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**Nanostructured electrodes for electrocatalytic advanced oxidation  
processes: from materials preparation to mechanisms  
understanding and wastewater treatment applications**

**Xuedong DU<sup>1</sup>, Mehmet A. OTURAN<sup>1,2,\*</sup>, Minghua ZHOU<sup>1,\*</sup>, Nacer BELKESSA<sup>3</sup>, Pei SU<sup>1</sup>,  
Jingju CAI<sup>1</sup>, Clément TRELLU<sup>2</sup>, Emmanuel MOUSSET<sup>3,\*</sup>**

<sup>1</sup> Key Laboratory of Pollution Process and Environmental Criteria, Ministry of Education, College of Environmental Science and Engineering, Nankai University, Tianjin 300350, China

<sup>2</sup> Université Gustave Eiffel, Laboratoire Géomatériaux et Environnement (EA 4508), UPEM, 77454, Marne-la-Vallée, France

<sup>3</sup> Laboratoire Réactions et Génie des Procédés, Université de Lorraine, CNRS, LRGP, F-54000 Nancy, France

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***APPLIED CATALYSIS B: ENVIRONMENTAL JOURNAL***

\* Corresponding authors' Emails: [mehmet.oturan@univ-eiffel.fr](mailto:mehmet.oturan@univ-eiffel.fr) (Mehmet A. Oturan), [zhoumh@nankai.edu.cn](mailto:zhoumh@nankai.edu.cn) (Minghua Zhou), [emmanuel.mousset@univ-lorraine.fr](mailto:emmanuel.mousset@univ-lorraine.fr) (Emmanuel Mousset)

## 1 **Abstract**

2 The implementation of nanostructured materials in electrochemistry implied the enhancement  
3 of conversion yield in fuel cell, in electrosynthesis of oxidants and electrolytic treatment for  
4 environmental protection, while it allowed reducing the detection limit in electroanalysis.  
5 Nanostructured materials are becoming a hot topic of research, especially in electrochemical  
6 treatment for environmental applications that is strongly related to the rise of graphene and  
7 subsequent 2D materials that emerged in the last ten years. Nano-structuration allows bringing  
8 new properties of the materials such as number of active sites and conductivity improvement.  
9 It can therefore enhance the heterogeneous catalysis mechanism at electrode surface. This is  
10 primordial since it makes increase the rate of electrochemical reactions that can be the rate  
11 limiting steps in electrocatalytic treatment. Such advanced materials contribute to make  
12 advanced electrochemical processes as “greener” processes than the conventional ones.  
13 This paper aims to be a comprehensive, critical, and accessible review of general interest. The  
14 literature covers mainly the last ten years’ period due to the recent topic, especially the last five  
15 years with the considerable increase of number of publications in this period. The contents  
16 particularly devote efforts to establish links between the nanostructured-based electrode  
17 properties and electrochemical treatment efficiency through the mechanisms involved. The  
18 perspectives about mechanisms understanding and electrodes stability improvement are  
19 especially discussed.

20

21 **Keywords:** Nanostructured electrodes; electrooxidation; Electro-Fenton; Oxygen reduction  
22 reaction, Oxygen evolution reaction, Wastewater treatment

23

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96		

97 **List of abbreviations**

<b>Abbreviation</b>	<b>Definition</b>
3D	Three-dimensional
ACF	Activated carbon fiber
AFM	Atomic force spectroscopy
AHPS	4-amino-3-hydroxy-2-p-tolylazo-naphthalene-1-sulfonic acid
ANC	Activated N-doped carbon
AOPs	Advanced oxidation processes
AR 73	Acid Red 73
ATZ	Atrazine
AY1	Acid Yellow 1
BDD	Boron-doped diamond
BDDNW	BDD nanowire
BET	Brunauer-Emmett-Teller
Blue-TNAs	Blue TiO <sub>2</sub> nanotube arrays (Blue-TNAs)
BOD <sub>5</sub>	Biochemical oxygen demand after 5 days
CF	Carbon felt
CHE	Computational hydrogen electrode
CNT	Carbon nanotube
COD	Chemical oxygen demand
CPET	Coupled proton-electron transfers
CV	Cyclic voltammetry
DFT	Density-functional theory
DO	Dissolved oxygen
DSA	Dimensionless stable anode
EAOPS	Electrochemical advanced oxidation processes
EDX	Energy-dispersive X-ray spectroscopy
EEGr	Electrochemically exfoliated graphene
EF	Electro-Fenton
EIS	Electrochemical impedance spectroscopy
FTIR	Fourier-transform infrared spectroscopy
FTO	Fluorine-doped tin oxide

GC	Glassy carbon
GDE	Gas diffusion electrode
GF	Graphite felt
HARN	High aspect ratio nanostructures
HER	Hydrogen evolution reaction
HF <sub>s</sub>	Hierarchical flower-like structure
HPCS-S	Hollow porous carbon sphere-sulfur composite
h-PEF	Heterogeneous photo-electro-Fenton
LSV	Linear sweep voltammetry
MCE	Mineralization current efficiency
MeOH	Methanol
MMO	Mixed metal oxide
MNC	Mesoporous N-doped carbon
MO	Methyl orange
MOF	Metal organic framework
MWCNTs	Multi-walled carbon nanotubes
NADE	Natural air diffusion electrode
NB	nitrobenzene
NCNT	N-doped multi-walled carbon nanotube
NF	Nickel foam
N/F-CNC	Nitrogen/fluoride co-doped carbon nanocages
NP	Nanoparticle
NS	Not specified
NTs	Nanotubes
NTA	Nanotube arrays
TNTs	TiO <sub>2</sub> nanotubes
OEP	Oxygen evolution potential
OER	Oxygen evolution reaction
ORR	Oxygen reduction reaction
PAN	Polyacrylonitrile
PANI	Polyaniline
PC	Photocatalysis
PEC	Photoelectrocatalysis

PEF	Photoelectro-Fenton
PFOA	Perfluorooctanoic acid
ppi	Pores per inch
PPM	Polymeric precursor method
PTFE	Polytetrafluoroethylene
PVD	Physical vapor deposition
R <sub>ct</sub>	Charge transfer resistance
R <sub>d</sub>	Dynamic resistance
REM	Reactive electrochemical membrane
RGO	Reduced graphene oxide
RHE	Reversible hydrogen electrode
ROS	Reactive oxygen species
RVC	Reticulated vitreous carbon
S <sub>BET</sub>	BET specific surface area
SBR	Sequencing batch reactor
SCE	Saturated calomel electrode
SEM	Scanning electron microscopy
SDBS	Sodium dodecyl benzene sulfonate
SHE	Standard hydrogen electrode
SS	Stainless steel
SWNT <sub>s</sub>	Single-walled carbon nanotubes
TBA	Tert-butyl alcohol
TEM	Transmission electron microscopy
TNA	Nanotube array
TGA	Thermal gravimetric analysis
TiO <sub>x</sub>	Sub-stoichiometric TiO <sub>2</sub>
TOC	Total organic carbon
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction



## 99        **1. Introduction**

100    Nanostructure materials have been widely developed, particularly in the last ten years, with the  
101    rise of graphene - sp<sup>2</sup>-hybridized carbon atoms arranged in a honeycomb structure - and  
102    associated Nobel prize attribution in 2010, and subsequent equivalent 2D materials as well as  
103    graphene-based materials [1,2]. Due to their ability to modify the raw material properties such  
104    as the electric and thermal conductivity, surface area, gas permeability as well as mechanical  
105    resistance, their implementation in electrochemistry area as electrode material became obvious  
106    [3]. It is important to note that nanostructured materials can be extended to nanostructured  
107    electrochemical interfaces that are usually encounter for example through defects and pinholes  
108    in self-assembled monolayers or catalytic nanoparticles spread throughout less reactive  
109    substrate [4].

110    In parallel, for more than 20 years, electrochemical applications for environmental protection  
111    especially in wastewater gained a considerable interest [5,6]. Those based on the generation of  
112    very strong oxidizing agents such as hydroxyl radical (<sup>•</sup>OH) ( $E^0(\text{<sup>•</sup>OH}/\text{H}_2\text{O}) = 2.80 \text{ V} / \text{SHE}$ ),  
113    namely electrochemical advanced oxidation processes (EAOPs), have shown impressive  
114    efficiency [7–13]. They have the ability to generate continuously and in situ the reactive agents  
115    in order to remove partially or completely - according to the treatment strategy [14] - a wide  
116    variety of organic pollutants, especially the most biorecalcitrant ones present either at high  
117    concentration (chemical oxygen demand (COD) = 1 – 100 g-O<sub>2</sub> L<sup>-1</sup>) or very low concentrations  
118    (i.e. micropollutant concentration in the range of ng L<sup>-1</sup> to μg L<sup>-1</sup>) [15–24]. Still, the possibility  
119    to improve their performance by incorporating nanostructured materials for both cathode and  
120    anode has been tested in the last decades. The promise of improvement came up with numerous  
121    studies on this specific topic with an increasing number without having an overview that could  
122    help giving some requirement and directions based on a critical literature review.

123 There are existing reviews on nanostructured carbon-based materials for some electrochemical  
124 applications, but mainly for fuel cell, water splitting and electro-analysis [4,25–31]. There are  
125 also few reviews on electrocatalytic treatments but the use of nanostructured electrode materials  
126 is not developed at all [5,7–9,11,14,22,32–35]. Thus, there is no detailed and systematic review  
127 on nanostructured (carbon-based, metallic-based) electrodes for EAOPs applications. Indeed,  
128 electrolytic treatment is implemented in EAOPs by applying current in order to make evolve  
129 non-spontaneous reactions. Contrastingly, spontaneous reactions are involved in fuel cell and  
130 microbial fuel cells systems to generate electrical energy. It means that the properties required  
131 for electrode materials are not the same in EAOPs and fuel cells, especially in terms of electrode  
132 potential and overvoltage requirements. Focusing only on electrocatalytic treatments is  
133 therefore a way to be exhaustive and to bring a critical overview on existing nanostructured  
134 materials and what could be the new insights required to improve the performance of such  
135 materials in terms of specific surface area, charge transfer kinetics, number of low-coordinated  
136 sites, quantum confinement, etc. [36].

137 This review intends to bring a synthetic and critical state of the art by screening the  
138 nanostructured electrode materials employed in electrocatalytic treatments that induce  
139 oxidative stress represented mainly by EAOPs, which excludes the other kinds of  
140 electrochemical processes such as fuel cells. As it is the first time that a detailed and exhaustive  
141 review is published on this topic, this review can further serve as a baseline in the targeted  
142 research area. The general electrolytic mechanisms involved at either cathode or anode  
143 materials are presented before exposing the main preparation routes and characterization  
144 techniques of the nanostructured materials. The properties obtained with these different kinds  
145 of materials are then reviewed in detail with added benefits of nano-structure, followed by the  
146 thorough presentation of their contribution in the EAOPs efficiency for wastewater treatment.

147 Finally, perspectives and outlook are disclosed regarding the mechanism understanding  
148 requirement and electrode stability improvement.

149

## 150 2. General electrocatalytic mechanisms

### 151 2.1. Two-electron oxygen reduction reaction (ORR) pathway

152 The two-electron oxygen reduction reaction (ORR) pathway leads to the electrogeneration of  
153 hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) at the cathode surface and involve adsorbed  $\ast\text{OOH}$  as intermediate  
154 species (Eq. 1) [25,37].



156  $\text{H}_2\text{O}_2$  is an interesting oxidant ( $E^0_{(\text{H}_2\text{O}_2/\text{H}_2\text{O})} = 1.76 \text{ V/SHE}$ ) since it is a precursor for the  
157 production of a strong oxidizing agent, i.e.,  $\ast\text{OH}$  ( $E^0_{(\ast\text{OH}/\text{H}_2\text{O})} = 2.80 \text{ V/SHE}$ ), that are produced  
158 through Fenton reaction (Eq. 2) [7,38].



160 This radical is widely implemented in environmental applications, as it is the main species  
161 responsible for the degradation and mineralization of organic pollutant as well as inhibition of  
162 microorganisms present in wastewater, as detailed in section 5. Moreover, the in situ production  
163 of  $\text{H}_2\text{O}_2$  offer a promising safer alternative compared to the use of Fenton's reagent ( $\text{H}_2\text{O}_2 +$   
164  $\text{Fe}^{2+}$ ) since the storage of  $\text{H}_2\text{O}_2$  is delicate due to its explosive nature [39]. The difficulties in  
165 involving the partial two-electron ORR is that the full four-electron ORR (Eq. 3) can also occur  
166 through either associative mechanism (Eqs. 4a-4d) or dissociative mechanism (Eqs. 5a-5c) by  
167 implementing adsorbed oxygenated intermediates species ( $\ast\text{OOH}$ ,  $\ast\text{O}$  and/or  $\ast\text{OH}$ ) at the  
168 cathode surface ( $\ast$ ) [25,37,40]. The contribution of associative versus dissociative pathway is  
169 depending on the kind of anode material employed and on the applied anodic potential [40].



178 The generation of  $H_2O$  is thermodynamically favorable, meaning that the selectivity towards  
 179 the two-electron instead of four-electron pathway is therefore an important key issue. This has  
 180 then an impact on the kinetics of Fenton reaction (section 6) to generate  $*OH$ . The ORR pathway  
 181 has been widely studied in its four-electron way [25,40], which is mainly due to the fuel cell  
 182 studies that currently occupy an important research area in electrochemistry, especially for the  
 183 promising industrial applications in energy (e.g.,  $H_2$  electrogeneration).

184 Still, two-electron ORR mechanism study could be find in literature. Thermodynamic analyses  
 185 have been proposed as first attempt to predict the reaction feasibility, especially regarding the  
 186 ORR selectivity. Density-functional theory (DFT) calculation permitted to estimate the free  
 187 energy ( $\Delta G$ ) describing the adsorption energies of intermediates (including solvated protons  
 188 and electron) at material surfaces [41]. Using the computational hydrogen electrode (CHE)  
 189 model [40],  $\Delta G$  could be drawn as function of reaction coordinate for two-electron ORR, as  
 190 shown in the diagram illustrated in Fig. 1a for PtHg<sub>4</sub> material [25,41]. It highlights that at 0.70  
 191 V (i.e., equilibrium potential) the first reaction step is uphill, which makes difficult the reaction,

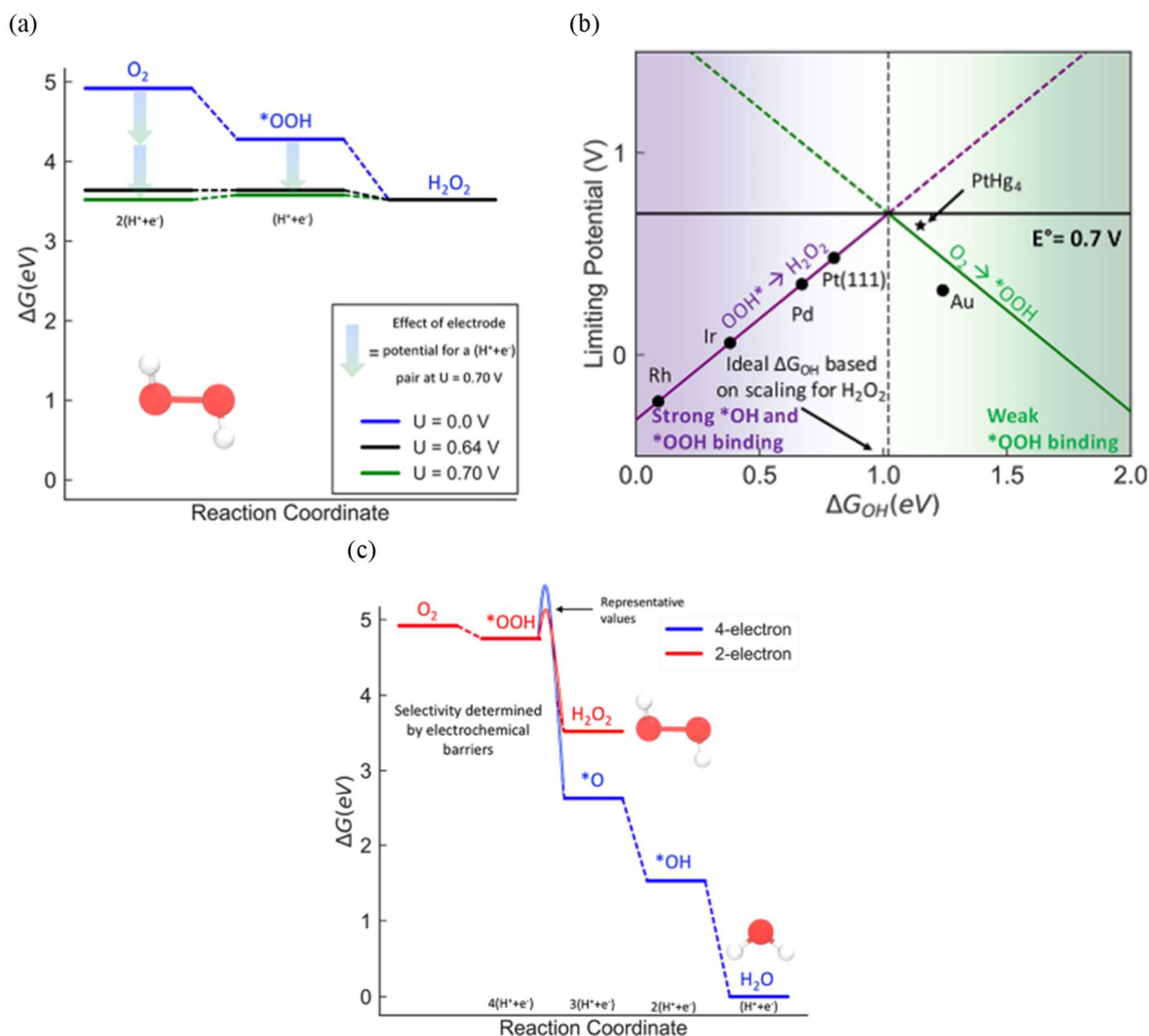
192 while at 0.63 V it is easier and it corresponds to the limiting potential since it is the maximum  
193 potential value for which the steps are downhill.

194 In addition, the electron transfer is fast in ORR, so that it is usually not considered as the kinetic  
195 rate limiting step [25]. Generally, the adsorption of oxygen ( $O_2$ ) on the cathode surface has been  
196 considered as the limiting step in literature, especially on carbon materials [42,43]. Deeper  
197 studies emphasized the fact that the formation or removal of  $^*OOH$  intermediates species from  
198 the surface are the limiting steps in two-electron ORR [25] (Fig. 1a). Volcano plot allowed  
199 visualizing the optimal binding energy of intermediate ( $^*OOH$ ) that need to be operated in order  
200 to have electrogeneration of  $H_2O_2$  (Fig. 1b). This binding need to be not too strong (solid purple  
201 line) and not too weak (solid green line). Several materials have shown to correspond to this  
202 property such as Pt and Pd mercury alloys [41,44] as well as some carbon structures [45].

203 Beyond these thermodynamics data, it has been shown that parallel reactions 1 and 4b interfere  
204 in the  $H_2O_2$  selectivity [41,46]:

205 It means that the O-O bond dissociation from adsorbed  $^*OOH$  should be avoided in order to  
206 favor  $H_2O_2$  generation [25]. It further indicates that the catalyst must have weak oxygen binding  
207 energies to avoid  $^*O$  formation [25]. Experimental data evidenced the selectivity towards  $H_2O_2$   
208 when using weak oxygen binding cathodes such as Au(111) [47] or carbon-based materials  
209 [48–51]. It is interesting to note that Au material does not thermodynamically favor the  
210 generation of  $H_2O_2$ , which is not in agreement with the laboratory results [25]. It means that the  
211 kinetics need also to be taken into account as highlighted in the free energy diagram for the  
212 two- and four-electron ORR on Au(111) in Fig. 1c.

213

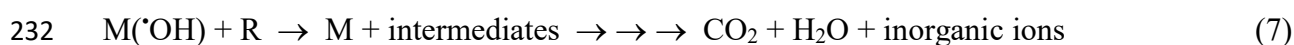


214  
 215 **Figure 1.** (a) Free energy diagram for the two-electron ORR on PtHg<sub>4</sub>, (b) volcano plot for  
 216 the two-electron ORR, (c) Free energy diagram for the two- and four-electron ORR on  
 217 Au(111). Reprinted with permission from [25]. Copyright 2018, American Chemical Society.  
 218

## 219 2.2. Oxygen evolution reaction (OER) pathway for high overvoltage anodes

220 Electrooxidation of pollutants in aqueous solution can be obtained by performing the  
 221 electrolysis at high anodic potentials. Depending on the potential at which the oxygen evolution  
 222 reaction (OER) occur, this process does not need to add catalysts into the solution and does not  
 223 produce any byproducts [52–54]. Generally, there are two types of anode materials: (1) active  
 224 anodes (Pt, IrO<sub>2</sub>, and RuO<sub>2</sub> and other mixed metal oxide (MMO) anodes) with low O<sub>2</sub> over-

225 potential and (2) non-active anodes (SnO<sub>2</sub>, PbO<sub>2</sub>, sub oxide of TiO<sub>2</sub> (like Ti<sub>4</sub>O<sub>7</sub>) and boron-  
226 doped diamond (BDD)) with high O<sub>2</sub> over-potential. It is supposed that H<sub>2</sub>O is oxidized on  
227 anode M to produce physisorbed hydroxyl radical (M(\*OH)) through Eq. 6, leading to the  
228 degradation and/or mineralization of organic pollutants as detailed in section 5. The surface of  
229 a non-active anode interacts so weakly with \*OH that it allows the direct reaction of organic  
230 pollutants (R) with M(\*OH) (Eq. 7) [33,55].



233 The oxygen evolution potential (OEP) of an anode is very important since the higher the OEP,  
234 the weaker the interaction of M(\*OH) with the anode surface and the higher is the chemical  
235 reactivity toward organics oxidation. To improve OEP, many approaches have been attempted,  
236 e.g., elemental doping and nano-structure construction. For example, when TiO<sub>2</sub> nanotubes  
237 (TNTs) were introduced to Ti/SnO<sub>2</sub>-Sb, the OEP was found to increase from 2.00 V to 2.18  
238 V/SHE [56]. In other works it was observed that the OEP increased from 1.73 V to 2.20 V/  
239 Saturated calomel electrode (SCE) after TiO<sub>2</sub> nanotubes (TNTs) base introduced into PbO<sub>2</sub>  
240 [57]. Therefore, nano-structure introduction could decline the activity of OER and improve the  
241 catalytic activity.

242

### 243 **3. Preparation and characterization of nanostructured-based electrodes**

#### 244 **3.1. Preparation methods**

##### 245 **3.1.1. Cathode materials**

246 The preparation of the material is a particularly important step regarding the properties and  
247 stability of the electrode once employed in electrochemical applications. The preparation of the

248 cathodes materials depends in general on the catalyst's composition and the desired structure.  
249 For this purpose, a wide range of methods is used to prepare or to modify the electrodes based  
250 on chemical, thermal and/or physicochemical methods.

251

#### 252 *3.1.1.1. Polymeric precursor method for metal oxide supported on carbon materials*

253 The polymeric precursor method (PPM) is used mainly in the preparation of nanostructured  
254 metal oxide electrocatalysts. Firstly, citric acid was dissolved in ethylene glycol at 60°C and  
255 then the metal precursor was added to this mixture to obtain a viscous resin [58]. Then, a desired  
256 amount of the carbon was added to the solution precursor prepared previously in order to  
257 produce the electrocatalyst. Finally, the mixture containing the electrocatalyst and the resin was  
258 homogenized in an ultrasonic bath for 1 h and then thermally treated at 400°C during 2 h under  
259 N<sub>2</sub> flow [59].

260

#### 261 *3.1.1.2. Hydrothermal functionalization for the heteroatoms-doped carbon nanomaterials*

262 Hydrothermal synthesis is largely used for the preparation of nanostructured materials as  
263 nanosheets, nanospheres and the famous carbon nanotubes (Fig. 2a). This method allows the  
264 morphology control of the desired compounds by the means of temperature flexibility reaching  
265 a very high values [60]. This approach is also commonly used in the case of the heteroatoms-  
266 doped carbon nanomaterials. An appropriate mass ratio of the desired heteroatoms source and  
267 the carbon nanomaterials were mixed in the autoclave and heated at high temperature for a  
268 necessary time, depending on the characteristics of the final product [61]. Then, the autoclave  
269 was cooled to room temperature and some post synthesis treatments like carbonization under  
270 inert gas (e.g., argon) were performed to form the nanostructure [62,63]. After that, a washing



271 treatment with hydrofluoric acid can be performed to dope the carbon with fluorine heteroatom  
272 [63] (Fig. 2a).

273

#### 274 *3.1.1.3. Plasma discharge treatment for nanostructured preparation*

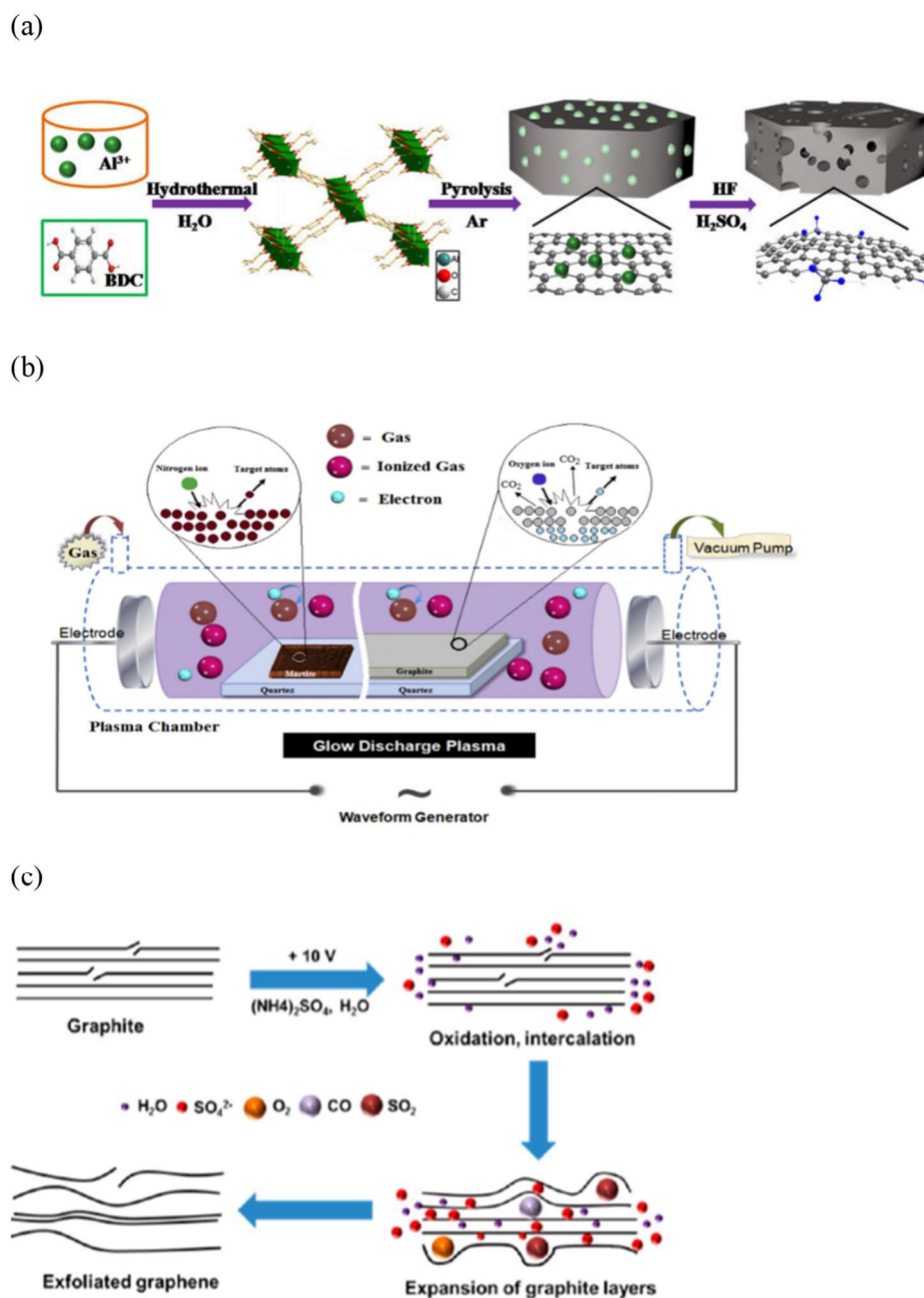
275 The plasma nanofabrication arouses a huge interest in the nanomaterials manufacturing (Fig.  
276 2b). This method exhibits more environmental and economic advantages compared to the  
277 chemical process and it allows achieving the wanted structural and electronics properties [64].  
278 For electro-Fenton cathode, this approach was used to create a nanostructure as the case for  
279 graphite. Khataee et al. [65] modified the graphite cathode to nanoflakes by the AC glow plasma  
280 discharge and they increase drastically the surface area of the cathode. Briefly the plasma was  
281 created by the interaction between the electric current with high voltage and gas generating  
282 several particles: ions, ionized ions, radicals and electrons inside the chamber reactor as shown  
283 in Fig. 2b [65], thus altering the targeted surface.

284

#### 285 *3.1.1.4. Electrochemical exfoliation synthesis of graphene followed by ink-coating method*

286 Electrochemical exfoliation synthesis is the method used only for the graphene cathode  
287 preparation from graphite powder [66–68]. The principle of this method consists on the  
288 application of voltage between two electrodes: the compressed graphite as working electrode  
289 and any counter electrode. Under the influence of the potential, the ionic species of the  
290 electrolyte goes into the graphite electrode creating an heterogeneity in the inter-layer distance,  
291 namely exfoliation step [69] (Fig. 2c).

292 The exfoliated graphene can then be mixed with a binder (e.g., PTFE, Nafion) in a water/ethanol  
293 mixture to obtain a suspension, namely ink, using ultrasonic bath for 1 h [67,70]. The raw  
294 carbon material can be then soaked in the ink and heated in furnace at 250°C for 1 h [67,70].



295

296 **Figure 2.** (a) Hydrothermal treatment for heteroatoms functionalization (Reprinted with  
 297 permission from [63]. Copyright 2018, Elsevier), (b) Plasma discharge reactor for  
 298 nanostructure preparation (Reprinted with permission from [65]. Copyright 2017, Elsevier)  
 299 and (c) electrochemical exfoliation mechanism of the graphite to graphene (Reprinted with  
 300 permission from [71]. Copyright 2014, American Chemical Society).

301

302 *3.1.1.5. Electrophoretic deposition*

303 Electrophoretic deposition consists in using the raw conductive substrate material to coat as an  
304 anode, while an inert counter-electrode (e.g., Pt) can be used [72,73]. Then the graphene oxide,  
305 which has a negative charge in solution, adheres to the anode material. A reduction is  
306 subsequently done by reversing the polarity so that the graphene oxide deposited on the material  
307 is reduced [72,73]. This method avoids the use of a binder.

308

309 *3.1.1.6. Microemulsion and co-precipitation to prepare bi metallic nanoparticles and mixed*  
310 *metal oxides nanostructures*

311 Microemulsion is among the known method used for the preparation of nanoparticles with an  
312 easier control of the particles size and distribution. It consists basically on the mixing of two  
313 surfactant microemulsions, i.e., one with the precursor metal and another one with a reducing  
314 agent [74,75]. The metallic nanoparticles were obtained after a series of chemical and physical  
315 transformation, including the interaction between the two microemulsions and then the  
316 chemical reaction occurs to allow the formation of the metal nuclei that is growing thereafter  
317 [74]. Félix-Navarro et al. [75] reported the formation of a bimetallic Pd-Pt nanoparticles using  
318 the microemulsion method.

319 Co-precipitation is another low-cost way used to prepare MMOs with high surface area. The  
320 obtained material surface contains an important number of active sites allowing an efficient  
321 adsorption of the molecules on the surface [76]. For the preparation of metal oxide  
322 nanoparticles, a salt precursor containing the metal was firstly dissolved in solvent with a base  
323 to favor the formation of the metal hydroxide precipitate. Then, the nucleation and the growth  
324 phases leads to the final dispersed nanoparticles [76]. A MMO nano spherical bismuth  
325 molybdates ( $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ ) by the co-precipitation route could be also synthesized [77]. The

326 prepared compound was served as a coating on titanium mesh to form a high effective  
327 nanostructured cathode for the electrogeneration of H<sub>2</sub>O<sub>2</sub> [77].

