

Closing the loop: upcycling secondary waste materials into nanoarchitected carbon composites for the electrochemical degradation of pharmaceuticals

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Abstract

In this study, we demonstrated the application of electrochemical oxidation as a safer and cleaner technology for minimizing the impact of pharmaceuticals in wastewaters, simultaneously mediated by upcycled secondary waste materials (SWMs)-derived electrodes, to further reduce their environmental impact. The modularity, scalability, ease of operation and reliability make electrochemical oxidation an ideal process for the destruction of emerging persistent pollutants; however, their full-scale application is hindered by energy efficiency and the potential release of toxic by-products. Thus, the answer to these issues can be found in the design of tailored multifunctional electrode material. For the first time, SWMs derived from combustion and industrial processes have been employed with the simultaneous dual function of functional fillers, in a polyacrylonitrile fibrous matrix, and as a catalyst for the growth of carbon nanofeatures over the fiber surface, to increase the surface area and charge transfer. Next, the tailored composites were employed as anodes for the electrochemical oxidation of acetaminophen, both in phosphate buffer and in a real wastewater sample. The results suggest

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28 that SWMs can substitute costly engineered fillers in carbon-based electrodes and that the
29 absence of reaction by-products (monitored by UHPLC-ESI-MS/MS), together with the low
30 energy consumption, make the tailored fibrous composite electrodes good candidates for the
31 development of safer and cleaner technologies with reduced environmental impact.

32 **Keywords**

33 Advanced Oxidation Process; fly ash; spent foundry sand; chemical vapor deposition; carbon
34 nanomaterial

35 **1. Introduction**

36 Utilization is one of the leading strategies for the management of hazardous industrial wastes
37 such as fly ash (FA) and spent foundry sand (FS), thus, developing new pathways to minimize
38 their environmental impact is currently a priority. Moreover, due to the ubiquitous presence
39 and persistence of pharmaceuticals and recalcitrant pollutants in the environment, the
40 development and implementation of efficient and cost-effective technologies to mineralize
41 such treats are of primary interest.

42 FA is a particulate material produced from the controlled combustion of fuels, biomass or
43 waste in thermal power plants and it constitutes a major concern for the environment, as it
44 causes water, soil, and air pollution, and because of its costly disposal as a hazardous waste
45 (Wang et al., 2019). For these reasons, diverting FA from landfills, where it also poses a
46 significant threat to the environment, thus finding new pathways for its utilization from the
47 perspective of the circular economy, also finds support in the European Commission guidelines
48 (Gharfalkar et al., 2015). FS is a by-product resulting from the ferrous and nonferrous metal
49 casting industries; it consists of high-quality silica particles, it has low absorption capacity, and
50 it is non-plastic. The spent foundry sand is either recycled in non-foundry applications or
51 landfilled. Indeed, the use of spent FS (originated only from iron, steel, and aluminum foundry
52 operations) has found application in manufactured soils, soil-less potting media, roadway
53 subbase, and as an aggregate for concrete production (Siddique and Singh, 2011), despite it
54 potentially containing heavy metals, and hazardous organics, such as polycyclic aromatic



55 hydrocarbons (PAHs), benzene, toluene, xylene (BTEX), polychlorinated-p-dioxins (PCDDs),
56 the related furans (PCDFs) and polychlorinated biphenyls (PCBs) (Environmental Protection
57 Agency, 2014).

58 Acetaminophen (APAP) is the most widely available and prescribed analgesic and antipyretic
59 pharmaceutical in the world, and its presence in the environment has started raising global
60 concerns (Zhang et al., 2018) since it easily accumulates in the aquatic environment, and has
61 been detected in surface waters, wastewater, and drinking water, and also because of its toxic
62 metabolites and hazardous degradation by-products (Wu et al., 2012; Pacheco-Álvarez et al.,
63 2022). While electrochemical oxidation has also been applied to the removal of APAP, the
64 formation of intermediates such as hydroquinone, p-aminophenol, p-nitrophenol, and p-
65 benzoquinone (Li et al., 2014; Zhang et al., 2022) has been reported, and these constitute a
66 potential threat to the environment because of their toxicity and difficulty to degrade (Li et al.,
67 2014; Al-Gharibi et al., 2021). For this reason, optimizing the degradation process, focusing on
68 energy efficiency, and tuning the reaction pathway can be done by intelligently tailoring the
69 material chemical structure and morphology at different scales.

70 Electrochemical oxidation is a reliable and effective water remediation technique for the
71 mineralization of a plethora of water pollutants of current concern, among per- and
72 polyfluoroalkyl substances (PFASs) (Pierpaoli et al., 2021c), pharmaceuticals, dyes and
73 herbicides (Martínez-Huitle and Panizza, 2018; Brillas, 2021; Santos et al., 2021), even in
74 complex and heavily concentrated matrices (Pierpaoli et al., 2021b). In our previous studies,
75 we demonstrated how intelligently nanoarchitected carbon hybrids possess superior
76 efficiency in micro- and macro-pollutant degradation, due to both their morphology and
77 chemical composition (Pierpaoli et al., 2021b), and that the chemical vapor deposition
78 technique constitutes a preferential path toward the development of highly efficient, critical
79 raw material (CRM)-free electrodes suitable for the designed process (Pierpaoli et al., 2020).
80 Among different carbon allotropes, graphite electrodes are one of the most widely investigated
81 electrode materials in the scientific literature, due to their low cost, availability, and non-
82 toxicity; however, their effectiveness is limited due to their high corrosion rate at potentials
83 higher than 1.7–1.9 versus SCE (Shestakova and Sillanpää, 2017). On the other hand, boron-

84 doped diamond electrodes (BDD) are known for their chemical and mechanical inertness, wide
85 potential window, and ability to generate strong oxidants (Martínez-Huitle and Panizza, 2018),
86 which makes them suitable for full-scale applications; however, commercially-available BDD
87 are usually grown by CVD on CRM-containing substrates, such as Nb, with direct effect on the
88 cost and sustainability. For this reason, alternative solutions charting a path towards greater
89 sustainability and lower impact are a major issue. Graphene-based electrodes have only been
90 developed in the last two decades, mostly by a bottom-up approach, being able to define a new
91 class of electrode materials characterized by intermediate properties, and able to adsorb and
92 degrade electrochemically a plethora of pollutants of emerging concern. Cui et al. fabricated a
93 three-dimensional carbon brush using reduced graphene oxide through simple one-step
94 electrodeposition and employed it as a cathode in a bio-electrochemical system for the removal
95 of the azo compound (AO7) (Cui et al., 2018). They attributed the enhanced conductivity and
96 increased electrochemical surface area to the improved AO7 removal efficiency. Similarly,
97 Ormeno-Cano and Radjenovic realized porous boron and nitrogen-doped graphene-based
98 sponge electrodes for the electrodegradation of selected antibiotics, attributing plane the
99 enhanced removal to the strong π - π interactions between the antibiotics and the graphene
100 basal (Ormeno-Cano and Radjenovic, 2022). The inclusion of different nano- and micro-fillers
101 into carbon fibers is generally beneficial to enhancing the mechanical and electrical properties,
102 both inherited by the filler itself and due to their intrinsic catalytic properties. Indeed,
103 Rajabpour and coworkers demonstrated how a graphene sheet can act as a seed to expedite the
104 alignment of all-carbon rings and can be responsible for enhancement of the mechanical
105 properties (Rajabpour et al., 2021).

