectiveness. This was in agreement with the results obtained from the PL spectra  
468 discussed earlier where increase in Pd loading resulted in light scattering effect on the surface of  
469 the catalyst, thereby diminishing its photocatalytic activity.

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

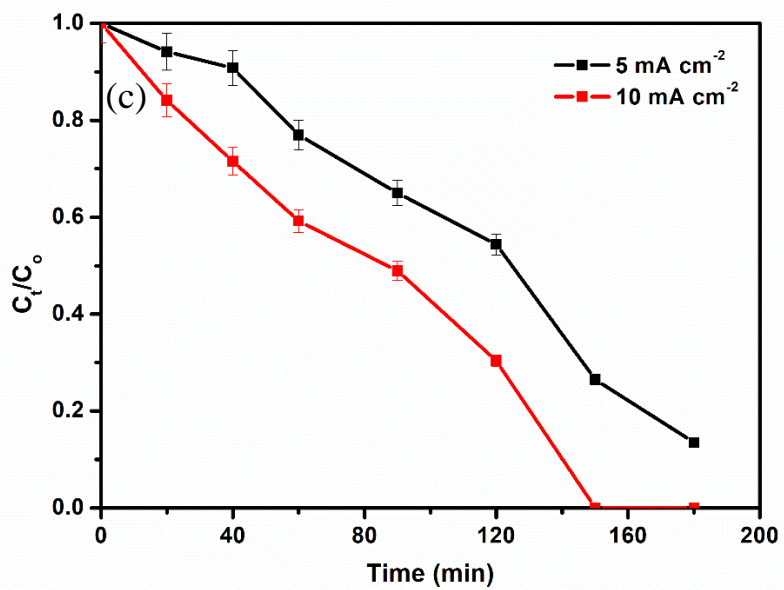


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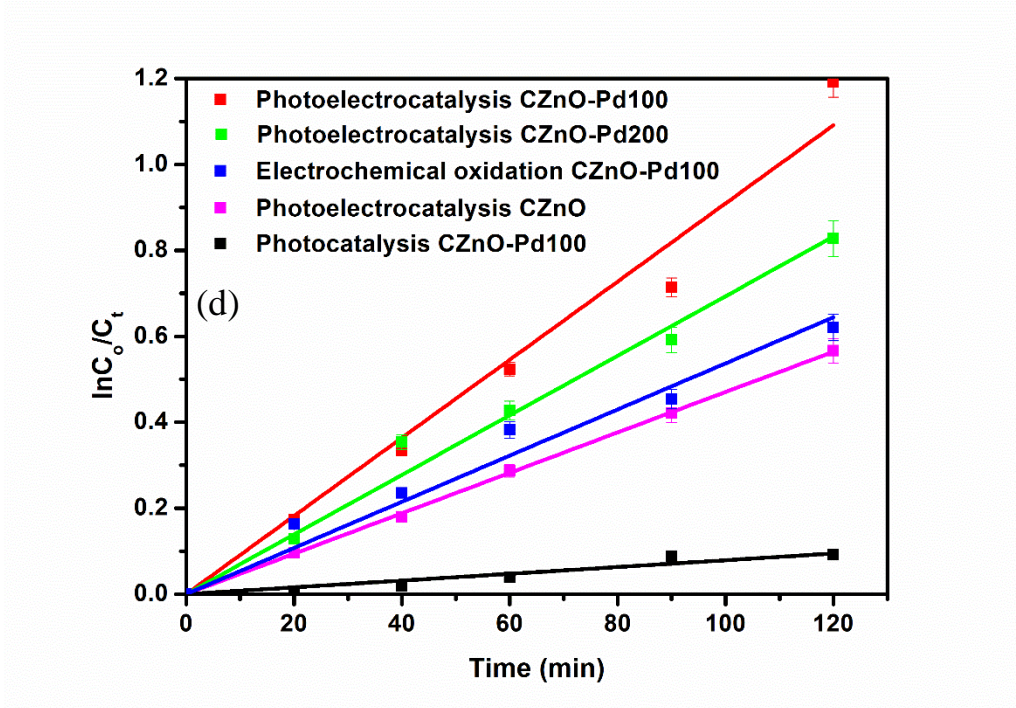
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480

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  $10 \text{ mAcm}^{-2}$  (0.1  
 485 mM paracetamol; pH 7; 50 mM  $\text{Na}_2\text{SO}_4$ )