328

### 329 *3.1.2. Anode materials*

330 In general, the preparation methods of nanostructured anode could be divided into two main  
331 groups: (1) chemical methods and (2) physical methods. For chemical methods, the techniques  
332 used consist of thermochemical deposition, electrodeposition and chemical vapor deposition  
333 (CVD). Physical vapor deposition (PVD) belongs to physical method. Different synthesis  
334 strategies have been chosen to introduce different components on anode support. Fig. 3  
335 summarizes some chemical methods for anode preparation including thermochemical  
336 decomposition, electrodeposition and CVD.

337

#### 338 *3.1.2.1. Thermochemical decomposition*

339 Thermochemical decomposition method is the most widely applied among all the chemical  
340 methods, especially for preparation of SnO<sub>2</sub> or IrO<sub>2</sub>-based anodes (Fig. 3a) [78–80]. In a typical  
341 thermochemical decomposition procedure, metal precursor and alcoholic solvent were mixed  
342 to drop or brush, and then dried and annealed at certain temperature. The isopropanol, ethanol  
343 or butanol was widely used as solvent to dissolve precursors. A high temperature is necessary  
344 for this method because it is beneficial to catalytic performance. The effects of preparation  
345 temperatures in the range of 450 - 850 °C for Eu doped Ti/SnO<sub>2</sub>-Sb electrodes on phenol  
346 removal were investigated [81]. It was observed that smaller SnO<sub>2</sub> grain sizes (e.g., 8 - 10 nm)  
347 were obtained at 750 °C. The removal efficiency first increased and then decreased with the  
348 increase of the pyrolysis temperature, and reached the maximum at 750 °C (96.4%) with the  
349 same energy consumption. However, high pyrolysis temperature (> 600 °C) was not conducive  
350 for the service life of Ti/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>5</sub> anode; it was only 0.5-24 h [82]. When the pyrolysis  
351 temperature was 500 °C, the service life exceeded 180 h.

352 The advantage of this method is to be easy in preparation and simple in operation. However,  
353 this method still faces some disadvantage [83]: (1) poor reproducibility due to generation of  
354 cracks at high internal pressure; (2) easy loss of some metals and (3) uneven surface coating.

355 To solve these problems, sol-gel method has been developed. This method is based on the  
356 solvolysis of organic solvent and inorganic or organic salts and water. The precursor was  
357 condensed at refluxing device, and achieved the required viscosity at room temperature. Thin  
358 films are prepared by dip or roll coating at intermediate temperatures and further annealed at  
359 high temperatures. Makgae et al. [79] prepared a series of MMOs ( $\text{SnO}_2\text{-RuO}_2\text{-IrO}_2$ ,  $\text{Ta}_2\text{O}_5\text{-}$   
360  $\text{IrO}_2$  and  $\text{RhO}_2\text{-IrO}_2$ ) fixed on a Ti substrate using sol-gel method, which exhibited higher  
361 stability with surface roughness and internal porosity. These anodes were used to degrade  
362 phenol, achieving more than 90% removal efficiency.

363

#### 364 3.1.2.2. Electrodeposition

365 Electrodeposition can be regarded as a facile method for the anode preparation [84–86]. In a  
366 typical electrodeposition procedure, plating bath containing metal precursor and electrolyte is  
367 controlled to regulate deposition performance via acidity and depositing current as well as  
368 depositing temperature to obtain oxide film (Fig. 3b). The advantage of this method [83] is that  
369 it is easy to prepare complex electrodes and that large surface areas can be deposited. However,  
370 this method still has some disadvantages [83]: (1) high energy consumption, (2) generation of  
371 acidic and toxic wastewater, and (3) uneven surface coating.

372 Electrodeposition method is more often used for electrodeposition of  $\text{PbO}_2$  anode (Fig. 3b). The  
373 temperature is one of the most critical parameters for electrodeposition of  $\text{PbO}_2$ , while high  
374 temperature is beneficial to nucleation, growth and rough coating [87,88]. The current density  
375 is favorable to improve the polycrystallinity due to massive nucleation and high degree of

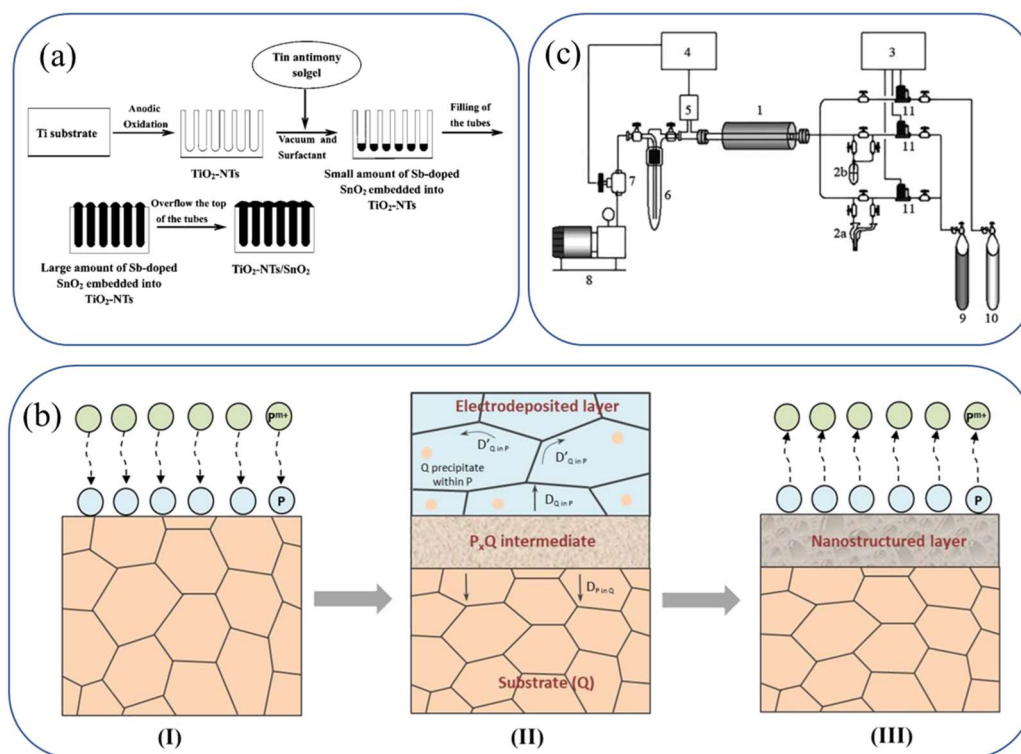
376 porosity [87]. A high current density or potential polarization is important to form high surface  
377 area [89]. Increasing of pH has significant influence on the surface morphology and crystal  
378 forms, resulting in the decrease of current density [90].

379

### 380 3.1.2.3. CVD

381 CVD is a relatively less used method for anode preparation because of complicated preparation,  
382 expensive equipment and troublesome preparation conditions (Fig. 3c). In a typical CVD  
383 procedure, chemical interaction is generated between the molecules of the volatile precursor  
384 and active sites of the substrate surface at vacuum conditions. This process can be repeated  
385 several times, and then an inert gas is purged to remove excess reactant and volatile by-products.

386 This method exhibits some advantages such as excellent reproducibility and uniform coating.  
387 SnO<sub>2</sub> coating on Ti plates via CVD method using SnEt<sub>4</sub> and O<sub>2</sub> as reactive gas mixture was  
388 prepared, which exhibited conformal-coverage of the surface roughness [91]. CVD method  
389 demonstrated excellent uniformity of coating, resulting in the increased service life and  
390 improved reproducibility compared with dip coating process [91,92]. The service life of BDD  
391 electrode prepared by CVD method was long and exhibited high removal and mineralization of  
392 phenol [93].



393

394 **Figure 3.** (a) Schematic illustration for the growth of a  $\text{TiO}_2\text{-NTs/SnO}_2$  electrode via  
 395 thermochemical decomposition. Reproduced with permission from Ref [94]. Copyright  
 396 (2009) American Chemical Society; (b) Electrodeposition method: schematic diagram for

397 electrolytic metal-atoms enabled manufacturing of nanostructured sensor electrodes. (I)

398 Electrodeposition of the metal atoms (P) from its corresponding ion form ( $\text{Pm}^+$ ) onto a

399 substrate (Q); (II) Representation of interactions at the interface between the electrodeposited

400 layer of P and the substrate Q; and (III) Electro-dissolution of P from the substrate.

401 Reproduced with permission from Ref [95]. Copyright (2020) Electrochemical Society. (c)

402 CVD apparatus: (1) Hot-wall CVD reactor. (2a) 1<sup>st</sup> bubbler for  $(\text{MeCp})\text{Ir}(\text{COD})$ . (2b) 2<sup>nd</sup>

403 bubbler for TET. (3) Gas flow controller. (4) Pressure controller. (5) Pressure gauge. (6) Cold

404 trap. (7) Throttle valve. (8) Vacuum pump. (9) He tank. (10)  $\text{O}_2$  tank. (11) Mass-flow

405 controller. Reproduced with permission from Ref [92]. Copyright (2010) Kluwer Academic

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407

#### 408 3.1.2.4. PVD

409 PVD is a physical method, applying metal oxides instead of volatile precursor in CVD. In a  
410 typical PVD procedure, the precursor is vapored to gas which is mixed with inert gas to deposit  
411 on substrate via condensation method to generate film. The advantage of this method is the  
412 careful controlling of the relative ratios of precursors.  $\text{Ir}_x\text{Ru}_{1-x}\text{O}_2$  mixed metal oxide nanowires  
413 were synthesized by PVD method using  $\text{IrO}_2$  and  $\text{RuO}_2$  as precursors, forming highly single  
414 crystalline [96]. However, because of troublesome preparation conditions such as complicated  
415 preparation, expensive equipment and limitations in complex substrate, very few reports have  
416 been found about anodic oxidation of organics using anode prepared by PVD.

417

### 418 3.2 Characterization techniques

419 Different characterization techniques have been applied to assess the physicochemical and  
420 electrochemical properties presented in section 4: "Nanostructured-based electrode properties"  
421 whose fabrication methods have been exposed in previous sub-section 3.1. The techniques  
422 include: scanning electron microscopy (SEM), transmission electron microscopy (TEM),  
423 energy-dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), contact angle  
424 measurements, X-Ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier-  
425 transform infrared (FTIR) spectroscopy, Raman spectroscopy, thermal gravimetric analysis  
426 (TGA), cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical  
427 impedance spectroscopy (EIS), Mott–Schottky measurements and UV–vis spectra.

428 Examples of characterization performance for some cathodes are illustrated in Figs. 4 and 6,  
429 while they are depicted in Figs. 5 and 7 for some anodes.

430 SEM, TEM and AFM could be used to observe the morphology and internal structure of  
431 materials. The nanoflowers made of carbon supported by  $\text{MnO}_2$  to enhance the ORR activity

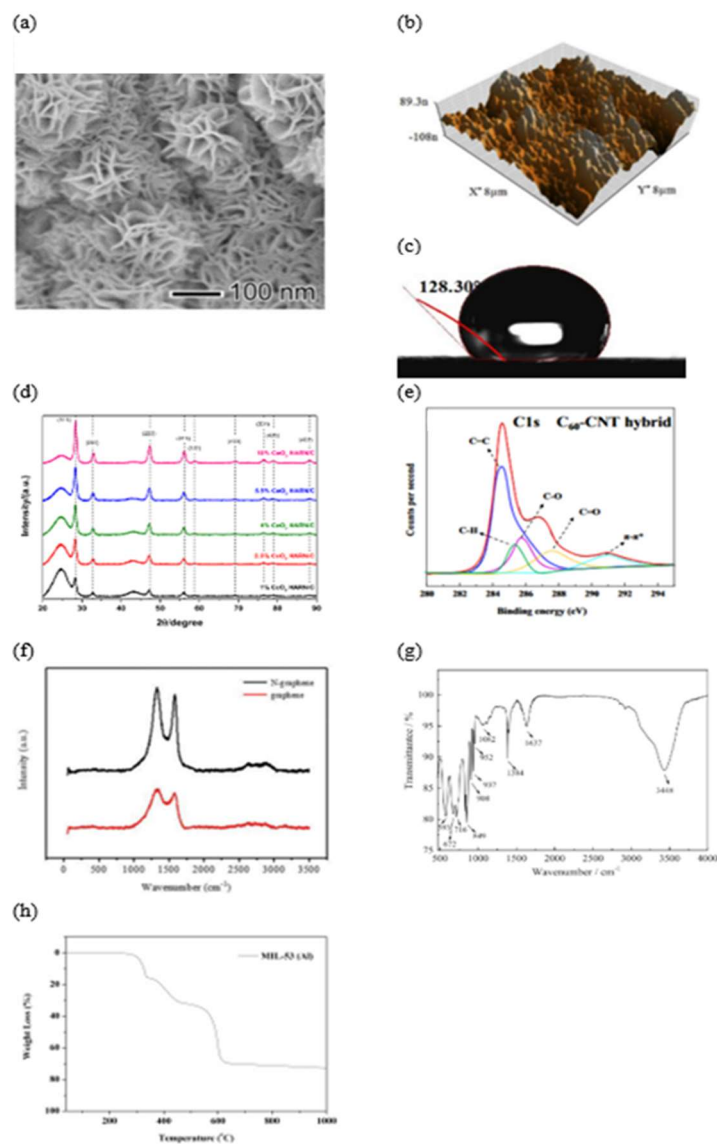


432 of cathode could be observed by SEM (Fig. 4a) [97]. AFM images of plasma treated graphite  
433 cathode could depict more roughness because of the higher number of peaks (bright part) and  
434 valley (dark part) allocated on all the surface of the material (Fig. 4b) [65]. Similarly, the more  
435 uniform nano-TiO<sub>2</sub> anode film prepared by CVD method was observed by Chang et al. [98];  
436 SEM and AFM observation showed that it exhibited smaller particle size ranged from 50 to 100  
437 nm with an average height of 250 nm (Fig. 5a). Besides, the Cr<sub>2</sub>O<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub> anode was showed  
438 with regular particles (15 nm) and uniform distribution of elements based on the TEM  
439 characterization and EDX elemental mapping (Fig. 5b) [99].

440 The hydrophilicity could be given by contact angle measurement as it has shown to play a role  
441 on ORR activity of cathodes. Graphene foam displayed high hydrophobicity, with a contact  
442 angle of 128.30° (Fig. 4c) [51], which was in concordance with the high number of apolar  
443 aromatic rings in such structure.

444 Crystal structure of electrodes could be obtained from XRD spectrum. For instance, CeO<sub>2</sub> high  
445 aspect ratio nanostructures (HARN)/C-based electrocatalyst was investigated by XRD and it  
446 showed no difference of spectra with the substrate (Fig. 4d) [100]. It meant that the  
447 semicrystalline structure was not altered during the hydrothermal synthesis of the material.  
448 Another example is given by the crystal lattices of TNTs on anode. The average size of anatase  
449 TiO<sub>2</sub> nanoparticles were found to be around 20 nm according to the Scherrer equation  
450 calculation from XRD spectra [98]. In addition, rutile and brookite TiO<sub>2</sub> were also observed  
451 from XRD spectrum (Fig. 5c) [101]. The surface electronic state and the composition of the  
452 electrodes could be obtained from XPS spectrum. C<sub>60</sub>-CNT cathode material in deconvoluted  
453 XPS plot (Fig. 4e) suggested the higher number of C=O and C-OH bonds on the hybrid structure  
454 compared to the raw materials [102]. Furthermore, the typical peak of Sn in nitrogen doped  
455 multi-walled CNTs (N-C@SnO<sub>2</sub>/MWCNTs) anode was obtained and the characteristic of Sn<sup>4+</sup>  
456 in Sn 3d<sub>3/2</sub> and Sn 3d<sub>5/2</sub> high-resolution spectra appeared (Fig. 5d) [103]. It indicated that the

457 content of nitrogen element was 3.4%, ascribed to the pyridinic N and pyrrolic N, which could  
458 enhance electrochemical reactivity and electronic conductivity. The Raman spectra could be  
459 used to evaluate defect structure and crystalline quality providing powerful information for peak  
460 shift, resulting in change of catalytic activity. The Raman spectra of graphene and N-doped  
461 graphene cathodes highlighted a higher  $I_D/I_G$  intensity ratio with the N-doped material (Fig. 4f)  
462 [104]. This resulted in an increase of defects that should increase the number of active sites. In  
463 addition, the blue-shift of anatase with peak broadening was observed in Raman spectra of the  
464 anode, ascribed to the localized defects related to  $Ti^{3+}$  or oxygen vacancies (Fig. 5e) [105].  
465 These findings were combined with XPS results, indicating that more surface hydroxyl groups  
466 were generated in new O1s peak. The FTIR spectra were used to analyze the surface functional  
467 group. The spectrum of  $Bi_2Mo_3O_{12}$  deposited on Ti cathode could highlight the Mo-O stretching  
468 vibration ( $952, 937, 908, 849\text{ cm}^{-1}$ ), the dioxo bridge vibration ( $716, 672\text{ cm}^{-1}$ ) and the Bi-O  
469 stretching vibration ( $593\text{ cm}^{-1}$ ) (Fig. 4g) [77]. Moreover, the N-H at around  $3100\text{-}3200\text{ cm}^{-1}$   
470 could be ascribed to the ammonium group vibrations in methylammonium lead bromide  
471 ( $MAPbBr_3$ ) microcrystals of anode material (Fig. 5f) [106]. The peaks at  $1546\text{ cm}^{-1}$ ,  $1471\text{ cm}^{-1}$   
472 and  $916\text{ cm}^{-1}$  were attributed to the N-H, C-H and  $-CH_3$  bonding modes, respectively. In  
473 addition, the TGA curve could be used to evaluate the thermochemical stability of electrode.  
474 TGA curve reported that the carbonization of aluminum-based metal organic framework (MOF)  
475 (MIL-53 (Al)) occurred at temperature higher than  $600^\circ\text{C}$  (Fig. 4h) [63]. Another example  
476 revealed that the content of  $SnO_2$  in N-C@ $SnO_2$ /MWCNTs composite anode was 64.35 wt%  
477 when the temperature was higher than  $500^\circ\text{C}$  (Fig. 5g) [103].

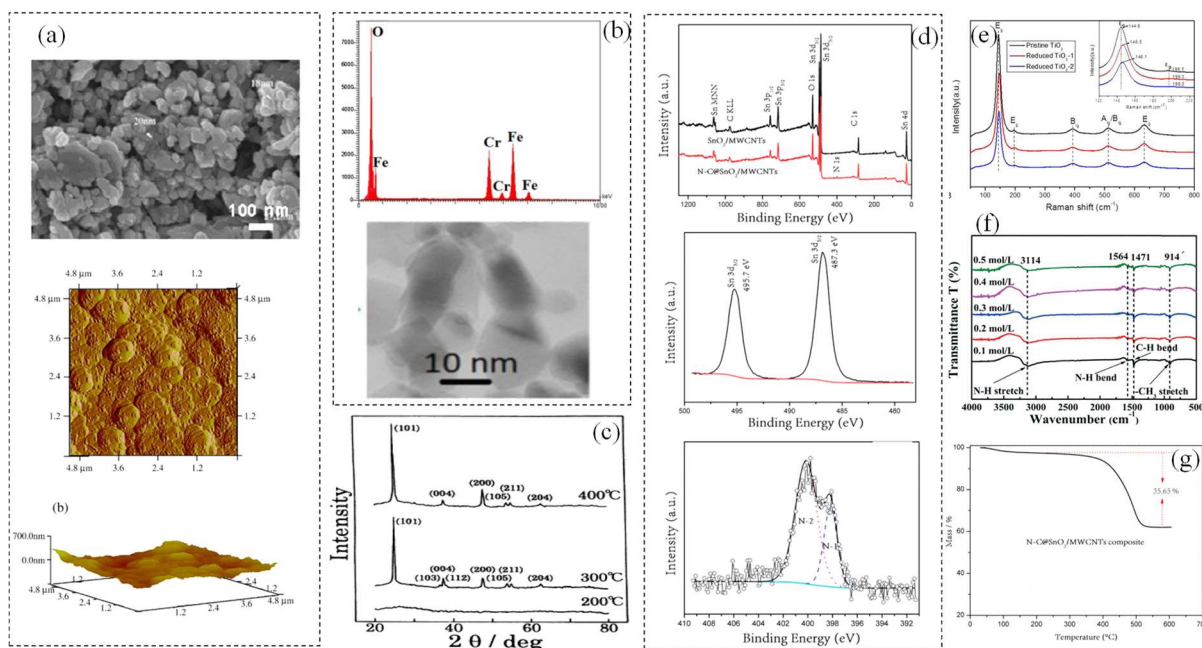


478

479 **Figure 4.** (a) SEM image of carbon supported MnO<sub>2</sub> nanoflowers (Reprinted with permission  
 480 from [97]. Copyright 2018, Elsevier), (b) 3D AFM images of plasma treated graphite  
 481 electrode (Reprinted with permission from [65]. Copyright 2017, Elsevier), (c) contact angle  
 482 measurement of graphene foam (Reprinted with permission from [51]. Copyright 2016,  
 483 Elsevier), (d) XRD patterns of CeO<sub>2</sub> HARN-based carbon cathodes with different proportions  
 484 of CeO<sub>2</sub> HARN (Reprinted with permission from [100]. Copyright 2018, Elsevier), (e) C 1s  
 485 core level of C<sub>60</sub>-CNT hybrid in deconvoluted XPS plot (Reprinted with permission from  
 486 [102]. Copyright 2019, Springer Nature), (f) Raman spectrum of graphene and N-doped  
 487 graphene cathodes (Reprinted with permission from [104]. Copyright 2019, Royal Society of

488 Chemistry), (g) FTIR spectrum of  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$  deposited on Ti cathode (Reprinted with  
 489 permission from [77]. Copyright 2019, Elsevier) and (h) TGA curve of aluminum-based metal  
 490 organic framework (MOF) (MIL-53 (Al)) (Reprinted with permission from [63]. Copyright  
 491 2018, Elsevier).

492



493

494 **Figure 5.** (a) FESEM and AFM images of nano- $\text{TiO}_2$  electrode films CVD coating.  
 495 Reproduced with permission from Ref. [98]. Copyright (2009) Elsevier; (b) EDX analysis and  
 496 SEM image of  $\text{Cr}_2\text{O}_3/\text{Fe}_2\text{O}_3$ . Reproduced with permission from Ref. [99]. Copyright (2019)  
 497 Elsevier; (c) XRD pattern of the nano- $\text{TiO}_2$  electrode. Reproduced with permission from Ref.  
 498 [101]. Copyright (1998) Elsevier; (d) XPS spectra for the  $\text{SnO}_2/\text{MWCNTs}$  composite and the  
 499  $\text{N-C@SnO}_2/\text{MWCNTs}$  composite, high-resolution spectra of  $\text{Sn}3d$  and  $\text{N}1s$  for the  $\text{N-C@SnO}_2/\text{MWCNTs}$   
 500 composite. Reproduced with permission from Ref [103]. Copyright  
 501 (2014) Royal Society of Chemistry; (e) Raman spectra of pristine and reduced  $\text{TiO}_2$  nanotube  
 502 arrays (NTA) after post-oxidation. Reproduced with permission from Ref [105]. Copyright  
 503 (2017) Elsevier; (f) FTIR of the methylammonium lead bromide with different sizes.

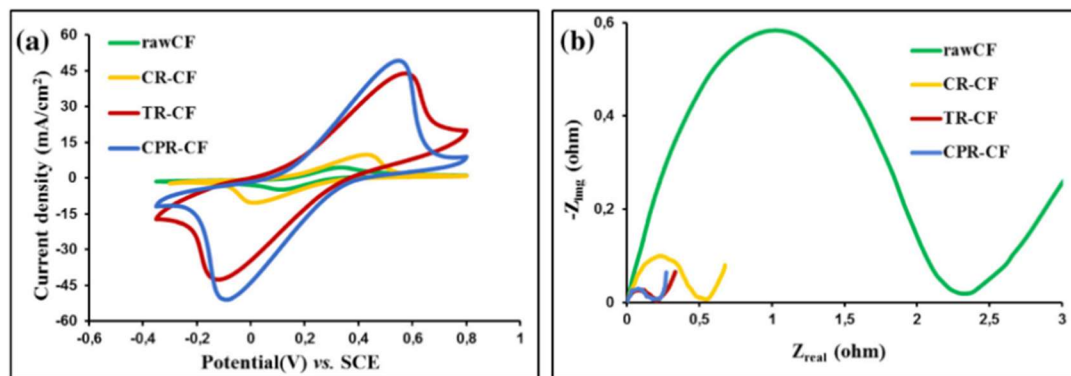
504 Reproduced with permission from Ref [106]. Copyright (2019) Royal Society of Chemistry;  
505 (g) TGA curve recorded for the N-C@SnO<sub>2</sub>/MWCNTs composite under air flow. Reproduced  
506 with permission from Ref [103]. Copyright (2014) Royal Society of Chemistry.

507

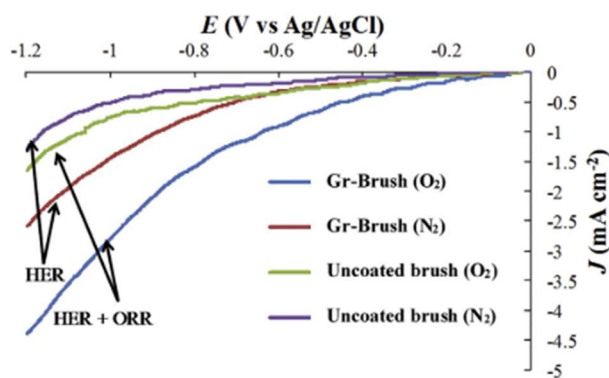
508 In general, CV, LSV and EIS curve were used to test electrical conductivity and electrochemical  
509 activity. CV of graphene modified and unmodified carbon felt (CF) cathodes (Fig. 6a) permit  
510 to show that the electroactive surface area was ten times higher than the reduced graphene oxide  
511 (RGO)/CF, determined by the Randles-Sevcik equation [73]. Moreover, EIS depicted through  
512 the Nyquist plot that the charge transfer resistance (R<sub>ct</sub>) value was 0.21 Ω against 2.38 Ω for  
513 RGO/CF and CF, respectively (Fig. 6b) [73]. The graphene-based material could enhance the  
514 cathode conductivity. LSV could further address the ORR activity by emphasizing the 3.1-fold  
515 enhancement of ORR using the graphene coated brush as compared to the raw carbon fiber  
516 brush cathode (Fig. 6c) [67]. Further examples with anode materials illustrated that the blue  
517 TiO<sub>2</sub> nanotube arrays (Blue-TNAs) exhibited much lower R<sub>ct</sub> (32 Ω) and dynamic resistance  
518 (R<sub>d</sub>) (682 Ω) compared with the TNA (333 Ω and 2848 Ω, respectively) (Fig. 7b) [55]. In  
519 addition, the higher O<sub>2</sub> overpotential (2.52 V/SCE) was obtained from CV curve (Fig. 7a).  
520 Furthermore, the LSV revealed that the current response increased with the increase of  
521 Co(NO<sub>3</sub>)<sub>2</sub> concentration until 5 mM, while the OEP decreased from 2.12 to 1.78 V/SCE,  
522 indicating that the anodic oxidation capacity would also decrease after Co doping (Fig. 7f)  
523 [107]. UV-vis reflectance spectra could be used to study the absorbance and bandgap. Blue-  
524 TNA had a stronger infrared adsorption than TNA, while the Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> NTs exhibited lower  
525 absorbance intensity in UV region, and higher absorbance intensity in visible light region than  
526 TNTs (Fig. 7d) [108]. Mott–Schottky was used to investigate the semiconductor lies in the  
527 Fermi. The Blue-TNA was still the n-type semiconductor characteristics from Mott–Schottky

528 plots. At the same time, the donor densities were calculated from the Mott-Schottky equation,  
 529 which increased to improve the charge conductivity (Fig. 7c) [55].

530 The service lifetime is also important for anode stability. The accelerated lifetime test indicated  
 531 that the incorporation of ruthenium for ruthenium doped  $\text{SnO}_2\text{-RuO}_2$  and  $\text{Ce-Ru-SnO}_2$  (318 h  
 532 and 340 h, respectively) could prolong the lifetime compared with  $\text{SnO}_2\text{-Sb}_2\text{O}_5$  anode (1.42 h)  
 533 (Fig. 7e) [80].



(c)



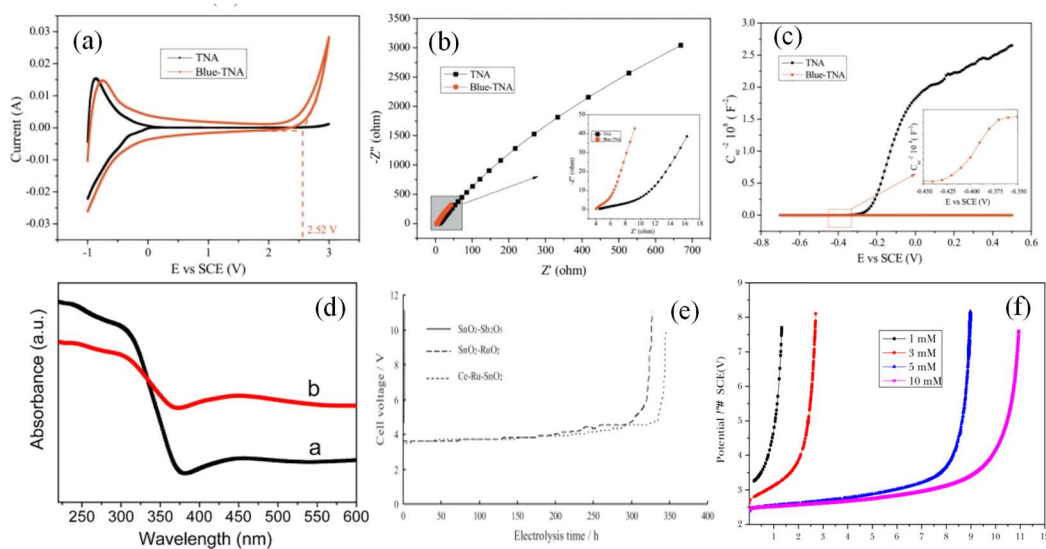
534

535 **Figure 6.** (a) CVs and (b) EIS of graphene modified and unmodified carbon felt (CF)  
 536 cathodes (Reprinted with permission from [73]. Copyright 2015, Elsevier), (c) ORR activity  
 537 of graphene-coated carbon fiber brush (Gr-Brush) compared with uncoated brush given by  
 538 LSV curves in  $\text{N}_2$ - and  $\text{O}_2$ -saturated solutions (Reprinted with permission from [67].

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540



541

542 **Figure 7.** (a) CV, (b) EIS and (c) Mott-Schottky plots of TNAs and blue-TNAs. Reproduced  
 543 with permission from Ref [55]. Copyright (2019) Elsevier; (d) UV-vis diffuse reflectance  
 544 spectra of TNTs and Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanotubes prepared by electrochemical deposition method.  
 545 Reproduced with permission from Ref [108]. Copyright (2012) Elsevier; (e) Accelerated life  
 546 tests of modified SnO<sub>2</sub> anodes. Reproduced with permission from Ref [80]. Copyright (2012)  
 547 Elsevier; (f) The effect of Co on LSV. Reproduced with permission from Ref [107].