106 For these reasons, in this study, novel carbon mesostructured electrodes were
107 synthesized for the first time by a simple phase inversion technique combined with a single
108 carbonization-surface decoration step performed in a CVD reactor. Hazardous secondary
109 materials (HSMs) were incorporated into the electrode bulk with the aim of both reducing their
110 environmental impact, by diverting them from landfilling, and acting as catalysts for the
111 development of nano/micro-sized carbon structures on the electrode surface. A comparison
112 with commercially-available graphene oxide flakes and diamonds fillers was also performed.

113 Finally, the acetaminophen degradation efficiency was evaluated for the different architected
 114 electrodes, both in phosphate buffer solution and in a real treated wastewater effluent, aiming
 115 to simulate their utilization as an advanced tertiary treatment.

116 **2. Materials and methods**

117 **2.1 Materials**

118 Polyacrylonitrile (PAN) and APAP (purity >98%) were purchased from Merck.
 119 Dimethylformamide (DMF, pure p.a) was bought from POCH (Poland). Phosphate buffer
 120 solution (PBS, 0.1 M) was prepared as described in our previous work (Pierpaoli et al., 2021a).
 121 Pharmaceutical standard (analytical standard grade) acetaminophen was purchased from
 122 Sigma-Aldrich (USA). A stock solution of 500mgL⁻¹ and a working solution of 100mgL⁻¹ for
 123 method calibration were prepared in LC-MS grade methanol (Optima, Fisher Scientific) and
 124 stored at -20 °C. Acetonitrile (ACN, LC-MS grade Optima) and formic acid (98–100%,
 125 LiChropur for LC-MS) were purchased from Fisher Scientific and Sigma-Aldrich (USA),
 126 respectively. Purified water (ultrapure water, resistivity 18.2 MΩ cm at 25 °C) was obtained via
 127 a Direct-Q® Water Purification System. The composition of the treated wastewater (TWW)
 128 was analyzed using the methods described in our previous work (Pierpaoli et al., 2021c).

129 Table 1 – Treated wastewater characteristics [mean±standard deviation]

	Parameter	Value
Organic matter characteristics	COD [mg L ⁻¹]	34.0±2.1
	BOD ₂₀ [mg L ⁻¹]	<LOD
	TSS [mg L ⁻¹]	3.2±0.1
	MSS [mg L ⁻¹]	1.6±0.1
	VSS [mg L ⁻¹]	1.6±0.1
Nitrogen forms	N-NH ₄ ⁺ [mg L ⁻¹]	0.103±0.015
	N-NO ₃ ⁻ [mg L ⁻¹]	4.69±0.50
	N-NO ₂ ⁻ [mg L ⁻¹]	6.11±0.61
	TN [mg L ⁻¹]	10.10±0.81
Phosphate forms	P-PO ₄ ³⁻ [mg L ⁻¹]	0.62±0.25
	TP [mg L ⁻¹]	0.768±0.016
Other ions	Cl ⁻ [mg L ⁻¹]	86.6±2.1
	SO ₄ ²⁻ [mg L ⁻¹]	37.9±1.8

	S ²⁻ [mg L ⁻¹]	<0.1
Basic physicochemical parameters	pH	8.37±0.10
	redox [mV]	187.8±9.8
	Conductivity [mS cm ⁻¹]	1164±2.2
Selected micropollutants	APAP [µg L ⁻¹]	<LOD

130 Abbreviations: COD – chemical oxygen demand, BOD – biological oxygen demand, TSS – total
 131 suspended solids, MSS – mineral suspended solids, VSS – volatile suspended solids, TN – total
 132 nitrogen, TP – total phosphorus, LOD – limit of detection

133 2.2 Creation and characterization of polymeric electrodes

134 A solution of 10%w PAN in DMF was prepared and stirred for 24 hours, then a selected filler
 135 (Table 2) was added into the mixture and vigorously stirred by a vibration shaker (Vibration
 136 stirrer ZX4 Vortex Mixer Velp) until a homogenous solution was obtained.

137 Table 2 – Description of the fillers used in bulk in the composite realization

Filler name	Filler type	Filler description	Filler dimensions
ND	Diamonds suspension	Commercially available micro-sized diamond suspension	0.6–1.3 µm
GO	Commercial graphene oxide	Commercially available flat graphene oxide flakes	0.2–2.8 µm
FA	Biomass fly ash	Fly ash from a biomass source, obtained from an oxidating atmosphere process	1.7–3.0 µm > 7.5 µm
FS	Foundry sand waste	Foundry sand used in a casting process at a temperature of up to 1400 °C	60–140 nm 140–830 nm > 5 µm

138
 139 In the case of ND, firstly, a dispersion of ND in dimethylformamide (DMF) was prepared by
 140 repeatedly centrifuging and replacing the original solvent (dimethylsulfoxide, DMSO) and
 141 finally sonicating. Due to the poor dispersion stability, the PAN was directly added to the
 142 ND/DMF solution and vigorously stirred until the polymer extruded in a water-based
 143 coagulation bath. Composite electrodes were obtained by the wet-spinning method, using an
 144 in-lab made apparatus, then compressed into cylinder electrodes, stabilized, and carbonized
 145 by CVD. The detailed procedure can be found in our previous work (Pierpaoli et al., 2022).
 146 Simultaneous carbonization and nanofeatures growth were performed by a microwave plasma-

