

Carbon nanoarchitectures as high-performance electrodes for the electrochemical oxidation of landfill leachate

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33

34 **Abstract**

35 Nanomaterials and assemblies of the aforementioned into complex architectures constitute an
36 opportunity to design efficient and selective solutions to widespread and emerging environmental
37 issues. The limited disposal of organic matter in modern landfills generates extremely
38 concentrated leachates characterised by high concentrations of refractory compounds.
39 Conventional biochemical treatment methods are unsuitable, while advanced treatment, such
40 coagulation, reverse osmosis and ultrafiltration can be very costly and generate additional waste.
41 Electrochemical oxidation is an established technique to efficiently mineralise a plethora of
42 recalcitrant pollutants, however the selectivity and efficiency of the process are strongly related to
43 the anode material. For this reason, a nanoarchitected carbon material has been designed and
44 synthesised to improve the capability of the anode towards the adsorption and decomposition of
45 pollutants. Instead of simple nanostructures, intelligently engineered nanomaterials can come in
46 handy for more efficient advanced treatment techniques. In this study, a carbon nanoarchitecture
47 comprising boron-doped vertically aligned graphene walls (BCNWs) were grown on a boron-
48 doped diamond (BDD) interfacial layer. The results show how the peculiar maze-like morphology
49 and the concurrence of different carbon hybridisations resulted in a higher current exchange
50 density. The BDD performed better for the removal of NH_4^+ while the BCNW-only sample
51 exhibited a faster deactivation. The BDD/BCNW nanoarchitecture resulted in an enhanced COD
52 removal and a NH_4^+ removal similar to that of BDD, without the intermediate production of NO_2^-
53 and NO_3^- .

54 **Keywords**

55 advanced oxidation, vertical graphene, carbon nanowalls, refractory pollutant, boron-doped
56 diamond

57 **1. Introduction**

58 Historical and current patterns of natural resource use have led to environmental degradation
59 and put human health at risk. With the introduction of the 1999/31/EC Directive (European
60 Parliament, 1999) and the 2013/39/EU Directive (European Parliament, 2013), a new waste
61 hierarchy has been introduced, jointly with a list of 45 new pollutants of emerging interest. This has
62 drawn attention to landfill leachates (LLs), which are significant sources of macro- and
63 micropollutants (Fudala-Ksiazek et al., 2017, 2016), and are characterised by low biodegradability.
64 Thus, conventional biochemical methods are unsuitable for the treatment of LLs, while other
65 processes such as chemical oxidation, coagulation, reverse osmosis and ultrafiltration can be very
66 costly. For this reason, the EU is supporting the development of innovative wastewater treatment
67 technologies to enable cheaper and more sustainable treatment (European Parliament, 2013).

68 Electrochemical oxidation (EO) of water pollutants is an advanced oxidation process (AOP), which
69 mineralises organic and inorganic pollutants. Among other AOPs, EO benefits from the lack of
70 added chemicals as well as the lack of the necessity to dispose of secondary waste products. The
71 main requirement for the electrodes is that they need to possess a wide electrochemical window, to
72 ensure stability for extended usage. For this reason, the electrode material plays a primary role in
73 the EO process (Pierpaoli et al., 2020b). Iridium, platinum, ruthenium and titanium oxide-based
74 anodes are characterised by high electrocatalytic activity, leading to faster degradation of organics
75 at lower potentials, while lead, tin oxides and boron-doped diamond (BDD) electrodes support the
76 complete mineralisation of organics due to their high oxygen evolution overpotential. Because of
77 the inexpensiveness and easy availability of graphite, graphitic electrodes have been tested by a few
78 authors for their potential at oxidising organic matter and ammonia from LLs (Bashir et al., 2009;
79 Chiang et al., 1995) However, the likelihood of the limited working potential range being exceeded
80 due to working conditions would lead to a significant dissolution of the graphite electrode (Qiao et
81 al., 2018). Dimensionally Stable Anodes (DSAs) form a class of electrodes including several kinds
82 of metal oxides (such as RuO_2 , IrO_2 , SnO_2) coated on titanium substrates. Given their ease of
83 preparation by the hydrothermal method, and their wider working potential, many authors have
84 investigated the removal efficiency of such electrodes. In particular, a few metal oxides in DSAs are
85 known to promote the formation of chloride radicals with respect to the water oxidation. The thus-
86 produced chlorine, hypochlorite, and hypochlorous acid play an important role in the indirect
87 pollutant oxidation; however, many organochlorinated species may be present as intermediate by-
88 products, which can constitute a hazard more harmful than the original pollutants (Sirés et al.,
89 2014).

90 Simultaneously to the investigation of the removal of new emerging pollutants using
91 conventional electrodes, the scientific community shift its attention to the realisation of novel
92 nanostructured electrode materials, as they exhibit better electrochemical properties than their bulk

93 counterparts (Pierpaoli et al., 2020a). Compared to naturally occurring porous materials with a pre-
94 determined pore dimension distribution, nanostructured hierarchical porous materials with well-
95 defined pore morphology offer a maximised surface area and a minimised diffusive resistance to
96 mass transport (Dutta et al., 2014). For this reason, the development of highly sophisticated
97 assemblies of nanomaterials may lead to further performance refinements (Kaneti et al., 2017;
98 Malgras et al., 2015; Wang et al., 2018), making them suitable for real-world application.

99 While a plethora of structured nanomaterials have been developed for environmental photocatalysis,
100 the enhanced selective adsorption of various pollutants and other functional applications (Dutta et
101 al., 2017), few examples in which they have been used for other remediation techniques are reported
102 in the literature. In particular, while nanostructured electrodes have been widely used for sensing
103 applications, a limited number of studies report their use for environmental remediation. Tan and
104 coauthors prepared a nanoporous PbO_2 electrode, firstly by synthesising highly-ordered TiO_2
105 nanotubes, then by depositing PbO_2 by the pulse electrodeposition method (Tan et al., 2011). Because
106 of the porous microstructure, in which the diffusion of the electrolyte is locally restricted, the pH is
107 much lower than in the bulk electrolyte. Similarly, Wang et al. prepared different nanotube-based
108 architectures by tailoring the electrode production conditions. By varying the anodisation time and
109 voltage, both morphological and electrochemical properties varied, resulting in an 85 nm pore
110 diameter, which is optimum for catalytic performance (Wang et al., 2013). The higher
111 electrochemical efficiency was correlated with a higher oxygen evolution potential. In another study,
112 Zhang and coworkers synthesised a $\text{Ti/SnO}_2\text{-Sb}$ electrode, modified by carbon nanotubes to
113 indirectly increase the specific surface area and the number of reaction active sites (Zhang et al.,
114 2014). In this work, carbon nanotubes played the role of a template, which was burned off during
115 calcination. When carbon-based electrodes are investigated, BDD is favoured because of its high
116 chemical inertness, corrosion resistance, and widest working potential, while graphite constitutes a
117 cost-effective solution. In BDD synthesis, the sp^3/sp^2 carbon hybridisation ratio has been found to
118 be an important parameter, linked to promoting the active or non-active electrode behaviour
119 (Medeiros De Araújo et al., 2014) and the boron inclusion into the diamond lattice (Bogdanowicz et
120 al., 2013), resulting in different EO selectivity (Fudala-Ksiazek et al., 2018). Boron-doped carbon
121 nanowalls (BCNWs) are open boundaries - vertically oriented few-layer graphene sheets - possessing
122 extraordinary electrochemical properties. Because of their peculiar maze-like morphology, the
123 specific surface area is increased, compared to a BDD electrode, which suggests an enhanced
124 efficiency towards the degradation of various pollutants, with a potential window comparable to
125 BDDs (Hiramatsu and Hori, 2010; Sobaszek et al., 2017). The vertical alignment of the carbon
126 nanostructures affects the electrochemical performance in different ways, both due to the chemistry
127 and to the morphology of the CVD-growth architecture. The larger extends of exposed edges,
128 compared to a parallel alignment, allows to have a greater number of functional groups and