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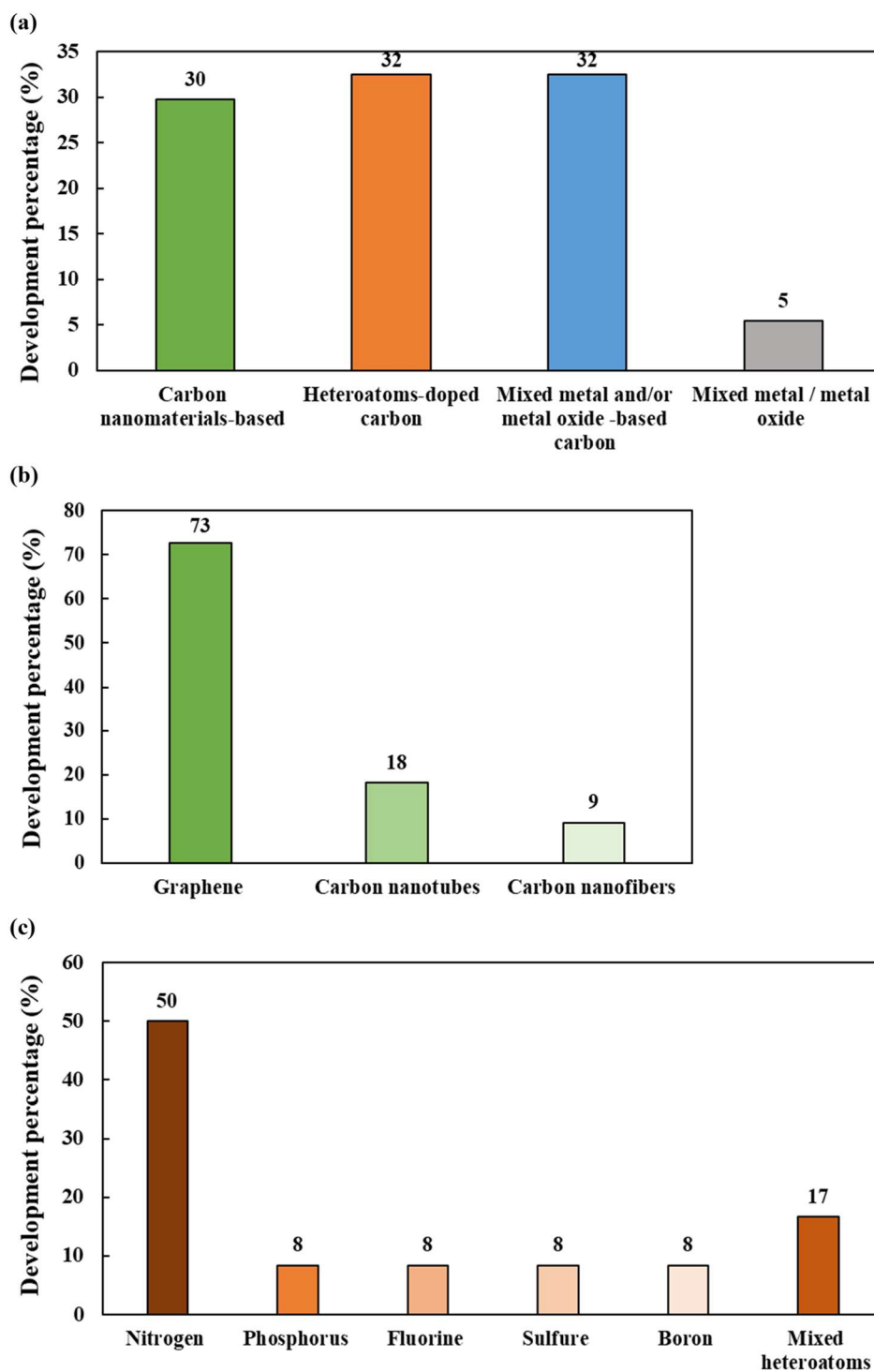
549

## 550 4. Nanostructured-based electrode properties

### 551 4.1. Nanostructured-based cathodes

552 The cathode property is an important parameter for H<sub>2</sub>O<sub>2</sub> electrogeneration efficiency. A wide  
 553 range of nanostructured cathodes have been developed in literature and they have been divided  
 554 into four category as follow: (i) carbon nanomaterials-based cathodes including carbon  
 555 nanotubes and graphene [102,109]; carbon and graphite felt modified with graphene  
 556 [66,67,110], (ii) heteroatoms-doped carbon cathodes, such as fluorine-doped [63,111],  
 557 nitrogen-doped [112] and phosphore-doped [61], (iii) metal or metal oxides deposited on carbon

558 support, like cerium oxide, vanadium, manganese oxide, tungsten oxide, zirconium and  
 559 tantalum [59,61,97,113–116], (4) metal oxide cathode. All the nanostructured-based cathodes  
 560 developed for H<sub>2</sub>O<sub>2</sub> electrogeneration have been listed in Table 1. The percentage of  
 561 development of each cathode category is illustrated in Fig. 8a, according to articles found in  
 562 literature.



563



564 **Figure 8.** (a) Percentage of development of each cathode category, (b) Carbon nanomaterials-  
565 based cathodes repartition, (c) Heteroatoms-doped carbon cathodes repartition.

566 It can be seen that heteroatoms-doped carbon materials as well as mixed metal /metal oxide-  
567 based carbon materials have been both developed at the same level (32.5%), while 30% of the  
568 nanostructured materials found in literature are made of carbon nanomaterials. Mixed metal /  
569 metal oxide materials have been studied in a lesser extent until now (5%). Generally, carbon-  
570 based materials used either as raw material or as nanomaterials catalysts have been developed  
571 extensively, since it represents 95% of the studies. This is to be linked with the reliable  
572 properties of carbon material to promote the two-electron ORR as discussed in section 2.1  
573 [\[66,117–124\]](#).

574

#### 575 *4.1.1. Carbon nanomaterials-based cathodes*

576 Among the carbon nanomaterials-based cathode developed, there is a variety of materials (Fig.  
577 8b) such as graphene, CNTs and carbon nanofibers coated on different carbon substrate like  
578 reticulated vitreous carbon (RVC), graphite felt (GF) and CF [\[125\]](#). The cathodes having a  
579 three-dimensional (3D) porous structure are known to favor H<sub>2</sub>O<sub>2</sub> electrogeneration thanks to  
580 their high active area, high chemical stability and low H<sub>2</sub> evolution overvoltage. In parallel, gas  
581 diffusion electrodes (GDEs) was proposed and could also reach high H<sub>2</sub>O<sub>2</sub> yields [\[123\]](#). The  
582 combination between 3D porous CF with GDEs could even improve the H<sub>2</sub>O<sub>2</sub> electrogeneration  
583 yield due to the enhanced oxygen mass transfer [\[51,126\]](#). Another way is to modify CF cathode  
584 for H<sub>2</sub>O<sub>2</sub> electrogeneration improvement [\[127\]](#).

585 Still the GDEs and/or 3D porous carbons modifications with nanostructured carbon based-  
586 materials have been suggested in literature to further raise the H<sub>2</sub>O<sub>2</sub> production. Thanks to their  
587 electrochemical and physical properties, the growth of graphene and CNTs is of great interest  
588 for electro-Fenton process as working electrodes. The honeycomb structure of graphene

589 containing  $sp^2$  hybridized carbon enhance the specific surface area [125]. The carbon containing  
590 oxygen groups serve as an active site for oxygen adsorption and conversion to  $H_2O_2$  through  
591 ORR [128]. Recently, Hasanzadeh et al. (2019) [102] performed a highly efficient nanocarbon  
592 cathode for the hydrogen peroxide electrogeneration with fullerene  $C_{60}$  covalently bonded to  
593 the CNT surface. This hybrid structure promotes the electron transfer and increase the surface  
594 area of the cathode offering to this material a high performance toward the oxygen reduction  
595 through the two-electron route, reaching a rate as high as  $28 \text{ mM (h cm}^2\text{)}^{-1}$  [102]. Other works  
596 focused on the modification of non-nanostructured cathodes with graphene or nanocarbon  
597 materials such as graphene ink-coated carbon cloth [70], graphite felt modified with  
598 electrochemically exfoliated graphene [66], GDEs with CNTs [129] and CF coated with  
599 reduced graphene [72]. It was highlighted that the nanostructured modification of the raw  
600 material improves the activity of the cathode and consequently its selectivity towards the  
601 hydrogen peroxide production [109].

602

#### 603 **4.1.2. Heteroatom-based cathodes**

604 Doping carbon materials is a way to control the ORR activity by incorporating heteroatoms in  
605 the carbon lattice atoms [130]. The most widely used dopants were nitrogen, phosphorus,  
606 fluorine, sulfur and boron (Fig. 8c) due to their different size and electronegativity with carbon  
607 atoms, the structure distortion and charge density were modulated [131].

608 Recently N-doped materials received more attention for  $H_2O_2$  electrosynthesis. The works  
609 about N-doped graphene and modified graphite felt electrode with nitrogen-doped porous  
610 carbon illustrated the ability of these cathodes to reach a high yield of  $H_2O_2$  production and  
611 selectivity, with high generation rate of  $1.6 \text{ mmol (h cm}^2\text{)}^{-1}$  and a current efficiency of 68%  
612 [112]. Yu et al. (2019) reported the performances of the modified graphite felt electrode with  
613 N-doped porous carbon, the  $H_2O_2$  generation rate was  $0.13 \text{ mmol (h cm}^2\text{)}^{-1}$  [132]. Moreover,

614 some recent works demonstrated that N-doped carbon materials could improve activity for H<sub>2</sub>O<sub>2</sub>  
615 synthesis, while the N-doped graphene could act as catalyst to convert the generated H<sub>2</sub>O<sub>2</sub> into free  
616 radicals [112,133]. Further, it was reported that graphite N could promote H<sub>2</sub>O<sub>2</sub> generation, while  
617 pyridinic N could catalyze H<sub>2</sub>O<sub>2</sub> conversion into <sup>•</sup>OH. Therefore, a novel in-situ metal-free EAOPs was  
618 developed for efficient degradation of organic pollutants at wide pH ranges in the absence of metal  
619 catalysts.

620 Fluorine is known as the highest electronegative atoms in Mendeleev table and its combination  
621 with carbon structure generate a redistribution in partials charges and more positives carbon  
622 atoms. This allows the adsorption of O<sub>2</sub> and the <sup>\*</sup>OOH desorption [134]. Fluorine-doped  
623 hierarchically porous carbon exhibited a high activity towards H<sub>2</sub>O<sub>2</sub> electro-generation with the  
624 enhancement of selectivity and yield with H<sub>2</sub>O<sub>2</sub> production rate of 3.11 mmol (h cm<sup>2</sup>)<sup>-1</sup> [63]. In  
625 addition, P-doped carbon single walled nanotube was also investigated for ORR activity, mainly  
626 for H<sub>2</sub>O<sub>2</sub> electrosynthesis. P as a donor atom presented a high affinity towards oxygen,  
627 modifying the charge transfer properties and improving the electrocatalysis of the doped  
628 material [135]. Moreover, according to Xia et al. [61] P-CNTs GDE cathode could reach 88%  
629 of current efficiency of H<sub>2</sub>O<sub>2</sub> formation against 65% with CNTs cathode.

630

#### 631 *4.1.3. Metal- and metal-oxide based cathodes*

632 The mixed metals or metal oxides have been generally used as an heterogeneous catalyst in a  
633 wide range of electrochemical and bio-electrochemical applications such as microbial fuel cells  
634 but rarely for H<sub>2</sub>O<sub>2</sub> electrosynthesis from oxygen reduction [136]. As reported in several works  
635 about the electrodes materials used for the H<sub>2</sub>O<sub>2</sub> electrosynthesis, the mixed metal or the metal  
636 oxides such as CaSnO<sub>3</sub>, BiVO<sub>4</sub>, TiO<sub>2</sub> and WO<sub>3</sub> were widely used for the anodic production of  
637 the H<sub>2</sub>O<sub>2</sub> or as a photocatalysts [137], instead of doing ORR at cathode.

638 Yuan et al. (2013) [138] performed the two-electron ORR at the MMO made of IrO<sub>2</sub>/Ta<sub>2</sub>O<sub>5</sub>  
639 coated on the titanium mesh (Ti/MMO). The maximum production of H<sub>2</sub>O<sub>2</sub> achieved with this

640 material was 0.06 mM, which is still very low compared to the metals oxide supported on  
641 carbon material [138]. The bismuth molybdate oxide coated on the titanium mesh  
642 ( $\text{Bi}_2\text{Mo}_3\text{O}_{12}/\text{Ti}$ ) cathode was also used by He et al. (2019) [77] for the production of hydrogen  
643 peroxide in electro-Fenton process. They report the effect of the catalyst structure on the  
644 electrochemical efficiency of the cathode. The catalyst performance was related to the presence  
645 of the oxygen vacancies in  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$  lattice, which allows the chemisorption of the oxygen  
646 and its reduction to  $\text{H}_2\text{O}_2$  [77].

647

#### 648 *4.1.4. Mixed metal / metal oxide and carbon-based cathodes*

649 Some metals and metal oxides supported on GDEs have depicted considerable performance for  
650 oxygen reduction catalysis. Due to their abundance, low cost and high performance towards  
651 ORR, scientists have given great interest for their uses as cathode materials for  $\text{H}_2\text{O}_2$   
652 electrogeneration [139].

653 GDEs made by  $\text{Ta}_2\text{O}_5$  nanoparticles supported on carbon black ( $\text{Ta}_2\text{O}_5/\text{C}$ ) demonstrated high  
654 catalytic efficiency making it as a promising candidate cathode for wastewater treatment.  
655 Tantalum (V), known as acid oxide, increases the surface wettability inducing more active site  
656 for ORR [115]. In another work,  $\text{MnO}_2/\text{Vulcan XC-72}$  carbon nanoflowers were used to  
657 optimize the oxygen vacancy sites.  $\text{MnO}_2/\text{C}$  3% displayed the optimal catalytic activity because  
658 of the uniform structure of  $\text{MnO}_2$  nanoflowers improving the distribution on carbon support,  
659 the high oxygen concentration vacancies and the high active surface area reached with metal  
660 oxide incorporation [97]. Paz et al. [113] prepared a new cathode material with tungsten oxide  
661 nanoparticles on carbon and the mass ratio of 1:100 (W:C) demonstrated the high  $\text{H}_2\text{O}_2$  yield  
662 and selectivity compared to the support without the metal oxide. Many other works about  $\text{H}_2\text{O}_2$   
663 electrogeneration by means of metal oxide nanostructured cathodes have been performed such  
664 as Vanadium/C [59],  $\text{CeO}_2$  [58] and  $\text{ZrO}_2$ -nanostructured GDE [114].

665 Furthermore, Félix-Navarro et al. (2013) [75] reported the electrocatalytic activity of the Pt-Pd  
666 bimetallic nanoparticles on CNTs towards the H<sub>2</sub>O<sub>2</sub> electrosynthesis. The mixed metal  
667 nanoparticles anchored on the multi-walled CNTs (MWCNTs) exhibited a high efficiency to  
668 produce H<sub>2</sub>O<sub>2</sub> compared to the MWCNTs alone. The enhancement of the H<sub>2</sub>O<sub>2</sub> yield is ascribed  
669 to the increase of the active surface area of the catalyst by the small particle sizes of the Pt-Pd  
670 distributed on the MWCNTs surface [75].

671 A heterogeneous cathode on which a confined interior iron cavity of CNTs (Fe<sup>0</sup>-in-CNTs) with  
672 extremely low iron leaching was prepared, observing a much higher H<sub>2</sub>O<sub>2</sub> yield and phenol  
673 removal rate (9.7 times faster) when compared with that of iron-confined external walls of  
674 CNTs (Fe<sup>0</sup>-out-CNTs) [140]. It was found that iron valence on CNTs played an important role  
675 on the heterogeneous Fenton activity, supporting that Fe<sup>0</sup> was beneficial for H<sub>2</sub>O<sub>2</sub> selectivity of  
676 two-electron process (2.4 times higher) and phenol removal rate (21.44 times faster) than iron  
677 oxide. Consequently, the CNT cavity provided an isolate space for Fe<sup>0</sup>, which is decisive for  
678 phenol removal based surface of Fe<sup>0</sup>-in-CNTs reaction.

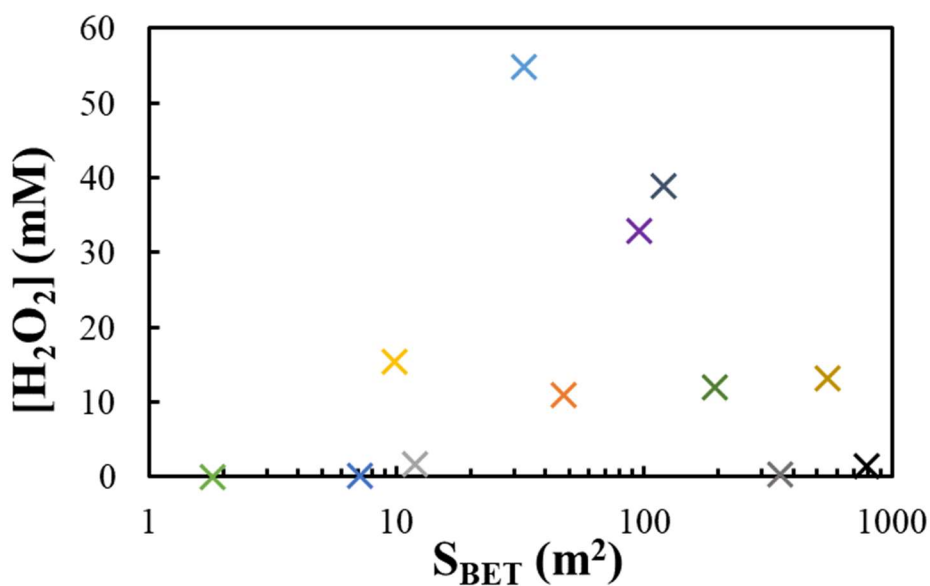
#### 679 **4.1.5. General requirement for cathode characteristics and operating conditions**

680 The nanostructure of the cathode plays a major role in the in-situ production of H<sub>2</sub>O<sub>2</sub>. The  
681 structural morphology and the introduction of new functional groups with various  
682 physicochemical properties affect drastically the cathode performance. It is reported in several  
683 works that the active surface area, the conductivity, the porosity, the surface composition and  
684 the wettability are the main parameter to consider in the ORR activity [109,141,142]. Some  
685 operating parameters play also an important role on two-electron-ORR activity such as  
686 electrode potential (or current density), solution pH and oxygen flow rate.

##### 687 *4.1.5.1. Effect of electrode surface area*

688 The surface area, defined by specific surface area using BET technique or electroactive surface  
689 area using EIS method, is a decisive parameter in the ORR activity enhancement [143]. The

690 influence of BET specific surface area ( $S_{\text{BET}}$ ) on the amount of  $\text{H}_2\text{O}_2$  electrogenerated at  
691 nanostructured-based cathode materials found in literature (Table 1) has been plotted in Fig. 9.  
692 It can be noted that the  $S_{\text{BET}}$  as high as around  $1000 \text{ m}^2$  can be obtained by nanostructuring the  
693 materials. Interestingly, the higher surface area does not systematically lead to higher  $\text{H}_2\text{O}_2$   
694 electrogeneration. It is known that increasing the surface area make increase the number of  
695 active sites for adsorption and subsequent desorption of intermediates species. However, this  
696 will increase the  $\text{H}_2\text{O}_2$  production until a certain optimal value of surface area. Fig. 9 defines  
697 this range of surface area between around 30 to  $100 \text{ m}^2$ . The high surface areas do not provide  
698 higher  $\text{H}_2\text{O}_2$  formation, since the rate of  $\text{O}_2$  transport from bulk to the electrode surface become  
699 then the rate-limiting step.



700  
701 **Figure 9.** Influence of BET specific surface area ( $S_{\text{BET}}$ ) on the amount of  $\text{H}_2\text{O}_2$   
702 electrogenerated at nanostructured-based cathode materials.

703  
704 *4.1.5.2. Effect of electrode porosity*

705 The porous structure effect of the nanostructured cathodes was investigated in many articles. It  
706 has been demonstrated that the presence of large number of pores in the cathode material  
707 increases the mass transfer and facilitates the diffusion of the reactants and products through

708 the cathode [109]. Also, this porous configuration limits the diffusion resistance and creates  
709 more active sites for oxygen reduction, enhancing in this way the ORR activity and the H<sub>2</sub>O<sub>2</sub>  
710 yield [63]. Park et al. [144] reported the correlation between the well-ordered mesoporous  
711 structure of N-doped-carbon (3-4 nm) catalyst and its high selectivity toward the H<sub>2</sub>O<sub>2</sub>  
712 electrosynthesis. In this work the effect of pores toward the H<sub>2</sub>O<sub>2</sub> selectivity was investigated  
713 through a comparison study between the mesoporous N-doped carbon (MNC) and activated N-  
714 doped carbon (ANC), using Koutecky-Levic plots and a rotating ring-disc electrode  
715 voltammetry [144]. High selectivity values are reached at MNC cathode compared to the ANC  
716 cathode; the mesopores of the MNC allow an easier release of the produced H<sub>2</sub>O<sub>2</sub>. In contrast,  
717 the micropores of the ANC increase the residence time and as a result, the formed H<sub>2</sub>O<sub>2</sub> evolves  
718 to H<sub>2</sub>O, thus affecting its selectivity [144].

719

#### 720 *4.1.5.3. Effect of electrode conductivity*

721 The electrical conductivity of cathode material is another important factor that increase the rate  
722 of electron transfer to let occur electrochemical reaction, though this is not usually the rate-  
723 limiting step. This conductivity has been often characterized by the R<sub>ct</sub> given by EIS  
724 measurement [67,70,73]. The conductivity is affected by the thickness of material and by the  
725 defects on the nanostructure. It has been shown that the increase of graphene thickness (from  
726 graphene single layer to graphene foam) could decrease the resistivity of the material  
727 [51,145,146]. Moreover, the presence of oxygen functional groups on carbon nanomaterial can  
728 localize the  $\pi$ -electrons, which decrease their mobility and therefore the material conductivity  
729 [147].

730

#### 731 *4.1.5.4. Effect of electrode wettability*

732 The hydrophilicity character of the cathode materials is considered in many studies about the  
733 electrogeneration of the H<sub>2</sub>O<sub>2</sub>. It has been shown that the hydrophobicity can also have a

734 positive influence on the ORR activity by enhancing the O<sub>2</sub> gas absorption on the porous  
735 carbon-based material [148]. Contrastingly, it was observed that the nanostructures with highest  
736 hydrophilic character exhibit a high H<sub>2</sub>O<sub>2</sub> production because it improved the dissolved oxygen  
737 diffusion in water and its subsequent adsorption on the cathode material [73]. The metal oxides  
738 nanostructures such as tantalum, vanadium and cerium oxides supported on carbon materials  
739 have a Lewis acid sites providing thus the wettability to the surface and allowing the interaction  
740 with adsorbed oxygen through the two-electron pathway [59,115].

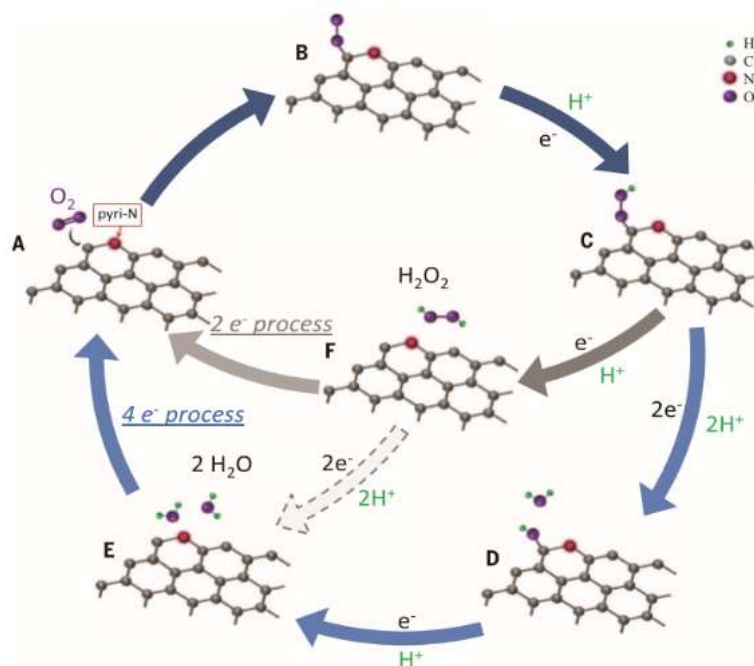
741 Paz et al. [149] reported improved performance of H<sub>2</sub>O<sub>2</sub> production at the tungsten oxide  
742 nanoparticles modified carbon cathode. Contact angle measurements performed emphasized  
743 the importance of hydrophilic character of the modified carbon compared to the unmodified  
744 one. Authors attributed this finding to the presence of tungsten nanoparticles as acidic entities  
745 on the surface. The presence of tungsten atoms as a Lewis acid promotes interactions with the  
746 oxygen entities through the Pauling model (two-electron way), resulting in the production of  
747 H<sub>2</sub>O<sub>2</sub> [149]. The selectivity toward H<sub>2</sub>O<sub>2</sub> formation was performed at modified carbon and  
748 unmodified carbon electrodes. The modified carbon materials (Printex 6L and Vulcan XC72)  
749 presented a higher H<sub>2</sub>O<sub>2</sub> selectivity than the unmodified one confirming the effect of the  
750 tungsten oxide on the wettability and therefore on the oxygen reduction through the two-  
751 electron mechanism [113].

#### 752 *4.1.5.5. Effect of surface composition*

753 The nanostructured carbon cathodes are widely used for the H<sub>2</sub>O<sub>2</sub> electrogeneration.  
754 Interestingly, the incorporation of some heteroatoms such as nitrogen, fluorine, phosphorus and  
755 sulfur to these material further increases their performance towards the oxygen reduction [150].  
756 The common feature of these dopant atoms is the difference of electronegativity and size with  
757 the carbon atoms.



758 N-doped carbon materials emerge as the main studied cathodes in literature for  $\text{H}_2\text{O}_2$   
759 electrosynthesis, and became models of heterostructured materials for mechanisms  
760 understanding. As known, the nitrogen is more electronegative and voluminous than carbon.  
761 Consequently, the C-N bond become polarized and creates a partial positive charge on the  
762 carbon atoms allowing its activation [132]. The oxygen is firstly adsorbed on the activated  
763 carbon and then protonated as illustrated in Fig. 10 [151].



764

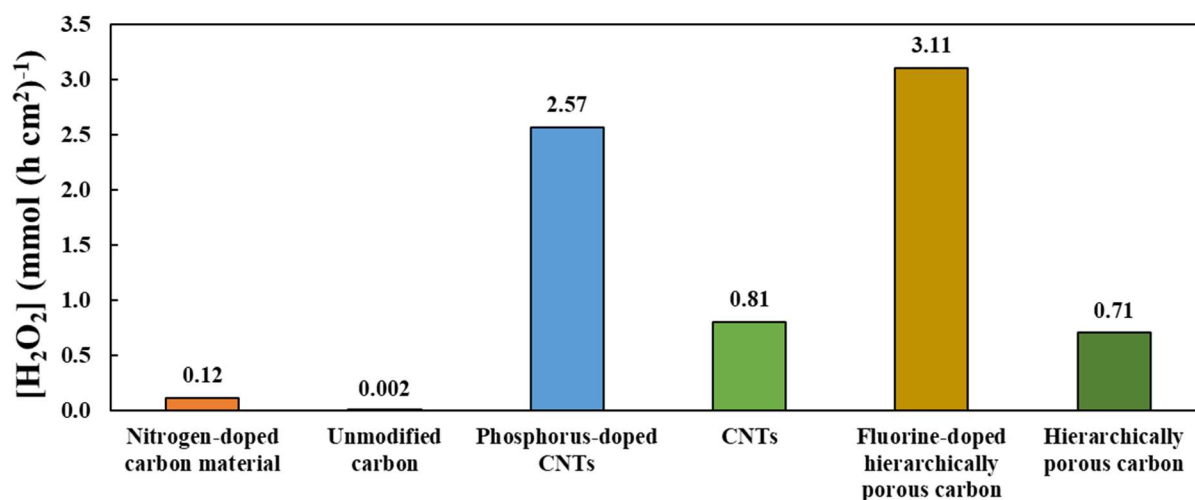
765 **Figure 10.** Mechanism of the ORR on nitrogen-doped carbon materials (Reproduced with  
766 permission from Ref [151]. Copyright (2018) Wiley).

767

768 In addition to the nitrogen dopant atom, other heteroatoms with similar properties have been  
769 used to dope carbon materials. Phosphorus incorporated on CNTs exhibits a high  $\text{H}_2\text{O}_2$  yield  
770 [61]. This result is assimilated to the structural distortion of the surface caused by the C-P  
771 bonding which promotes the oxygen adsorption. Moreover, the electron donor character of the  
772 phosphorus atom boosts the electron density of the CNTs surface and enhances the  
773 electroactivity of the cathode towards the ORR [150]. Furthermore, at molecular level, it was

774 demonstrated that the fluorine doped on carbon material played a determining role in H<sub>2</sub>O<sub>2</sub>  
775 selectivity. The incorporation of heteroatoms in carbon framework promotes the oxygen  
776 adsorption on the surface and the \*OOH desorption leading to the two-electron route mechanism  
777 as shown in the Fig. 11 [63].

778



779

780 **Figure 11.** H<sub>2</sub>O<sub>2</sub> generation rate at heteroatoms doped-carbon and the corresponding  
781 unmodified cathode (Adapted with permission from Ref [61,63,132]. Copyrights (2018, 2019)  
782 Elsevier).

783

#### 784 4.1.5.6. Effect of cathode potential / current density and H<sub>2</sub> evolution overvoltage

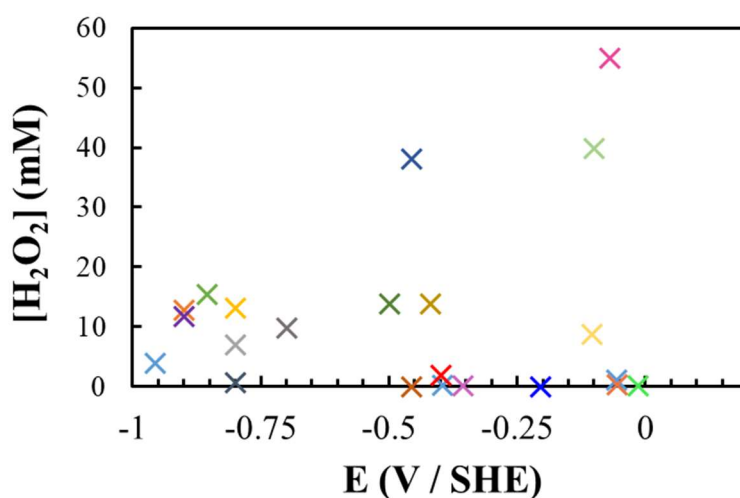
785 The electrogeneration of H<sub>2</sub>O<sub>2</sub> is often performed at a fixed potential value (potentiostatic) or  
786 at constant current (galvanostatic) mode in an undivided cell [125]. In this configuration, the  
787 concentration profile of H<sub>2</sub>O<sub>2</sub> increases during the first minutes of the electrolysis and then  
788 achieves a plateau with constant H<sub>2</sub>O<sub>2</sub> concentration [114].

789 Mousset et al. [51] investigated the effect of current density on H<sub>2</sub>O<sub>2</sub> production on the range  
790 of 0.0016-1.6 mA cm<sup>-2</sup> with three graphene cathodes. The increase in current density does not  
791 allow the increase in H<sub>2</sub>O<sub>2</sub> concentration but there is an optimal applied current density giving  
792 the highest concentration that can be reached [51]. This behavior could be explained by the

793 occurring of parallel reactions including the electroreduction of the  $\text{H}_2\text{O}_2$  at the cathode (Eq. 8),  
 794 the decomposition in the bulk electrolyte (Eq. 9) and the oxidation at anode following Eq. 10.  
 795 The  $\text{H}_2$  evolution reaction (HER) was also evoked to be a parasite reaction under some cathode  
 796 potential (Eq. 11) [67].



801 The influence of optimal cathode potential (reported versus SHE for reliable comparison)  
 802 applied in literature (Table 1) at nanostructured-based cathode materials to electrogenerate  
 803  $\text{H}_2\text{O}_2$  has been displayed in Fig. 12. This optimal potential can vary from 0 to -1 V/SHE  
 804 according the cathode material. It is important to note that low cathode potentials could be  
 805 applied thanks to the low hydrogen evolution overvoltage of such nanostructured-based  
 806 material permitting the two-electron ORR to occur. The highest amount of  $\text{H}_2\text{O}_2$  could be  
 807 obtained at cathode potentials between -0.5 V/SHE and -0.1 V/SHE. Too high cathode  
 808 potentials then favor the four-electron ORR.



809  
 810 **Figure 12.** Influence of optimal cathode potential on the amount of  $\text{H}_2\text{O}_2$  electrogenerated at  
 811 nanostructured-based cathode materials.