147 assisted chemical vapor deposition (MWPECVD) system (SEKI Technotron AX5400S, Japan).
148 During the CVD process, which lasted for 40 minutes, the microwave power and the total
149 pressure were kept at 1100 W and 40 Torr, respectively. The substrate holder temperature was
150 set at 550 °C. A gas mixture of H₂, CH₄, and B₂H₆, with a total flow of 328 sccm, was used for
151 the BDD growth. After the fiber wet-spinning procedure and stabilization process in cylindrical
152 mold, flattened cylindric-shaped electrodes, having diameter of 9.45mm (SD=1.0mm) and
153 thickness of 2.0mm (SD=0.17mm) are produced, for a total area of approximately 2 cm² (1.96
154 ± 0.42 cm²). After carbonization/CVD-growth process, different shrinkage occurs dependently
155 on the filler employed, resulting in a decrease of the electrode geometrical area (ranging
156 between 30% for the only PAN to 7% for the FA) but in an increase of the total exposed one.
157 Scanning electron microscopy (SEM) imaging was carried out using an FEI Quanta 250 FEG
158 (ThermoFisher Scientific) equipped with a Schottky field emission gun and operating with
159 secondary electrons under a 20 kV accelerating voltage. X-ray Photoelectron Spectroscopy
160 (XPS) analyses were done with an Escalab 250Xi (ThermoFisher Scientific) multispectroscopie.
161 The spectroscopie was operating with an AlK α X-ray source and a spot diameter of 650 μ m. The
162 pass energy through the hemispherical analyzer was set to 20 eV. The charge compensation
163 was guaranteed by a low-energy electron and low-energy Ar⁺ ion flow, with a final peak
164 calibration at adventitious C 1s at 284.6 eV. Raman spectra were acquired using a commercial
165 Raman microscope (LabRam Aramis, Horiba) on excitation by a 632.8 nm HeNe laser with up
166 to 20 mW optical power at the sample. An integration time of 5 s (20 averages) with a
167 diffraction grating of 300 lines per mm was set, using a 50x magnification objective. All of the
168 peaks were fitted with Lorentzian functions after the spectra were baseline subtracted. Peak
169 ratios were calculated by considering their area, instead of intensity, due to the heterogeneity
170 of the composite material. An Inductively Coupled Plasma – Optical Emission Spectroscopy
171 (ICP-OES) analysis was carried out to assess the presence of metals in trace quantities from
172 the SWMs after performing an acid (HNO₃/HCl 1:3 solution) digestion procedure. The
173 electrochemical properties of the electrode were measured by a VMP-300 BioLogic
174 potentiostat, in a three-electrode cell configuration, in which the BDD, a platinum wire, and
175 an Ag/AgCl 3M KCl electrode were used, respectively, as the working, counter and reference

176 electrodes in PBS 1M as the electrolyte. The EIS experimental data was fitted using the
177 BioLogic EC-lab software.

178 **2.3 Electrochemical oxidation setup**

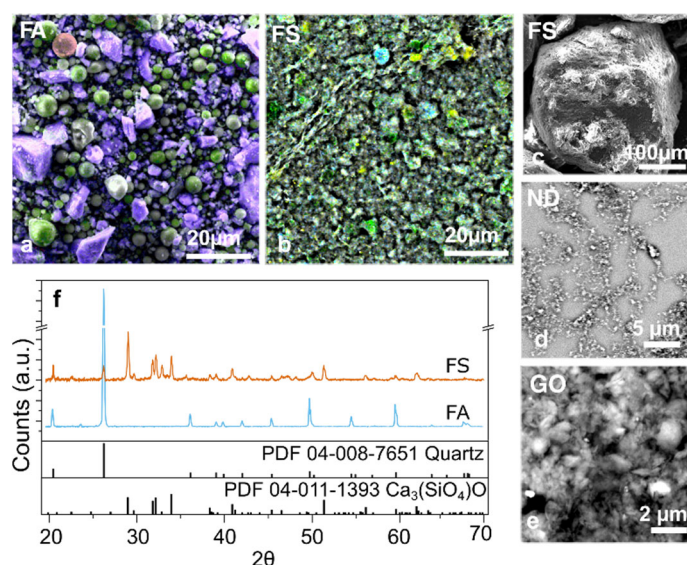
179 Electrochemical oxidation batch tests were performed in a completely stirred borosilicate
180 beaker as reactor, with an initial volume of 35 mL, in which the electrode sample is completely
181 immersed (Fig. S1). Twenty minutes after the APAP solution was added to the reactor, to
182 distinguish the adsorption phase from the oxidative, a 2 mL sample was taken from the beaker
183 and a constant voltage of +3 V was applied to the electrode. At 5, 15, 30, and 60 minutes,
184 samples having a volume of 1 mL each were taken and directed to an ultra-high performance
185 liquid chromatography tandem mass spectrometry with electrospray ionization (UHPLC-ESI-
186 MS/MS) analysis. The current density was measured during the process. Chemical analyses of
187 the APAP were performed by UHPLC-ESI-MS/MS (UHPLC Nexera XR coupled with LC/MS-
188 8050, Shimadzu Company) using an external calibration method. Shim-pack SP-C18, 2.1 x 150
189 mm, and 2.7 μm was used as an analytical column. A gradient flow was applied starting at 0.15
190 mlmin^{-1} , ramped up to 0.25 mlmin^{-1} over 4 min, kept at this level until the 9.5 min mark, then
191 returned to 0.15 ml (11 min), and maintained here until the 12 min mark. A gradient mobile
192 phase was used; starting at 95% mobile phase A (0.3 % formic acid in ultrapure water, and 5%
193 of mobile phase B (1:1 MeOH, ACN, solution) kept until the 4 min mark, followed by a linear
194 increase over 8 min to 65% A and 35% B, a second increase to 100 % B at the 9 min mark,
195 maintained until 9.5 mins. (washing stage), then returned to the initial conditions (11 min
196 mark), and held for 1 min (re-equilibration to initial condition). The column temperature was
197 maintained at 40 °C and the autosampler at 4 °C. The total run time was 12 min. LC eluate was
198 sprayed into a tandem mass spectrometer by electrospray ionization in the positive ion mode.
199 The interface setup parameters were as follows: nebulizing gas flow (N_2 , 2 Lmin^{-1}), heating
200 gas flow (N_2 , 8 Lmin^{-1}), interface temperature (150 °C), desolvation temperature (261 °C), heat
201 block temperature (400 °C). The APAP eluted at 6.75 ± 0.05 min and was a monitored by
202 multiple reaction monitoring (MRM) transition m/z 152.0 > 110.2 (collision energy (-17 eV);
203 quantifier transition) and m/z 152.0 > 65.2 (collision energy (-29 eV); qualifier transition).

204 Potential APAP oxidation products include hydroquinone (ESI+, MS m/z=123), p-
205 benzoquinone (ESI+, MS m/z=121), ketomalonic acid (ESI+, MS m/z=119), maleic acid (ESI+,
206 MS m/z=117), oxalic acid (ESI+, MS m/z=91), oxamic acid (ESI+, MS m/z=90), and acetamide
207 (ESI+, MS m/z=60), and were evaluated using scanning single ion monitoring mode (SIM)
208 under the same chromatographic conditions after Li et al. (Li et al., 2014). The sample injection
209 volume was 1 μL . The calibration curve was plotted using 5-level calibration (linearity 1–1000
210 μgL^{-1} . The method detection limit (MDL) and method quantification limit (MQL) were 1 and 3
211 μgL^{-1} and 1.5 and 4.5 μgL^{-1} for water and wastewater matrix, respectively. For this method, no
212 analyte pre-concentration was applied. To evaluate the APAP removal efficiency as function of
213 the energy consumed, the specific electrical charge (Q) is reported as follow: $Q=Jt/V$ where Jt
214 is the integral of the measured current over time ($\text{A}\cdot\text{h}$) and V is the solution volume (L)
215 (Anglada et al., 2009). Since the applied potential is constant, Q is directly proportional to the
216 power used.