129 chemisorbed heteroatoms, in particular oxygen, which allows a higher reactivity of the carbonaceous
130 nanostructure (Dettlaff et al., 2020). Many physical properties of the synthesized carbon
131 nanomaterials, in particular the wetting and adsorption behaviour, are decisively influenced by
132 chemisorbed oxygen. Oxygen, in the plane edges, can be bound in the form of various functional
133 groups, thus they play an important contribution to the capacitance through faradic processes which
134 involve one or two-electron transfer reactions, which aspect is limited in the case of a parallel
135 disposition of the carbon layers.

136 In this study, for the first time, a hybrid 3D/2D carbon nanoarchitected electrode was
137 fabricated, and the oxidation efficiency was assessed by the electrochemical mineralisation of
138 recalcitrant landfill leachate pollutants. The three-dimensional layer consisted of a BDD sheet
139 grown by microwave plasma-enhanced chemical vapour deposition (MPECVD) on a roughened
140 niobium substrate. By changing the composition of the gas during the synthesis process, it was
141 possible to grow vertically aligned graphene sheets on the uneven surface of the substrate, with a
142 BDD interlayer, covered by “nano-flap” surface nanotextures. BDD and graphite electrodes were
143 used as a reference for comparison.

144 **2. Materials and methods**

145 *2.1 Landfill leachate analysis*

146 In this study, LL was collected from a waste cell at a municipal solid waste plant (MSWP)
147 located in northern Poland (N 54°51'742' S 18°36'854") which serves a metropolitan area of
148 approximately 460,000 people and receives approximately 200,000 Mg of waste annually. The
149 landfill was operated from January 2003 to November 2011. During that time, the cells were
150 arranged in an ad-hoc manner without any liner or pollution-control systems, and with unlimited
151 disposal of organic wastes. While in operation, the landfill received up to 90% of indistinct
152 municipal waste, including the deposition of highly biodegradable waste. The LL was collected in
153 March 2019, after 195 months (16 years and 3 months) of operation. This explains the high COD
154 (2854 mg O₂/l), and low BOD₅ (mg O₂/l) and BOD₂₀ (345 mg O₂/l) concentrations. The LL was also
155 characterised by a high ammonia concentration (1940 mg N-NH₄⁺/l), which constituted the main
156 fraction of the total nitrogen (98% of TN). Ammonia forms in a landfill cell during the
157 decomposition of organic matter (mainly proteins) and, as a water-soluble compound, is easily
158 released into the leachate, because its microbiological utilisation is limited under low oxygen
159 availability. Phosphorus was also detected, mainly in mineral form, as P-PO₄³⁻ mg/l and constituted
160 about 89% of the total phosphorous (TP). The presence of phosphorus and nitrogen mainly in
161 mineral form as well as the low BOD₅/COD (0.08) and BOD₅/BOD₂₀ (0.63) ratios indicated that the
162 biodegradable organic matter from the solid waste was efficiently consumed. In manure landfills,
163 the organic matter becomes refractory and is mainly represented by humic and fulvic-like fractions



164 (Pelaez et al., 2009), which can be indirectly confirmed by the leachate colour. It is worth
 165 highlighting that the WC/PP generates landfill gas which is stable in quantity (44,881 m³ in March)
 166 and quality (about 73% methane), suggesting that this cell still undergoes a methanogenic phase
 167 (Spagni et al., 2008). The leachate characteristics are reported in Table 1.

168

Table 1 – Leachate characteristics

Parameter	Value
pH	7.78
Redox potential (mV)	-409.7
BOD ₅ (mg O ₂ /l)	218
BOD ₂₀ (mg O ₂ /l)	345
COD (mg O ₂ /l)	2854
N-NH ₄ ⁺ (mg/l)	1940
S ²⁻ (mg/l)	10.5
Cl ⁻ (mg/l)	2758
SO ₄ ⁻ (mg/l)	1035
TN (mg/l)	1975
N-NO ₃ ⁻ (mg/l)	15.2
N-NO ₂ ⁻ (mg/l)	0.229
P-PO ₄ ³⁻ (mg/l)	12.98
TP (mg/l)	14.6

169

170 *2.2 Nanoarchitected electrode fabrication*

171 The carbon nanoarchitectures were fabricated as follows: a 2-inch diameter niobium substrate
 172 was sandblasted, washed and rinsed with acetone and 2-propanol in an ultrasonic bath, to roughen
 173 the surface. Next, the substrate was sonicated in a water-based nanodiamond-slurry, in order to
 174 provide the nucleation sites for the growth of thin diamond film (Sobaszek et al., 2017). BDD and
 175 BCNW were grown by MPECVD (SEKI Technotron AX5400S, 2.45 GHz, 1300 W), using a gas
 176 mixture of H₂, CH₄, B₂H₆, and N₂ (N₂ was used only for growing the BCNW structure). The chamber
 177 pressure was kept at 50 Torr for all of the processes. The gas composition, substrate holder
 178 temperature and process duration were varied according to Table 2. As can be seen, the process
 179 duration between the BCNW and BDD differs because of the different nanostructure growth rates.
 180 While the doped diamond can be deposited directly onto the niobium substrate at 700°C, the
 181 growth of vertical carbon on Nb has been found to be facilitated by a higher temperature. In order
 182 to minimise the internal thermal stresses, both layers of the nanoarchitected composite were

183 grown at the same temperature. The growth duration is substantially reduced for the CNW growth
 184 because of the higher CH₄ flow and growth rate. To obtain a hierarchical structure, the growth of
 185 the graphene “nano-flap”, perpendicular to the principal BCNW, was obtained by deliberately
 186 switching off the DC bias. In the absence of an electrical field perpendicular to the niobium
 187 substrate, the growth proceeds in multiple directions, thus realising a complex interconnected
 188 morphology.