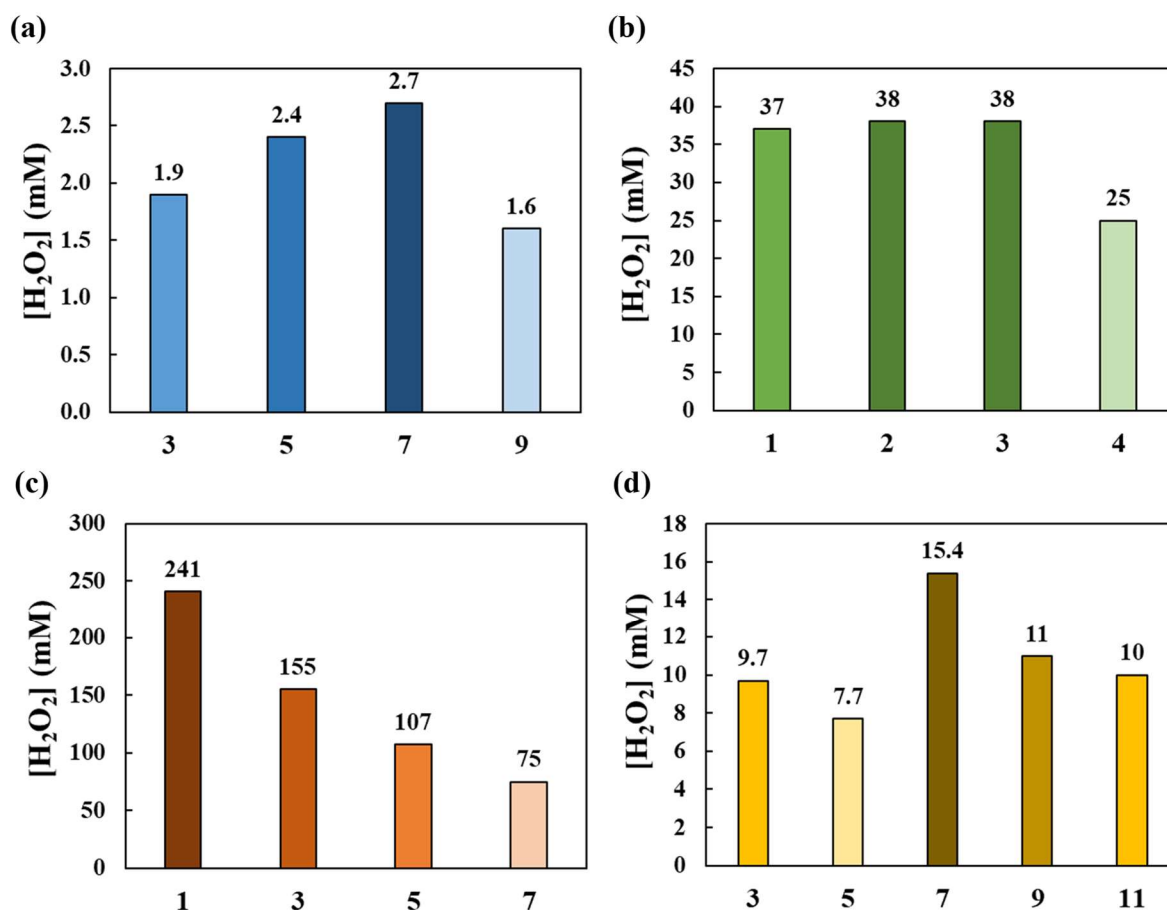
812

#### 813 *4.1.5.7. Effect of solution pH*

814 The proton content of the electrolyte has a significant weight on the H<sub>2</sub>O<sub>2</sub> production. In fact,  
815 the acidic or the alkaline medium can influence the parallel reactions and consequently the H<sub>2</sub>O<sub>2</sub>  
816 yield. On the one hand, the electrogeneration of H<sub>2</sub>O<sub>2</sub> at the cathode from the dissolved oxygen  
817 needs the presence of protons. On the other hand, the higher amount of protons in the solution  
818 can promote the hydrogen peroxide decomposition following Eq. 8 or the HER (Eq. 11) [132].  
819 Moreover, at low pH value the ORR occurs via the four-electron mechanism to produce water  
820 at the cathode, leading to the decrease in H<sub>2</sub>O<sub>2</sub> concentration [61]. It is further important to note  
821 that the acid dissociation constant (pKa) of H<sub>2</sub>O<sub>2</sub>/HO<sub>2</sub><sup>-</sup> couple is 11.7, and HO<sub>2</sub><sup>-</sup> is not only a  
822 weaker oxidant but also is not able to produce <sup>•</sup>OH from Fenton reaction. Consequently, the  
823 implementation of ORR in alkaline media (Eq. 12) has to be avoided [61]:



825 Many researches have studied the effect of the electrolyte pH medium on the electrogeneration  
826 of H<sub>2</sub>O<sub>2</sub>. Yu et al. [132] have performed the electrogeneration of H<sub>2</sub>O<sub>2</sub> at different pH values  
827 of 3, 5, 7 and 9 and they have observed the increase of the H<sub>2</sub>O<sub>2</sub> concentration with increase of  
828 the pH from 3 to 7 and it decrease significantly at pH equal to 9. This trend is confirmed by Xia  
829 et al. [61] with a similar study. Depending on the nanostructured cathode material an optimum  
830 pH value lead to a maximum H<sub>2</sub>O<sub>2</sub> concentration (Fig. 13). At the acidic pH, an excess of  
831 protons are released in the solution and can be reduced at the cathode to form H<sub>2</sub>, competing  
832 with the H<sub>2</sub>O<sub>2</sub> formation [66]. When the pH increase, the quantity of protons needed to form  
833 H<sub>2</sub>O<sub>2</sub> become insufficient, resulting in low H<sub>2</sub>O<sub>2</sub> yield [132].



834

835 **Figure 13.** pH effect on the H<sub>2</sub>O<sub>2</sub> electrogeneration at different nanostructured cathode

836 materials: (a) nitrogen-porous based carbon, (b) phosphorus-CNTs, (c) fluorine-doped

837 hierarchically porous carbon, (d) exfoliated graphene. (Adapted with permission from

838 [\[61,63,66,132\]](#). Copyrights (2018, 2019) Elsevier and Copyright (2017) Royal Society of

839 Chemistry).

840

#### 841 4.1.5.8. Effect of oxygen flow rate

842 Oxygen is the main reagent for H<sub>2</sub>O<sub>2</sub> electrogeneration. It has been demonstrated that the

843 oxygen flow rate controls the kinetic of the ORR and consequently the H<sub>2</sub>O<sub>2</sub> yield and the

844 current efficiency [\[125\]](#). The dissolved oxygen (DO) concentration depends on the nature of

845 oxygen supply. With air supply, the DO concentration is 8 mg L<sup>-1</sup> at 23 °C and this value depend

846 remarkably on the purity of the oxygen supplies, and solution temperature [\[152\]](#).

847 The accumulation of hydrogen peroxide at P-doped CNTs cathode was studied at different  
848 oxygen flow rates [61]. Despite the absence of oxygen supply, the H<sub>2</sub>O<sub>2</sub> was accumulated at  
849 the cathode thanks to the oxygen formed at the anode level from water oxidation. The increase  
850 of O<sub>2</sub> flow rate improves the oxygen mass transfer to the cathode and promotes the H<sub>2</sub>O<sub>2</sub>  
851 formation. However, the high flow rates create an excessive mass bubbles at the cathode surface  
852 minimizing the access to the active sites. Additionally, the superfluous conditions maximize  
853 the electrolyte resistance and consequently decrease the ORR activity [153].

854 **Table 1.** Experimental conditions and hydrogen peroxide production performances at the  
 855 different kinds of nanostructured cathode materials.

Cathode	pH	Specific surface area ( $S_{BET}$ ) ( $m^2 g^{-1}$ )	Current density (mA $cm^{-2}$ ) or cathodic potential (V/SHE)	O <sub>2</sub> flow rate (L $min^{-1}$ )	[H <sub>2</sub> O <sub>2</sub> ] ( $mmol (h cm^2)^{-1}$ )*	Current efficiency (%)	Ref.
<b>Nanostructured carbon-based material</b>							
Carbon fiber brush coated with graphene ink	3	NS	1.25 -0.8	0.2	0.07	95	[67]
Pristine graphene	3	NS	0.4 -0.39	NS	0.0117	13	[51]
Graphene/graphite	3	11.8	20 NS <sup>1</sup>	0.06	0.23	16	[109]
Graphene ink coated carbon cloth	3	NS	1.25 -0.4	0.2	0.03	23	[70]
Graphite felt modified with electrochemically exfoliated graphene	7	9.8	NS -0.856	0.7	0.23	60	[66]
Modified graphite felt	7	NS	300 mA NS	0.8	0.163	19.5	[110]
Fullerene C60-Carbon nanotubes	3	422	NS 0.044	NS	28 mM (h $cm^2$ ) <sup>-1</sup>	82.60	[102]
Covalent hybrid CF modified with electrochemically exfoliated graphene	3	NS	16.66 NS	1	0.90	23.5	[127]
CF coated with reduced graphene	3	NS	40 mA NS	NS	-	NS	[72]
Carbon nanofiber	NS	NS	200 mA NS	NS	0.05	27.6	[154]
PANI <sup>2</sup> /MWCNT <sup>3</sup> Nanocomposite on Stainless Steel	2	7.1	NS -0.356	0.3	1.37 mM h <sup>-1</sup>	40	[155]
<b>Heteroatom-doped carbon cathode</b>							
Phosphorus-doped Carbon nanotubes GDE <sup>4</sup>	7	119	NS -0.456	0.21	2.57	88.5	[61]
N-Doped graphene	7	NS	NS -0.9	0.75	1.6175	68	[112]
Fluorine-doped porous carbon	1	1001	NS -0.156	NS	3.11	NS	[63]

Modified graphite felt electrode with Nitrogen-Doped porous Carbon	7	1453	12.5 NS	NS	0.12	10	[132]
Graphite felt modified with nitrogen doped graphene	3	13.8	7 -0.106	0.3	0.13	33	[104]
Graphite felt modified with nitrogen doped exfoliated graphene	7	NS	NS NS	1	-	NS	[156]
NCNT <sup>5</sup> /NF <sup>6</sup> /CNT <sup>7</sup>	3	NS	30 NS	0.4	0.18	33	[157]
N/F-CNC <sup>8</sup>	13 0.35	NS	NS -1.36 NS 0.33	NS	92% (S) 88% (S)	89.6 88	[158]
Glassy carbon coated with HPCS-S <sup>9</sup> nanocrystals	NS	794	NS 0.3	NS	1.35 mmol	70	[159]
Nitrogen and sulfur doped carbon cathode on GC <sup>10</sup>	2.4	NS	NS NS	NS	-	NS	[160]
BDD	3	NS	40 NS	0.3	0.04	0.09	[161]
PAN <sup>11</sup> -Carbon Fiber Brush on Ti wire	3	NS	300 mA -0.95	3	0.063 mmol h <sup>-1</sup>	68	[162]

---

#### Mixed metal/metal oxide and carbon-based cathode

Ta <sub>2</sub> O <sub>5</sub> nanoparticles On carbon black	2	NS	NS -0.8	0.2 bar	0.186	83.2	[115]
ZrO <sub>2</sub> -Nanostructured GDE <sup>4</sup>	2	NS	75 NS	0.2 bar	0.39	9	[114]
Tungsten oxide Nanoparticles modified carbon	2	NS	NS -0.42	0.2 bar	8.21	96	[113]
CoS <sub>2</sub> -Based Air-diffusion cathode	3	32.5	100 -0.071	0.5	2.75	49	[163]
12% V/C GDE <sup>4</sup>	NS	NS	NS -1.36	0.2 bar	18.23 mM h <sup>-1</sup>	NS	[59]
4 % CeO <sub>2</sub> /C GDE <sup>4</sup>	NS	NS	NS -1.1	0.2 bar	19.4 mM h <sup>-1</sup>	NS	[58]
Carbon-Supported MnO <sub>2</sub> Nanoflowers	3	191	NS -0.9	0.2 bar	0.6	NS	[97]
Tungsten oxide Nanoparticles modified carbon	3	NS	NS -2.3	0.2 bar	1.93	44	[149]



Pt-Pd bimetallic nanoparticles on MWCNTs <sup>3</sup> /RVC	NS	NS	NS 0.699	NS	0.43	-	[75]
Mn/Fe nanoparticles porous carbon	NS	351	NS -0.056	NS	0.07	-	[62]
Gold nanoparticles deposited on the graphite cathode	3	NS	0.5 mA -0.056	NS	0.84 mM (h cm <sup>2</sup> ) <sup>-1</sup>	-	[164]
Cobalt (II) Phthalocyanine/C GDE <sup>4</sup>	NS	NS	NS -0.7	NS	0.14	81.5	[165]
NiFe nanostructure /Graphite	2	NS	300 mA -0.016	NS	0.015	0.15	[166]
Nanostructured martite	6	1.8	300 mA -0.206	NS	0.038	0.2	[65]
<b>Mixed metal/metal oxide cathode</b>							
Bi <sub>2</sub> Mo <sub>3</sub> O <sub>12</sub> /Ti cathode	3	NS	0.9 -0.456	NS	0.044 mmol h <sup>-1</sup>	-	[77]
MMO <sup>12</sup> /Ti	4	NS	40 mA NS	NS	0.1	6	[138]

856 \*calculated by dividing with the geometric surface of cathode

857 <sup>1</sup>NS: not specified, <sup>2</sup>PANI: polyaniline, <sup>3</sup>MWCNT: multi-walled carbon nanotube, <sup>4</sup>GDE: gas diffusion electrode, <sup>5</sup>NCNT: N-  
858 doped multi-walled carbon nanotube, <sup>6</sup>NF: nickel foam, <sup>7</sup>CNT: carbon nanotube, <sup>8</sup>N/F-CNC: nitrogen/fluoride co-doped carbon  
859 nanocages, <sup>9</sup>HPCS-S: hollow porous carbon sphere-sulfur composite, <sup>10</sup>GC: glassy carbon, <sup>11</sup>PAN: polyacrylonitrile, <sup>12</sup>MMO: mixed  
860 metal oxide

861

862

## 863 **4.2. Nanostructured-based anodes**

### 864 *4.2.1. General requirement for anode characteristics*

865 Different anodes have different electrochemical properties, e.g., electrode area, OEP and  
866 conductivity. Thus some electrochemical characterization methods are employed, for example,  
867 CV and EIS Nyquist plot [167]. When nanostructure is introduced into anode, some electrode  
868 properties would change. It was found that the introduction of TiO<sub>2</sub> nanostructure into Ti/SnO<sub>2</sub>-  
869 Sb anode resulted in a higher oxidation peak. The R<sub>ct</sub> obtained from EIS was 203 and 380 Ω  
870 for Ti/TiO<sub>2</sub>/SnO<sub>2</sub>-Sb and Ti/SnO<sub>2</sub>-Sb anodes, respectively, indicating the enhanced  
871 electrochemical conductivity [56]. This result was also supported by another work according to  
872 which the value of R<sub>ct</sub> was decreased from 74.62 Ω to 2.57 Ω after the introduction of Pt at the  
873 nanoscale into Ti/SnO<sub>2</sub>-Sb electrode [168].

### 874 *4.2.2. Carbon nanomaterials-based electrodes*

#### 875 *4.2.2.1. CNTs*

876 CNT as anode is prone to corrosion at potential higher than 1.7-1.9 V/SCE [83], but it has been  
877 widely used as adsorbents for pollutants adsorption and electrocatalysts for pollutants  
878 electrooxidation or electrosorption in a range of small potentials and currents due to unique  
879 hollow structure and high surface area [169,170].

#### 880 • **Raw CNTs**

881 In order to improve the electrochemical oxidation kinetics and mass transport, electrochemical  
882 filters with 3D nanostructure have attracted much attention (Fig. 14a). In general, CNT was  
883 filtered onto the PTFE membrane as anode for use in electrochemical filtration system. A five-  
884 layer electrochemical CNT-polyvinylidene fluoride filter was constructed for single-pass  
885 nitrobenzene removal by sequential reduction-oxidation, but not oxidation–reduction [171].

886 Aqueous dyes could be adsorbed by CNT filter surface without current application. However,  
887 over 90% of dyes from influent could be oxidized when anodic potential was 2 and 3  
888 V/(Ag/AgCl) (residence time  $\leq 1.2$  s) [172,173]. When CNT networks were used for removal  
889 of methyl orange (MO), the primary removal mechanism during electrochemical filtration was  
890 oxidative degradation rather than physical adsorption. Compared with MO, tetracycline (TC)  
891 with multiple functional groups/moieties, tended to adsorb onto the  $sp^2$  conjugated CNT  
892 sidewalls. However, the MO removal was more effective at high potential with high energy  
893 consumption [174]. It was observed that the efficiency of electrochemical filtration was a  
894 function of CNT surface chemistry [172]. When CNT networks were used to remove non-  
895 sorptive ferrocyanide, electro-oxidation kinetics of ferrocyanide had good relationship with  
896 BET specific surface area of the CNT at a low anodic potential ( $\leq 0.2$  V/(Ag/AgCl), indicating  
897 that the  $sp^2$  sidewalls were the predominant reaction sites. At a higher anodic potential ( $\geq 0.3$   
898 V/(Ag/AgCl), the differential ferrocyanide electrooxidation kinetics in CNT tips and sidewalls  
899 correlated well with the O/C ratio of the CNT networks. It illustrated that the oxy-tips also  
900 contributed to attain faster electrochemical kinetics [175]. Aqueous chloride and iodide were  
901 also oxidized with minimal overpotential, which was limited by active sites on CNT surface  
902 [173].

903 Therefore, many parameters have effected the electrochemical filtration system, e.g., oxidative  
904 fluxes and anodic potential. 95% 17 $\beta$ -estradiol and 17 $\alpha$ -ethinylestradiol were removed by CNT  
905 electrochemical filter when the oxidative fluxes were more than  $2.94 \pm 0.05$  mmol h<sup>-1</sup> m<sup>-2</sup> at  
906 the voltage of 2.5 V [176]. An anodic MWCNT micro-filter was applied to remove and  
907 inactivate viruses (MS<sub>2</sub>) and bacteria (*Escherichia coli* (*E. coli*)). When the anodic potential  
908 was 2 V and 3 V/(Ag/AgCl), the sieved bacteria and adsorbed viruses could be removed over  
909 75.0% and 99.6% for 30 s post-filtration, respectively, indicating that it was promising at the  
910 point-of-use of drinking water treatment [173]. In addition, graphene is another kind of carbon

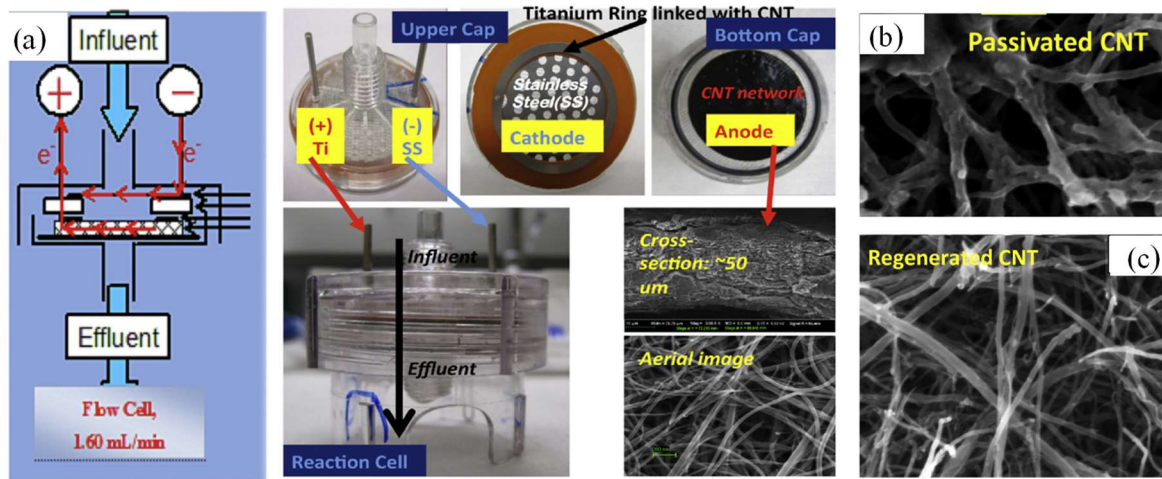
911 nanomaterials with large surface area and conductivity, which also exhibit  $sp^2$  carbon atoms  
912 with CNT. The addition of graphene to CNT increased the water permeation rate and decreased  
913 the liquid residence time to 0.44 s. When graphene: CNT ratio was 7:3, the filter performance  
914 was the best because it achieved the balance between low specific surface area and high  
915 conductivity of CNTs [177].

916 Additionally, the target pollutants were degraded into intermediates, which coated electrodes  
917 by forming polymer. The presence of polymer and intermediate may negatively affect the  
918 efficacy and efficiency of the device toward practical application. When an anodic potential of  
919 1.6 V/(Ag/AgCl) was applied to CNT network for 4 h, CNT film was passivated due to  
920 pollutants polymerization on the CNT network, reducing reaction current and electrochemical  
921 performance (Fig. 14b). To obtain an active (non-passivated) CNT network to remove polymer  
922 on electrode, electrode regeneration was necessary, and it was more effective to prevent the  
923 formation of polymers at higher potentials (Fig. 14c). The method of calcination and  
924 redispersion was effective (> 97%) for the removal of the passivating electropolymer coating  
925 [178].

926 The oxidation and adsorption at the CNT electrode, especially for Fenton reaction (Fe was  
927 loaded in cathode materials), could be combined, allowing a promising process for effective  
928 wastewater treatment [179–182]. The increase in surface area of cathode led to decrease the  
929 cathodic resistance for charge transfer, which was beneficial to anodic potential and  
930 electrooxidation [183]. The total organic carbon (TOC) removal rate by the coupled process  
931 between anodic oxidation and EF was 4 times higher than that of individual processes [184]. In  
932 addition, electrochemical oxidation could combine with other technology (forward osmosis and  
933 ozonation) based on the CNT filter [175,185]. This could simultaneously achieve the removal  
934 of both phenol (3.2-fold increase) and soluble salts in forward osmosis, and decrease polymer

935 formation and deposition on CNT. It is therefore promising for commercially available water  
936 purification system.

937



938

939 **Figure 14.** (a) Depiction and images of the CNT electrochemical filtration apparatus, i.e. real  
940 images of the whole reaction cell (including the upper cap and bottom cap), anode  
941 components (titanium ring and CNT network with cross-section and aerial images) and  
942 cathode (the perforated stainless steel), (b) SEM image of the fresh and passivated CNT  
943 network, respectively, and (c) SEM image of regenerated CNT. Reproduced with permission  
944 from Ref. [178]. Copyright (2013) Elsevier.

945

## 946 • CNTs modification

### 947 (1) Chemical surface treatments

948 After anodic oxidation, CNT will inevitably undergo surface oxidation, which has certain effect  
949 on electrochemical performance. Calcination of CNT to remove amorphous carbon can lead to  
950 the opening of the ends of crude CNTs. Oxygen functional groups were generated during acid  
951 treatment. HCl treatment is advantageous compared to HNO<sub>3</sub> treatment since CNT exhibits

952 more surface  $sp^2$ -bonded carbon positively charged in the former case and this leads to adsorb  
953 pollutants negatively charged. In the case of  $HNO_3$  treatment CNT has negatively charged  
954 surface oxy-groups that have a longer effective retention time for adsorption and oxidation of  
955 pollutants with positive charged [172]. The pre-anodization of CNT sodium sulfate electrolyte  
956 increased hydroxyl group (-COH) and decreased carboxyl group (-COOH) compared with raw  
957 CNT, resulting in an increased anodic phenol mineralization by two-time [184]. However, when  
958 CNT was refluxed in nitric acid, the decisive functional group was -COOH, resulting in a  
959 decrease of phenol mineralization by two-time (Fig. 15a). The reason was that hydrophilic -  
960 COH groups were beneficial to electron transfer (Fig. 15b) and exhibited more defect sites  
961 under a similar O/C ratio. In addition, the formation of -COOH would lead to breaking of C-C  
962 bond conducting to a negative effect on CNT electrochemical activity [184].

963 In another work, CNT was modified by sodium dodecyl benzene sulfonate (SDBS) and then  
964 dipped on polyurethane sponges as conductive nano-sponge filtration [186]. The removal  
965 efficiency of tetracycline decreased when excess SDBS was treated by concentrated  $HNO_3$ . The  
966 electro-oxidation flux of this system could reach  $0.87 \pm 0.04 \text{ mol h}^{-1} \text{ m}^{-2}$ , which was 36-folds  
967 more than raw CNT filtration due to the decrease of the actual filter cross-sectional area [183].  
968 However, forming polymer/precipitate from intermediates was easier to block the active sites,  
969 decreasing the catalytic activity.

## 970 (2) Heteroatom doping

971 Heteroatom doping of CNT was developed to improve its electrochemical filtration action for  
972 effective oxidation of pollutants. Boron and nitrogen-doping (B-CNT, N-CNT) with 1% of  
973 heteroatom as well as raw CNT were used as anode for phenol removal. It was found that the  
974 three anodes were all able to remove approximately 7 to 8  $\text{mg C L}^{-1}$  of the influent TOC within  
975 the 1 s liquid residence time at the anodic potential of 1.6 V/(Ag/AgCl) (Fig. 15c) [187].

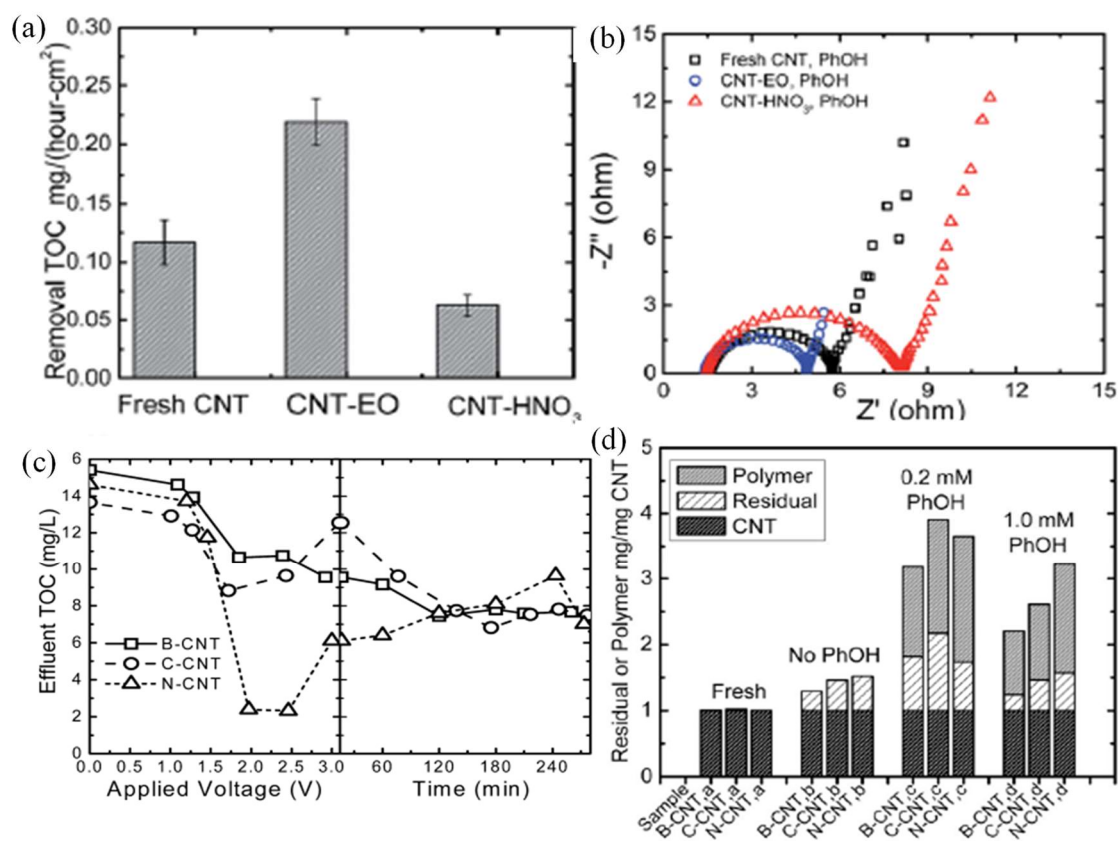
976 Although, the TOC removal was similar for all anodes, B-CNT led to a greater extent of phenol  
977 oxidation and yield to a higher fraction of by-products that did not polymerize. According to  
978 the TGA and current change measurements, the B-CNT exhibited most stable and resistance  
979 performance toward electrochemical passivation with the lowest extent of electrochemical  
980 polymer and precipitate formation (Fig. 15d). It was suggested that it might be the optimal CNT  
981 for anodic processes [187].

### 982 (3) Metal doping

983 Sb-doped SnO<sub>2</sub> CNT (Sb-SnO<sub>2</sub>-CNT) exhibited high over-potential and electrocatalytic surface  
984 area compared with heteroatom doping CNT [172]. A nanoscale tin oxide modified CNT  
985 (SnO<sub>2</sub>-CNT) was prepared via electrosorption-hydrothermal protocol to apply it in a  
986 continuous-flow system as anode. SnO<sub>2</sub> nanoparticles were uniformly distributed on the  
987 sidewalls of CNT, resulting in a rougher tubular surface and an increased tube diameter [188].  
988 The OEP of SnO<sub>2</sub>-CNT and BTO-CNT (CNT uniformly coated with bismuth-doped tin oxide  
989 nanoparticles) was, respectively, 580 mV and 440 mV higher than that of raw CNT (1.27 V vs  
990 Ag/AgCl). It resulted in an excellent anodic stability for ammonia transformation over three  
991 consecutive cycles [188,189]. TOC removal by BTO-CNT was two to eight-time higher and  
992 energy consumption was 0.2-time than that of raw CNT anode [189]. CNT loaded with Sb-  
993 SnO<sub>2</sub> and Bi-Sb-SnO<sub>2</sub> enhanced the degradation rate of phenol by 1.5 and 2.1-folds,  
994 respectively and this enhancement was attributed to an effective generation of <sup>•</sup>OH [190]. Only  
995 0.8 mg L<sup>-1</sup> Sn<sup>4+</sup> was measured after 1.5 h electrolysis, indicating good stability of the anode  
996 materials [188]. In addition, Ti<sup>4+</sup> was adsorbed on the CNT surface and further formed the TiO<sub>2</sub>  
997 modified CNT filters (TiO<sub>2</sub>-CNT) via electrosorption-hydrothermal process. In this  
998 electroactive filter system, simultaneous detoxification and sequestration of Sb(III) were  
999 fulfilled within pH ranging from 3 to 11 [188]. Therefore, metal doping CNTs as anode

1000 exhibited excellent reactivity, current efficiency and lower energy consumption due to  
 1001 increased conductivity, OEP and stability.

1002



1003

1004 **Figure 15.** Anodic performance evaluation of the CNT samples. Electrochemical conditions

1005 were flow rate = 1.6 mL min<sup>-1</sup>, [phenol] = 1.0 mM and [Na<sub>2</sub>SO<sub>4</sub>] = 100 mM unless otherwise

1006 noted. (a) Average TOC removal rate over 180 minutes of continued electrochemical filtration

1007 at an anodic potential of 1.6 V/(Ag/AgCl); (b). EIS was measured with a three-electrode

1008 system over a frequency range of 0.1-10<sup>6</sup> Hz. Reproduced with permission from Ref. [184].

1009 Copyright (2015) Royal Society of Chemistry. Effluent total organic carbon (mg C L<sup>-1</sup>) versus

1010 applied voltage (V) and time (min) (c) and percent CNT, residual, and polymer versus CNT

1011 network (d). Reproduced with permission from Ref. [187]. Copyright (2012) American

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1013

#### 1014 4.2.2.2. Boron-doped diamond (BDD) anode

1015 BDD is one of the most promising electrodes in the field of electrocatalysis due to its low  
1016 background current, noise signals, wide potential window, high mechanical strength and  
1017 corrosion resistance and long-term response stability [191]. BDD has been considered as an  
1018 excellent anode material for the electrochemical treatment of wastewater at a wide pH range,  
1019 due to its unique and excellent properties compared with dimensionally stable anodes (DSA)  
1020 [192–194]. At present, BDD electrode has promising prospect in wastewater treatment  
1021 especially for mineralization of bio-refractory organic pollutants [195,196]. Furthermore, when  
1022 BDD was used as anode in electro-Fenton (EF) process, the pollutants removal would be greatly  
1023 improved [17,197]. It has been proved that boron doping level of BDD had obvious effect on  
1024 the diamond crystallites and the active sites on the surface, resulting in a better oxidation  
1025 performance.