217 **3. Results and discussion**

218 **3.1 Electrode characterization**

219 Due to their nature as combustion products, FA and FS do not possess a well-defined
220 morphology and chemical composition, but they are rather dependent on the combustion
221 process parameters and feedstock composition. For this reason, a more in-depth analysis was
222 performed to characterize the waste materials. From Fig. 1a, it is possible to observe the
223 presence of both spherical and irregularly shaped particles.



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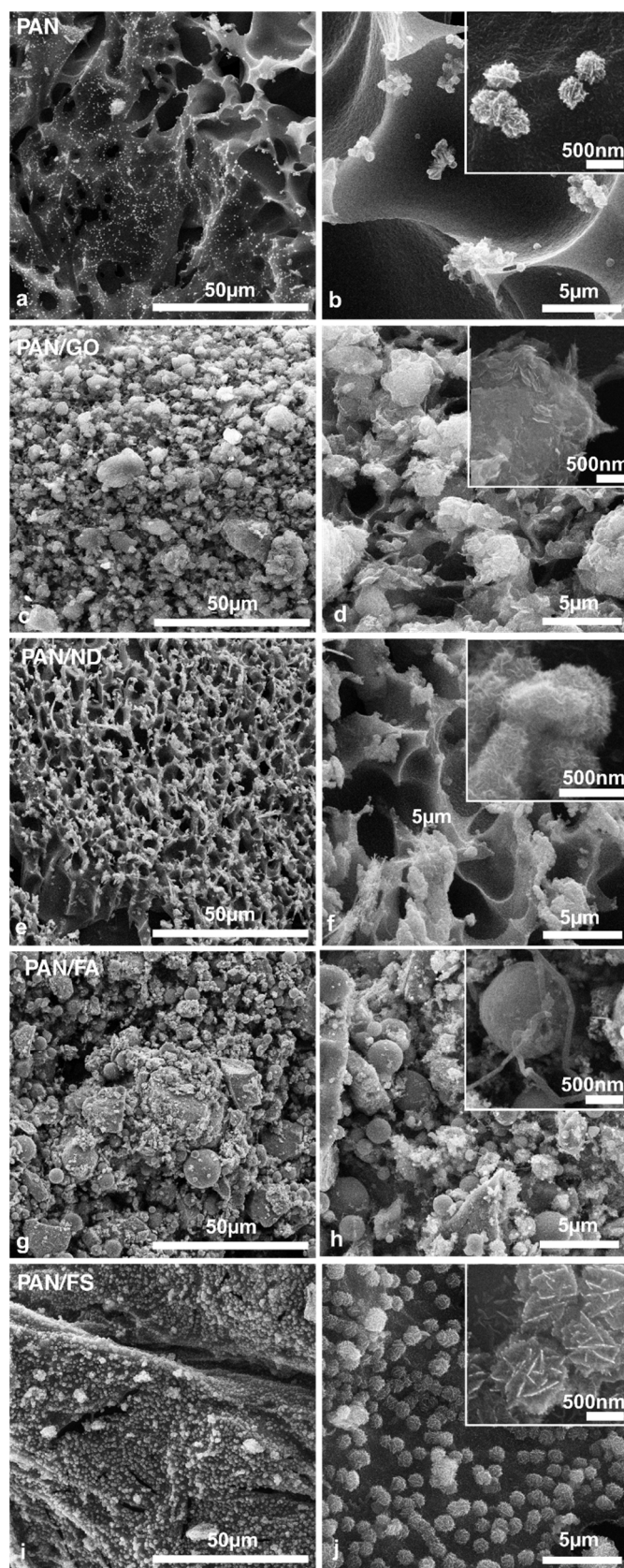
225 *Fig. 1 – SEM-EDX pictures of (a) FA (in yellow aluminum silicates, in blue calcium silicates and in*
 226 *red Fe-rich particles; (b) fine fraction of FS (in green calcium carbonates, in yellow calcium silicates*
 227 *and in blue Fe-rich) and (c) large fraction of FS. SEM of (d) ND solution dried on Si substrate; (e)*
 228 *GO flakes, and XRD diffractograms of FS and FA. The reader is referred to the web version of this*
 229 *paper for the color representation of this figure.*

230

231 In particular, a bimodal particle size distribution is present in the FA sample, with the smaller
 232 fraction accounting for particles having a diameter between 1 and 3 μm and the larger one
 233 having an equivalent diameter larger than 8 μm . FS is mostly constituted by subangular sand
 234 with obtuse angles, with a diameter ranging from tens to hundreds of micrometers (Fig. 1c)
 235 and a superfine fraction (0.05–1 μm , Fig. 1b), which results from the presence of inorganic and
 236 organic binders, and other additives used during the casting process (Siddique and Singh,
 237 2011). Quartz and calcium silicate are the prevalent crystalline form (Fig. 1e); however, Al is
 238 predominant as well, as determined by the EDX analysis, and other elements are present in
 239 minor quantities, as reported in Table S1. Indeed, a major difference arises between FA and
 240 FS, related to the Fe content, especially after acid treatment, suggesting a different composition
 241 (Table S2). The commercial ND suspension presents particles agglomerating into larger
 242 structures (Fig. 1d), as well as for the graphene oxide flakes (Fig. 1e).

243 GO, NDs, FA and FS were then added to the PAN/DMF solution, and the electrodes were

244 synthesized. SEM images of the different electrode composites, after CVD-carbonization, are
245 reported in Fig. 2.



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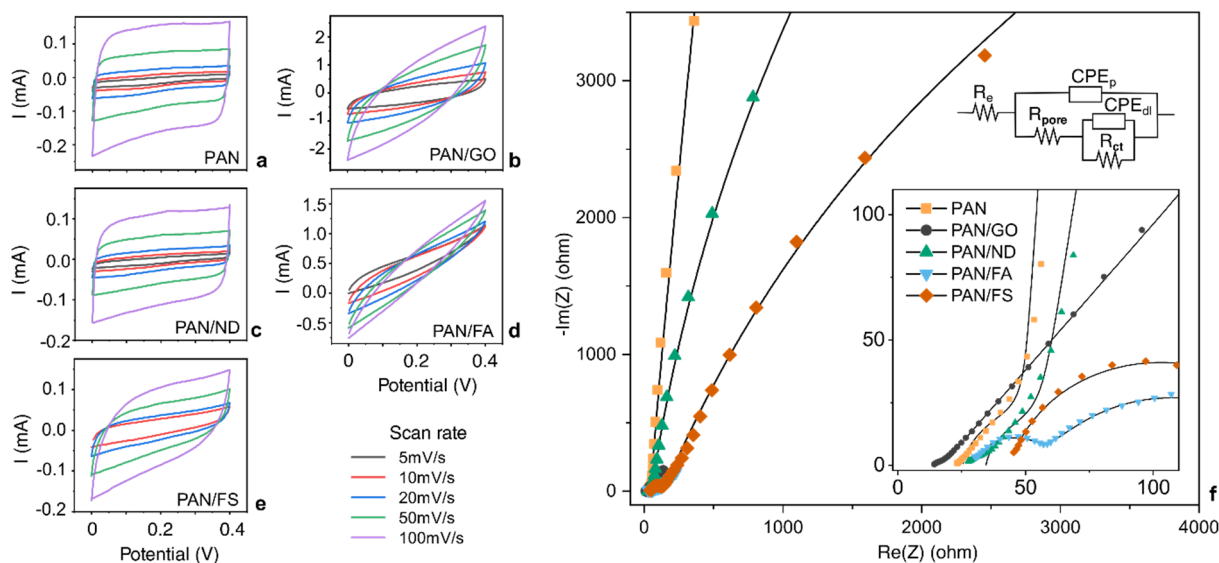
Fig. 2 – SEM of the differently synthesized composite materials before the oxidation tests.