189 *Table 2 – Growth parameters for the nanoarchitected electrode fabrication*

	BDD	BCNW	BDD/BCNW
Substrate		Nb	
Sample holder temperature (°C)	700	850	850
Growth duration (h)	12	3	3+2
B ₂ H ₆ /CH ₄	2.5	0.3	0.3
N ₂ /CH ₄	0	0.12	0+0.12

190
 191 The graphite electrode was used as purchased and consists of a 50*40*3mm 99.99% graphitic plate.
 192 The sample was cut and covered with resin to have the same dimension as the exposed surface.

193 *2.2 Nanoarchitected electrode characterisation*

194 For all of the samples, morphological, chemical, and electrochemical characterisations were
 195 performed both prior to and after the EO tests. The nomenclature report “pre” or “post”,
 196 corresponding to whether the test was performed before or after the EO.

197 Scanning electron microscopy and energy-dispersive X-ray spectroscopy were performed with a
 198 Phenom XL instrument (Thermo Fisher Scientific), using a 10 kV beam accelerating voltage with
 199 BSD or EDS detectors working in high vacuum mode.

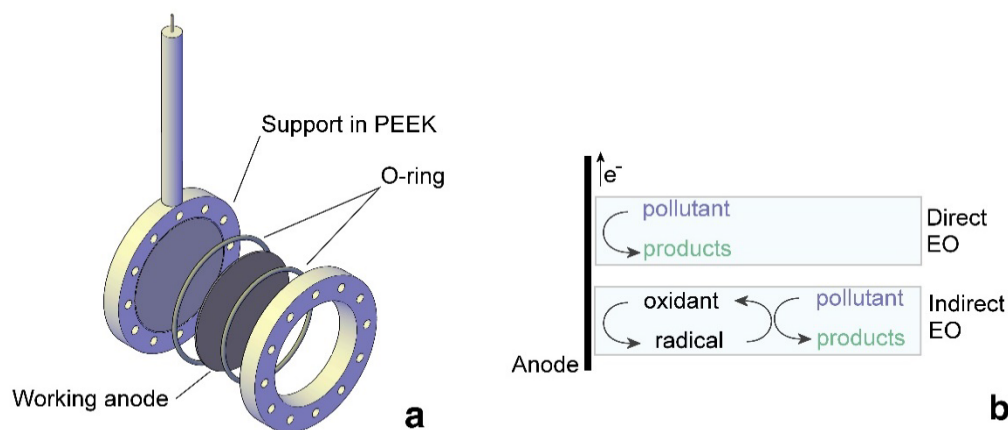
200 Raman spectra were recorded in the 100–1740 cm⁻¹ range, using a micro Raman spectrometer
 201 (InVia Renishaw, UK) equipped with a 514 nm argon-ion laser. For each sample, spectra were
 202 acquired in three different spots, and the measured values were averaged, smoothed (using a
 203 Savitzky-Golay method: 15 points, second polynomial order), and the baseline (approximated with
 204 a cubic polynomial) was subtracted and normalised.

205 The electrochemical properties of the samples were investigated by cyclic voltammetry (CV),
 206 electrochemical impedance spectroscopy (EIS), and linear sweep voltammetry (LSV). For each
 207 investigation technique, the working electrode was the considered anode, having a working area of
 208 0.0314 cm², the counter electrode was a platinum wire, and the reference electrode was an AgCl-

209 coated Ag wire. The measurement was carried out in 0.5 M H₂SO₄ as the electrolyte, at a scan rate
210 of 50 mV/s, using a potentiostat-galvanostat (VMP-300, *Bio-Logic*, France) driven by the EC-Lab
211 software.

212 2.3 Nanoarchitected electrochemical oxidation test

213 EO tests were performed in a cylindrical single-cell reactor containing 400 mL of solution.
214 The leachate was diluted 1:1 with deionised water. The anode had a total area of 10.5 cm², and was
215 secured in a PEEK sample holder (Figure 1a), while a stainless steel net of approximately 10x7 cm
216 served as the cathode. A constant potential of 12V was applied to the electrodes, and the current
217 was measured during the process. The leachate was stirred and thermostated in a water bath for
218 the whole process. The N-NH₄⁺ and COD removal processes can happen both by direct and indirect
219 electrochemical oxidation (Figure 1b). The pH, redox potential, and concentration of selected
220 pollutants were monitored every 2 hours. In particular, the following parameters were analysed
221 according to American Public Health Association guidelines (D. Eaton et al., 2005): pH and redox
222 potential (mV) using a portable multi-parameter meter (HL-HQ40d multi, HACH, Germany); total
223 (TN) and inorganic N compounds (N-NH₄⁺, N-NO₃⁻, and N-NO₂⁻), and chemical oxygen demand
224 (COD), using a XION 500 spectrophotometer (Dr. Lange, GmbH, Germany); 5- and 20-day
225 biochemical oxygen demand (BOD5 and BOD20) using the manometric respirometric BOD OxiTop
226 method.



227
228 *Figure 1 – (a) Sample holder used in the electrochemical oxidation batch test; (b) schematic of the process*
229 *occurring in the electrochemical oxidation process*

230 3. Results and discussion

231 3.1 Leachate electrochemical oxidation

232 The decrease in pollutant concentration during the electrochemical oxidative tests is
233 expressed against the specific electrical charge (Q), as follows:

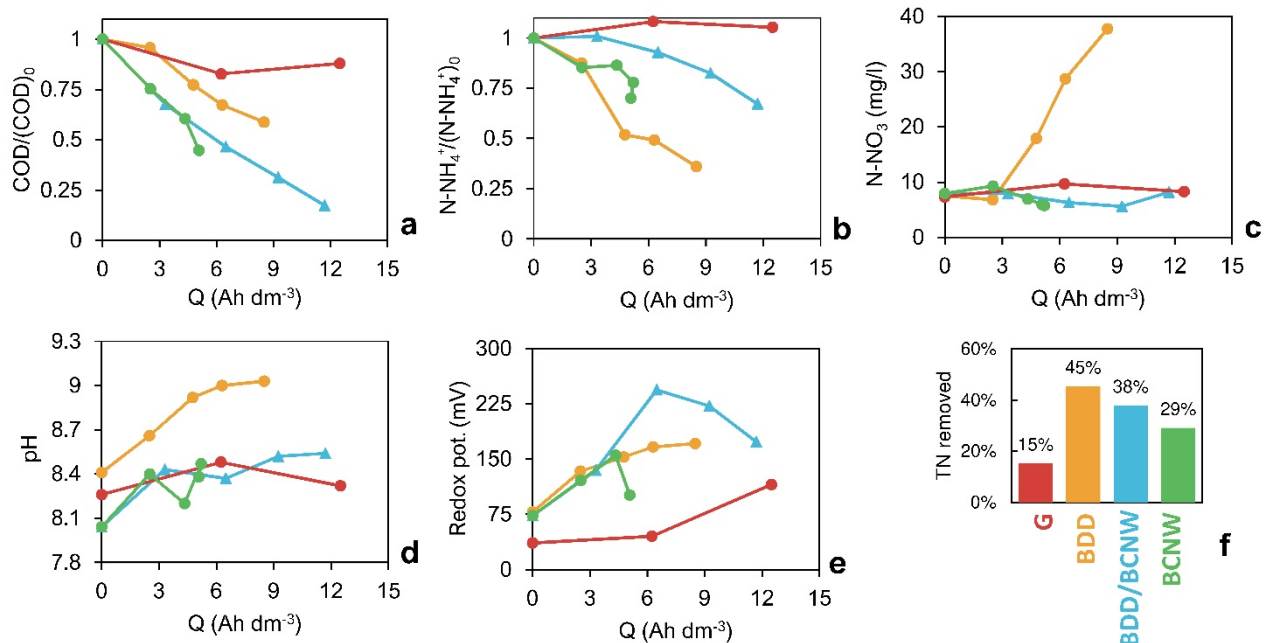
234

$$Q = \frac{JAt}{V}$$

235 Where J is the current density (Am^{-2}), A is the electrode surface (m^2), t is the time (s), and V is the
236 volume of the electrolytic solution (L). While a representation of the physicochemical parameters
237 against time would determine the oxidation rate, the representation against Q provides information
238 about the process efficiency (Anglada et al., 2009).

239 Figure 2a shows the trend of the COD with Q for the different anode types. After 8 hours of tests, the
240 COD was reduced by about 50% for the BDD electrode; the same result was achieved by the BCNW
241 electrode, but at a lower specific electrical charge (40% lower). The BDD/BCNW sample had the best
242 performance, removing 83% of the COD. The graphite electrode test was performed for only 4 hours
243 because of the accelerated exfoliation of the electrode, and only 12% of the COD was oxidised. BOD_{20}
244 removal was equal to 55% for the BDD electrode, 37% for the BCNW, and it reached 70% for the
245 BDD/BCNW electrode. Interestingly, the ammonium removal was faster with the BDD (Figure 2b),
246 followed by the BCNW and by the nanostructured composite electrode. As ammonia removal is
247 mainly promoted by a reaction with active chlorine, the electrodes which performed better at directly
248 oxidising organic matter resulted in being disadvantaged for the indirect N-NH_4^+ oxidation because
249 of the competitive behaviour. While hypochlorite ions and hypochlorous acid can oxidise ammonium
250 into nitrogen gas due to their high oxidative potentials, BDD has a tendency to oxidise ammonium
251 to nitrates (Figure 2c). The variation of pH for the three nanostructured electrodes (Figure 2d) was
252 small (an increase of 7% after 8 hours), and was constant for the graphite electrode. However, it has
253 to be considered that the pH is significantly lower in the vicinity of the electrode, especially within
254 the pores, due to the CNW maze-like structure, because of the limited electrolyte diffusion (Wang et
255 al., 2013). The presence of chlorine concentration and other oxidants results in an increase of the
256 redox potential. While, for the BDD/BCNW electrode, the oxidation-reduction potential (ORP)
257 increase is higher at 4h, followed by a decrease, this results in an acceleration of the N-NH_4^+ removal.
258 Controversially, the ORP of the BDD sample increases slowly with the time, until a plateau is reached
259 (Figure 2e). Despite the N-NH_4^+ removal being slower with the nanostructured composite, the total
260 nitrogen removal efficiency was similar to the BDD electrode, mostly because of the direct oxidation
261 to nitrogen gas by the chlorine reaction, without the production of nitrates.

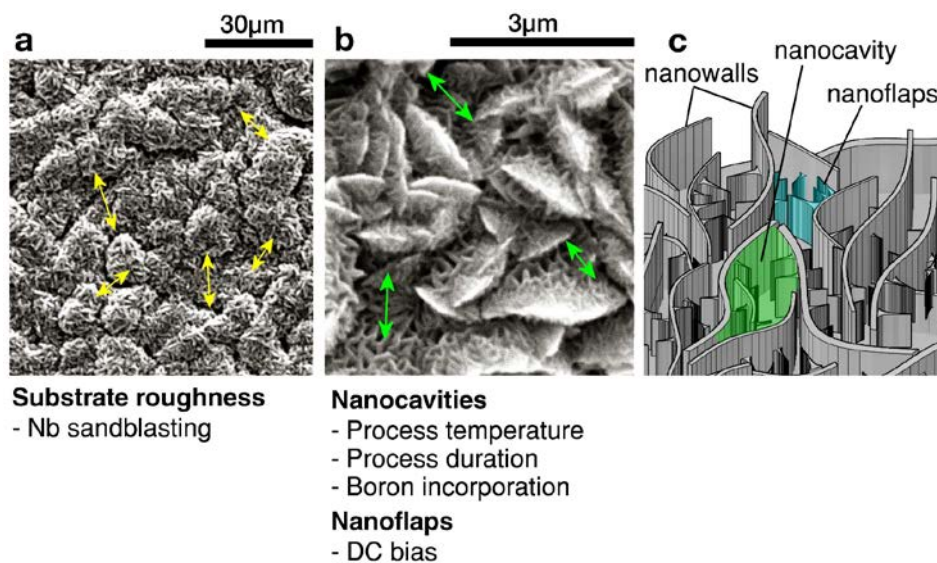




262
 263 *Figure 2 – (a-e) The variation of COD, N-NH₄⁺, N-NO₃⁻, pH and redox potential with Q for the different*
 264 *consider electrodes; (f) the total nitrogen removed within 8 h (4 h for the graphite electrode) of the test.*