#### 1026 • Substrates-based BDD anode

##### 1027 (1) Titanium substrate

1028 After BDD film deposition on Ti substrate via CVD process (Fig. 15a), porous Ti was uniformly  
1029 covered by BDD film, showing well-faceted crystal with the crystal size being in the range of  
1030 1-2  $\mu\text{m}$  [198]. 3D structure of porous Ti/BDD exhibited excellent electrochemical effective  
1031 surface area for electron transfer (3.2-time) and high OEP for  $\cdot\text{OH}$  generation compared to flat  
1032 Ti/BDD [199]. The contact angle of porous Ti/BDD electrodes were  $135^\circ$  compared to  $72^\circ$  of  
1033 flat Ti/BDD electrodes, indicating that the microstructure of polycrystalline BDD could also  
1034 improve the hydrophobicity to some extent. The thickness of diffusion layer of porous Ti/BDD  
1035 ( $69\ \mu\text{m}$ ) was much less than that of flat BDD ( $117\ \mu\text{m}$ ), which was decisive for mass transfer  
1036 coefficient of porous Ti/BDD ( $1.31 \times 10^{-5}\ \text{m s}^{-1}$ ) compared to that of flat BDD ( $7.71 \times 10^{-6}\ \text{m s}^{-1}$ )

1037 [200]. With the increase of boron concentration, the grain size of Ti/BDD was more obvious,  
1038 exhibiting more stable electrochemical properties (Fig. 17a-b) [201]. Through LSV curve  
1039 measurements, it was found that oxidation peak for aspirin was observed, shifting positively  
1040 with the increase of aspirin concentration. Importantly, porous Ti/BDD electrode exhibited  
1041 outstanding direct electrochemical oxidation ability for aspirin with the step currents 1.4-1.8  
1042 times of the values of flat Ti/BDD electrode, which was beneficial to direct oxidation of aspirin.  
1043 The apparent rate constants ( $k_{app}$ ) of porous Ti/BDD for anodic oxidation of aspirin was 1.98  
1044 times of flat BDD and 7.20 times of PbO<sub>2</sub> electrode, which could be ascribed to the more active  
1045 sites provided by porous film to generate  $\cdot\text{OH}$  [202]. Porous Ti/BDD electrodes exhibited  
1046 excellent stability (service life: 111 h) than plate Ti/BDD (89 h), indicating that porous Ti  
1047 improved the stability of Ti/BDD electrode (Fig. 17c) [198]. The different utilization efficiency  
1048 of porous electrode surface led to discrepancy between promotion of current efficiency and  
1049 enhancement of  $\cdot\text{OH}$  [203]. On the other hand, the current efficiency of porous Ti/BDD was  
1050 smaller than that of plate anode because the surface could not be exploited completely in a mass  
1051 transport control situation (Fig. 17d).

1052 Porous Ti/BDD anode presented excellent potential in anodic oxidation and mineralization of  
1053 different pollutants (e.g., dyes, pharmaceuticals, phenols, etc.) [199,202,204,205].

## 1054 (2) Silicon substrate

1055 A BDD nanowire (BDDNW) electrode via metal-assisted chemical etching of Si and  
1056 electrostatic self-assembly of nanodiamond seeding was prepared (Fig. 16b) [206]. The average  
1057 length and thickness of nanocrystalline BDD on Si substrate were 200 nm and 750 nm,  
1058 respectively. The effective surface area of BDDNW was 3 times higher than that of plat BDD,  
1059 providing substantially greater electrochemical reaction sites for  $\cdot\text{OH}$  generation. The phenol  
1060 removal by BDDNW and plate BDD was 97% and 79%, respectively, and the phenol

1061 mineralization by BDDNW was 2.27-folds than that of plate BDD anode. These results  
1062 suggested that BDDNW electrode was much more efficient in electrooxidation of phenol.

### 1063 **(3) Platinum substrate**

1064 In addition, 3D-Pt nanosheet perpendicular to BDD film was prepared by the double  
1065 template method (hydrogen bubble template and metallic Zn template for displacement  
1066 reaction) to control the morphology. The length and thickness of the Pt nanosheet were about 1  
1067  $\mu\text{m}$  and 10 nm, respectively. Due to the size effect of the Pt and active effect of the BDD, Pt  
1068 nanosheet/BDD electrode had higher electrocatalytic activity and active sites, facilitating the  
1069 pollutants degradation [207].

### 1070 **(4) Nickel foam substrate**

1071 The BDD could also be loaded on the Ni foam by CVD to form the 3D-BDD [208]. Compared  
1072 with 2D-BDD (Ti sheet as substrate), the electroactive surface area of 3D-BDD increased by  
1073 20-time. Thanks to the fluid flow channel, the 3D-BDD electrode exhibited highly efficient  
1074 electrochemical oxidation of RB-19. The apparent reaction rate constant, energy consumption,  
1075 and mineralization current efficiency (MCE) were  $1.487 \text{ min}^{-1}$ ,  $0.03 \text{ kWh (gTOC)}^{-1}$  and 326%,  
1076 respectively (electrolyte: 0.1 M  $\text{Na}_2\text{SO}_4$  was 0.1 M; current was 0.3 A;  $400 \text{ mg L}^{-1}$  RB-19; time:  
1077 180 min) 3D-BDD electrodes prepared with different ppi (pores per inch) of Ni foam had  
1078 different electro-oxidation performance [209]. The COD removal rate and energy consumption  
1079 of 3D-BDD<sub>1</sub> (50 ppi) were 1.5-time and 25% of that of 3D-BDD<sub>2</sub> (35 ppi-30), respectively.

## 1080 **• Composite electrodes with BDD and other materials**

### 1081 **(1) $\text{TiO}_2$**

1082  $\text{TiO}_2$ /BDD heterojunction electrodes were prepared via CVD method by dip-coating  $\text{TiO}_2$   
1083 nanoparticles onto BDD electrodes at  $700 \text{ }^\circ\text{C}$ , exhibiting 20 nm  $\text{TiO}_2$  nanoparticles. When boron  
1084 ( $2 \times 10^{21} \text{ cm}^{-3}$ )/carbon ( $(2 \times 10^{19} \text{ cm}^{-3})$ )\_ratio in gas phase 1000 ppm and covered 500 nm thick

1085 TiO<sub>2</sub> layer, this nanostructure of p-n junction was beneficial to the hole injection [210]. The  
1086 photoelectrocatalytic activity of mixed-phase TiO<sub>2</sub>/BDD electrode in 700 °C was 3-fold of that  
1087 obtained at pure anatase TiO<sub>2</sub>/BDD electrode in 450 °C, which was caused by the improvement  
1088 of the active area [211]. When composite TiO<sub>2</sub>/BDD electrode was prepared via  
1089 electrophoretically deposited method, the thickness of TiO<sub>2</sub> layer on the BDD surface was 14.68  
1090 μm, exhibiting great ability and stability [212]. The electrocatalytic activity of TiO<sub>2</sub>/BDD was  
1091 proved to be improved due to the greater electroactive area compared with BDD. For instance,  
1092 the degradation of Acid Blue 80 by TiO<sub>2</sub>/BDD in photoelectrocatalysis (PEC) was enhanced  
1093 compared to BDD due to the higher electroactive area of the nanostructured TiO<sub>2</sub> deposition,  
1094 showing promising prospect for application [212].

## 1095 (2) SnO<sub>2</sub>

1096 Sb-doped SnO<sub>2</sub> film was constructed on BDD (Sb-SnO<sub>2</sub>/BDD) by a sol-gel method [213] with  
1097 a bifunctional electrode interface: innumerable, uniform, nanosized SnO<sub>2</sub> particles and some  
1098 BDD polycrystallites. For clofibric acid degradation, the reaction rate constant of Sb-  
1099 SnO<sub>2</sub>/BDD was 1.6-time higher than with BDD. This effect has been explained by its high OEP  
1100 (2.23 V/SCE) versus that of BDD (2.35 V/SCE) and good conductivity (with electrical  
1101 resistance of 175 Ω compared to that of BDD: 3850 Ω). It would therefore be a promising anode  
1102 for wastewater remediation.

## 1103 (3) Ni

1104 Polycrystalline BDD on Ta substrate via electron-assisted hot filament CVD and Ni-  
1105 nanoparticle-assisted plasma etching was prepared, providing a method for obtaining a regular  
1106 porous nanostructure on the BDD surface (Fig. 16c) [214]. The etching process and the  
1107 formation of the porous nanostructure on the BDD were investigated by changing the Ni  
1108 sputtering time and the BDD etching time. When a porous BDD film was sputtered with Ni for  
1109 10 s and etched for 2 min, holes less than 200 nm size were densely distributed on the BDD

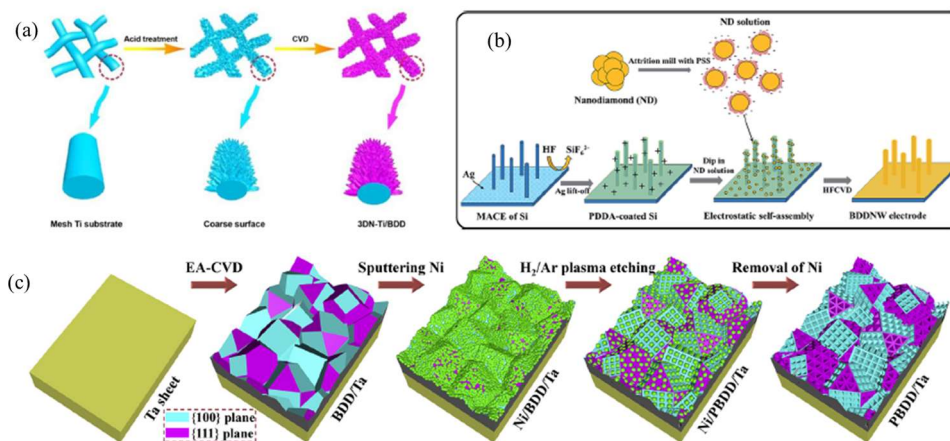
1110 surface, with square and triangular holes present on the (100) and (111) phases, respectively.  
1111 Compared with plate BDD electrode, porous BDD/Ta exhibited excellent electron transfer via  
1112 effective electroactive surface area (2.43-fold) and a pseudo-first-order reaction rate of 0.02  
1113  $\text{min}^{-1}$  for electrochemical oxidation of methylene blue.

#### 1114 (4) Au

1115 The dendritic Au/BDD was successfully prepared with well-defined fractal structure and 0.24  
1116 nm space between the branch and the trunk [215]. This structure exhibited better reversibility  
1117 than BDD electrode due to the difference between anodic and cathodic peaks. The dendritic  
1118 Au/BDD with single crystal dendritic Au with dominant (111) facet exhibited numerous  
1119 physisorption and chemisorption sites [215]. It was indicated that dendritic Au/BDD exhibited  
1120 better electrocatalytic oxidation for the sulfur containing target contaminant with higher  
1121 selectivity than phenol due to preferential adsorption of target molecules to form Au–S bonds,  
1122 resulting in electron transfer between Au and S [215].

1123 In summary, nanostructuring the surface of BDD anodes (e.g., porous diamond, diamond  
1124 nanowires, etc.) enhanced the degradation performance towards organic pollutants. It could  
1125 further improve the electrochemical performance due to the increasing surface area for  
1126 adsorption capacity, porous structure for electron transfer and rough surface for extending the  
1127 life of the composite electrode.

1128



1129

1130 **Figure 16.** (a) Schematic diagram of fabrication process for 3DN-BDD film electrode.

1131 Reproduced with permission from Ref. [200]. Copyright (2016) Royal Society of Chemistry;

1132 (b) Schematic of the fabrication process for a BDDNW electrode. Reproduced with

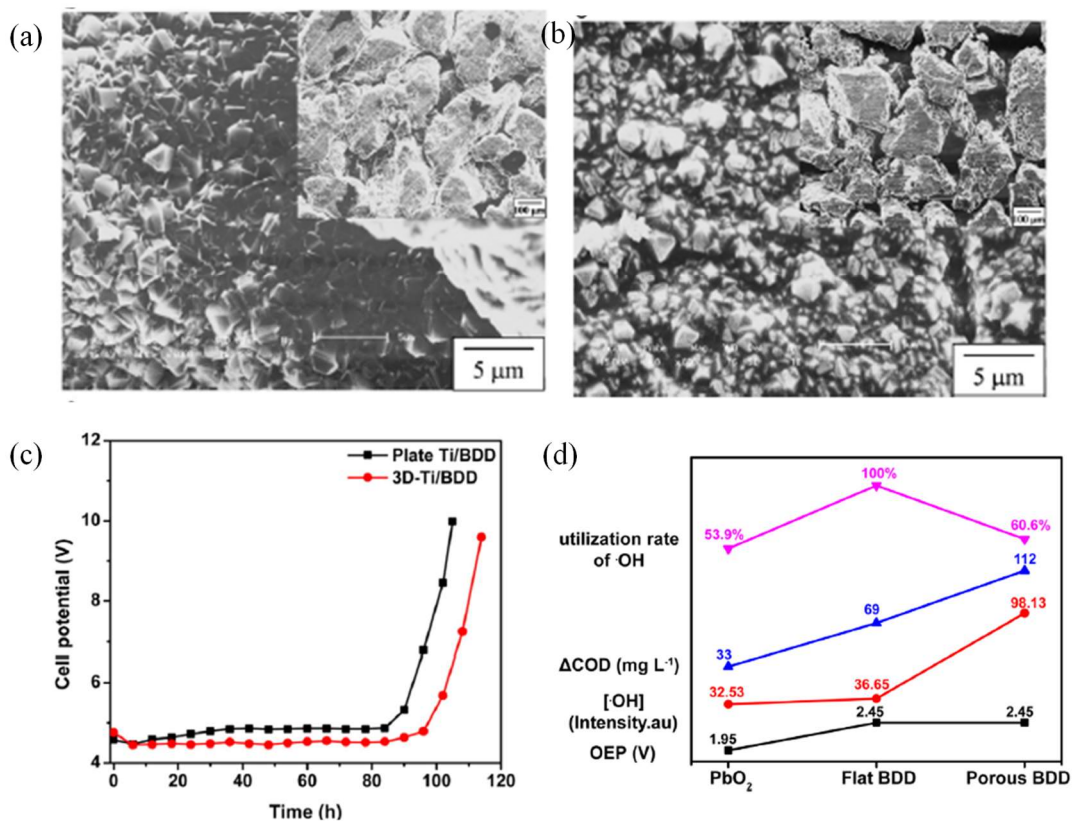
1133 permission from Ref. [206]. Copyright (2017) Royal Society of Chemistry; (c) Schematic

1134 diagram depicting the preparation of a porous BDD/Ta films. (c) Reproduced with

1135 permission from Ref. [214]. Copyright (2018) Elsevier.

1136

1137



1138

1139 **Figure 17.** SEM images porous Ti/BDD electrodes: (a) Ti/BDD electrode for high boron  
 1140 concentration and (b) low boron concentration; inset: SEM images with low magnification  
 1141 corresponding to the electrodes. Reproduced with permission from Ref. [201]. Copyright  
 1142 (2012) Elsevier. (c) Accelerated life between plate and 3D-Ti/BDD electrodes in 3 mol L<sup>-1</sup>  
 1143 H<sub>2</sub>SO<sub>4</sub> solution. Reproduced with permission from Ref. [198]. Copyright (2015) Elsevier.  
 1144 Hydroxyl radical utilization rate as a function of electrode material (d) Reproduced with  
 1145 permission from Ref. [202]. Copyright (2015) Elsevier.

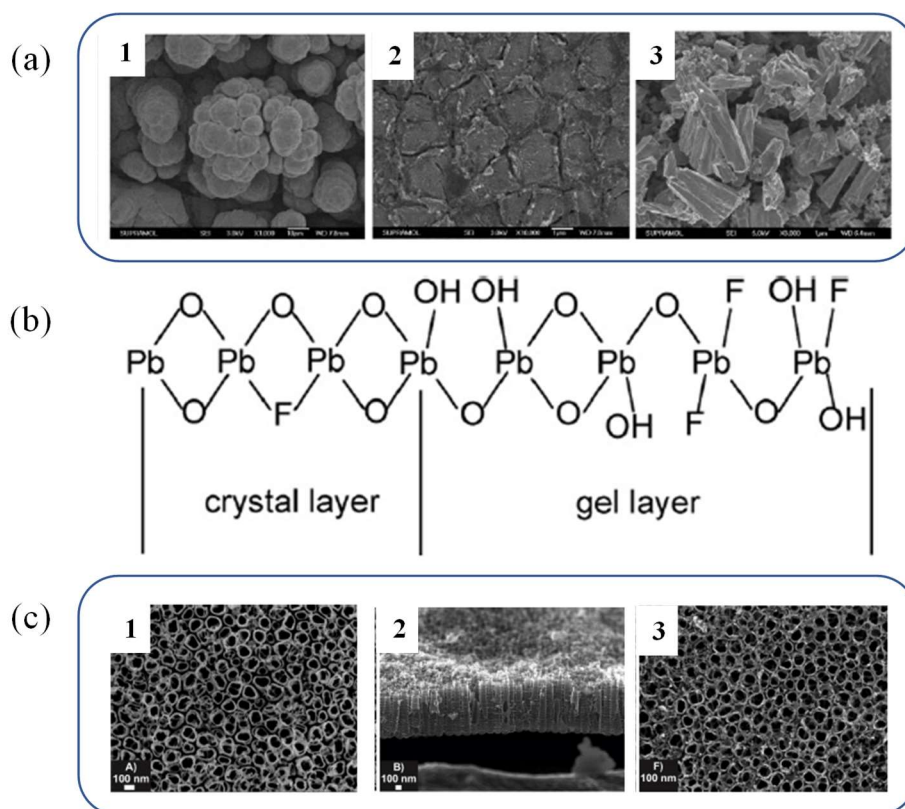
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#### 1147 4.2.3. Heteroatom-based electrodes

1148 The interaction between the catalyst and interacting media could be improved when heteroatom  
 1149 was doped in nanostructured materials to increased active surface area and electric properties  
 1150 [216].

1151 4.2.3.1. Fluorine-doped electrodes

1152 Fluorine (F) doping with high potential anode could inhibit O<sub>2</sub> evolution to improve the anodic  
1153 oxidation of pollutants [217]. Because F<sup>-</sup> and O<sup>2-</sup> have similar ionic radius, the oxygen sites on  
1154 the surfaces can be replaced by F<sup>-</sup> anions [218], so that F-PbO<sub>2</sub> exhibit more regular morphology  
1155 with better oriented crystals of lower size (16.203 nm) than for raw PbO<sub>2</sub> (24.305 nm)  
1156 [219,220]. When F-PbO<sub>2</sub> film electrode was prepared by anode co-deposition, the deposition  
1157 potential had obvious effect on morphology, resulting in thinner crystal grains on the F-doped  
1158 PbO<sub>2</sub> surface (Fig. 18). The spherical crystallites appeared when deposition potential was low,  
1159 i.e. when F content was high (Fig. 18a-1). On the contrary, when the deposition potential was  
1160 high, cracks were observed on the electrode surface (Fig. 18a-2).



1161  
1162 **Figure 18.** (a) SEM micrographs of the F-PbO<sub>2</sub> electrode with different doping content of F  
1163 (atomic ratio of F to Pb, 1: 0.075: 2: 0.07: 1, 3: free-doped PbO<sub>2</sub> electrode). Reproduced with  
1164 permission from Ref [218]. Copyright (2013) Wiley. (b) Schematic diagram of the structure



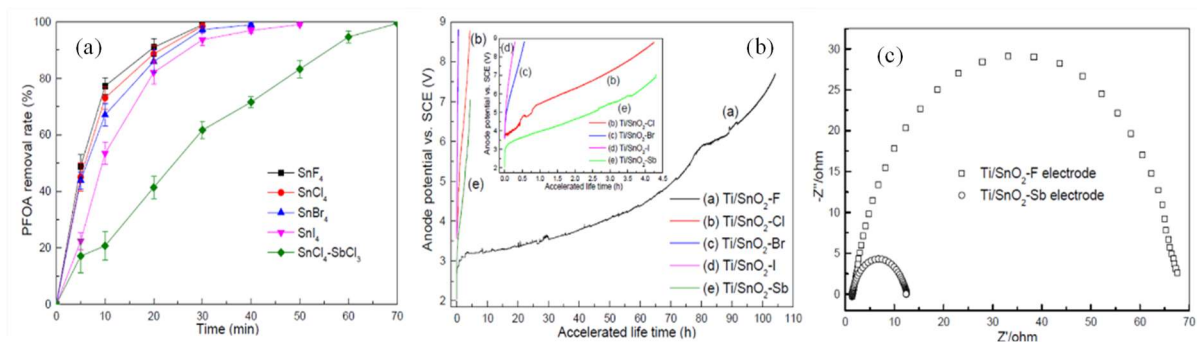
1165 of F-PbO<sub>2</sub> electrode system. Reproduced with permission from Ref. [220]. Copyright (2009)  
1166 Elsevier. (c) FEG-SEM images of (1) top view of TiO<sub>2</sub>NTs; (2) cross-section of TiO<sub>2</sub> NTs;  
1167 and (3) top view of boron-doped TiO<sub>2</sub>NTs with addition of 560 ppm of NaBF<sub>4</sub> in the  
1168 electrolyte of nanotubes growth. Reproduced with permission from Ref [221]. Copyright  
1169 (2015) Elsevier.

1170 F-PbO<sub>2</sub> anode via decomposition methods was prepared to explore the mechanism of the effect  
1171 of F doping on lifetime and electrochemical and degradation activity of PbO<sub>2</sub> [220]. In Fig. 17b,  
1172 -OH sites in gel layer were replaced by F<sup>-</sup> anions in F-PbO<sub>2</sub>, decreasing free move of oxygen  
1173 atoms and coverage of reactive oxygen species (ROS) [222]. The O<sup>2-</sup> sites in crystal layer were  
1174 also replaced by F<sup>-</sup> anions, decreasing the formation of free oxygen and occupying the channels  
1175 of the diffusion of the free oxygen atoms [219,222]. Therefore, the service life of F-PbO<sub>2</sub> anode  
1176 (140 h) was three times higher than that of PbO<sub>2</sub>. Because the average surface coverage by F  
1177 doping was only 6%, ROS on F-PbO<sub>2</sub> was still higher than raw PbO<sub>2</sub>, and the weight loss of F-  
1178 PbO<sub>2</sub> after 140 h was only 2.1%. In addition, removal efficiency of 4-chlorophenol reached  
1179 97% at 120 min by F-PbO<sub>2</sub> anode, while it was 88% for non-doped PbO<sub>2</sub>. The doping of the  
1180 PbO<sub>2</sub> electrode with F atom only had a significant effect on the pollutant degradation, but TOC  
1181 removal was barely altered [223,224] because of modification of surface properties to improve  
1182 pollutants adsorption.

1183 At present, fluorine-doped tin oxide (FTO), which exhibits good chemical and physical  
1184 stability, high temperature resistance, low preparation cost and high electrochemical  
1185 performance, was widely used as anode [225,226]. The FTO as non-active anode could produce  
1186 reactive ·OH to enhance oxidation efficiency. The degradation rate and mineralization yield of  
1187 phenol by FTO anode could reach 0.014 min<sup>-1</sup> and (76 ± 1)%, respectively [227]. Besides, FTO

1188 have a sufficiently transparent material to allow UV penetration. Therefore, it was modified in  
1189 many photochemical processes [227,228].

1190 In addition, the novel F-doped Ti/SnO<sub>2</sub> electrode prepared by SnF<sub>4</sub> as the single-source  
1191 precursor was used for electrochemical degradation of aqueous perfluorooctanoic acid (PFOA)  
1192 [229]. Compared with other Ti/SnO<sub>2</sub>-X (X=Cl, Br, I, or Sb) anode, Ti/SnO<sub>2</sub>-F anode exhibited  
1193 smooth surface, even after accelerated lifetime test, preventing penetrating of electrolyte and  
1194 generating bubbles. Therefore, higher PFOA degradation within 30 min and improved  
1195 accelerated lifetime (104 h) was achieved by Ti/SnO<sub>2</sub>-F than with other halogen-doped  
1196 electrodes (less than 5h) (Figs. 18b and 19a). In Fig. 19c, Ti/SnO<sub>2</sub>-F electrode had larger  
1197 resistance and higher OEP [218,219], which was benefit to obtain electron from H<sub>2</sub>O or PFOA  
1198 and to physical adsorption of •OH on non-active anode. Therefore, it was possible that F-doping  
1199 decreased the amount of oxygen vacancy in SnO<sub>2</sub> and provided lower possibility of oxygen  
1200 transfer from •OH into crystal lattice. This further improved the stability of electrode material.



1201  
1202 **Figure 19.** Effect of different precursors on the degradation rate of PFOA using different Sn-  
1203 based anodes (a); Accelerated life test of freshly prepared electrodes (b), the inset being the  
1204 enlarged view of accelerated life tests for the prepared electrodes except Ti/SnO<sub>2</sub>-F  
1205 electrode); and Nyquist plot for Ti/SnO<sub>2</sub>-F and Ti/SnO<sub>2</sub>-Sb electrode (c). Measurement  
1206 conditions: EIS (solution = 10 mM NaClO<sub>4</sub>, voltage amplitude = 5 mV, frequency range = 10<sup>-2</sup>

1207  $1\sim 10^5$  Hz, bias = 1.8 V/SCE). Reproduced with permission from Ref [229]. Copyright (2015)  
1208 Elsevier.

#### 1209 *4.2.3.2. Boron-doped electrodes*

1210 Due to its high electrical conductivity, the BDD anode was widely used in EAOPs. Therefore,  
1211 the boron doped on other anode materials were suggested to achieve even higher activity. B-  
1212 doped TiO<sub>2</sub> nanotubes (B-TiO<sub>2</sub> NTs) made by electrochemical anodization (one-step doping)  
1213 using NaBF<sub>4</sub> as a boron source were prepared to degrade the dye Acid Yellow 1 (AY1) in  
1214 photoelectrocatalytic processes [221]. The introduction of B did not change the morphology of  
1215 TiO<sub>2</sub> nanotubes. Different content of NaBF<sub>4</sub> was introduced to have the B content from 0.4 to  
1216 0.7 at. % in B-TiO<sub>2</sub> NTs. The mineralization efficiency (90%) of PEC for AY1 was higher than  
1217 that of photocatalysis (PC) process at 90 min, indicating the effectiveness of B-TiO<sub>2</sub> NTs in  
1218 electrocatalysis process. However, the photogenerated holes can produce more hydroxyl  
1219 radicals, promoting an increased mineralization rate after B-doping. There is still very limited  
1220 understanding in the mechanism of B-doped electrodes for electrocatalysis. In addition, B-  
1221 doped porous Si (B-doped pSi) nanoplates were design via air-oxidation process to decrease  
1222 the resistance and surface oxidation and obtain high crystallinity, achieving high initial  
1223 coulombic efficiency and long cycling stability [230].

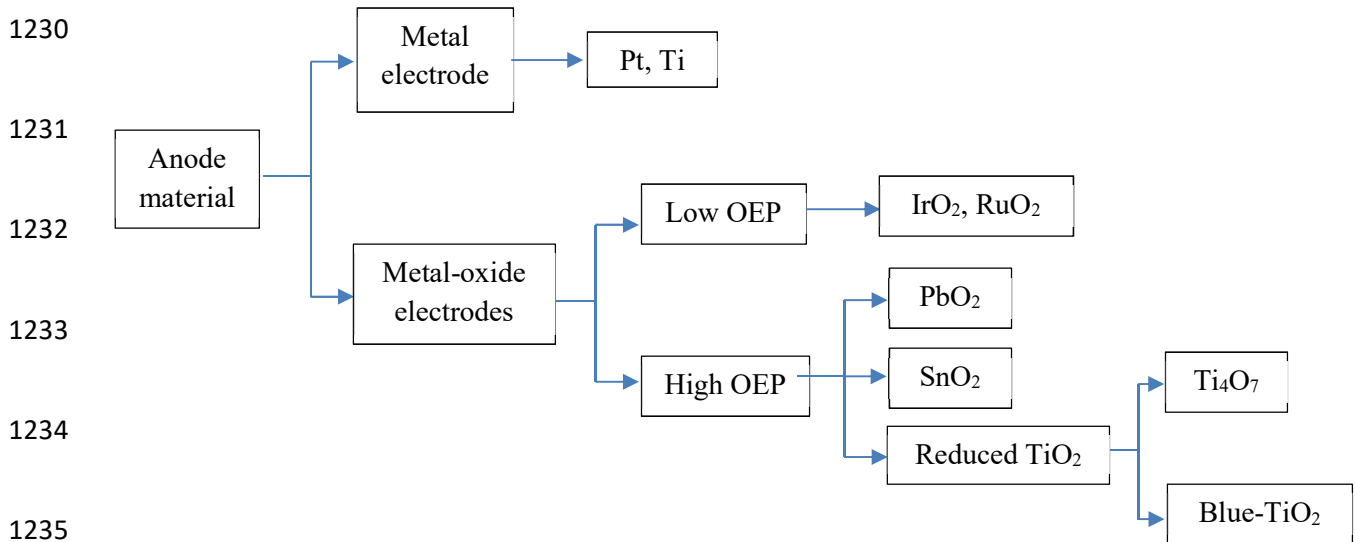
1224

#### 1225 *4.2.4. Metal- and metal oxide- based electrodes*

1226 The main employed anodes categorized as either metal or metal oxide based nanostructured  
1227 material are summarized in Fig. 20.

1228

1229



1236 **Figure 20.** Classification of metal and metal-oxide based nanostructured anodes.

1237

1238 *4.2.4.1. Metal-based electrodes*

1239 As an active anode, Pt electrode is probably the most used metal electrode for pollutants  
 1240 degradation due to its excellent electrocatalysis performance [231,232]. Yoon et al. (2012)  
 1241 investigated the use of Pt for degradation of phenol and 2-chlorophenol, observing 94% phenol  
 1242 and 95% 2-chlorophenol degradation at the current 300 mA for 3 h. However, this performance  
 1243 was worse when compared to BDD anode [232]. To improve the performance of Pt anode,  
 1244 Chen et al. (2019) introduced nano-sized Pt (1.2-2.2 nm) into Al<sub>2</sub>O<sub>3</sub> using the ethylene glycol  
 1245 reduction method, confirming that the decrease of the Pt particle size led to the enhancement of  
 1246 the catalyst ability of degrading benzene [233].

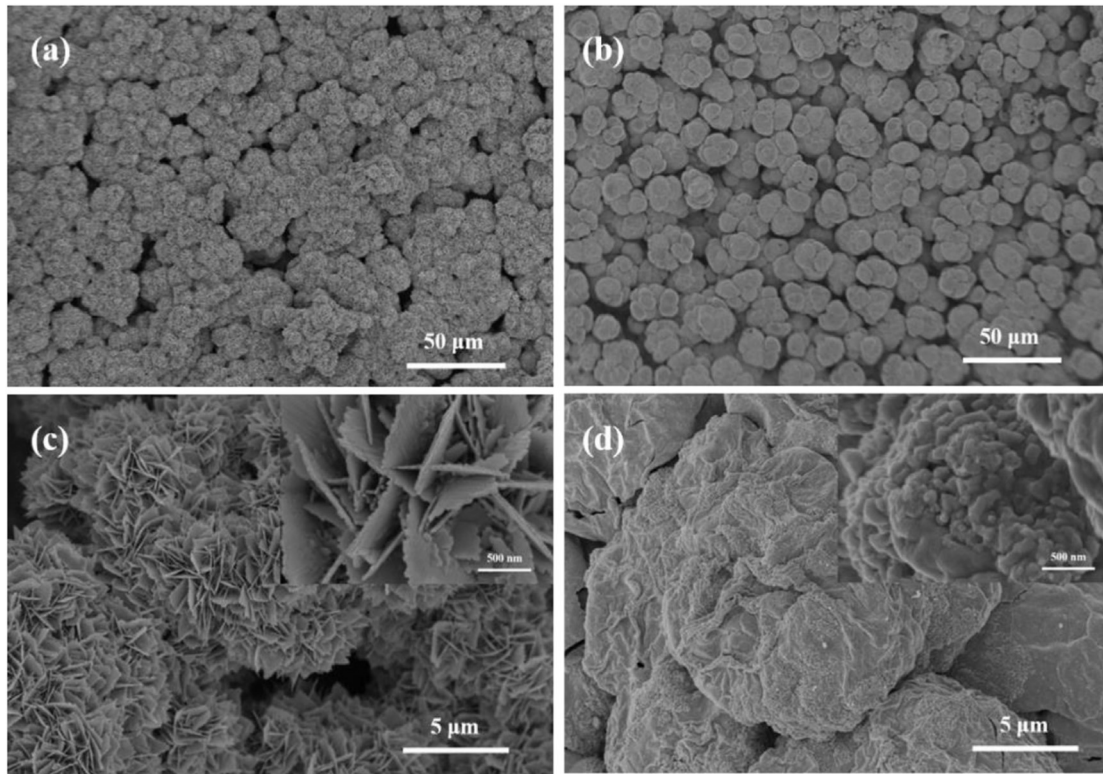
1247 *4.2.4.2. Metal oxide-based electrodes*

- 1248 • SnO<sub>2</sub> electrodes

1249 Pure SnO<sub>2</sub> cannot be used as electrode material due to a low conductivity at room temperature;  
 1250 however, its conductivity can be improved by doping with Ar, B, Bi, F, Cl, P and Sb [234–

1251 [236](#)]. In particular, Sb-SnO<sub>2</sub> is one of the most commonly used anode in electrochemical  
1252 applications.