248 It is possible to observe the characteristic fiber morphology in Fig. 2a, obtained by the
249 combined action of phase inversion during the wet-spinning process, and the effect of the
250 plasma in etching the outer fiber interfacial layer. A few micrometer-sized carbon nanowalls-
251 flakes are present on the pores' edges as a result of the locally-enhanced plasma during CVD
252 (Fig. 2f). The addition of different powders dramatically affects the composite morphology. For
253 both GO and NDs, it is still possible to observe a similar porous structure, which is more open
254 for the PAN/ND composite, while it is partially clogged by the GO flakes in the case of PAN/GO
255 (Fig. 2g), where it is possible to observe the presence of the wrinkled graphene sheets on the
256 composite surface. Indeed, the GO flakes hinder the transport of ionic species toward the PAN
257 microporous structure, as also demonstrated by the electrochemical characterization, in Fig.
258 3. The presence of NDs leads to the formation of a highly developed agglomerated structure
259 during the CVD process constituted by tiny carbon nanowalls (Fig. 2h). The presence of
260 different carbon architectures in the PAN/FA composite is the result of the FA chemical
261 heterogeneity. In particular, it is possible to observe both amorphous carbon and the formation
262 of fibers and nanotubes, catalyzed by the presence of Fe within FA (Fig. 2i). Nevertheless, in
263 the PAN/FS composite, most of the larger particles have sedimented in the spinning solution,
264 thus only the finer FS fraction is present in the composite; moreover, it is interesting to observe
265 the formation and a high density of nanowall-coated spherical structures which cover most of
266 the fiber surface, with a very limited porosity (Fig. 2j).

267 The electrochemical behaviors of the different carbon electrodes were systematically tested in-
268 situ, using the same reactor for the APAP EO tests. Fig. 3a–e reports the voltammograms at
269 different scan rates for all five of the composites in 1M PBS, at a potential window from 0 to
270 0.4 V. The CV curves of bare PAN, PAN/ND, and PAN/FS composites present the characteristic
271 shape of an electrochemical double-layer capacitor (EDL). The large rectangular-shaped area
272 for these two composites suggests better electrolyte penetration in the pores compared to the
273 PAN/GO and PAN/FA. Indeed, in the later ones, at high scan rates, an oval-shaped resistive-
274 capacitive behavior is observed, which is related to a high instability of EDL and the poor
275 capacitive nature of the electrodes. The main factor affecting ionic diffusion within the porous
276 structure of carbon materials is the structure of the porous network itself. By plotting current

277 versus the scan rate, straight interpolating lines were obtained, to estimate the EDL
 278 capacitance values (Fig. S2).

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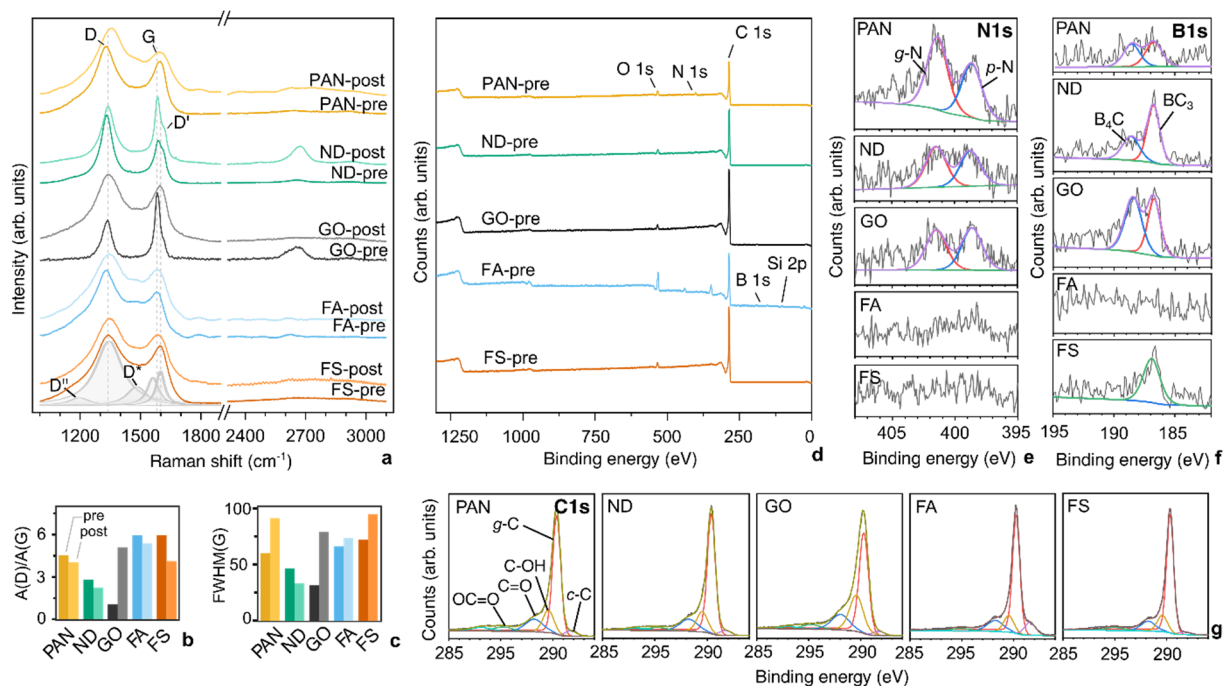
281 Fig. 3 – (a–e) Cyclic voltammograms at different scan rates for all 5 composites in 1M PBS, at a
 282 potential window from 0 to 0.4 V. (f) EIS Nyquist plot. Straight lines are results of EEC fit. The

283 reader is referred to the web version of this paper for the color representation of this figure.