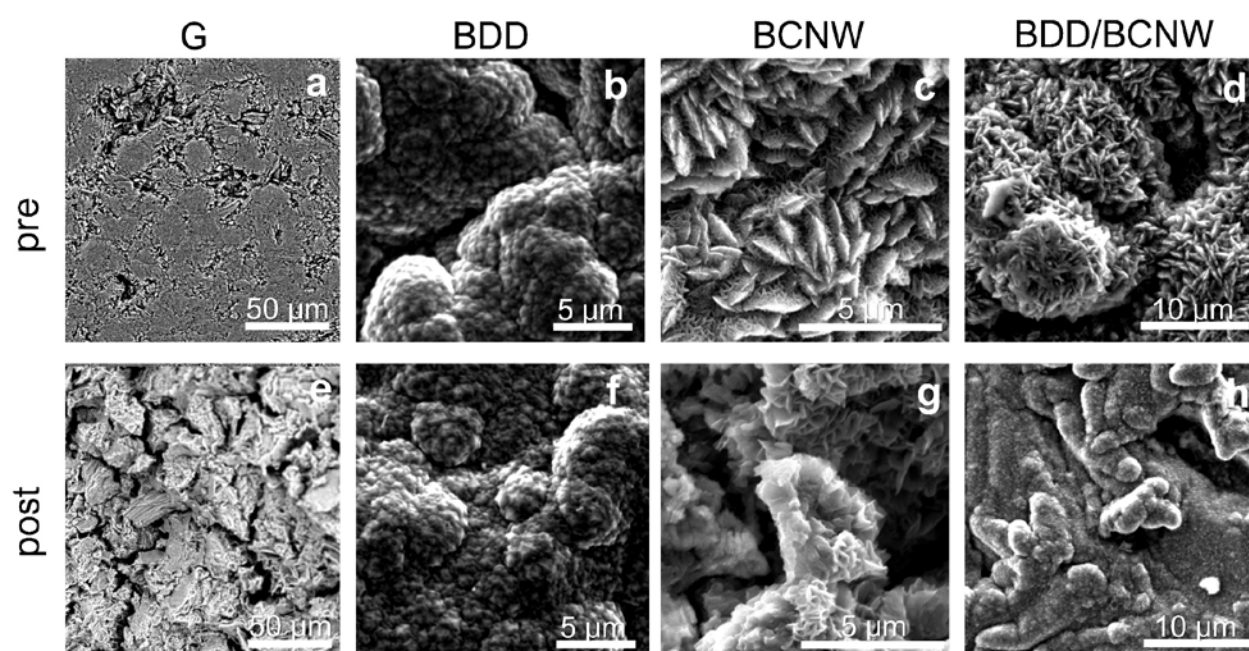
265 3.2 Electrode morphology

266 The morphology of all of the synthesised samples is affected by the surface pretreatment,
 267 resulting from the sandblasting process, which produces microscale valleys having a diameter of tens
 268 of micrometers (Figure 3a). Altering the support surface prior to the CVD process is an innovative
 269 approach to obtain a carbon nanostructure with concave and convex curvatures in a simple way
 270 (Huang et al., 2019).



271
 272 *Figure 3 – (a,b) SEM images of the BDD/BCNW grown on Nb. (c) Schematic representation of the BCNW*
 273 *morphology*

274 While this is the only roughness present for the BDD (Figure 4b), where the carbon grows vertically,
 275 microcavities, having an opening in the range between tens and hundreds of nanometres, are formed
 276 between the nanowall boundaries (Figure 3b). It is easy to tune these openings by varying the
 277 synthesis parameters (Pierpaoli et al., 2019). The “nano-flaps” are secondary protuberances grown
 278 perpendicularly to the surface of the nanowalls due to the absence of a uniform electric field. The
 279 density of the “nano-flaps” can be modified *a posteriori* by a capillarity-driven modification process
 280 (Bo et al., 2017). The production of uniaxially aligned, controlled porosity may bring the benefits of
 281 an effective perpendicular diffusion to the electrode, and minimise the diffusion around it (Ariga et
 282 al., 2012). Scanning electron micrographs of the different electrodes, before and after the EO
 283 experiment, are reported in Figure 4.

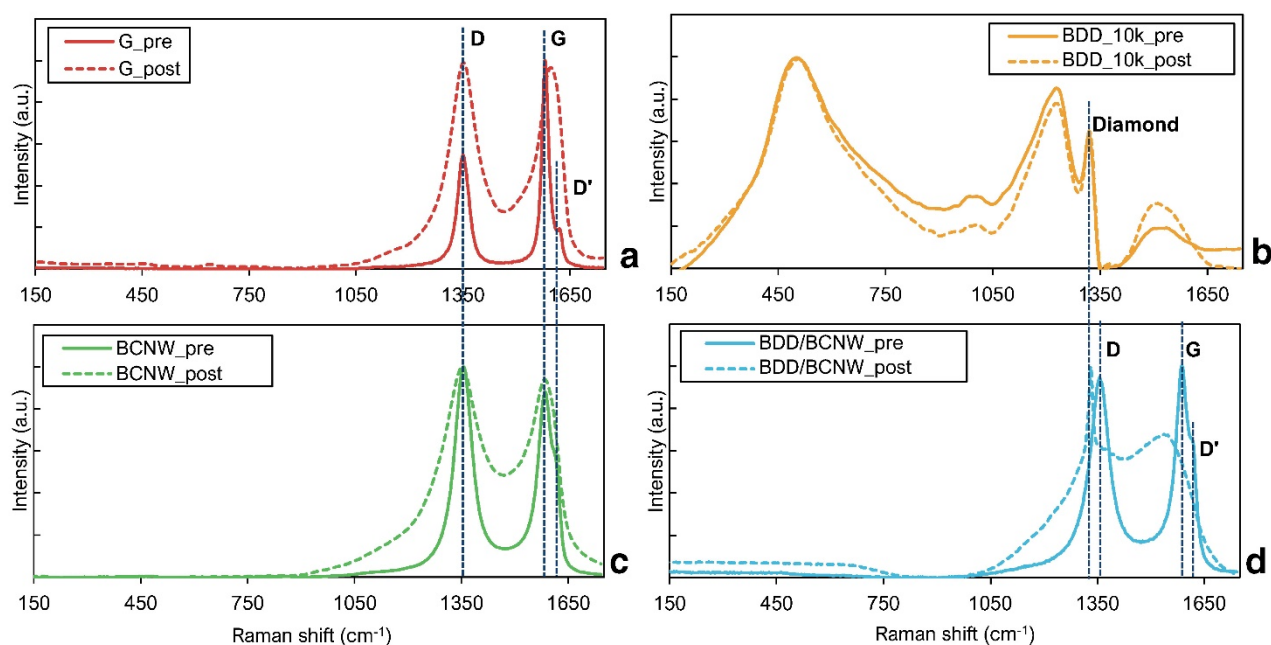


284
 285 *Figure 4 – SEM images of the graphite (G), boron-doped diamond (BDD), boron-doped carbon nanowall*
 286 *(BCNW), and composite (BDD/BCNW) electrodes before (pre) and after (post) the LL EO test.*

287 The graphite electrode (Figure 4a) appears visibly altered after the EO process (Figure 4e), so the
 288 test was concluded after 4 h, instead of 8 h. The porosity of the electrode surface significantly
 289 increased, as a result of the graphite oxidation and the ion intercalation, present in the leachate.
 290 The morphology of the BDD electrode (Figure 4b/f) appears unchanged, while the BCNW electrode
 291 (Figure 4c/g) exhibits a partial loss of the thinner nanowalls and the shedding of carbon flakes,
 292 partially revealing the Nb substrate. The BDD/BCNW nanoarchitecture, prior the the EO test,
 293 exhibits a similar morphology to the BCWN and it visibly change after, tending to look like to the
 294 BDD structure, with localized protrusions (Figure 4d/h).

295 Raman spectroscopy is a relatively simple, quick and non-destructive method to measure the

296 inelastic light scattering from the sample surface, and is a widely used technique for the
 297 characterisation of carbonaceous materials, which can provide useful information on the chemical
 298 and molecular morphology. Figure 5 contains the Raman spectra for the four electrodes, before and
 299 after the EO test.