1253 Acting as the catalytic layer, SnO<sub>2</sub> electrode has been widely used for pollutants degradation  
1254 through the formation of heterogeneous <sup>•</sup>OH. Zhou et al. (2019) used sol-gel method to prepare  
1255 a porous Ti/SnO<sub>2</sub>-Sb electrode, achieving the degradation efficiency of more than 97% in only  
1256 10 min at a current density of 0.2 mA cm<sup>-2</sup> [\[237\]](#). Recently, self-assembled 3D hierarchical  
1257 nano-structures from low dimensional nanoscale building blocks via interactions has received  
1258 considerable attention. The 3D hierarchical structure assembled by two-dimensional nanoplates  
1259 or nanosheets can expose larger specific surface area, therefore, they are more suitable and  
1260 efficient [\[208,234\]](#). Wang et al. (2019) introduced a 3D hierarchical flower-like structure (HFs)  
1261 constructed by 2D nanosheets on Ti-based SnO<sub>2</sub> electrode by hydrothermal method.  
1262 Characterized by SEM, this Ti/SnO<sub>2</sub>-Sb-HFs electrode showed a denser surface layer with the  
1263 nanosheet of 29 nm than traditional Ti/SnO<sub>2</sub>-Sb electrode (Fig. 21). It also had a higher oxygen  
1264 evolution potential 2.25 V/SCE, and a larger electrochemical active surface area (2.28-times  
1265 higher) than traditional Ti/SnO<sub>2</sub>-Sb electrode. Thus, for the degradation of Acid Red 73 (AR  
1266 73), the rate constant on Ti/SnO<sub>2</sub>-Sb-HFs electrode was 1.58-time higher than that of Ti/SnO<sub>2</sub>-  
1267 Sb electrodes [\[238\]](#).



1268

1269 **Figure 21.** Surface morphologies of (a and c) Ti/SnO<sub>2</sub>-Sb-HFs electrode, (b and d) Ti/SnO<sub>2</sub>-  
 1270 Sb electrode. Reproduced with permission from Ref [238]. Copyright (2019) Elsevier

1271 On the other hand, the practical application of SnO<sub>2</sub> anode is hampered by its poor stability  
 1272 because SnO<sub>2</sub> film is easily fall of the substrate. To overcome this problem, SnO<sub>2</sub> is always  
 1273 applied as the middle layer while other metal oxide as catalytic layer [239–241]. Wang et al.  
 1274 (2020) introduced PbO<sub>2</sub> as the catalytic layer into SnO<sub>2</sub> middle layer, which improved the  
 1275 electrocatalytic activity of PbO<sub>2</sub> electrode because the SnO<sub>2</sub> particles in PbO<sub>2</sub> films improved  
 1276 the amount of active sites on the surface, oxygen evolution potential and ·OH generation rate  
 1277 [242]. Duan et al. (2019) also introduced SnO<sub>2</sub> nanoparticle as the middle layer, which reduced  
 1278 the grain size of PbO<sub>2</sub> crystal and improved the EOP and ·OH generation capacity obtaining a  
 1279 better electrochemical activity for degradation of 3-chlorophenol [243].

1280 Besides, the substrate is also an important factor for anode materials. When the nanostructure  
 1281 is introduced into the anode, it exhibits good electron transportation properties and help to

1282 generate  $\cdot\text{OH}$  on electrode surface. For example, the  $\text{TiO}_2$  NTA, due to its stake structure,  
1283 effectively improved the service life of the combination of  $\text{SnO}_2$ -Sb function layer  
1284 [241,244,245]. Chen et al. (2019) prepared a novel enhanced  $\text{TiO}_2$  nanotube arrays  
1285 (ENTA)/ $\text{SnO}_2$ -Sb electrode by the sol-gel method, which possessed a higher oxygen evolution  
1286 potential and electrochemical stability when compared with the conventional  $\text{Ti}/\text{SnO}_2$ -Sb  
1287 electrode. Its performance for the destruction of a common biocide of 2-methyl-4-isothiazolin-  
1288 3-one was better than that of  $\text{Ti}/\text{SnO}_2$ -Sb [56].

1289       •  **$\text{PbO}_2$  electrodes**

1290  $\text{PbO}_2$  electrode has been extensively studied for organic pollutant degradation due to its good  
1291 conductivity and high OEP. However, its catalysis performance is still not as satisfactory as  
1292 BDD anodes [239,246–248]. Therefore, nanostructured  $\text{PbO}_2$  study has been a research trend.  
1293 Tan et al. (2011) fabricated  $\text{PbO}_2/\text{TNTs}$  anode which possessed stronger oxidation ability than  
1294 that traditional  $\text{PbO}_2$  electrode owing to the unique microstructure [247].

1295       •  **$\text{ZnO}$  electrodes**

1296 El Kacemi et al. (2017) prepared a nanostructured  $\text{ZnO-TiO}_2$  tin film oxide deposited on  
1297 graphite felt for degradation of organic pollutants [249]. This electrode was used as anode in  
1298 anodic oxidation and EF processes to remove efficiently the dye Amido Black 10B. Complete  
1299 mineralization of  $74 \text{ mg L}^{-1}$  dye solution was achieved in 6 h at 100 mA constant current  
1300 electrolysis [249].

1301       • **Reduced TNT anode:  $\text{Ti}_4\text{O}_7$  electrodes**

1302 TNT has a poor conductivity, and many efforts have been made to improve its conductivity.  
1303 One of the approach is the hydrogen reduction to obtain  $\text{Ti}_4\text{O}_7$  electrode. Prepared by the gas  
1304 mixture of  $\text{H}_2$  and  $\text{N}_2$  or Ar at high temperature,  $\text{Ti}_4\text{O}_7$  electrode was used for degradation of  
1305 organic pollutants because of its high conductivity and corrosion resistance. Geng et al. (2015)

1306 fabricated pure Magnéli Ti<sub>4</sub>O<sub>7</sub> NTA by reducing TiO<sub>2</sub>/NTA with hydrogen at 850 °C for 30  
1307 min [167]. The as-prepared NTA/Ti<sub>4</sub>O<sub>7</sub> had a highly-ordered tubular structure with high  
1308 crystallinity, large electrochemical window of water electrolysis (2.4 V/(Ag/AgCl at pH= 6.0))  
1309 and low Rct. This anode had a 20% higher COD removal than Ti<sub>4</sub>O<sub>7</sub>, and was even more  
1310 efficient than BDD and other types of Magnéli NTA. Wang et al. (2018) prepared Ti/Ti<sub>4</sub>O<sub>7</sub>  
1311 electrode by plasma spraying through reducing TiO<sub>2</sub> nanopowder [250]. They used it for the  
1312 degradation of tetracycline and obtained 95.8% of degradation efficiency in 40 min [250]. A  
1313 reactive electrochemical membrane (REM) composed of high purity Ti<sub>4</sub>O<sub>7</sub> was found to be  
1314 promising for water treatment applications. It achieved the highest convection-enhanced rate  
1315 constant for Fe(CN)<sub>6</sub><sup>4-</sup> oxidation in an electrochemical flow-through reactor [251]. Oturan's  
1316 group found that plasma elaborated sub-stoichiometric Ti<sub>4</sub>O<sub>7</sub> ceramic electrode could constitute  
1317 an alternative to BDD anode for a cost effective electro-oxidation process, and this electrode  
1318 was more efficient for paracetamol degradation in SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> media, but less  
1319 effective in Cl<sup>-</sup> medium [252,253]. Their other works on imatinib degradation by EF process  
1320 proved that the Ti<sub>4</sub>O<sub>7</sub> anode exhibited better mineralization performance than DSA and Pt  
1321 anode, reaching 82% TOC removal efficiency at 12.5 mA cm<sup>-2</sup> [254].

1322       • **Reduced TNT anode: Blue-TNA electrodes**

1323 The second approach to improve the conductivity of TNT is the electrochemical reduction into  
1324 Blue-TNT anode. During the electrochemical reduction of TNA, the color of TNA turns from  
1325 gray to blue, forming the so-called Blue-TNA, which has been explored as the anode for electro-  
1326 oxidation [105,255–260]. Kim et al. (2014) revealed that Blue-TNA exhibited excellent electro-  
1327 catalytic activity in generating chlorine and hydroxyl radicals, which was comparable to the  
1328 commercial DSA and BDD electrodes, respectively. Thus this Blue-TNA was suggested as a  
1329 potential cost-effective anodic material in industrial electrochemistry [261]. Chang et al. (2014)  
1330 investigated the performance of Blue-TNA for degradation of salicylic acid (SA) [262]. It



1331 possessed a much higher over-potential than Pt electrode for OER, exhibiting a 6.3 times higher  
1332 electrocatalytic activity toward SA oxidation. Stability tests indicated that Blue-TNA electrodes  
1333 were very stable during eight cycles of electrochemical oxidation of SA [262]. The high  
1334 electrocatalytic activity and stability of Blue-TNA enabled by the facile electrochemical  
1335 reduction can be attributed to the decrease of Ti(IV), the increase of Ti(II) and Ti(III) and the  
1336 increase of the oxygen vacancies, as well as significant improvement in the donor density. Cai  
1337 et al. (2019) prepared Blue-TNA having a higher  $\cdot\text{OH}$  production activity than BDD), inducing  
1338 a higher TOC and COD removal of phenol with a lower energy consumption of 9.9 kWh (kg  
1339 COD)<sup>-1</sup> [55].

1340

#### 1341 ***4.2.5. Mixed metal- / metal-oxide and carbon-based electrodes***

1342 Due to the fact that carbon-based materials are cheaper and more modular to be adapted to  
1343 specific reactor design, nanostructured metal or metal oxide deposited on the carbon material  
1344 would reduce the cost of metal-based material while the electrocatalytic activity would be  
1345 usually enhanced [263–266].

1346 For the carbon based metal electrodes, the commonly used one is Pt/C. Li et al. (2013) prepared  
1347 the Pt–Bi/C nanostructured electrode using square-wave potential method for the degradation  
1348 of MO dye, greatly reducing the energy consumption when compared with carbon fiber  
1349 electrode [263]. Besides, different supporting carbon materials significantly affect the  
1350 performance of the supported Pt nano-particles. Chen et al. (2010) compared single-walled  
1351 carbon nanotubes (SWNTs), MWNTs and Vulcan XC-72 carbon as the supporting carbon  
1352 materials to prepare Pt electrode [264]. It indicated that Pt/SWNTs exhibited the highest current  
1353 density, the lowest onset oxidation potential and the best stability for methanol electro-  
1354 oxidation [264].

1355 For the carbon-based metal oxide anodes, the mainly used one is RuO<sub>2</sub>-TiO<sub>2</sub> electrodes. Li et  
1356 al. (2018) prepared RuO<sub>2</sub>-TiO<sub>2</sub> nano-graphite electrode using sol-gel and hot press technology  
1357 for the degradation of ceftriaxone sodium, achieving a 97% removal efficiency which was much  
1358 higher than that on raw nano-graphite electrode (77%) [266]. Tsele et al. (2017) indicated that  
1359 the prepared TiO<sub>2</sub>-MWCNT and RuO<sub>2</sub>-MWCNT electrodes gave the best electron transport  
1360 properties towards the oxidation of epinephrine compared with MWCNT, RuO<sub>2</sub> and TiO<sub>2</sub>  
1361 electrodes [265].

## 1362 **5 Assessment of electrodes performance in water/wastewater**

### 1363 **treatment**

1364 The treatment at the source of water polluted by toxic/persistent micropollutants turns out to be  
1365 the most efficient and cost-effective way to avoid the contamination of natural water body  
1366 [7,267–269]. The so-called methods advanced oxidation processes (AOPs) have been  
1367 developed to offset the non-effectiveness of conventional treatment techniques to remove such  
1368 contaminants from water [9,33,270]. The AOPs are the processes based on the in situ generation  
1369 of strong oxidants (mainly the hydroxyl (\*OH) radicals) under mild conditions [271]. The  
1370 EAOPs were emerged during last decades as among the most efficient processes for the  
1371 degradation of persistent organic micropollutant [8,16,34,272,273].

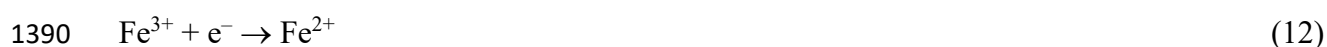
#### 1372 **5.1. Electro-Fenton process**

1373 Among the EAOPs, the electro-Fenton (EF) process has become a popular electrochemical  
1374 process for effective destruction of organic pollutants [7,273].

1375 EF is an indirect EAOPs; it originates from Fenton's chemistry, which constitutes a chemical  
1376 way to produce \*OH in acidic medium from activation of H<sub>2</sub>O<sub>2</sub> by ferrous iron, via the Fenton  
1377 reaction (Eq. 2) [274,275]. Although the Fenton process has been applied to the treatment of

1378 industrial wastewater since the 1980s, the presence of several inconveniences (use of large  
1379 amount of chemicals, the generation of process sludge, low efficiency due to the involvement  
1380 of parasitic reactions) disadvantaged its development [267,276,277]. Therefore, the EF process  
1381 has been implemented and developed in the late 1990s in two versions; gas diffusion cathode  
1382 (Brillas' team) and CF cathode (Oturán's team) to overcome the major drawbacks of  
1383 conventional Fenton process [278,279].

1384 The main features of EF process are the continuous electrogeneration of H<sub>2</sub>O<sub>2</sub> in the solution  
1385 to be treated from electroreduction of DO (Eq. 1), avoiding the cost and risks associated to the  
1386 production, transport and storage of H<sub>2</sub>O<sub>2</sub> and the electro-regeneration of the catalyst (Fe<sup>2+</sup>)  
1387 (Eq. 12), avoiding thus the formation and management of process sludge. Therefore, reactions  
1388 (1), (2) and (12) ensure a permanent catalytic production of <sup>•</sup>OH, allowing destruction of  
1389 organic micropollutants [7,280,281].



1391 The in situ generation of H<sub>2</sub>O<sub>2</sub> in a controlled way by the application of an appropriate current  
1392 or potential to the electrochemical reactor is one of the main characteristics of the EF process.  
1393 Therefore, the use of suitable cathode materials is primordial. The first cathode materials used  
1394 in this process to produce H<sub>2</sub>O<sub>2</sub> were mercury pool [282], carbon-PTFE-O<sub>2</sub> gas diffusion  
1395 cathode [278]. Then 3D carbonaceous materials such as CF [280], carbon sponge [124,283],  
1396 activated carbon fiber [284], graphite [285,286], [287] and graphene foam were introduced and  
1397 applied as a cathode in the EF process. Indeed, carbon-based cathodes are material of interest  
1398 as discussed in sections 2.1, 3.1 and 4.1, especially because of their large H<sub>2</sub> evolution  
1399 overpotential, good electrical conductivity stability and low cost. Recently, modified carbon-  
1400 based materials [254,288–291] in which iron ions incorporated were successfully used to  
1401 perform the heterogeneous EF process in mild pH conditions. The development and use of CNT  
1402 composite cathodes [292,293] or graphene-based cathodes [156,294] constitutes new trends in

1403 EF process. For instance, Yang et al. (2019) [156] reported strongly high concentration (400  
1404 mg L<sup>-1</sup>) of H<sub>2</sub>O<sub>2</sub>, using CF modified with electrochemically exfoliated graphene (EEGr)  
1405 cathode compared to the raw CF cathode (400 mg L<sup>-1</sup>). Once produced, H<sub>2</sub>O<sub>2</sub> reacts with Fe<sup>2+</sup>  
1406 ion to produce <sup>•</sup>OH, which is a nonselective strong oxidant and is able to oxidize any organic  
1407 pollutants [10,254,295]. The Fe<sup>2+</sup> ion is externally added at a catalytic amount (mostly in sulfate  
1408 salt) and regenerated in the process through Fe<sup>3+</sup>/Fe<sup>2+</sup> cycle. Therefore, there is no accumulation  
1409 of the following wasting reactions (Eqs. 13 and 14) of the Fenton process because they occur  
1410 at high H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> concentrations, respectively:



1413 Moreover, this process has other practical advantages such as easy handling,  
1414 degradation/mineralization efficiency, amenability and versatility since it can be applied to  
1415 effluents with a large range of organic matter [7,273,290,296].

1416 The nature of anode material is also of great importance in the EF process efficiency. In fact,  
1417 by using an appropriate anode (M) material, the anodic oxidation processes can be incorporated  
1418 into the EF process. In this case, there is production of supplementary hydroxyl radicals M(<sup>•</sup>OH)  
1419 on the surface of the anodes from oxidation of water (Eq. 15), increasing thus the process  
1420 efficiency.

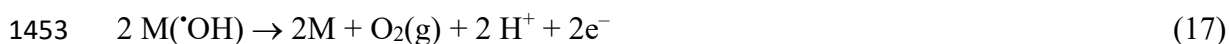


1422 The extent of the contribution of the heterogeneous hydroxyl radicals, M(<sup>•</sup>OH), to the EF  
1423 process efficiency is directly related to the anode material. In the case of active anodes, i.e., Pt,  
1424 DSA, M(<sup>•</sup>OH) are strongly adsorbed on the anode surface and therefore less available for  
1425 reacting with organic pollutants [7,267]. In contrast, M(<sup>•</sup>OH) generated on non-active anodes  
1426 (BDD, PbO<sub>2</sub>, Ti<sub>4</sub>O<sub>7</sub>) are loosely adsorbed on the surface and are more available for participating

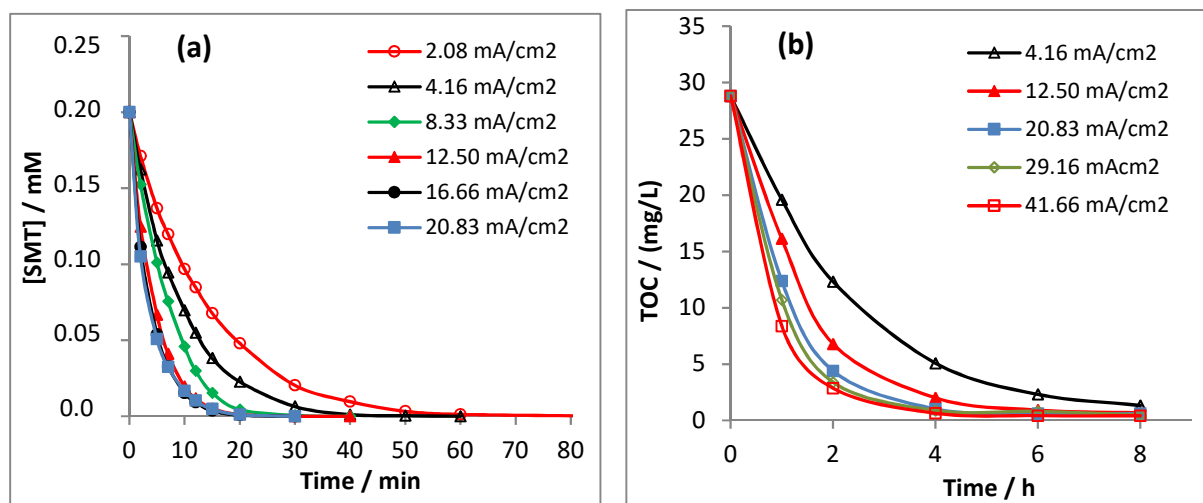
1427 in the oxidative degradation/mineralization of organic pollutants [197,252,297,298].  $M(\cdot\text{OH})$   
1428 generated from the latter kind of anodes are particularly efficient for the mineralization of  
1429 carboxylic acids resistant to homogeneous  $\cdot\text{OH}$ . Nanostructured materials have also been  
1430 developed for enhancing the oxidation of pollutants at the anode, as discussed in the next section  
1431 (5.2).

1432 Apart from electrode material, several operating parameters such as solution pH, applied  
1433 current, catalyst nature and concentration, electrolyte composition, etc., influence the EF  
1434 efficiency for the removal of organics from water [7]. The optimal value of some of these  
1435 parameters, such as the solution pH value (around 3), nature and concentration of the electrolyte  
1436 (0.05 M  $\text{Na}_2\text{SO}_4$ ) for the CF version and catalyst nature and concentration (about 0.1 mM  $\text{Fe}^{2+}$ )  
1437 are now well-known [8,299,300]. The inconvenient of working at pH 3 can be overcome using  
1438 the heterogeneous EF process as explained above or by using solid catalysts such as pyrite, iron  
1439 oxides (magnetite, goethite, hematite) and MOF derived composite catalysts [301–305].

1440 Since EF is an electrochemical process, the current (undivided cell) or potential (divided cell)  
1441 applied to the cell are obviously of great importance for the process efficiency because these  
1442 parameters directly affect the rate of  $\text{H}_2\text{O}_2$  generation (Eq. 1), the rate of regeneration of  $\text{Fe}^{2+}$   
1443 (Eq. 12) and consequently the rate of formation of  $\cdot\text{OH}$  (Eq. 14) [285,306–308]. It influences  
1444 also strongly the production of  $M(\cdot\text{OH})$ , particularly at low currents [7,309,310]. In general,  
1445 oxidation/mineralization efficiency increases with rising the current up to an optimal value for  
1446 which parasitic reactions (HER at the cathode and/or  $\text{O}_2$  evolution reaction at the anode) start  
1447 to harm the efficiency of the process. High currents above this optimal value can also lead to  
1448 the enhancement of wasting reactions given in Eqs. 16 and 17. This situation also conducts to  
1449 lower current efficiency and increases energy consumption [8,123,311–314]. An example of  
1450 the effect of current on the oxidation efficiency of the antibiotic sulfamethazine and TOC  
1451 removal rate of its aqueous solution is depicted in Fig. 22.



1454 Therefore, to reach a high oxidation efficiency, MCE and low energy cost, the EF process  
 1455 should be conducted under optimized conditions: optimal current, suitable electrodes (anode  
 1456 and cathode), solution pH near 3 (for homogeneous process), suitable catalyst nature ( $\text{Fe}^{2+}$ ) and  
 1457 concentration, air/ $\text{O}_2$  flow rate to saturate the solution to be treated and high stirring rate (batch  
 1458 reactor) or liquid flow rate (flow reactor) [7,272,273,313]. The electrolyte composition is also  
 1459 important, since chloride and ammonia ions can lead to the formation of chlorinated and  
 1460 nitrogen intermediates that can be unwanted (e.g. chlorate, nitrate, etc.) [315,316]. Considering  
 1461 the high numbers of influent parameters, the modeling of the EF process is not easy. However,  
 1462 an interesting kinetic modeling for mineralization route of phenol, including the formation of  
 1463 several intermediates and their successive oxidation steps until complete mineralization was  
 1464 recently carried out by Mousset et al. (2016) [317].



1465  
 1466 **Figure 22.** Effect of applied current density on (a) the decay kinetics and (b) TOC removal  
 1467 efficiency during EF treatment of 0.2 mM ( $57.5 \text{ mg L}^{-1}$ ) of 300 mL sulfamethazine solution in  
 1468 0.05 M  $\text{Na}_2\text{SO}_4$  solution at pH 3 and room temperature using the BDD anode/graphite felt  
 1469 cathode. Reprinted with permission from Sopaj et al., 2016 [248]. Copyright 2016 Elsevier.

1470

## 1471 **5.2. Advanced electro-oxidation process**

1472 Advanced electro-oxidation processes are based on the development of suitable anode materials  
1473 for promotion of the oxidation of organic pollutants. Various mechanisms can be involved as  
1474 thoroughly described in section 2.2. Direct electron transfer can occur at the electrode-solution  
1475 interface, thus resulting in selective oxidation of some organic compounds. Anode materials  
1476 with high overvoltage for OER can also generate physisorbed hydroxyl radicals ( $\cdot\text{OH}$ ) (Eq. 19)  
1477 from the one-electron oxidation of water [9,33]. These radicals are available for reaction with  
1478 organic compounds in a non-selective way, but they are accumulated only in a thin layer close  
1479 to the anode surface ( $<1.0\ \mu\text{m}$ ) because of their short lifetime [318]. The formation of sulfate  
1480 radicals ( $\text{SO}_4^{\cdot-}$ ), known as very powerful oxidant species, have also been reported in the  
1481 literature [9,55] during the electro-oxidation process when using sodium sulfate as electrolyte.  
1482 Besides, mediated oxidation in the bulk solution can be promoted depending on the reaction of  
1483 inorganic compounds in the solution to treat. Particularly, the formation of active chlorine from  
1484 oxidation of chloride ions as well as persulfate (that can be then further activated to sulfate  
1485 radicals) from oxidation of sulfate ions are usually the most predominant mechanisms of  
1486 mediated oxidation of organic compounds in the bulk [9,319]. The reactivity of nanostructured  
1487 electrodes and their ability to promote these different reaction mechanisms tightly depend on  
1488 their chemical characteristics, as described in section 4. Another important parameter is the  
1489 electro-active surface area of anode materials to favour reactions with organic pollutants at the  
1490 electrode-solution interface. Nano-structured electrodes present a key advantage in this area.

1491 The advanced electro-oxidation process also faces the problem of mass transport of organic  
1492 pollutants from the bulk to the anode surface [24,33,251,320,321]. As a result of the fast kinetic  
1493 processes at the anode surface, treatment systems using electrodes in parallel plate  
1494 configuration are usually limited by the diffusion of organics to the electrode surface,  
1495 particularly for treating low concentrations of pollutants. The diffusion boundary layer is

1496 usually in the range of 10 – 100  $\mu\text{m}$ . Thus, features of nanostructured electrode roughness are  
1497 smaller than the diffusion length and become averaged into the diffusion field [322]. The use  
1498 of nanostructured electrode in flow-through configuration is therefore a key parameter to really  
1499 take advantage of their high electro-active surface area. In fact, electro-oxidation is strongly  
1500 enhanced because of the fast mass transport inside small pores as well as the possibility to  
1501 increase the convective mass transport by simply increasing the filtration flux [251,323].

1502 The Table 2 gives an overview of the efficiency of advanced electro-oxidation process using  
1503 nanostructured electrodes. Two groups of materials have been mainly investigated. First,  
1504 several studies have focused on the use of materials based on CNTs. This kind of nanostructured  
1505 material present several advantages including high conductivity, large specific surface area (50  
1506 – 1000  $\text{m}^2 \text{g}^{-1}$ ) and good mechanical strength [323]. Both sorption and oxidation mechanisms  
1507 have to be taken into consideration in order to explain the removal of organic pollutants from  
1508 water. CNT-based electrodes have been mainly used in flow-through configuration. Most of  
1509 CNT-based electrochemical filters are made of a thin layer (e.g., 41  $\mu\text{m}$ ) of randomly oriented  
1510 multi-walled CNT supported by a porous membrane (e.g., PTFE membrane). Small pore size  
1511 can be obtained depending on the nature of CNT. For example, the average pore size was 115  
1512  $\pm 47$  nm by using CNT of 15 nm diameter and 100  $\mu\text{m}$  of length [323]. Thus, convection-  
1513 enhanced mass transport combined with fast mass transport inside the CNT network can result  
1514 in very fast degradation of target compounds. A single passage through the CNT network with  
1515 a flow rate of 130  $\text{L m}^{-2} \text{h}^{-1}$  (resulting in a residence time in the filter of  $\tau \leq 1.2$  s) was able to  
1516 achieve 80% degradation of 89  $\text{mg L}^{-1}$  of tetracycline with a total cell potential of 2 V [183].  
1517 Most importantly, the energy consumption of advanced electro-oxidation can be significantly  
1518 improved. For example, energy consumption below 1.0  $\text{kWh m}^{-3}$  or even below 0.1  $\text{kWh m}^{-3}$   
1519 was reported (Table 2). However, CNT-based electrodes also present some critical drawbacks.  
1520 CNTs are usually operated under very low current density or anodic potential (Table 2) in order



1521 to avoid corrosion. For example, corrosion of uncoated CNT was reported to start from 1.4  
1522 V/(Ag/AgCl) [189]. CNTs also present low overpotential for OER (active electrode), thus  
1523 limiting the generation of nonselective oxidizing species such as  $\cdot\text{OH}$ . The OEP of uncoated  
1524 CNT was, for example, 1.27 V/(Ag/AgCl) in 0.5 M  $\text{H}_2\text{SO}_4$  [189]. By comparison, the OEP of  
1525 BDD (gold standard for advanced electro-oxidation) is around 2.1 V/(Ag/AgCl). As a  
1526 consequence, CNT-based electrodes present selective oxidation features. While fast  
1527 degradation of target pollutants is usually reported, only partial mineralization is achieved  
1528 because of the recalcitrance of some degradation by-products. One of the most explored ways  
1529 to improve the effectiveness of CNTs is to synthesize modified CNTs (e.g., chemical surface  
1530 modification, incorporation of Bi-doped  $\text{SnO}_2$  NPs) in order to increase the overvoltage of OER  
1531 or to promote interaction (particularly adsorption) between the electrode surface and target  
1532 pollutants. For example, negligible corrosion was obtained up to 2.2 V/(Ag/AgCl) and the OEP  
1533 was increased to 1.71 V/(Ag/AgCl) by using a Bi-doped  $\text{SnO}_2$ -coated CNT network [189].

**Table 2.** Overview of the efficiency of advanced electro-oxidation processes for the removal of organic pollutants reported in recent studies using nano-structured electrode materials.