284 To further examine the interfacial charge transport dynamics of the synthesized composite
 285 electrodes, electrochemical impedance spectroscopy (EIS) was employed. Fig. 3f shows the
 286 Nyquist plots, highlighting the different behaviors across the 200 kHz – 20 mHz frequency
 287 range. The obtained semicircles were fitted with an equivalent electrical circuit (EEC) model,
 288 reported in the inset, which includes the solution resistance (R_s), pore resistance (R_p), pore
 289 capacitance (CPE_p), charge transfer resistance (R_{ct}), and double-layer capacitance (CPE_{dl}); the
 290 fitted parameters are tabulated in Table S4. Unexpectedly, despite the different origin and
 291 chemical composition of the powders, their incorporation within the PAN composite was found
 292 to have a minor effect on the conductivity of the electrode, as described by the comparable
 293 value of R_s , equal to $30 \pm 15 \Omega$. The reason for such a finding may be that the CVD-growth
 294 electrode surface constitutes the preferential path for the charge transfer rather than the fiber
 295 bulk. Indeed, the lowest R_s belongs to the PAN/GO, for which stacks of GO flakes are
 296 recognizable from the SEM picture (Fig. 2g). Similarly, the first semicircle in high-frequency

297 regions is easily distinguishable for all of the samples, which is attributed to the combined
298 effect of charge transport resistances at the electrode/electrolyte interfaces (R_{ct}). At a first look,
299 PAN, PAN/ND, and PAN/FS exhibit similar behavior and they fit the EEC well, characterized
300 by a large semicircle at low frequencies related to the bulk Nernst diffusion. However,
301 examining the different Nyquist plots individually, the smaller semicircle at high frequencies
302 indicates a faster ionic transference within the EDL for the PAN/GO sample, followed by a
303 linear response in the low-frequency region, resulting in an angle of 45° with the axis, which
304 corresponds to low ionic diffusion resistance (well-represented by a Warburg element
305 (Randles, 1947). EDL capacitance values obtained from CV and EIS studies were compared
306 and used to estimate the electrochemical surface area (ECSA), since this method allows for
307 accounting the total surface accessible to the solution. ECSA was estimated utilizing the
308 relationship $ECSA = C_{dl} / C_s$, where C_s is the specific capacitance of the investigated material.
309 However, the exact C_s value is typically unknown, leading to substantial errors in ECSA
310 determination from CDL. It is commonly accepted to use a single C_s value for ECSA for
311 comparative purposes, yet the numbers obtained this way may be under- or overestimated
312 (Morales and Risch, 2021; de Freitas Araújo et al., 2022). For comparison, we considered 0.06
313 $mF\ cm^{-2}$ based on the previous literature reports for porous carbonaceous materials (de Freitas
314 Araújo et al., 2022). The estimated ECSA it is between 16 cm^2 for PAN and ND and almost
315 double for FA and FS (22 and 34 cm^2 respectively), while for GO is 150 cm^2 , which could be
316 overestimated.

317 The Raman spectra presented in Fig. 4a show the difference between the different composites,
318 before and after the EO tests. The spectra were deconvoluted and the peak was analyzed, by
319 considering bands at 1577 (9), 1337 (6), 1612 (8), 1493 (12), and 1189 (12) cm^{-1} (standard
320 deviation in brackets), attributed to the G (graphitic, attributed to E_{2g} phonon vibrations of sp^2
321 carbon atoms), D (corresponding to the A_{1g} breathing mode, attributed to the disorder-induced
322 defects), D' (appearing as a shoulder of the G peak, observed in microcrystalline graphite and
323 glassy carbon), D* (a broad band, attributed to amorphous carbon and to the presence of
324 hetero-atoms as impurities in the carbon lattice) and D'' (trans-polyacetylene) bands (Lee et
325 al., 2022).



326
 327 Fig. 4 – (a) Raman spectra, with an example of the peaks used for the deconvolution, (b) $A(D)/A(G)$
 328 ratios, (c) $FWHM(G)$ of the samples before and after EO tests. (d) $A(D)/A(G)$ versus ratio
 329 $A(D')/A(G)$. X-ray photoelectron spectroscopy (XPS) spectra of the different samples: (d) survey
 330 spectra; (e) N 1s spectra; (f) B 1s spectra; and (g) C 1s spectra. The reader is referred to the web
 331 version of this paper for the color representation of this figure.

332 The position, intensity (relative to the G-band, expressed as a ratio) and broadening of the D
 333 band depends on the type of disorder, the presence of impurities, and functional groups. The
 334 intensity ratio of $A(D)/A(G)$ is commonly used as an estimator of the defect density in carbon
 335 materials since it is sensitive only to defects in the rings. In particular, the relative peak
 336 intensity, expressed as the ratio of the integrated area of the D and D' bands, has been preferred
 337 because the area under the band represents the probability of the whole scattering process
 338 (Martins Ferreira et al., 2010; Del Corro et al., 2014). Firstly, by comparing the $A(D)/A(G)$ of
 339 the different composites, before EO, it is possible to observe that the ratio is lower for the
 340 composites containing ND and GO. Thus, the presence of such engineered carbon nanofillers
 341 may improve the formation of a large ladder structure, being converted into a large graphene
 342 layer. All of the samples, with the exception of the PAN-GO, show a slight decrease in the
 343 $A(D)/A(G)$ ratios after the EO tests (Fig. 4b and Table S4), which can probably be attributed to

344 the oxidation and elimination of amorphous and disordered carbons, leaving exposed the
345 better-crystallized fiber surface, as also supported by their FWHM(G). It is interesting to
346 observe that the biggest difference belongs to the PAN/GO sample, already visible by
347 qualitatively comparing the spectra (Fig. 4a). In contrast, the A(D)/A(G) ratio for the PAN/ND
348 sample after EO is significantly lower than the others. On the other hand, the FWHM of the G
349 peak always increases for the increasing disorder, since this parameter is sensitive to all types
350 of defects, either in the sp² rings or chains (Eckmann et al., 2013), making it a good indicator
351 of the degree of graphitization of carbonaceous materials. Thus, the widening of the D and G
352 peaks after the EO process (Fig. 4c) was also observed in our previous studies (Pierpaoli et al.,
353 2021b) for sp²-C-rich carbon nanoarchitected electrodes, while almost no difference was
354 found for boron-doped diamond ones. Indeed, it is interesting to find that the PAN-ND
355 composite belongs to the lowest FWHM, probably due to the beneficial effect of NDs within
356 the structure of the fiber acting as nucleation seeds, in a similar fashion as reported by
357 (Rajabpour et al., 2021).

358 Furthermore, XPS was performed on CVD-carbonized PAN composites to quantify the
359 differently hybridized carbon and functional groups. XPS survey spectra are shown in Fig. 4d.
360 The N1s XPS spectra were deconvoluted into two peaks: at around 398.7 eV, attributed to
361 pyridinic N, and at around 401.5 eV, corresponding to graphitic N. The presence of the pyrrolic
362 N peak can overlap the graphitic N; however, due to the low N content (< 4%), it is difficult to
363 distinguish the peaks, especially for the PAN-FA and PAN-FS composites, for which a higher
364 amount of fillers is present. Thus, it is possible to affirm that the nitrogen is related to the bare
365 PAN structure, differently from the boron which is associated with the nanostructure growth,
366 due to the introduction of B₂H₆ during the MPECVD process. Indeed, it is also possible to
367 qualitatively compare the grown nanostructure by the SEM reported in Fig. 2, with the
368 presence of the B1s profiles. The B1s profiles shown in Fig. 4f indicate that several B species
369 are present and incorporated within the CVD-grown nanostructure, and the two peaks, at
370 approximately 188.6 and 186.8 eV, could correspond to B₄C and BC₃, respectively (Bepete et
371 al., 2013). The BN peak is not present (191 eV), due to the low N content, limited to the PAN
372 fiber, and not available as a gas precursor, while the presence of B₄C is inhibited in the PAN-

373 FS composite. Finally, the C1s spectra (Fig. 4g) show five peaks after deconvolution. The peak
374 at 284.7 eV corresponds to graphitic carbon. The peak at 283.3 eV can be associated with the
375 carbidic components (SiC, BC) for the PAN/FS and PAN/FA composites. The peak at 285.4 eV
376 is likely to arise from the graphene domain edges and defects, or by C-OH. The higher binding
377 energy peaks at ca. 286.8 and 289.9 eV are attributed to the formation of C–O bonds. For a
378 quantitative comparison, fitted results of C1s, N1s and B1s core level XPS spectra for the different
379 composite electrodes are reported in Table S5.