300
 301 *Figure 5 – Raman spectra of the graphite (G), boron-doped diamond (BDD), boron-doped carbon*
 302 *nanowall (BCNW), and composite (BDD/BCNW) electrodes before (pre) and after (post) the LL EO test.*

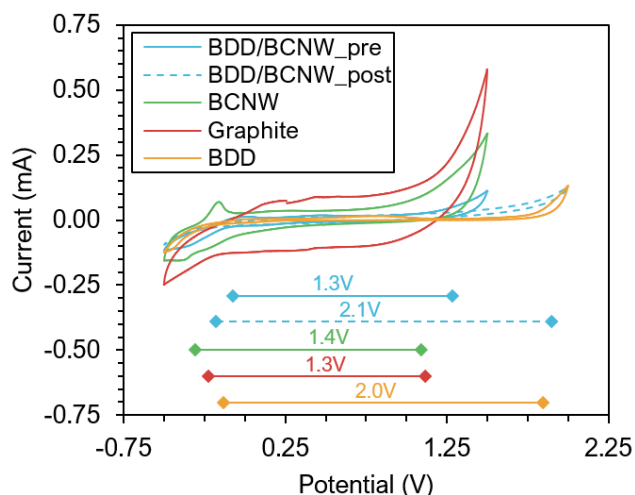
303 The spectra of the graphite electrode (Figure 5a) report two prominent peaks at about 1353cm⁻¹ and
 304 1583 cm⁻¹, corresponding to the G and D bands, respectively, where the D band corresponds to
 305 defects or disorders in sp² structure especially occurring at the edges of graphene sheets. The G band
 306 corresponds to hexagonal carbon rings that arise from in-plane C-C bond stretching vibrations. The
 307 broadening and intensity increase of the D band may indicate an increase of disorder after the EO
 308 process resulting from oxidation processes and leading to the formation of functional groups,
 309 resulting in an increased I_D/I_G ratio (Zhang et al., 2016). The increase of this ratio confirms an
 310 increase in defect density in the carbon sp² structure (Sahoo and Mallik, 2015). The splitting of the
 311 G-band into the D'-band highlights the transformation into a graphitic structure and the formation
 312 of defects in the formed sp² layers.

313 In the case of BDD, for both spectra (Figure 5b), it is possible to easily distinguish the diamond peak
 314 at 1332 cm⁻¹. The broad band at around 500 cm⁻¹ is related to the lesser presence of amorphous
 315 carbon, while the additional band at 1520 cm⁻¹ was attributed to the C-H bending bonds (Fudala-
 316 Ksiazek et al., 2018). As was previously seen in the SEM images, the EO process did not affect the
 317 BDD molecular structure. For the BCNW spectra (Figure 5c), two main bands at around 1356 cm⁻¹

318 and 1590 cm^{-1} are found, generally attributed to the G and D bands. Similarly, for the graphite
319 electrode, the EO process induces a peak widening, due to the increased amount of disorder, even if
320 to a lesser extent due to the almost unaltered I_D/I_G ratio. The pristine BDD/BCNW sample exhibits
321 a spectrum (Figure 5d) similar to that of the BCNW. However, after the EO process, it is possible to
322 observe the appearing of a microcrystalline diamond peak at 1331 cm^{-1} , due to the partial detachment
323 of the overlying BCNW layer. The co-presence of the diamond peak with the D and G bands suggests
324 the mixed presence of sp^2 - and sp^3 -bonded carbon.

325 3.3 Electrode electrochemical characterisation

326 Voltammetric curves are useful for testing the surface quality of electrodes because the
327 electrochemical response is very sensitive to the physicochemical properties of the surface. One of
328 the important parameters describing anodes is their oxygen overpotential. Otherwise, a large
329 amount of delivered electrical energy will be wasted on O_2 production. The nature of the formed
330 oxidants is determined by the electrode's potential window, especially by the one characterised by
331 the high oxygen evolution potential. The anode's oxidation power is directly related to the anode
332 material; the higher O_2 overvoltage, the higher its oxidation power is. Figure 6 shows the resulting
333 cyclic voltammetry curve obtained for the graphite, BDD, BCNW, and BDD/BCNW electrodes.



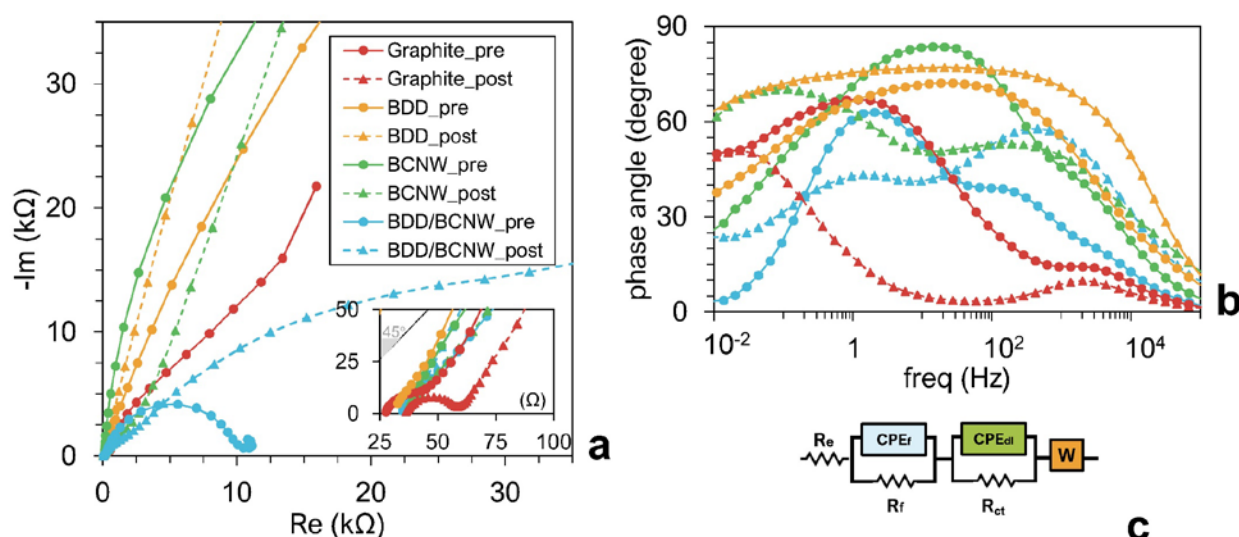
334
335 *Figure 6 – Cyclic voltammograms of G, BDD, BCNW, and BDD/BCNW electrodes before the EO test. The*
336 *voltammogram after the EO test has also been reported for the BDD/BCNW electrodes.*