Anode	Cathode	Operating conditions								Treated solution		Process efficiency					Ref	
		P/G	CD <i>mA cm<sup>-2</sup></i>	An. Pot. <i>V/(Ag/AgCl)</i>	Cell Pot. <i>V</i>	An. Surface <i>cm<sup>2</sup></i>	Batch (Volume) <i>mL</i>	S/V <i>cm<sup>-1</sup></i>	Flow-through (flux) <i>L m<sup>-2</sup> h<sup>-1</sup></i>	Pollutant C <i>mg L<sup>-1</sup></i>	Electrolyte C <i>mM</i>	Deg. / Time <i>% / h</i>	k <sub>app</sub> <i>min<sup>-1</sup> (x10<sup>2</sup>)</i>	Min. / Time <i>% / h</i>	MCE <i>%</i>	EC <i>kWh m<sup>-3</sup></i> <i>kgCOD<sup>-1</sup></i>		
CNT	CNT	P	-	-	10	28	-	-	1700	X-3B 50	-	94 / 1.5	-	58 / 1.5	26	-	150	[324]
Modified CNT	SS	P	-	-	2	-	-	-	-	MO 327	Na <sub>2</sub> SO <sub>4</sub> 100	70 / SP	-	-	-	0.22	4	[172]
			-	-	3	7	-	-	130	Phenol 97		-	-	20 / SP	-	-	-	
CNT/Bi-doped SnO <sub>2</sub> NP	SS	G	1.4	<1.1	2.7	-	-	-	-	Oxalate 367	Na <sub>2</sub> SO <sub>4</sub> 10	50 / SP	-	50 / SP	100	-	5 (TOC)	[189]
			8.6	2	4.3	7	-	-	130	95 / SP		-	95 / SP	30	-	30 (TOC)		
CNT/Graphene	Ti	P	0.4	0.8	2.5	7	-	-	130	Phenol 51	real reservoir water	76 / SP	-	Partial	-	0.075	1.9	[177]
CNT	CNT	P	1	-	2	7	-	-	130	Tetracycline 89	Na <sub>2</sub> SO <sub>4</sub> 10	80 / SP	-	Partial	-	0.084	-	[183]
Carboxylated CNT	Ti	P	-	0.9	2	9.5	-	-	130	Ibuprofene 20	NaCl 10	75 / SP	-	Partial	-	-	-	[325]
CNT/PANI UF membrane	Ti	P	0.17	-	3	4	40	0.1	-	MB 5	Cl from MB salt	32 / 1	-	-	-	-	-	[326]
			-	1.7	-	-	-	-	20	85 / SP	-	-	-	2.5	-			
BDD/Sb-doped SnO <sub>2</sub> NP	Ti	G	20	-	-	1.2	Batch	-	-	2,4-D 100	Na <sub>2</sub> SO <sub>4</sub> 100	98.5 / 2	-	82.2 / 2	19.8	3.3	-	[327]

<b>Ti/Sb-doped SnO<sub>2</sub> modified with CNT</b>	Ti	G	50	-	-	8	150	0.05	-	AR 73 1000	Na <sub>2</sub> SO <sub>4</sub> 100	96 / 3	1.6	80 / 3	58	-	121	[241]
<b>TNT/Fe-doped PbO<sub>2</sub></b>	Ti	G	-	-	-	5	100	0.05	-	p- nitrophenol 50	Na <sub>2</sub> SO <sub>4</sub> 30	90 / 1	6.9	-	-	-	280	[328]
<b>TNT</b>	Pt	G	5	-	-	1	-	-	-	Salicyclic acid 30	H <sub>2</sub> SO <sub>4</sub> 100	-	11.5	-	-	-	-	[262]
<b>TNT/PbO<sub>2</sub></b>	Ti	G	10	-	-	5	100	0.05	-	p- nitrophenol 50	Na <sub>2</sub> SO <sub>4</sub> 30	82 / 3	-	42 / 3	-	9.5	-	[329]
<b>Nano-graphite/TiO<sub>2</sub>-RuO<sub>2</sub></b>	Ti	P	-	-	2	-	40	-	-	Ceftriaxone 10	Na <sub>2</sub> SO <sub>4</sub> 100	90 / 1.7	-	-	-	-	-	[330]
<b>Ti<sub>4</sub>O<sub>7</sub> NT</b>	Ti <sub>4</sub> O <sub>7</sub> NT	G	2.5	-	-	-	Batch	-	-	Phenol 100	Na <sub>2</sub> SO <sub>4</sub> 100	85 / 2	1.5	95 / 3	43	-	-	[167]
<b>TNT/Sb-doped SnO<sub>2</sub></b>	SS	G	10	-	-	5	100	0.05	-	Phenol 50	Na <sub>2</sub> SO <sub>4</sub> 100	70 / 2	1	-	-	-	-	[244]
<b>Blue TNT</b>	Blue TNT	G	5	-	5.2	6	Batch	-	-	Wastewater 330 (COD)	-	-	-	60 / 2	-	-	150	[331]
<b>Ti<sub>4</sub>O<sub>7</sub></b>	SS	P	-	2.65	-	0.35	-	-	789	Terephthalic acid 16.6	NaClO <sub>4</sub> 100	60 / SP	-	-	-	-	-	[332]
<b>Blue TNT</b>	SS	G	2.5	-	-	3	100	0.05	-	Phenol 100	Na <sub>2</sub> SO <sub>4</sub> 100	97 / 5	0.7	60 / 5	90	-	9.9	[55]

2,4-D: 2,4-dichlorophénoxyacétique ; An. Pot.: anodic potential; An. Surface: geometric anodic surface ; AR 73 : acid red 73 ; C: concentration ; CD: current density ; Cell Pot.: cell potential ; CNT: carbon nanotube ; COD : chemical oxygen demand ; Deg.: degradation ; EC : energy consumption ; G: galvanostatic ; k<sub>app</sub> : apparent degradation rate constant ; MB : methylene blue ; MCE : mineralization current efficiency ; Min.: mineralization ; MO : methyl orange ; NP: nanoparticles ; NT: nanotube ; P: potentiostatic ; PANI : polyaniline ; S: surface ; SP : single passage ; TNT: TiO<sub>2</sub> nanotube ; TOC : total organic carbon ; UF : ultrafiltration ; V: volume ; X-3B : reactive brilliant red

1534 The second group of materials is those having high overvoltage for OER, also called as non-  
1535 active electrodes. Materials based on TiO<sub>2</sub> NTA have been mostly studied. They present an  
1536 interesting nanostructuration for the application in water treatment. For example, by following  
1537 a conventional anodization method, TiO<sub>2</sub> NTA obtained by [55] presented a length of  
1538 approximately 15 μm, a diameter of 100 nm and a tube wall of 54 nm. However, anatase TiO<sub>2</sub>  
1539 NTA present a very low conductivity [261]. One of the strategies for solving this issue is the  
1540 deposition of conductive metal oxide layer. IrO<sub>2</sub> and RuO<sub>2</sub> layers resulted in the formation of  
1541 active anodes with low overpotential for OER, while a layer of PbO<sub>2</sub> and SnO<sub>2</sub> (with possible  
1542 addition of doping agents such as Sb) can form non-active anodes with high overpotential for  
1543 OER. Therefore, these latter are able to generate nonselective oxidants such as M(<sup>•</sup>OH) and  
1544 both degradation and mineralization of complex organic compounds can be achieved as  
1545 reported in Table 2. Another strategy for improving the reactivity and stability of TNT arrays  
1546 comes from the synthesis of Blue and Black TiO<sub>2</sub> NTA from cathodic polarization and  
1547 reduction of a variable number of Ti(IV) sites to Ti(III). By comparison with Magnéli phases  
1548 obtained from high temperature thermal processes, cathodic polarization might be more a cost-  
1549 effective method. These materials are able to generate both <sup>•</sup>OH and SO<sub>4</sub><sup>•-</sup> radicals [55,331],  
1550 thus resulting also in high mineralization rate of organic compounds (see Table 2). However,  
1551 none studies have been reported on the use of electrodes based on TiO<sub>2</sub> NTA in flow-through  
1552 configuration. Advanced electro-oxidation in batch configuration is therefore limited by the  
1553 mass transport of organic compounds through the diffusion boundary layer. Therefore, such  
1554 nanostructured electrodes do not significantly improve energy consumption of advanced  
1555 electro-oxidation and become only cost-effective for treating concentrated effluents. As regards  
1556 to non-active electrodes, only sub-stoichiometric titanium oxide (TiO<sub>x</sub>) electrodes have been  
1557 successfully applied in flow-through configuration. Most of recent studies have focused on  
1558 microstructured materials with pore size in the range 1 – 5 μm [251,322,333], however Nayak

1559 and Chaplin (2018) [332] also showed that nanostructuring of such materials (using a simple  
1560 chemical etching step) was also able to increase the rate of oxidation of probe molecules such  
1561 as oxalic acid or terephthalic acid.

1562 Overall, CNT-based electrodes operated in flow-through configuration are promising materials  
1563 for improving the energy consumption of advanced electro-oxidation because of the high  
1564 electro-active surface area and suitable properties for optimization of mass transport of organic  
1565 pollutants at the electrode/solution interface. A high degradation rate of organic pollutants can  
1566 be achieved after only a single passage through such electrochemical filter. The main drawback  
1567 of these electrodes is their low overvoltage for OEP that reduces their capacity for generation  
1568 of nonselective oxidant species and results in selective oxidation of organic compounds and  
1569 low mineralization rate. By comparison, electrodes based on TiO<sub>2</sub> NTA arrays or TiO<sub>x</sub> are able  
1570 to achieve a higher mineralization rate of complex organics, thanks to the generation of  
1571 hydroxyl and/or sulphate radicals. However, further studies are required on the implementation  
1572 of such nanostructured electrodes in flow-through configuration in order to avoid mass  
1573 transport limitations.

1574 For all nanostructured electrodes used in advanced electro-oxidation, two important challenges  
1575 can be highlighted. The first one is related to the development of methods for synthesizing large  
1576 geometric surface area to scale-up such processes. Most of data reported in the literature have  
1577 been obtained with electrodes presenting a geometric surface area in the range of 3 to 9 cm<sup>2</sup>  
1578 (Table 2). The second challenge is related to the lifetime of these electrodes. The optimization  
1579 of the synthesis method [331], surface modification [172] and the addition of doping agents  
1580 [189] have been mainly studied for improving corrosion resistance and lifetime. However, in  
1581 the case of TiO<sub>2</sub> NTA-based and TiO<sub>x</sub> electrodes, a promising strategy for the regeneration of  
1582 the oxidation capacity might also be the implementation of sequential cathodic polarization  
1583 [331,334].

### 1584 **5.3. Solar/artificial light induced photo-electrocatalytic processes**

1585 As reported previously, organic pollutants can be electrochemically oxidized through different  
1586 pathways. Solar or artificial light represents an additional source of energy allowing the  
1587 generation of further oxidant species. The main pathways of degradation of organic pollutants  
1588 during photochemical processes include, (i) direct photolysis and (ii) reaction with  $\cdot\text{OH}$   
1589 generated from PC when using a suitable photocatalyst. Photoelectrocatalytic processes can be  
1590 implemented either in sequential reactors or in hybrid reactors where photochemical and  
1591 electrochemical mechanisms are combined into a single reactor. This latter type of reactor  
1592 allows for the promotion of synergistic effects and is therefore the focus of most of recent  
1593 studies [296,335–341].

1594 The photoelectro-Fenton (PEF) has been developed to obtain a more efficient process, mainly  
1595 by Brillas and coworkers and great results have been obtained for the degradation and  
1596 mineralization of organic compounds [335,337]. It is based on the application of the EF process  
1597 as described in section 5.1 but with an additional source of energy from artificial or solar light.  
1598 Therefore, as described previously, nanostructured materials can be mainly used for the  
1599 enhancement of the  $\text{H}_2\text{O}_2$  production at the cathode or for improving the reactivity of the iron  
1600 source when using heterogeneous catalysts. The main synergistic effects induced from the  
1601 artificial/solar light is related to the photolysis of Fe(III)-monohydroxy complex under UVA  
1602 irradiation that leads to the formation of additional  $\cdot\text{OH}$  and the enhanced regeneration of Fe(III)  
1603 into Fe(II) (Eq. 18).



1605 Therefore, faster degradation and mineralization kinetics are observed compared to the EF  
1606 process. Several authors have also proposed various reactor designs for pre-industrial  
1607 applications using the well-known CF or gas-diffusion carbon cathodes [342,343]. Compared

1608 to the EF process, reactor design must also take into consideration the optimization of the  
1609 irradiation of the solution.

1610 There are also several different ways to combine electrochemical and photochemical processes.  
1611 EAOPs can also be implemented as described in sections 5.1 and 5.2, while, in addition, a  
1612 photocatalytic material as well as artificial or solar light is provided to the system. Such  
1613 treatment strategies allow the formation of additional oxidant species by combining different  
1614 pathways for the generation of oxidant species into a single reactor [227,339,344].  
1615 Nanostructured materials can therefore be used for improving the effectiveness of each single  
1616 pathway. Various synergistic effects can also take place such as the formation of  $\cdot\text{OH}$  by  
1617 homolytic cleavage of electrochemically generated  $\text{H}_2\text{O}_2$  or photoactivation of other  
1618 electrochemically generated species such as  $\text{S}_2\text{O}_8^{2-}$  into sulfate radicals or  $\text{HClO}$  into chloride  
1619 and hydroxyl radicals [339,345]. A particular attention must also be given to the reactor design  
1620 in order to be able to promote all the different pathways at the same time. For example, the use  
1621 of transparent electrode materials (e.g. fluorine-doped  $\text{SnO}_2$ ) has been proposed for improving  
1622 light irradiation inside the reactor [227].

1623 Interestingly, it is also possible to combine electrochemical and photochemical processes by  
1624 using a single material playing the role of both photocatalyst and electrode. These photo-  
1625 electrocatalytic (PEC) processes aim at reducing charge recombination occurring during PC by  
1626 coating the photocatalytic material on a so-called photo-anode. Thus, both photocatalytic and  
1627 electrooxidation processes can take place at the same time with high synergistic effects. In this  
1628 area, several nanostructured materials have been recently developed in order to increase the  
1629 reactive surface area of the heterogeneous photo-electrocatalysts. An overview of the  
1630 effectiveness of the PEC process using nanostructured materials is given in Table 3. The  
1631 synergistic effects occurring during PEC have been highlighted in several publications  
1632 comparing the effectiveness of PC, electro-oxidation and PEC. For example, using blue- $\text{TiO}_2$

1633 nanotubes as photo-anode for the degradation of  $100 \mu\text{g L}^{-1}$  of 4-chlorophenol at anodic  
1634 potential of  $1.43 \text{ V}/(\text{Ag}/\text{AgCl})$  ( $\text{KCl}$ ,  $3 \text{ M}$ ) during 2 h, standalone electrooxidation and PC only  
1635 achieved  $<5\%$  and  $30\%$  degradation, respectively, while PEC achieved  $>99\%$  abatement of 4-  
1636 chlorophenol [346]. In an another example, RGO-polyaniline/ $\text{TiO}_2$  was used as photo-anode for  
1637 the degradation of  $10 \text{ mg L}^{-1}$  of phenol at anodic potential of  $1.03 \text{ V}/(\text{Ag}/\text{AgCl})$  ( $\text{KCl}$ ,  $3 \text{ M}$ )  
1638 during 8 h; standalone electrooxidation and PC only achieved  $68\%$  and  $42\%$  degradation,  
1639 respectively, while PEC achieved  $>99\%$  degradation [347]. The Table 3 highlights also some  
1640 important trends on the way to implement PEC as well as on the effectiveness of this process.  
1641 Degradation kinetics reported in the literature are usually lower than the ones reported for  
1642 advanced electro-oxidation. First-order apparent degradation kinetics reported in the literature  
1643 are usually in the range  $0.4 - 3 \text{ min}^{-1}$  and more than one hour of treatment is usually required  
1644 for achieving  $90\%$  degradation of the target pollutant. Complete mineralization of organic  
1645 pollutant is not always reported but several studies have shown promising results with more  
1646 than  $80\%$  of TOC removal in a few hours. It is also interesting to highlight that PEC has been  
1647 mainly implemented using anodic potential in the range  $0.5 - 1.5 \text{ V}/(\text{Ag}/\text{AgCl})$ . These values  
1648 are lower than anodic potentials usually reported for advanced electro-oxidation. In fact, the  
1649 generation of hydroxyl radicals from water oxidation at the surface of electrodes with high  
1650 overpotential for OER requires performing electro-oxidation in the potential region of water  
1651 discharge. Similarly, low current density (in the range  $0.1 - 5 \text{ mA cm}^{-2}$ ) is usually used for  
1652 performing experiments under galvanostatic conditions. Performing electrochemical processes  
1653 at low current density/potential is usually beneficial for lowering the energy consumption.  
1654 However, such data are still very rare in the literature. Ding et al. (2014) [348] reported high  
1655 MCE ( $47\%$ ), which seems to confirm the potential high energy-efficiency of PEC. It is also  
1656 important to note that mainly potentiostatic experiments in small-scale stirred batch reactors  
1657 have been performed for testing the effectiveness of this emerging process. It is therefore



1658 currently difficult to assess the potential of PEC for full-scale applications. Besides, mass  
1659 transport limitations related to the transfer of pollutants from the bulk to the photo-electrode  
1660 could also be further investigated in order to improve the effectiveness of PEC.

1661 Very interesting results have also been obtained by combination of PEC and PEF using either  
1662 a homogeneous or heterogeneous iron source. This treatment strategy seems very promising  
1663 since it allows the combination of the synergistic effects from both electro-Fenton/PC and  
1664 electrooxidation/PCs. Compared to PEC, PEC/PEF process allows a strong increase of  
1665 degradation kinetics. For example, Hernandez et al. (2018) reported 57% and >99%  
1666 degradation of 78.6 mg L<sup>-1</sup> of paracetamol by using PEC and combined PEC/PEF processes,  
1667 respectively [349]. Thus, degradation kinetics are usually much more rapid for PEC/PEF  
1668 compared to PEC. Complete degradation of the target pollutants are usually reported in less  
1669 than 1 h. Furthermore, high MCE can be achieved, as reported by [340], who achieved 84.6%  
1670 to TOC removal with a quiet high MCE of 87.6% during the treatment of Indigo Carmine dye  
1671 solution.

1672 A new PEF system using a superhydrophobic natural air diffusion electrode (NADE) for the  
1673 fast H<sub>2</sub>O<sub>2</sub> production (101.67 mg h<sup>-1</sup> cm<sup>-2</sup>) and high oxygen utilization efficiency (44.5%-  
1674 64.9%) without external oxygen-pumping equipment was suggested [50]. In this system,  
1675 organic contaminants can be efficiently destroyed by the combined action of Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>,  
1676 UV/H<sub>2</sub>O<sub>2</sub> and UV radiation to reach high mineralization rate (>83.5%) at low current (50 mA).  
1677 In addition, the use of the NADE in EAOPs significantly reduced energy consumption  
1678 compared with aeration system [111].

1679 .

**Table 3.** Overview of the efficiency of nanostructured materials for photo-electrocatalytic (PEC) processes and combined photo-electrocatalytic / photo-electro-Fenton (PEC / PEF) processes

Process	Anode Surface (cm <sup>2</sup> )	Cathode Surface (cm <sup>2</sup> )	Operating conditions										Treated solution		Process efficiency				Ref
			Light source	Light intensity W m <sup>-2</sup>	P/G	CD mA cm <sup>-2</sup>	An. Pot. V/(Ag/AgCl)	Cell Pot. V	pH	[Fe <sup>2+</sup> ] mM	V mL	S/V cm <sup>-1</sup>	Pollutant mg L <sup>-1</sup>	Electrolyte mM	Deg. / Time % / h	k <sub>app</sub> min <sup>-1</sup> (×10 <sup>2</sup> )	Min. / Time % / h	MCE %	
PEC	Indium SnO <sub>2</sub> 15	-	Hg lamp	-	P	-	0.545	-	5.25	0	15	1	Direct Yellow 42 6.8	NaCl 500	90 / 2	1.02			[350]
PEC	CNT/TiO <sub>2</sub> 2.5	Quartz 4.9	UVC	65	P	-	0.8	-	-	0	50	0.05	Methylene blue 5	NaCl 100	55 / 3	-			[351]
PEC	TiO <sub>2</sub> nanopore	Pt	UVC	25	P	-	0.5	-	5.5	0	20	-	Tetracycline 20	Na <sub>2</sub> SO <sub>4</sub> 20	80 / 3	0.93			[352]
PEC	Bi <sub>2</sub> MoO <sub>6</sub> / BDD 10	Pt	Xe lamp	250	P	-	2.045	-	-	0	100	0.1	Naproxen 15	Na <sub>2</sub> SO <sub>4</sub> 100	85 / 6		78 / 6		[353]
PEC	ZnWO <sub>4</sub> / BDD 11	Pt	Xe lamp	200	P	-	2.045	-	-	0	60	0.18	Red X-3B 30	Na <sub>2</sub> SO <sub>4</sub> 100	95 / 3				[354]

PEC	TiO <sub>2</sub> 25	Pt	Hg lamp	27.3	G	0.4	-	-	2	0	1000	0.025	Indigo Carmine 24	Na <sub>2</sub> SO <sub>4</sub> 100	99 / 0.5	3	75 / 6	75	[355]
PEC	TiO <sub>2</sub> NTA	Pt	Hg lamp	-	P	-	0.645	-	-	0	60	-	Methyl orange 10	Na <sub>2</sub> SO <sub>4</sub> 100	58 / 3	0.49			[356]
PEC	WO <sub>3</sub> / TiO <sub>2</sub> 1	Pt	Xe lamp	-	P	-	1	-	2	0	30	0.033	Indigo Carmine 24	Na <sub>2</sub> SO <sub>4</sub> 100	96 / 2	1.13	62 / 2		[357]
PEC	B-doped TiO <sub>2</sub> NTA 25	Ti/Ru	Hg lamp	-	P	-	1.2	-	2	0	500	0.05	Acid Yellow 1	Na <sub>2</sub> SO <sub>4</sub> 10	95 / 1	2.35	95 / 2		[221]
PEC	Reduced TiO <sub>2</sub> NTA 4	-	Xe lamp	-	P	-	0.445	-	-	0	80	0.05	diclofenac 5	Na <sub>2</sub> SO <sub>4</sub> 100	99 / 8				[358]
PEC	Au / TiO <sub>2</sub> 7	Pt	Hg lamp	-	G	4.3	-	-	6.7	0	-	-	Methyl Orange 5.2	Na <sub>2</sub> SO <sub>4</sub> 100	83 / 1.5				[359]
PEC	Blue TiO <sub>2</sub> NTA 4	SS 4	Xe lamp	10000	P	-	1.43	-	6	0	80	0.05	4-chlorophenol 12.8	Na <sub>2</sub> SO <sub>4</sub> 100	99 / 2		99 / 6		[346]

PEC	RGO / polyaniline / TiO <sub>2</sub> 5	Pt	Hg lamp	-	P	-	1.045	-	-	0	100	0.05	Phenol 10	Na <sub>2</sub> SO <sub>4</sub> 1	90 / 6	89.5 / 10	[347]
PEC	WO <sub>3</sub> / graphite 1.3	Pt	Xe lamp	1000	G	10	-	-	6	0	100	0.013	2-nitrophenol 20	Na <sub>2</sub> SO <sub>4</sub> 100	82 / 3		[360]
PEC	Cu <sub>2</sub> O / TiO <sub>2</sub> NTA 15	Pt	Xe lamp	-	P	-	1.5	-	-	0	50	0.3	Ciprofloxacin 10	Na <sub>2</sub> SO <sub>4</sub> 100	73 / 4		[361]
PEC	BiVO <sub>4</sub> / MnO <sub>2</sub> / fluorine SnO <sub>2</sub> 6.5	Pt	Xe lamp	-	P	-	1.5	-	-	0	100	0.065	Ciprofloxacin 10	Na <sub>2</sub> SO <sub>4</sub> 100	76 / 2		[341]
PEC	B-doped BiVO <sub>4</sub> / WO <sub>3</sub> / carbon NP 4	Pt	Xe lamp	-	P	-	1.2	-	-	0	250	0.016	Orange II 5	Na <sub>2</sub> SO <sub>4</sub> 100	92 / 3		[362]
PEC	ZnO / TiO <sub>2</sub> / Ag <sub>2</sub> Se / fluorine SnO <sub>2</sub>	Pt	blue LED 450-460 nm	173	P	-	1.0	-	5.8	0	100	-	Oxytetracycline 5	Na <sub>2</sub> SO <sub>4</sub> 50	96.5 / 6	0.82	[363]
													Spiked urban wastewater effluent	Na <sub>2</sub> SO <sub>4</sub> 20	91 / 6	0.67	

PEC	BiVO <sub>4</sub> / Ag <sub>2</sub> S / fluorine SnO <sub>2</sub> 6.5	Pt	Xe lamp	-	P	-	1.2	-	-	0	50	0.13	Sulfamethoxazole 10	Na <sub>2</sub> SO <sub>4</sub> 100	86 / 2					[364]
PEC	Blue TiO <sub>2</sub> NTA 3.7	SS 3.75	Xe lamp	800	P	-	-	2.4	5	0	100	-	2,4- dichlorophenoxyacetic acid 10	Na <sub>2</sub> SO <sub>4</sub> 50	80 / 1	2.95				[365]
PEC / PEF	TiO <sub>2</sub> 9.4	Carbon cloth 265	Hg lamp	750	P	-	Cat. Pot. -0.27	-	2	0.25	250	0.038 (an.) 1.06 (cat.)	Direct Yellow 52 2	Na <sub>2</sub> SO <sub>4</sub> 50	74 / 0.83	-	66 / 0.33			[366]
PEC / h PEF	α-Fe <sub>2</sub> O <sub>3</sub> / TiO <sub>2</sub> NTA 5	Nickel	W lamp	-	P	-	-	5	3	0	100	0.05	Phenol 10	Na <sub>2</sub> SO <sub>4</sub> 200	99 / 1					[108]
PEC / h PEF	Bi <sub>2</sub> WO <sub>6</sub> / fluorine SnO <sub>2</sub> 3	Fe@Fe <sub>2</sub> O <sub>3</sub> ACF 3	W lamp		G	0.1	-	1.2	6.2	0	-	-	Rhodamine B 5	Na <sub>2</sub> SO <sub>4</sub> 50	80 / 2	1.36	87 / 3	47		[348]
PEC / PEF	TiO <sub>2</sub> NT 4	Carbon PTFE air diffusion 3	Hg lamp	-	G	16.7	-	-	3	0.5	500	0.008	Orange G 84.5	Na <sub>2</sub> SO <sub>4</sub> 50	99 / 0.1	65	97 / 2	10		[367]
PEC / Fenton	RGO / CeO <sub>2</sub> / TiO <sub>2</sub> NTA 6	Pt	Xe lamp	1100	P	-	-	9	5	1	100		Bisphenol A 10	Na <sub>2</sub> SO <sub>4</sub> 50	80 / 2	1.46				[368]



## 1680 **5.4. Other combined or hybrid processes**

1681 To enhance process efficiency and applicability of the EF process or to overcome some of its  
1682 inconvenience, different couplings with other techniques have been performed. PEF or solar  
1683 PEF (see section 5.3) are among such hybrid processes. Bio-electro-Fenton (bio-EF),  
1684 sonoelectro-Fenton (SEF), pyrite-electro-Fenton (pyrite-EF) and peroxi-electrocoagulation are  
1685 some of these combined processes [7,273].

### 1686 **5.4.1. Bio-EAOPs**

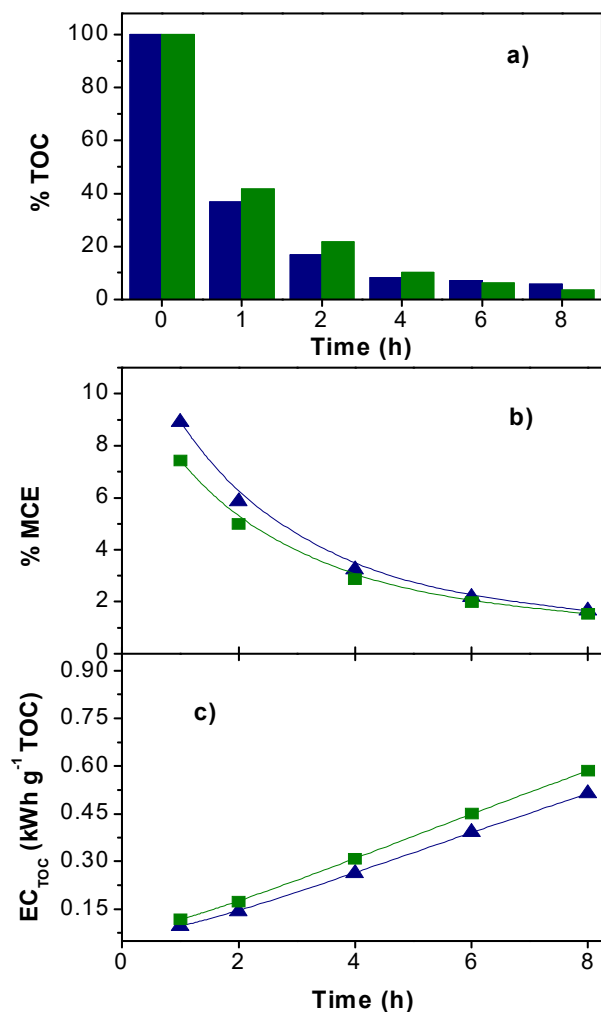
1687 Hybrid processes coupling EAOPs with biological process were developed in order achieve  
1688 cost-effective treatments [14]. The goal is to decrease the treatment time in order to save  
1689 electrical energy or to produce electrical energy that is needed for EF treatment. Therefore,  
1690 there are two types of bio-EF process: the coupling between EF and biological degradation that  
1691 can be performed sequentially between EF and microbial degradation reactors (EF being  
1692 generally the pretreatment step) or the coupling between two cells in a one-pot process:  
1693 microbial fuel cell (MFC) and EF cell. In the latter case, a MFC containing biodegradable  
1694 organic substrates generates electrical energy that is used by EF cell containing pollutants to be  
1695 degraded; where the latter cell is operated by using the electrical energy generated by the MFC  
1696 [370–372]. In fact, MCF works in this system as a “renewable energy” device converting  
1697 chemical energy available in organic compounds into electricity, which is used to operate the  
1698 EF reactor. This system has not yet managed to produce a high amount of electricity so that the  
1699 EF reactor cannot operate with high degradation rate, and needs more investigation in the  
1700 future.

1701 In this chapter, our attention will be focused mainly on the bio-EF process performed  
1702 sequentially between EF and biological treatment. It is well known that the treatment of  
1703 persistent organics by EAOPs leads to the formation of more persistent or toxic intermediate

1704 products [373]. It causes a longer treatment time and consequently more energy consumption  
1705 to reach a quasi-complete mineralization ( $EC_{TOC}$ ) [374,375]. As shown in Fig. 23, long  
1706 electrolysis times (to reach high mineralization rate) result in lower current efficiency and  
1707 higher energy consumption. To avoid these drawbacks, a pioneer study coupling the EF process  
1708 as a pretreatment step for a post-biological degradation was performed by Olvera-Vargas et al.  
1709 (2016) [376]. In this scenario, the EF process serves to convert recalcitrant organic pollutants  
1710 to biologically degradable end-products, in a relatively short electrolysis time. Indeed, several  
1711 reports have demonstrated that the treatment of recalcitrant organic pollutants by AOPs  
1712 enhances the biodegradability index, measured by  $BOD_5/COD$  ratio (with  $BOD_5$ , the  
1713 biochemical oxygen demand after 5 days) of treated solutions [377–380]. It has been  
1714 demonstrated that EF treatment allows the oxidation of mother molecules and leads to the  
1715 formation of by-products with lower molecular weight, mainly short-chain carboxylic acids,  
1716 that are biodegradables [381,382]. The key parameter taken into consideration in enhancement  
1717 of biodegradability during combination of EF (as a pretreatment step) with biological  
1718 degradation is the  $BOD_5/COD$  ratio [383]. A threshold value of 0.4 attained during EF  
1719 pretreatment allows the application of biological processes to mineralize the remaining organic  
1720 substrates.

1721





1722

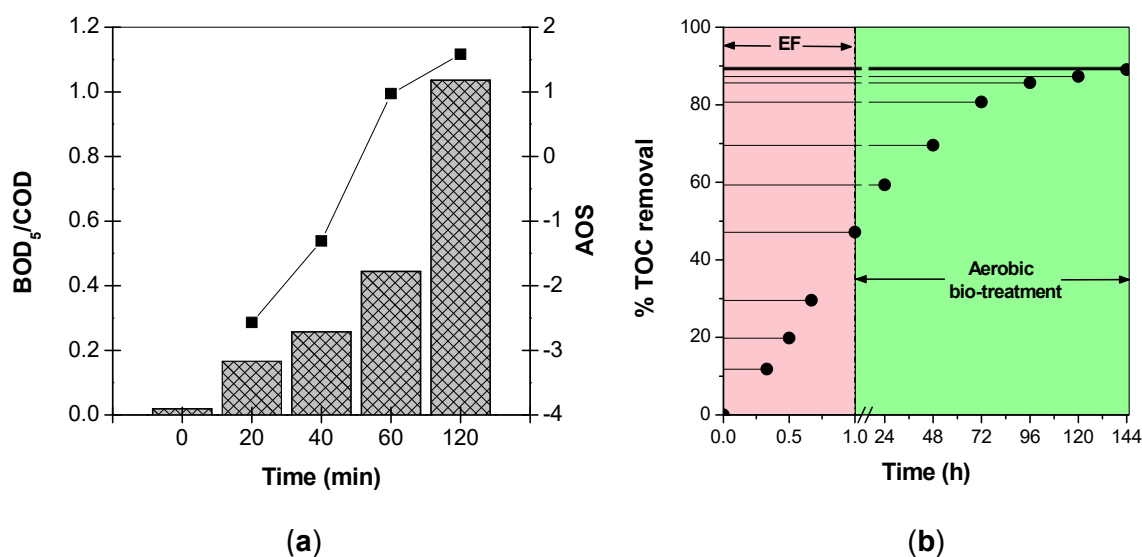
1723 **Figure 23.** (a) Evolution of TOC removal, (b) MCE and (c) EC<sub>TOC</sub> during the mineralization  
 1724 of 230 mL of 0.1 mM FRSM (■) and RNTD (■) aqueous solutions (both in 0.05 M Na<sub>2</sub>SO<sub>4</sub>  
 1725 medium at pH 3.0, room temperature and 500 mA of current) using a BDD/CF cell with  
 1726 [Fe<sup>2+</sup>] = 0.1 mM. The equations used to determine MCE and EC<sub>TOC</sub> (in kWh (g TOC)<sup>-1</sup>) are  
 1727 given in the reference Brillas et al., 2009 [7]. Reprinted from Olvera-Vargas et al. 2016 [375],  
 1728 with permission. Copyright 2016 Elsevier.

1729

1730 In this context, an outstanding work showing the applicability of bio-EF hybrid process has  
 1731 been conducted by Olvera-Vargas et al. (2016) [376]. The solutions of 0.1 mM β-blocker  
 1732 metoprolol (MTPL) were treated by the EF process and an increase in the biodegradability  
 1733 index of treated solutions from 0.012 (strongly non-biodegradable) to 0.44 (biodegradable) was  
 1734 reached after a short electrolysis time of 1 h at 300 mA. The evolution of the BOD<sub>5</sub>/COD ratio

1735 and that of average oxidation state (AOS) is depicted in Fig. 24a. These values clearly indicate  
 1736 that the remaining organic carbon is mainly composed of biocompatible short-chain carboxylic  
 1737 acids.

1738 The initial TOC was reduced by 46% after 1 h EF pretreatment, and then it was efficiently  
 1739 decreased by 90% during the following 4 days-incubation under aerobic conditions (Fig. 24b).  
 1740 Moreover, toxicity tests based on the use of *V. fischeri* bioluminescent bacteria (Microtox®  
 1741 test) evidenced the presence of harmful intermediates formed during the EF treatment, which  
 1742 were also destroyed, as attested by the absence of toxicity after the EF stage [376]. Recently,  
 1743 Arellano et al. (2020) [384] have successfully applied this hybrid process to the removal of  
 1744 ionic liquids from water.