380 **3.2 Electrochemical oxidation tests**

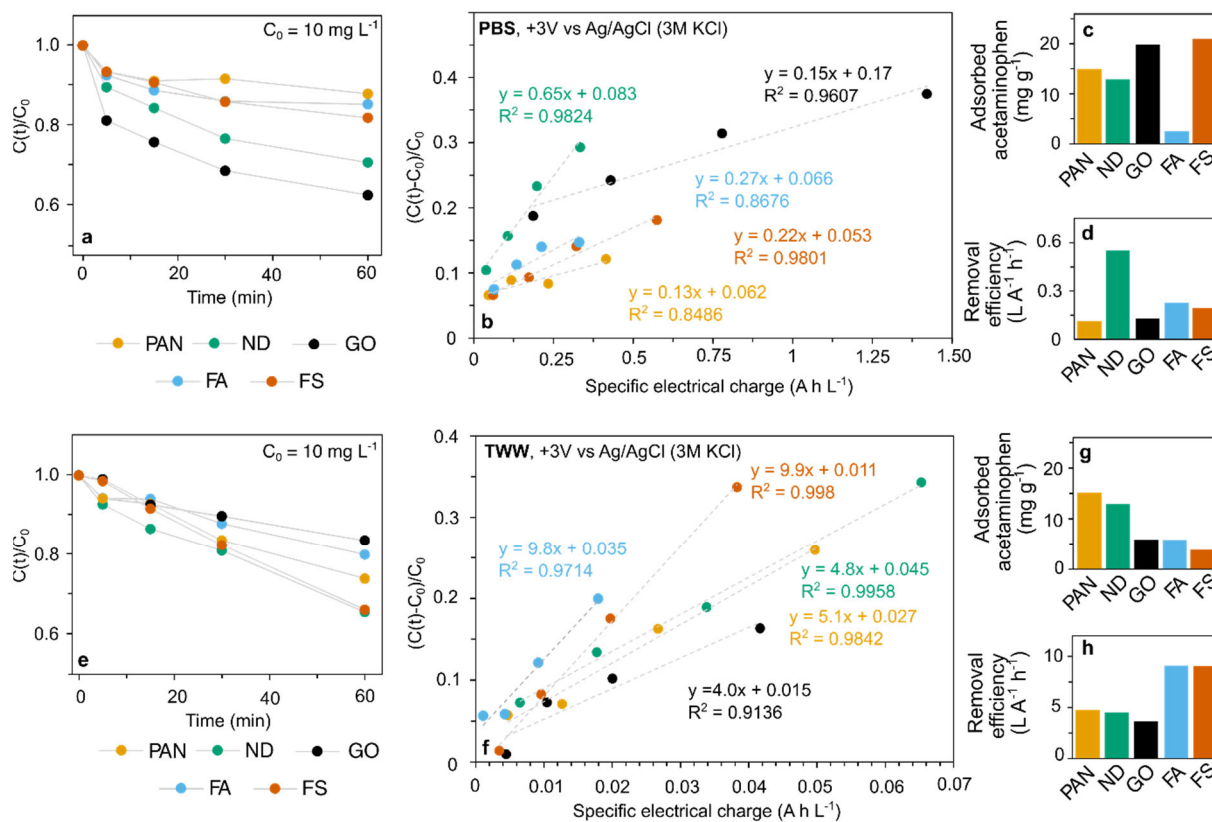
381 The oxidation of organic compounds by electrochemical technique involves two different
382 mechanisms acting simultaneously: direct anodic and indirect oxidations. In the first, the
383 electron transfer between the organic compound and the anode occurs directly on its surface,
384 while in the indirect oxidation, the electrochemical process is mediated by highly reactive
385 oxidant generated by the reaction with other species (e.g. hydroxyl radical, chlorine active
386 species), which are electro-generated at the anode surface (Martínez-Huitle and Panizza, 2018;
387 Wilk et al., 2022). Moreover, secondary oxidants reactive sulfate species (sulfate radicals,
388 peroxydisulfates) at appropriate current density may also occur during EO (Ganiyu et al.,
389 2021). Possibility of their in-situ EO generation, especially in sulphate-rich matrix constitute
390 additional influence for effective degrading organic contaminants. Indeed, $S_2O_8^{2-}$ can be
391 electrosynthesized from the SO_4^{2-} oxidation, resulting, then, in the cathodic production of $SO_4^{\bullet-}$
392 (Araújo et al., 2022) also by sp²-C rich boron-doped diamond hybrid electrodes (de Freitas
393 Araújo et al., 2022). However, considering the relatively low concentrations of chloride and
394 sulphate ions in the studied matrix (Table 1), the contribution of such electrogenerated
395 oxidants, may play a minor role in the mineralization process. However, the anode material
396 plays a predominant role in favoring one or other pathway (Brito et al., 2021). In particular,
397 the higher charge transferability, the larger active surface, and superior stability are
398 preferential for ideal electrode material (Faber et al., 2014). Indeed, it has been reported that
399 B, N co-doping reduces the charge transfer resistance, induces high electrical conductivity, and
400 fosters quicker EOP kinetics (Zhang et al., 2020).

401 To oxidize APAP on gassy carbon electrodes, a potential ranging between 0.2 and 0.7 V vs SCE
402 should be applied to the anode, depending on the solution's pH, as has been reported
403 (Nematollahi et al., 2009). However, a higher applied potential may be necessary to directly
404 transfer electrons from the APAP to the anode, and to allow the formation of different oxidants.
405 Moreover, the APAP oxidation pathway is known to follow complex kinetics, due to the variable
406 OH concentration caused by the parallel consumption of this oxidant in fast reactions with
407 products (Brillas et al., 2005). The electrochemical degradations of APAP were evaluated both
408 in phosphate buffer (PB) and treated wastewater (TWW) by the different composite electrodes.