337 BDD is characterised by a very wide electrochemical window. The results showed that the
338 BDD/BCNW electrode, before the oxidation, was electrochemically stable to a potential of about
339 1.35V which is determined versus an Ag/AgCl electrode. The graphite and BCNW electrodes had a
340 similar oxygen evolution voltage of about 1.2V vs. the Ag/AgCl reference electrode, but the forming
341 double layer capacity was much larger for the graphite electrode, which caused energy loss and a
342 lower current efficiency of the electrochemical oxidation of the leachate. The graphite, BCNW, and
343 BDD/BCNW electrodes had lower oxygen evolution potentials, which produced weaker oxidants



344 than the anode with a higher oxygen evolution potential (BDD) (Chang et al., 2009). Different
 345 anode materials, as well as the type of wastewater, affect the efficiency obtained during
 346 electrooxidation. The high overpotential of water decomposition can be an advantage due to the
 347 formation of strong oxidants, but it resulted in higher energy consumption during the
 348 electrooxidation of pollutants. The electrooxidation mechanism is determined by the formed
 349 oxidants as well as the surface adsorption properties, hence the similar BCNW and BDD/BCNW
 350 electrooxidation products, and different products for BDD (Martí and Ferro, 2006). After the EO
 351 process, the BDD/BCNW composite electrode changed its character tending to a characteristic
 352 curve for BDD. High O_2 overvoltage anodes are associated with weaker interaction with the
 353 electrode surface and lower ion adsorption (Bergmann et al., 2009; Vatistas, 2012).

354 Electrochemical impedance spectroscopy (EIS) is a method to characterise the interfacial
 355 properties of electrodes (B. Oliveira and Oliveira-Brett, 2010). The impedance measurements were
 356 performed in sulphuric acid media at the graphite, BDD, BDD/BCNW, and BCNW electrode
 357 surfaces immediately before and after EO of the leachates (Figure 7).



358
 359 *Figure 7 – Impedance spectra of electrodes tested in 0.5m H₂SO₄ as electrolyte vs. Ag/AgCl and electrical*
 360 *equivalent circuit.*

361 The Nyquist spectra (Figure 7a) for the BDD/BCNW prior to the oxidation process had the
 362 shape of a flattened semicircle with two visible time constants. For the BDD and BCNW materials
 363 before and after the oxidation process, for graphite prior the EO, and for BDD/BCNW after the EO
 364 process, the part of the diagrams responsible for diffusion and the semicircle from the charge transfer
 365 reactions overlap and create a curved plot line. The curves of Graphite_post, and BDD/BCNW_pre
 366 show flattened semicircles and a significant diffusion part for graphite post, while it is inappreciable

367 at high frequencies for BDD/BCNW_pre.

368 The two-time constants are visible on the bode curves for the graphite, BDD/BCNW, and BCNW
 369 electrodes. Due to the low porosity of BDD, the second time constant is not clearly visible (Figure
 370 7b). The curves shown in Figure 7a were fitted taking into account two-time constants (RC), the
 371 reflect film resistance (R_f , CPE_f) and the charge transfer process which took place at the
 372 electrode/electrolyte interface (R_{ct} , CPE_{dl}) (Levi and Aurbach, 1997; Siuzdak et al., 2015; Wang et al.,
 373 2010). The equivalent electrical circuit (EqEC) is reported in Figure 7c, and the fitted values of the
 374 elements in the EqEC are displayed in Table 3.

375 *Table 3 – EIS fitting parameters of the G, BDD, BCNW, and BDD/BCNW electrodes before and after the*
 376 *leachate EO test.*

Electrode	R_e Ω	R_{ct} Ω	CPE_{dl}		R_f	CPE_f	
			Y_{dl}	α_{dl}		Y_f	α_f
			$Fs^{(\alpha-1)}$			$Fs^{(\alpha-1)}$	
Graphite_pre	29.6	$5.1 \cdot 10^9$	$1.26 \cdot 10^{-4}$	0.91	$2.69 \cdot 10^3$	$5.0 \cdot 10^{-4}$	0.78
Graphite_post	34.8	$2.7 \cdot 10^3$	$1.14 \cdot 10^{-2}$	0.72	11.9	$3.7 \cdot 10^{-3}$	0.46
BDD_pre	30.2	$7.3 \cdot 10^5$	$1.59 \cdot 10^{-5}$	0.82	$1.1 \cdot 10^5$	$1.3 \cdot 10^{-3}$	0.82
BDD_post	10.6	$9.8 \cdot 10^6$	$5.19 \cdot 10^{-6}$	0.87	$1.1 \cdot 10^5$	$1.5 \cdot 10^{-5}$	0.87
BCNW_pre	33.7	$4.9 \cdot 10^5$	$1.52 \cdot 10^{-5}$	0.90	$1.1 \cdot 10^5$	$6.2 \cdot 10^{-6}$	0.96
BCNW_post	30.2	$1.9 \cdot 10^6$	$1.95 \cdot 10^{-5}$	0.83	$3.6 \cdot 10^3$	$2.8 \cdot 10^{-5}$	0.62
BDD/BCNW_pre	33.2	$1.0 \cdot 10^4$	$7.59 \cdot 10^{-5}$	0.87	$1.72 \cdot 10^2$	$4.8 \cdot 10^{-5}$	0.78
BDD/BCNW_post	31.6	$5.5 \cdot 10^4$	$3.82 \cdot 10^{-5}$	0.65	$1.40 \cdot 10^3$	$4.0 \cdot 10^{-6}$	0.94

377
 378 Under perfect conditions, diffusion is represented on a Nyquist plot in the low-frequency part by a
 379 45-degree slope line. For BDD and BCNW before and after the oxidation process, for graphite prior
 380 the EO, and for BDD/BCNW post EO, the line (diffusion part) is overlaid with semicircles from
 381 charge transfer processes and the film resistance. The recorded spectra (Figure 7a) were analysed
 382 using the equivalent electrical circuit consisting of electrolyte resistance (R_{el}) in series with two-time
 383 constants (R and C in parallel), including in-place capacitance (C), constant phase element (CPE):
 384 R_f , CPE_f and R_{ct} , CPE_{dl} and Warburg element W (Figure 7c). A CPE is generally used when interfacial
 385 impedance occurs, and is particularly helpful in describing interface processes on sp^2 -based carbon
 386 electrodes and other heterogeneous materials.

387 In contrast to the impedance equation of capacitor C, the expression characterising the impedance
 388 (Z) of the CPE contains additional parameter α in the range $0 < \alpha \leq 1$: $Z=Y^{-1}(i\omega)^{-\alpha}$, where ω is the

389 angular frequency, and Y is the CPE parameter in $F s^{(\alpha-1)}$. The Warburg element is related to the
 390 diffusion of charged ions from the bulk of the electrolyte to the surface of the electrode (Ryl et al.,
 391 2014; *EC-Lab – Application Note #42*, 2012). The value of the charge transfer resistance, taking into
 392 account the electrode surface, evaluated by applying the EqEC was $5.2 \cdot 10^2 \Omega \cdot \text{cm}^2$ for
 393 BDD/BCNW_pre, and was an order of magnitude lower than for BDD_pre ($5.27 \cdot 10^3 \Omega \cdot \text{cm}^2$) and two
 394 orders of magnitude lower than for BCNW_pre (Table 4).