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

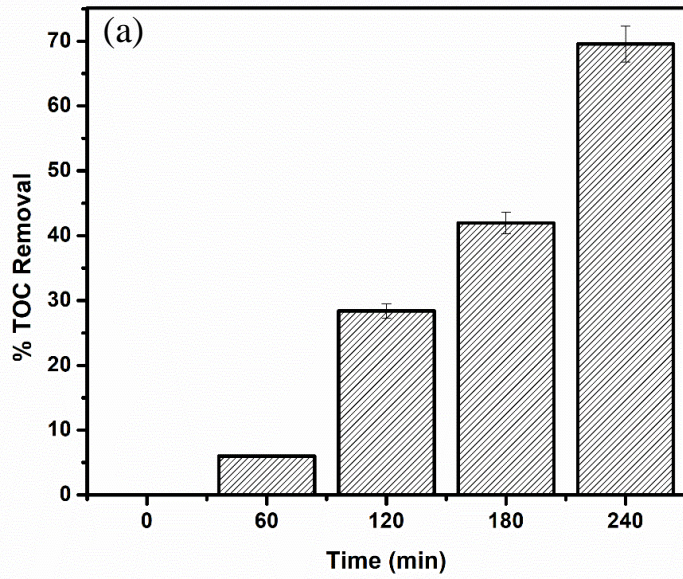
493 71.20  $\pm$  0.31% after 4 h. This clearly revealed that significant mineralization of paracetamol  
494 molecules occurred in the PEC degradation. From the TOC results obtained, it became obvious  
495 that the paracetamol was broken down totally to other smaller organics first, and this accounted  
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.