409 **3.2.1 EO in phosphate buffer**

410 Degradation of APAP was quantified as a pseudo-first-order kinetic in PBS (Fig. 5a) and a
411 pseudo-zero-order kinetic in TWW (Fig. 5e), under the application of a +3V vs Ag/AgCL 3M
412 KCl electrode. The initial concentration of APAP was set as 10 mg/L for all of the reported
413 experiments, in a 0.1M PBS. Before the application of a constant potential to the electrode, the
414 solution was stirred with the PAN-based electrode composite and allowed to rest for 20
415 minutes to allow adsorption (Fig. 5c). The presence of a high level of graphitization on the
416 carbon surface seems to play an important role in adsorption, allowing for the π - π interaction
417 with the benzene ring present in the organic molecules (Tian et al., 2020). As can be observed
418 in Fig. 2i, the PAN/FA morphology lacks a porous carbon-rich coating, while it catalyzes the
419 growth of nanofiber-like structures, thus exhibiting the lowest adsorption. To compare the
420 APAP removal efficiencies with the energy consumed, Fig. 5b reports the plot between the
421 efficiency and specific current density, measured during the tests. It is possible to observe that,
422 while the PAN-GO electrode exhibits the faster removal kinetic (Fig. 5a), it also has the highest
423 energy consumption, since part of the energy is consumed by the electrode oxidation, as is also
424 well documented by the big difference in the Raman spectra before and after the EO process
425 (Fig. 4a). For this reason, it was deemed appropriate to compare the angular coefficients of the
426 linear regressions, which express the APAP oxidation efficiency at a specific energy density
427 (Fig. 5b), which have been reported in Fig. 5d. The APAP adsorption, evaluated at the
428 beginning of the tests (Fig. 5c) shows a comparable effect between the different composites,

429 except for the PAN/FA sample, which does not show an outer carbon “skin” at the solid/liquid
 430 interface, which can be simply explained by the low π - π interactions.



431
 432 Fig. 5 – (a,e) normalized APAP concentration versus time. (b,f) comparison between APAP removed
 433 and specific energy density measured. (c,g) APAP initially adsorbed by the electrode and (d,h) their
 434 corresponding removal efficiency in 0.1M PBS at the applied potential of 3 V vs AgAgCl 3KCl. The
 435 reader is referred to the web version of this paper for the color representation of this figure.

436 We also further investigated the impact of chloride species on the AC degradation, (PBS
 437 containing 0.137 M NaCl, 2.7 mM KCl, 8 mM Na₂HPO₄, 2 mM KH₂PO₄) on the degradation of
 438 AC, finding that more than 99% was degraded in the first 5 minutes, for all of the electrodes.
 439 The redox chemistry of aqueous chlorine species depends on several experimental conditions,
 440 such as the solution pH, which results in the different fractioning of different aqueous active
 441 chlorine species. Indeed, during the electrochemical oxidation process, Cl⁻ could be oxidized
 442 to Cl₂, Cl₂O, or HClO, all of which indirectly participate in the APAP oxidation reactions (Wilk
 443 et al., 2022), thus explaining the abrupt APAP degradation.

444 3.2.2 EO in TWW

445 To assess the effectiveness of employing the synthesized electrodes for the electrochemical
446 degradation of pharmaceuticals in relevant environments as an advanced treatment, the
447 oxidation of APAP, as a representative widespread drug, from a real TWW matrix was
448 investigated. Firstly, TWW is characterized by a lower conductivity than PBS, which implies an
449 increase in the applied potential for the same current density. On the other hand, the higher
450 potential may result in the formation of different active species that may participate both in
451 the indirect oxidation processes, oxygen evolution, and accelerated electrode degradation;
452 thus, it was decided to apply the same potential, with the result of a lower current density on
453 the electrode, thus a reduced removal efficiency. Similar behaviors were observed in other
454 studies, such as in tap water, due to the lower conductivity (Ormeno-Cano and Radjenovic,
455 2022) and the absence of organic matter (Pierpaoli et al., 2021c). It is worth reporting that the
456 PAN/ND composite exhibits a higher removal efficiency in PBS (Fig. 5d). BDD electrodes are
457 known to possess a distinct advantage over other electrode materials of their stability, chemical
458 inertness, due to the C atoms in sp^3 hybridization (Martínez-Huitle and Panizza, 2018). Even
459 if their presence was not directly probed on the PAN/ND surface, their presence in the PAN
460 bulk may induce a less defective structure (Fig. 4), therefore resulting in a wider active surface,
461 not limited to the single BDD grain boundaries exposed to the electrolyte. The highest
462 efficiencies attributable to FA and FS (Fig. 5h) may also be attributable to their lower capacitive
463 behavior (Table S4), favoring faradaic processes instead. For both tests, pH increases with
464 time, more remarkably in TWW (from 7.7 to 10.5 after 1h of treatment), rather than PBS (from
465 7.8 to 8.0).

466 In summary, both the electrode morphology and the chemical structures play important roles
467 in the APAP degradation: Zhang et al. reported that co-doped atoms and the unsaturated
468 carbon atoms provide a series of potential active sites; in particular, the copresence of B,
469 carrying negative charges due to the strong electronegativity, with C neighboring atoms,
470 represent a preferential site for the adsorption of O and O_2 intermediates (Zhang et al., 2020).
471 Interestingly, no by-products, inc. hydroquinone, p-benzoquinone, ketomalonic acid, maleic
472 acid, oxalic acid, oxamic acid, and acetamide, were identified during the EO processes (Fig. S3,

473 S4).

474 **4. Conclusion**

475 In this study, we demonstrated how to upcycle hazardous waste into architected
476 electroactive carbon-based electrodes and demonstrated their potential for the oxidation of
477 acetaminophen, as a putative pharmaceutical, in real wastewater. Combustion by-products
478 and industrial waste can be used as inexpensive fillers in polyacrylonitrile-based composites
479 and as catalysts, able to induce the growth of different carbon nanostructures by catalytic
480 chemical vapor deposition. The introduction of fly-ashes and foundry sand waste into the PAN
481 matrix resulted in an acetaminophen electrochemical removal efficiency twice that of the bare
482 PAN-based electrode, which acts differently as a catalyst during the CVD process: while large
483 the Fe-rich particles in the FA catalyze the formation of tubular carbon nanostructures, the
484 complex sub-micron FS fraction enhances the degree of graphitization of the composite
485 electrode. The addition of nanodiamonds, acting as a nucleation seed, positively affect the
486 CVD-grown interfacial structure, resulting in a more ordered graphitic structure, which is
487 related to the fastest degradation kinetics, both in PBS and TWW. On the other hand, the
488 addition of graphene oxide into the electrode is detrimental, since most of the energy is
489 consumed in the electrode oxidation. No by-products, inc. hydroquinone, p-benzoquinone,
490 ketomalonic acid, maleic acid, oxalic acid, oxamic acid, and acetamide, were identified during
491 the EO processes. The most remarkable result of the present study is the demonstration of
492 upcycling hazardous materials into valuable catalysts for the creation of electrodes to degrade
493 hazardous water pollutants. Further investigations are intended to apply the current
494 modulation technique, by continuously adjusting the applied current, to reduce the energy
495 consumption, and develop topologically optimized flow-through electrodes, for developing a
496 more efficient process.

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