395 *Table 4 – Electrochemical parameters of the equivalent electrical circuit for the prepared electrodes before*
 396 *and after electrochemical oxidation immersed in 0.5 M H₂SO₄*

Electrode	S*R_{ct} cm²·Ω	j₀EIS A·cm⁻²	j₀Tafel A·cm⁻²
Graphite_pre	$2.95 \cdot 10^5$	$8.86 \cdot 10^{-8}$	$7.38 \cdot 10^{-6}$
Graphite_post	$1.35 \cdot 10^2$	$1.95 \cdot 10^{-4}$	$4.40 \cdot 10^{-4}$
BDD-10k_pre	$5.27 \cdot 10^3$	$4.96 \cdot 10^{-6}$	$5.00 \cdot 10^{-7}$
BDD-10_post	$5.34 \cdot 10^3$	$4.90 \cdot 10^{-6}$	$6.20 \cdot 10^{-7}$
BCNW_pre	$2.45 \cdot 10^4$	$1.07 \cdot 10^{-6}$	$1.50 \cdot 10^{-6}$
BCNW_post	$9.52 \cdot 10^4$	$2.75 \cdot 10^{-7}$	$3.80 \cdot 10^{-7}$
BDD/BCNW_pre	$5.20 \cdot 10^2$	$5.03 \cdot 10^{-5}$	$2.86 \cdot 10^{-6}$
BDD/BCNW_post	$2.74 \cdot 10^3$	$9.54 \cdot 10^{-6}$	$1.06 \cdot 10^{-5}$

397

398 Charge transfer resistances may be converted into exchange current densities (j_0) by the following
 399 equation:

400
$$j_0 = \frac{RT}{F} \frac{1}{SR_{ct}}$$

401 where R is the gas constant, F is the Faraday constant, and SR_{ct} leads the resistance of the real
 402 electrode surface.

403 The exchange current density shown in Table 4 is on the order of $10^{-8} \text{ A} \cdot \text{cm}^{-2}$ ($8.86 \cdot 10^{-8} \text{ A} \cdot \text{cm}^{-2}$) for
 404 the graphite, prior to the EO test, and about four orders of magnitude higher for the graphite after
 405 the EO test ($1.95 \cdot 10^{-4} \text{ A} \cdot \text{cm}^{-2}$). This behaviour is caused by the increase of the surface area by
 406 graphite exfoliation (Zhang et al., 2016) during oxidation of organic compounds on the graphite
 407 electrode.

408 For the BCNW and BDD/BCNW electrodes, a decrease in the exchange current density for the
 409 electrodes after the EO process by one order of magnitude was observed, according to the R_{ct} values
 410 obtained from EIS. For the BDD electrodes, the exchange current density remained unchanged after

411 the electrooxidation process. This indicates the stability of the BDD electrodes. However, it should
412 be noted that the largest exchange current density is was revealed by the BDD/BCNW electrodes,
413 which relates to the larger active surface area of the resulting BDD/BCNW electrodes than the
414 electrodes grown directly on the niobium surface. The BCNW electrodes had the same order of
415 magnitude of exchange current density as the BDD electrodes. After the oxidation process, the
416 exchange current density of the BDD/BCNW electrode decreased to a value equivalent to the
417 exchange current density of the BDD electrodes. This suggests degradation of the BCNW layer on
418 the BDD electrode with mainly the BDD layer remaining.

419 The exchange current density values were low and indicate that the charge transfer process may be
420 a stage limiting the EO process. Therefore, the BDD/BCNW_pre exchange current was greater by
421 one order of magnitude than for BDD_pre, and BCNW_pre indicates a good direction of
422 modification of electrodes, and shows that the charge transfer process prefers BDD/BCNW as the
423 electrode for the electrochemical oxidation reaction. A lower charge transfer resistance means a
424 higher exchange current and thus a faster electrochemical oxidation process. It should be
425 emphasised that an increase in the current density does not necessarily lead to an increase in the
426 oxidation efficiency or oxidation rate. For a given anode material, the impact of current density on
427 the electrooxidation efficiency of treated wastewater depends on their physicochemical properties
428 such as the type and concentration of the electrolyte, pH value, and temperature (Anglada et al.,
429 2009). However, the adhesion to the substrate of the material being produced will need to be
430 improved so that it does not degrade during electrooxidation.

431 The exchange current density can be estimated using also the Tafel extrapolation method and a
432 transformation of the Butler-Volmer equation. It should be taken into account that the error of this
433 method increases in the presence of adsorbed or passive layers. In these cases, thanks to the use of
434 EIS, we can afford to evaluate the kinetics of the oxidation process on electrodes. Table 4 reports the
435 comparison of the exchange current density estimated with the two methods. It can be seen that the
436 exchange current density obtained from the Tafel plots differs from the exchange current density
437 estimated by the EIS method for most electrodes. The obtained values of exchange current are only
438 of the same order for the BCNW electrodes.

439 **4. Conclusions**

440 Architecturing carbon nanostructures represents valuable support to enhance the
441 electrochemical properties of anodes for environmental remediation. Because of the lower surface
442 resistance, higher surface area and current exchange density, the fabricated nanostructured
443 electrodes exhibit an increased process efficiency.

444 The localised pH variation within the BCNW nanostructure may be responsible for the limited

445 competition between the direct oxidation of organics and other secondary undesired electrochemical
446 reactions initiated by chlorate intermediates. This aspect results in enhanced COD (and BOD)
447 removal by the composite nanostructure, compared to BDD, at the expense of N-NH₄⁺
448 mineralisation, which is mediated mainly by secondary reactions, despite both electrodes working at
449 the same potential.

450 The potential of oxygen evolution revealed by cyclic voltammetry was similar for graphite, BCNW,
451 and BDD/BCNW, and higher for BDD. The maze-like structure of the BCNW significantly increased
452 the active sites, improving the exchange current density. After the EO test, the morphology and
453 electrochemical character of the BDD/BCNW architecture changed, exhibiting a coexistence of sp²
454 and sp³ carbon. While a higher sp²/sp³ ratio is generally used as a descriptor of the BDD quality,
455 which negatively affects the mineralisation efficiency, the localised sp² inhomogeneity left by the
456 etched BCNW may be the reason for the improved efficiency.

457

458 **Acknowledgements**

459 This research was supported by the Polish National Agency for Academic Exchange (NAWA),
460 under the Ulam program, Agreement no. PPN/ULM/2019/1/00061/DEC/1 (M.Pierpaoli).

461 This work was also supported by the Provincial Fund for Environmental Protection and Water
462 management in Gdansk under Grant No. RX15/13/2017.

463

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