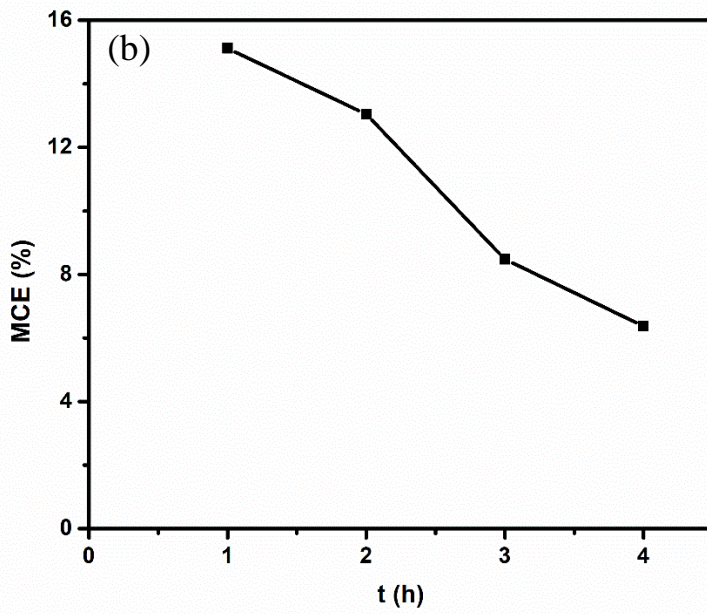
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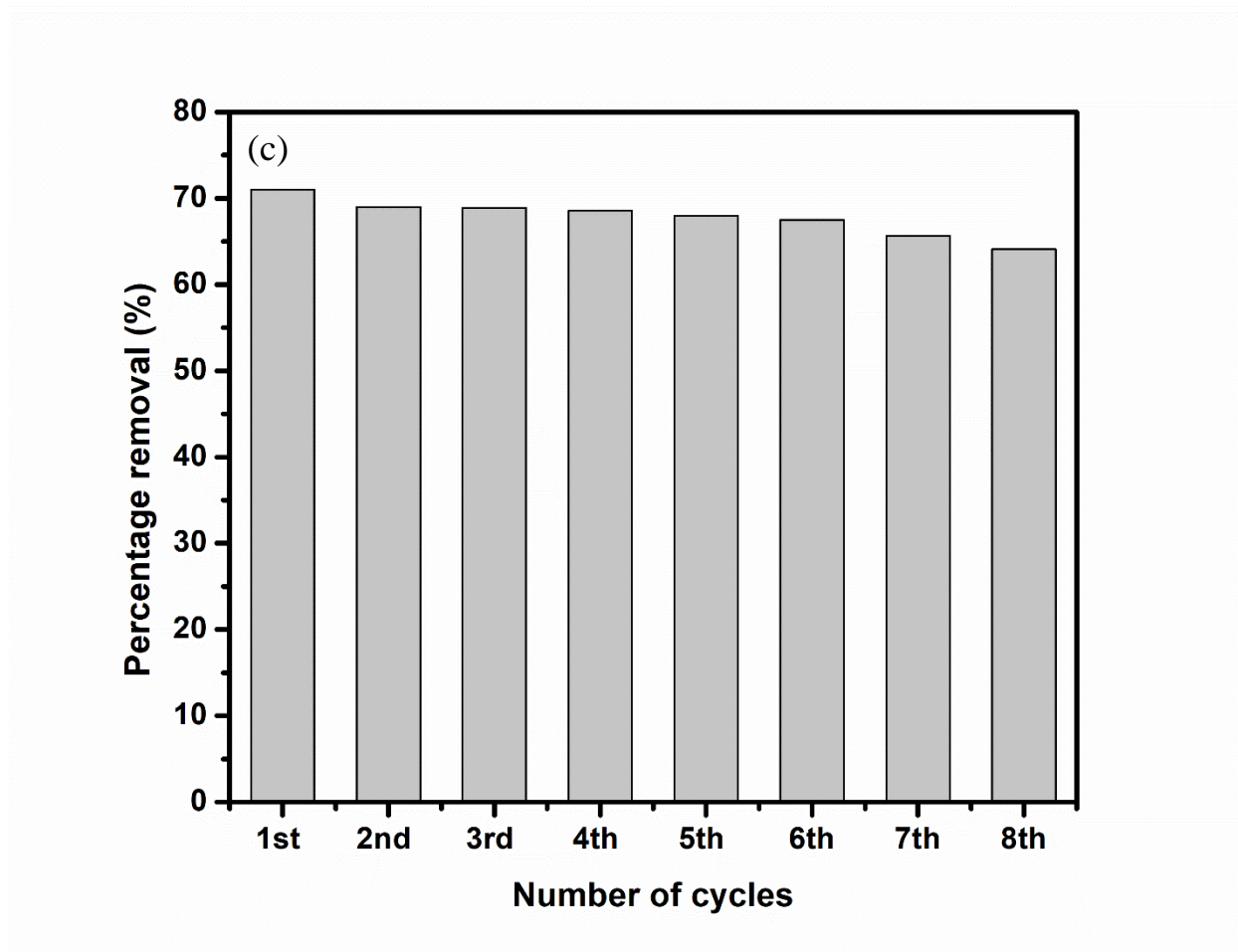




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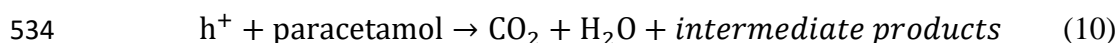
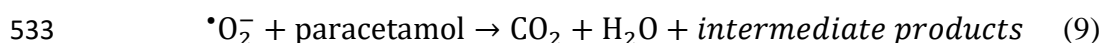
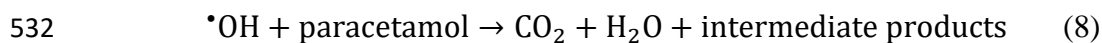
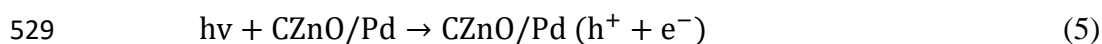
520 Figure 6: (a) Percentage total organic carbon removal in the PEC degradation of paracetamol; (b)  
521 Corresponding percentage mineralization current efficiency with time; (c) Reusability tests (0.1  
522 mM paracetamol; pH 7; CZnO-Pd100; 10 mA cm<sup>-2</sup>)

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:



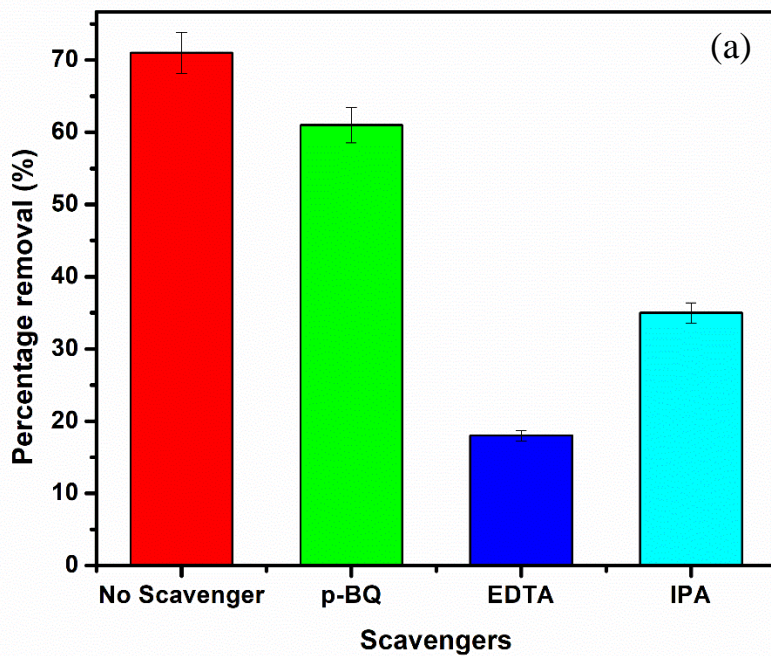
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536 Trapping experiments were therefore conducted to understand the specific roles of hydroxyl  
537 radicals, photogenerated holes and superoxide radicals in the PEC degradation of paracetamol by  
538 the addition of 0.001 M Isopropanol (IPA), 0.02 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



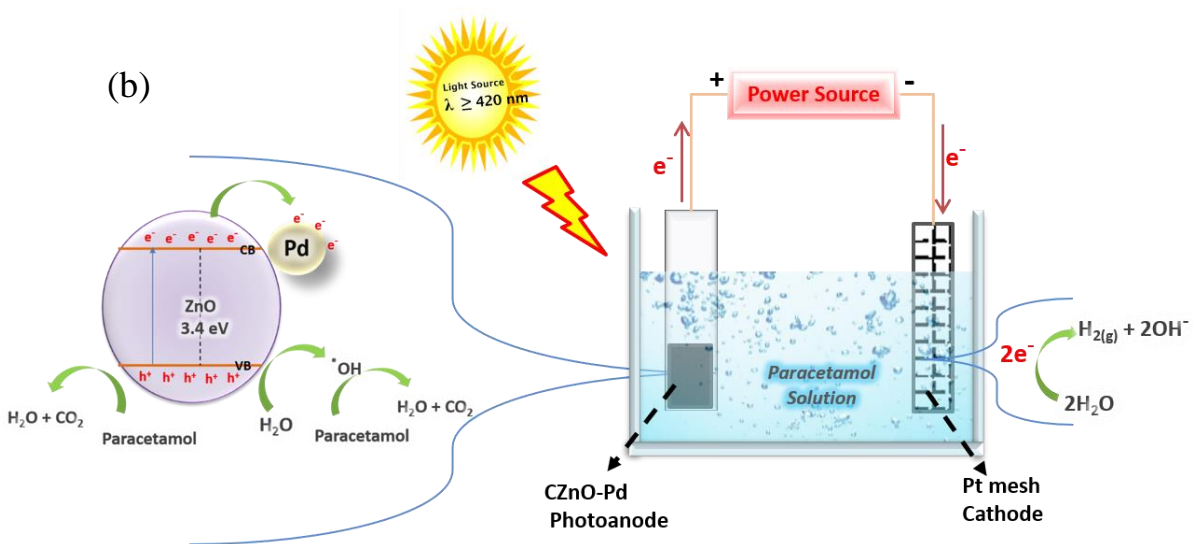
550 molecules using the CZnO-Pd photoanode depends largely on the photogenerated holes.  
551 Generally, when a semiconductor is irradiated with light of appropriate energy, the photo excited  
552 electrons transfer from the valence band to the conduction band while holes occupy the valence  
553 band. 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<sup>-2</sup>;

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 <sup>-1</sup> )	Percentage Removal	%TOC removal	References
Au-TiO <sub>2</sub>	78.5	66% after 3 h	20% after 3 h	[101]
TiO <sub>2</sub>	60	100% after 70 min	-	[102]
BiVO <sub>4</sub> /BiOI	10	68% after 2 h	59% after 2 h	[103]
TiO <sub>2</sub>	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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