1745  
 1746  
 1747 **Figure 24.** Treatment of beta-blocker metoprolol by Bio-EF process: (a) Evolution of the  
 1748 BOD<sub>5</sub>/COD (▨) ratio and of AOS (—■—) during EF treatment of 220 mL of 0.1 mM of MTPL  
 1749 solution in 0.05 M Na<sub>2</sub>SO<sub>4</sub> and 0.1 mM Fe<sup>2+</sup> at pH 3.0 using a CF/BDD cell operating at 300  
 1750 mA and room temperature, and (b) Time-course of the overall TOC removal 26.74 mg L<sup>-1</sup>  
 1751 (corresponding to 0.1 mM) solution. Biological phase was conducted under aerobic  
 1752 conditions using a mixture of 12 pure cultures of microorganisms. Reprinted with permission  
 1753 from Olvera-Vargas et al. (2016) [376]. Copyright 2016 Elsevier.

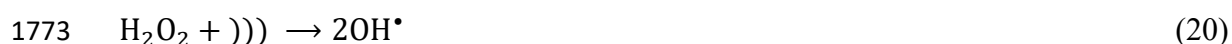
1754 The bio-EF can also be used as post-treatment step after a biological treatment step. Ganzenko  
1755 et al., (2018) [380] investigated the application of the EF process as a pre- or post-treatment  
1756 step coupled with a biological process using a sequencing batch reactor during the treatment of  
1757 a pharmaceutical wastewater spiked with the pharmaceutical caffeine and 5-fluoracil and found  
1758 the first scenario (EF as pretreatment) more efficient. Indeed, EF could completely degrade  
1759 both drugs and reached 60% COD removal in 2 h at 200 mA. The post SBR removed 30% COD  
1760 attaining an overall 90% COD removal. It is noteworthy to use low currents during EF treatment  
1761 to avoid higher energy consumption and mineralization of the biodegradable intermediates so  
1762 that they will be removed by biological post-treatment.

#### 1763 **5.4.2. Sonoelectro-Fenton (SEF)**

1764 The coupling between EF and sonolysis was performed by Oturan et al. (2008) [385] where the  
1765 term SEF was defined for the first time. In SEF, the solutions to be treated are submitted  
1766 simultaneously to the degradation of pollutants by EF and ultrasonic irradiation [385–389]. The  
1767 collapse of cavitation bubbles results in local high pressures and temperatures, leading to the  
1768 formation of  $\cdot\text{OH}$  (Eq. 19) [386]:



1770 The application of ultrasound to the solutions under EF treatment, leads also to the formation  
1771 of additional  $\cdot\text{OH}$  from the dissociation of electrogenerated  $\text{H}_2\text{O}_2$  under ultrasonic irradiation  
1772 (Eq. 20).



1774 It was shown that a synergistic effect is obtained during SEF process, because of the additional  
1775 effect of the enhancement of the mass transfer rate to the electrode by sonication [385]. A Pt/CF  
1776 tank reactor was placed on a ceramic piezoelectric transducer placed on the base of EF (Pt/CF)

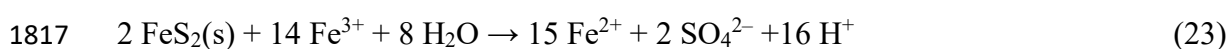
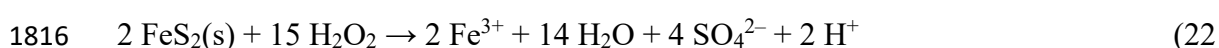
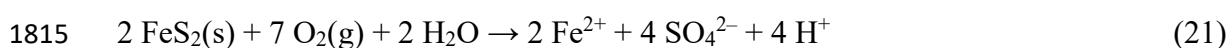
1777 batch used to compare the performance of the EF and the SEF processes during the degradation  
1778 of the herbicides 2,4-dichlorophenoxyacetic acid and 4,6-dinitro-*o*-cresol. Results highlighted  
1779 better performance of SEF compared with EF alone at low frequencies of 28 kHz with low  
1780 energy ultrasounds of 20 and 60 W. In contrast, higher energy ultrasounds (i.e., 80 W) inhibited  
1781 the efficiency of the hybrid process, due to the depletion of O<sub>2</sub> required for the EF process  
1782 [385].

1783 Later, there were several studies on the application of the SEF. Li et al. (2010) [386] reported  
1784 an enhancement in H<sub>2</sub>O<sub>2</sub> production and dye degradation rate when using low frequency  
1785 ultrasounds. Martínez and Uribe (2012) [390] reported quick degradation and efficient  
1786 mineralization (85% TOC removal) of the dye Azur B by the SEF. Lounis et al. (2016) [391]  
1787 studied the degradation of Orange G by SEF in seawater and natural mineral water obtaining  
1788 complete degradation rate in the former medium while 94% of the dye is degraded in the latter  
1789 one. All above results concerned the application of SEF to dye solutions. Few studies have been  
1790 conducted with other pollutants such as nitrotoluenes and 4-chlorophenol. SEF was applied to  
1791 the degradation of dinitrotoluene and 2,4,6-trinitrotoluene) in wastewater [392]. Complete  
1792 degradation of both nitrotoluenes was obtained despite the absence of oxygen bubbling in the  
1793 solution. Authors explained this situation by O<sub>2</sub> generation at the anode and its rapid transfer  
1794 toward the cathode (for H<sub>2</sub>O<sub>2</sub> generation) thanks to enhanced mass transfer rate of O<sub>2</sub> caused  
1795 by ultrasonic irradiation. On the other hand, Nazari et al. (2018) [393] investigated the  
1796 degradation of 4-chlorophenol (4-CP) in aqueous solution using two Ti/mixed metal oxide  
1797 electrodes. 4-CP was hardly degraded by sonolysis while a degradation rate of 83% was reached  
1798 by EF. Complete degradation of 4-CP was attained by hybrid process SEF at in min under low  
1799 energy (20 kHz) ultrasounds. The main contribution of ultrasound irradiation was explained by  
1800 the enhancement of the mass transfer rate. The use of low energy ultrasounds was suggested as

1801 a practical and efficient approach to support the EF process in order to work without the need  
1802 to cool the solution.

### 1803 *5.4.3. EF-pyrite*

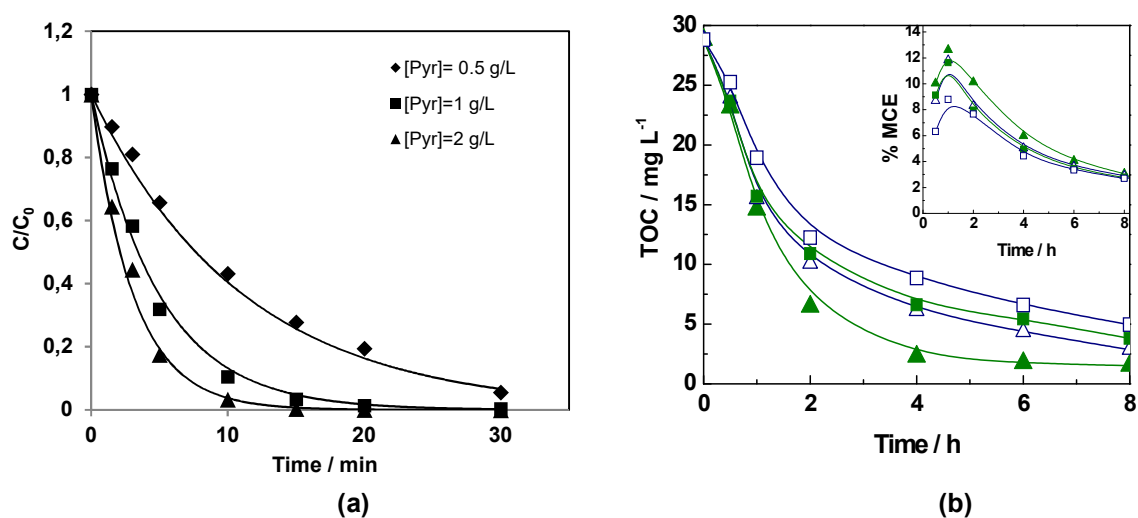
1804 The EF-pyrite is the heterogeneous version of the classical EF in which the soluble iron salt (as  
1805 source of Fe<sup>2+</sup> ion as catalyst) is replaced by natural pyrite (FeS<sub>2</sub>) mineral as solid catalyst. The  
1806 use of pyrite as catalyst in the EF process conducted to the description of a novel EF process,  
1807 so-called EF-pyrite [268,277,302,394]. In contrast to other solid catalysts to perform  
1808 heterogeneous EF processes, pyrite provides some additional interesting characteristics  
1809 [272,301,395]. Besides its abundance in the nature and reusability, it possesses some very  
1810 interesting properties for EF process. Indeed, once introduced into the solution to be treated, it  
1811 behaves as a source of H<sup>+</sup> and Fe<sup>2+</sup> ions according to Eqs. 21-23. Therefore, its use as a solid  
1812 catalyst in the EF process presents several advantages such as self-regulation of solution pH  
1813 and the possibility to avoid external addition of acid and soluble salt catalyst (Fe<sup>2+</sup>) source  
1814 [303].



1818 Another advantage is related to the reaction of pyrite reaction with electrogenerated H<sub>2</sub>O<sub>2</sub>  
1819 producing Fe<sup>3+</sup> (Eq. 22) which is then reduced to Fe<sup>2+</sup> (Eq. 23) contributing to the self-  
1820 regulation of catalyst. Therefore, pyrite dosage constitutes a key parameter for oxidation  
1821 kinetics of organic pollutants. The effect of this parameter has been investigated by Labiadh et  
1822 al. (2015) [301] during the removal of the azo dye AHPS (4-amino-3-hydroxy-2-p-tolylazo-  
1823 naphthalene-1-sulfonic acid) from water (Fig. 25a). The increase in pyrite dosage from 0.5 to 2

1824  $\text{g L}^{-1}$  enhanced the degradation kinetics of AHPS but a further raising led to a weakened  
 1825 degradation kinetics, probably due to the release of an excess of  $\text{Fe}^{2+}$  ions wasting the  $\cdot\text{OH}$  (Eq.  
 1826 14).

1827 The EF-pyrite process was successfully applied to the efficient removal (oxidative  
 1828 degradation/mineralization) of different organic pollutants from water. An example of  
 1829 mineralization kinetics, including MCE is given in Fig. 25b. An overview of other studies on  
 1830 the performance of the EF-pyrite process with experimental conditions and mineralization rates  
 1831 of treated solutions, are gathered in Table 4. This Table also includes a comparative study  
 1832 between EF-pyrite and classical EF with  $\text{Fe}^{2+}$  ions as a homogeneous catalyst. It is worthy of  
 1833 note that the excellent results were obtained with chalcopyrite ( $\text{CuFeS}_2$ ) as a solid catalyst  
 1834 [396].



1835  
 1836  
 1837 **Figure 25.** (a): Effect of pyrite dosage on the oxidative degradation kinetics of AHPS ( $C_0 =$   
 1838  $175 \text{ mg L}^{-1}$ ) in the EF-pyrite process and (b): Mineralization kinetics of  $0.2 \text{ mM}$   
 1839 sulfamethazine using ( $\blacktriangle, \Delta$ ) BDD/CF and ( $\blacksquare, \square$ ) Pt/CF cells. The inset panel shows the  
 1840 corresponding MCE curves for ( $\blacktriangle, \blacksquare$ ) EF-pyrite with  $2.0 \text{ g L}^{-1}$  pyrite and ( $\Delta, \square$ ) classical EF  
 1841 with  $0.2 \text{ mM Fe}^{2+}$ . Experimental conditions:  $I = 300 \text{ mA}$ ,  $[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$ . Adapted from  
 1842 Labiadh et al., 2015 [301] (a) and Barhoumi et al., 2016 [303] (b) with permission. Copyright  
 1843 2015, 2016, Elsevier.

**Table 4.** TOC removal efficiencies obtained during the EF-pyrite treatment of different contaminants and comparison with classic (homogeneous) EF process. Adapted from the reference [272], Copyright 2018, Springer

Contaminant	Cell configuration	% TOC removal (EF-Pyrite)	%TOC removal (Classic EF)	Reference
Levofloxacin	BDD-CF undivided cell (300 mA) 1 g L <sup>-1</sup> of pyrite	95 in 8 h-treatment	-	[395]
Tyrosol	BDD-CF undivided cell (300 mA) 1 g L <sup>-1</sup> of pyrite	89 in 6 h-treatment	88 in 6 h-treatment	[394]
Synthetic dye AHPS	BDD-CF undivided cell (450 mA) 2 g L <sup>-1</sup> of pyrite	>90 in 5 h-treatment	70 in 5 h-treatment	[301]
Sulfamethazine	BDD-CF undivided cell (300 mA) 2 g L <sup>-1</sup> of pyrite	95 in 8 h-treatment	90 in 8 h-treatment	[303]
Tetracycline	BDD-CF undivided cell (500 mA) 1 g L <sup>-1</sup> of chalcopyrite	92 in 2 h, 99 in 6 h-treatment	90 in 2 h, 98 in 6 h-treatment	[396]
Tetracycline	BDD-CF undivided cell (300 mA) 2 g L <sup>-1</sup> of pyrite	99 in 8 h-treatment 87% with Pt anode at 300 mA	96 in 8 h-treatment	[397]
Vanillic acid	Pt-CF undivided cell (300 mA) 1 g L <sup>-1</sup> of pyrite	89 in 4 h-treatment	-	[398]

1844

#### 1845 **5.4.4. Peroxi-electrocoagulation**

1846 Peroxi-electrocoagulation (called also peroxi-coagulation) is a coupling between electrocoagulation and EF  
1847 processes, developed and applied to wastewater treatment by Brillas et al. [399,400]. This hybrid process  
1848 involves the EF process using a sacrificial iron anode to generate iron ions (Eq. 24) and a carbonaceous  
1849 cathode to produce H<sub>2</sub>O<sub>2</sub> according to Eq. 1 allowing the Fenton reaction (Eq. 2) to take place.



1851 In addition, ferrous iron ions leached to the solution from the iron anode (Eq. 24) is oxidized in the solution  
1852 by the DO and electrogenerate H<sub>2</sub>O<sub>2</sub> (Eq. 1) to form ferric iron ions that promote the coagulation process  
1853 through the formation of ferric hydroxide (Fe(OH)<sub>3</sub>). Thus, pollutants contained in wastewater are removed  
1854 by both oxidative attacks of •OH (produced from the Fenton reaction (Eq. 2)), and by coagulation  
1855 (adsorption and entrapment in Fe(OH)<sub>3</sub> precipitates). Therefore, Brillas and Casado (2002) [400] observed  
1856 higher pollutants removal efficiency in peroxi-electrocoagulation compared to the EF process. In contrast  
1857 to the electrocoagulation process in which pollutants are only eliminated by coagulation, the peroxi-  
1858 electrocoagulation allows high organics removal efficiencies thank to the action of strong oxidant •OH  
1859 generated through EF process [401–404]. Moreover, to enhance the process efficiency, the peroxi-  
1860 electrocoagulation has also been coupled with UV irradiation [405,406] for degradation of chlorophenoxy  
1861 acid herbicides in aqueous media.

1862 Inversely to the EF, solution pH increases during the peroxi-electrocoagulation process due to the HER at  
1863 the cathode (Eq. 11) [407–409]. This increase promotes coagulation and results in a high amount of sludge  
1864 production in the electrochemical reactor. The formation of sludge production can be reduced by setting the  
1865 solution pH to approximately 3. Under this condition, ferrous iron predominates in the solution, thus  
1866 allowing the Fenton reaction to occur more efficiently.



1867 The peroxi-electrocoagulation process was recently applied to the treatment of different types of wastewater.  
1868 Lizama-Bahena et al., 2015 [410] studied a mixture of three herbicides (alachlor, atrazine, and  
1869 chlorbromuron) and obtained complete removal of herbicides and COD at 75 min when combined with UV  
1870 irradiation. Recently different research groups successfully applied this hybrid process to the treatment of  
1871 composite wastewater [411], acrylonitrile [110], cooking wastewater [412], coke-plant wastewater [413],  
1872 laundry wastewater [414] with 70% COD removal in most of the cases.

#### 1873 ***5.4.5. Coupling with a pre-concentration step***

1874 EAOPs are generally not cost-effective in the case of low/very low pollutant concentrations ( $< 10^{-3}$  mM or  
1875 between  $\mu\text{g L}^{-1}$  to  $\text{mg L}^{-1}$ ) because of slow mass transfer rate requiring long electrolysis times and  
1876 consequently high energy consumption for the removal of low amounts of pollutants. An appropriate pre-  
1877 concentration step before EAOPs can constitute a solution. In this context, Trellu et al. (2018) [415] reported  
1878 the adsorption of phenol on activated carbon fiber (ACF) and then the ACF was used as cathode in EF  
1879 process with efficient desorption and mineralization efficiency. Furthermore, such a process was suggested  
1880 for regeneration of spend ACF with high regeneration efficiency [415]. Thus, ACF can be used as filter to  
1881 concentrate the pollutants of a very dilute (but toxic even at low concentration) pollutants and remove  
1882 completely these pollutants by EF process with regeneration of ACF. Banuelos et al. (2013) [416] also  
1883 proposed such approach for regeneration of granular activated carbon. Using sawdust as adsorbent material,  
1884 Bouaziz et al. (2014) [417] also studied the regeneration of this material using advanced electro-oxidation  
1885 with a BDD anode. Recently, Muñoz-Morales et al. (2020) [418] also applied this technique to the pre-  
1886 concentration on granular activated carbon using a sequential three step processes: adsorption-desorption-  
1887 electrolysis to treat low concentrated wastewater containing organochlorinated compounds. The process  
1888 was successful for chlopyralid and perchloroethylene (8-time concentration) before electrochemical  
1889 oxidation step while lindane was poorly concentrated.

Another strategy is to combine EAOPs with a pre-concentration step based on membrane filtration. The objective is to apply the electrochemical process on the retentate obtained after membrane filtration. For example, Lan et al. (2015) [419] have used nanofiltration for the removal of ciprofloxacin from an hospital effluent and have subsequently treated the retentate by advanced electro-oxidation using BDD anode with an energy consumption of 50 kWh per kg of COD removed.

#### 5.4.6. *Electro-peroxone*

The peroxone process is an AOP used for the abatement of organic pollutants in water. This enhanced ozonation technology consists of the combination of conventional ozonation with H<sub>2</sub>O<sub>2</sub>. In fact, the reaction of O<sub>3</sub> with H<sub>2</sub>O<sub>2</sub> leads to the generation of <sup>•</sup>OH according to the Eq. 25 [420,421]. Thus, the O<sub>3</sub> (E° = 2.07 V/SHE) is transformed to a stronger oxidant (E° = 2.80 V/SHE), able to oxidize pollutants until their mineralization.



When the H<sub>2</sub>O<sub>2</sub> is electrochemically in situ generated from electro-reduction of O<sub>2</sub> (Eq. 1), the process is called electro-peroxone [422,423] and considered as one of emerging EAOPs [424,425]. This process overcomes the limitation of conventional ozonation, such as the formation of toxic intermediates remaining in the treated solution, and can be easily implemented by installing a pair of electrodes (including a carbonaceous cathode) in existing ozone reactor with a minimal capital cost [426]. Therefore, different configurations of electro-peroxone process were applied to the treatment of organic pollutants. For example, Yang et al. (2018) [427] developed a dual electrode system to generate simultaneously O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> for efficient removal (97.6%) of carbamazepine solution after 90 min electrolysis. A coupling between electro-peroxone and biological treatment was developed for the treatment of a simulated hospital wastewater with 92.8% of TOC removal efficiency [428]. Ghalebizade and Ayati (2019) [429] showed the ability of this process to treat the effluents with high pollutant concentration using a continuous circular flow reactor with 99% degradation efficiency of 500 mg L<sup>-1</sup> of Acid Orange solution at 40 min. Finally, Cornejo and Nava

(2021) [430] compared ozonation, AO-H<sub>2</sub>O<sub>2</sub> and electro-peroxone processes for the treatment of levofloxacin in a lab scale flow plant and reported the oxidation power in the following order: electro-peroxone > ozonation > AO-H<sub>2</sub>O<sub>2</sub>. Electro-peroxone was able to reach 63% of mineralization of levofloxacin solution with a low energy consumption of 0.27 kWh (gTOC)<sup>-1</sup>. A flow-through electro-peroxone system was developed for the disinfection of two kinds of simulated ballast water, fulfilling the efficient generation of ·OH through the reaction of ozone with in-situ electrochemical generation H<sub>2</sub>O<sub>2</sub>. As a result, a higher *E. coli* inactivation of one order of magnitude was reached, with a very low energy consumption (0.33 and 0.12 kWh m<sup>-3</sup> for treating both solutions) compared to ozonation and electrolysis [431]. This process was found also cost-effective and promising for simultaneous tetracycline removal and disinfection of municipal secondary effluents. The main disinfection by-products such as trihalomethanes, haloacetonitrile and halonitromethanes were particularly much lower than the WHO's thresholds for drinking water [432].

## 6. Perspectives and outlook

### 6.1. Electrocatalytic mechanism understanding requirement

#### 6.1.1. ORR mechanisms

Investigations about existing ORR studies illustrate the difficulties to predict the selectivity of ORR; more developed kinetic models are required in combination with thermodynamic analysis as well as pH dependence studies to deeper understand these mechanisms of selectivity [25].

Moreover, there is a lack of studies about the influence of nanostructure on the ORR mechanisms. Still, a recent paper attempt to investigate in detail the influence of nitrogen-doped RGO on two- and four-electron ORR [433]. The authors identified the ORR active sites on sp<sup>2</sup> carbon close to oxide location and highlighted the influence of oxygen functional groups. Moreover, heteroatom structure could interfere with the catalytic activity and selectivity through modification of chemical structure. They also highlighted that a coupled

1938 proton-electron transfers (CPETs) mechanism, i.e. the proton and electron are transferred simultaneously  
1939 with a single transition state, mainly occurs with metal cathode. Contrastingly, there are different possible  
1940 ORR pathways with carbon-based materials. It can occur through either CPETs or non-CPETs (i.e.  
1941 decoupled proton and electron transfer) mechanisms, depending on the material composition, the surface  
1942 functionalization and the solution pH. This complexity of different ORR mechanisms emphasized in this  
1943 specific study, has to be enlarged to other types of nanostructured-based cathode materials, which will help  
1944 to get an overview of the different ORR mechanisms.

### 1945 **6.1.2. OER and oxidation mechanisms**

1946 The mechanism of anodic oxidation of pollutants is mainly classified by two ways: direct electron transfer,  
1947 and oxidation through the generated radicals. The direct electron transfer is usually verified by the LSV  
1948 characterization via comparison of the output current in the presence/absence of pollutants. If the output  
1949 current in the presence of pollutant is higher than that in the absence of pollutants, it can prove the role of  
1950 direct electron transfer.

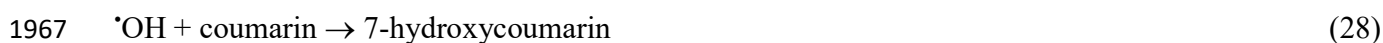
1951 For the role of radical oxidation, there are qualitative and quantitative methods including quenching study,  
1952 radical probes and electron paramagnetic resonance method [434]. Table 5 lists some common radical  
1953 scavenger and probes. Methanol (MeOH) is the scavenger for  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$ , and tert-butyl alcohol (TBA)  
1954 is supposed to scavenge only  $\cdot\text{OH}$ . Atrazine (ATZ) can distinguish the role of radical and non-radical  
1955 oxidation.  $\text{SO}_4^{\cdot-}$  has a low reactivity to nitrobenzene (NB) oxidation and can determine the role of  $\cdot\text{OH}$  and  
1956  $\text{SO}_4^{\cdot-}$ . From the quenching study, it can be distinguished the role of  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$ , and furthermore the  
1957 contribution of these two radicals could be calculated by Eqs. (26) and (27). In addition, there are two kinds  
1958 of  $\cdot\text{OH}$  that supposed to exist in electrochemical oxidation, homogeneous (free  $\cdot\text{OH}$ ) and heterogeneous  
1959 (surface  $\cdot\text{OH}$ ), which can be detected using coumarin as the  $\cdot\text{OH}$  probe. An  $\cdot\text{OH}$  adduct product of 7-  
1960 hydroxycoumarin can be formed through Eq. (28) which is considered to be non-oxidizable by  $\cdot\text{OH}$  [255].

1961 Therefore, the higher the intensity of 7-hydroxycoumarin, the higher contribution of  $\cdot\text{OH}$  tended to be free  
 1962  $\cdot\text{OH}$ . On the contrary,  $\cdot\text{OH}$  is tended to be surface  $\cdot\text{OH}$ .

1963 
$$\lambda_{\cdot\text{OH}} = \frac{k - k_{\text{TBA}}}{k} \times 100\% \quad (26)$$

1964 
$$\lambda_{\text{SO}_4^{\cdot-}} = \frac{k_{\text{MeOH}} - k_{\text{TBA}}}{k} \times 100\% \quad (27)$$

1965 where  $k$  was the rate constant of phenol degradation without addition of scavenger,  $k_{\text{TBA}}$  was the rate constant  
 1966 with addition of TBA,  $k_{\text{MeOH}}$  was the rate constant with addition of MeOH.



1968

1969

**Table 5.** Common scavengers and reactive radicals.

Scavengers	Rate constant with	Rate constant with	Reactive species	Ref.
	$\cdot\text{OH}$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$\text{SO}_4^{\cdot-}$ ( $\text{M}^{-1} \text{s}^{-1}$ )		
MeOH	$1.2 - 2.8 \times 10^9$	$1.6 - 7.7 \times 10^7$	$\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$	[435]
TBA <sup>1</sup>	$3.8 - 7.6 \times 10^8$	$4.0 - 9.1 \times 10^5$	$\cdot\text{OH}$	[436]
ATZ <sup>2</sup>	$2.6 \times 10^9$	$2.6 \times 10^9$	$\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$	[437]
NB <sup>3</sup>	$3.9 \times 10^9$	$< 10^6$	$\cdot\text{OH}$	[437]

1970

<sup>1</sup> TBA: tert-butyl alcohol, <sup>2</sup> ATZ: atrazine, <sup>3</sup> NB: nitrobenzene

1971 Besides, the degradation intermediates are also important to disclose the possible degradation pathway and  
 1972 mechanism through analysis via gas chromatography mass spectrometry (GC-MS) or liquid  
 1973 chromatography mass spectrometry (LC-MS). However, these measurements are not sufficient for

1974 understanding OER and oxidation mechanism. As an anodic interface process, there is an urgent need to  
1975 develop the characterization and identification method for surface reaction especially for the real-time or in  
1976 situ detection of possible radicals involved in the pollutant degradation, so that an intrinsic mechanism  
1977 would be well disclosed to benefit OER mechanism understanding.

## 1978 **6.2. Electrode stability improvement**

### 1979 **6.2.1. Cathodes stability**

1980 The cathode performances does not stop at achieving the desired amount of the H<sub>2</sub>O<sub>2</sub> but, the challenge is  
1981 to keep the production capacity constant for a long time and to develop the process in a large-scale  
1982 application [125]. Some papers focused on the nanostructured cathode stability or reusability by assessing  
1983 either the H<sub>2</sub>O<sub>2</sub> generation efficiency or contaminant degradation performances after several successive  
1984 cycles of electrolysis. Table 6 presents some different works that deal with the stability of the cathode toward  
1985 H<sub>2</sub>O<sub>2</sub> electrogeneration.

1986 Yu et al. [132] used CF modified with nitrogen-doped carbon as the cathode for the production of H<sub>2</sub>O<sub>2</sub>. It  
1987 was concluded that the H<sub>2</sub>O<sub>2</sub> yield was kept relatively constant after 5 cycles with a slight loss of the  
1988 concentration during the last run. Yang et al. [66] carried out the H<sub>2</sub>O<sub>2</sub> electrogeneration rate at the EEGr/GF  
1989 cathode. Due to the cathode modification, the stability of the material was boosted and the production rate  
1990 stayed almost constant after 10 cycles.

1991 In another work Zhao et al. [63] evaluated the stability of the fluorine-doped carbon cathodes toward the  
1992 H<sub>2</sub>O<sub>2</sub> after 8 cycles of 3 h each, and no significant decrease of performance was observed. Xia et al. [61]  
1993 prepared a phosphorus-doped CNTs GDE and the reusability of the electrode was explored through the  
1994 H<sub>2</sub>O<sub>2</sub> yield after 6 cycles during 1 h each. The authors reported the unchanged cathode performance after  
1995 the test, which was explained by the strong covalent bond between the phosphorus atoms and carbons  
1996 framework.

1997 Though promising stability have been assessed with some nanostructured modified raw cathode materials,  
 1998 especially those that favor chemical binding, the stability has to be proven for long-term use, i.e., over  
 1999 several weeks and months. Moreover, standard protocol to assess the life span performance should be  
 2000 established so that the international community would have a comparable and viable way to perform them.

2001

2002 **Table 6.** Literature on the nanostructured cathode stability towards the hydrogen peroxide yield.

Nanostructured cathode	pH	Current density or cathode potential	O <sub>2</sub> flow rate (L min <sup>-1</sup> )	Time (min)	[H <sub>2</sub> O <sub>2</sub> ] (mM cm <sup>-2</sup> )	Number of successive cycles	Stability (% loss of yield)	Reference
Phosphorus-doped carbon nanotubes	7	-0.45 V vs SHE	0.21	60	1.41	6	UP <sup>1</sup>	[61]
Fluorine-doped HPC	1	-0.1 V vs RHE <sup>4</sup>	NS	180	11.42	8	UP <sup>1</sup>	[63]
NiFe nanostructure /Graphite	3	300 mA cm <sup>-2</sup>	NS	NS	0.015	15	3.59 <sup>2</sup>	[166]
Tungsten oxide nanoparticles/C	NS	-0.5 V vs SHE	NS	180	2.34	12	6 <sup>2</sup>	[113]
Exfoliated Graphene/graphite felt	7	-0.856 V vs SHE	0.7	NS	7.72 <sup>2</sup>	10	UP <sup>1</sup>	[66]
Nitrogen-doped carbon/graphite felt	7	12.5 mA cm <sup>-2</sup>	0	NS	0.4	5	9	[132]
GDE-CX 80	7	-0.8 V vs SHE	NS	120	6.60 <sup>2</sup>	10	10 <sup>2</sup>	[438]
Carbon nanotubes hybrid fullerene	3	0.044 V vs SHE	NS	NS	29	15	11.7	[102]

2003 <sup>1</sup> UP: unchanged performance, <sup>2</sup>unit: (% loss of H<sub>2</sub>O<sub>2</sub> yield), <sup>3</sup>unit: (mM h<sup>-1</sup>), <sup>4</sup>RHE: reversible hydrogen electrode

2004

### 2005 6.2.2. Anodes stability

2006 As known, the electrode stability is an important parameter for industrial applications. There are two  
 2007 strategies to improve the electrode stability, one is the intermediate layer modification, the other is the

2008 electrode surface modification. Huang et al. (2020) introduced clustered TNTs intermediate layer on Ti  
2009 mesh as substrate for mesh Sb-SnO<sub>2</sub> electrode (M-TNTs-SnO<sub>2</sub>), which exhibited a higher TOC removal and  
2010 MCE, and longer accelerated service lifetime of 105 h for electrochemical degradation of phenol when  
2011 compared with Ti mesh or Ti plate /TNTs electrodes (Fig. 26a) [235]. This enhanced performance was  
2012 mainly ascribed to the introduction of mutually self-supported TNTs clusters in different orientations [235].  
2013 Xu et al. (2017) explored Nb-doped TNTs interlayer for Sb-SnO<sub>2</sub> electrode [439]. The novel electrode has  
2014 a larger surface area and smaller crystallite particles than conventional SnO<sub>2</sub>-Sb electrodes. Compared with  
2015 Ti/SnO<sub>2</sub>-Sb and Ti/TiO<sub>2</sub>-NTs/SnO<sub>2</sub>-Sb, the electrode modified by Nb-TiO<sub>2</sub>-NTs has a higher OEP of 2.29  
2016 V/(Ag/AgCl), and a lower R<sub>ct</sub> with a decrease by 65% and 79%, respectively. The service lifetime of Nb-  
2017 Ti/Nb-TiO<sub>2</sub>-NTs/SnO<sub>2</sub>-Sb was 4.9-time longer than that of Ti/SnO<sub>2</sub>-Sb and 1.9-time longer than that of  
2018 Ti/TiO<sub>2</sub>-NTs/SnO<sub>2</sub>-Sb (Fig. 26b) [439].

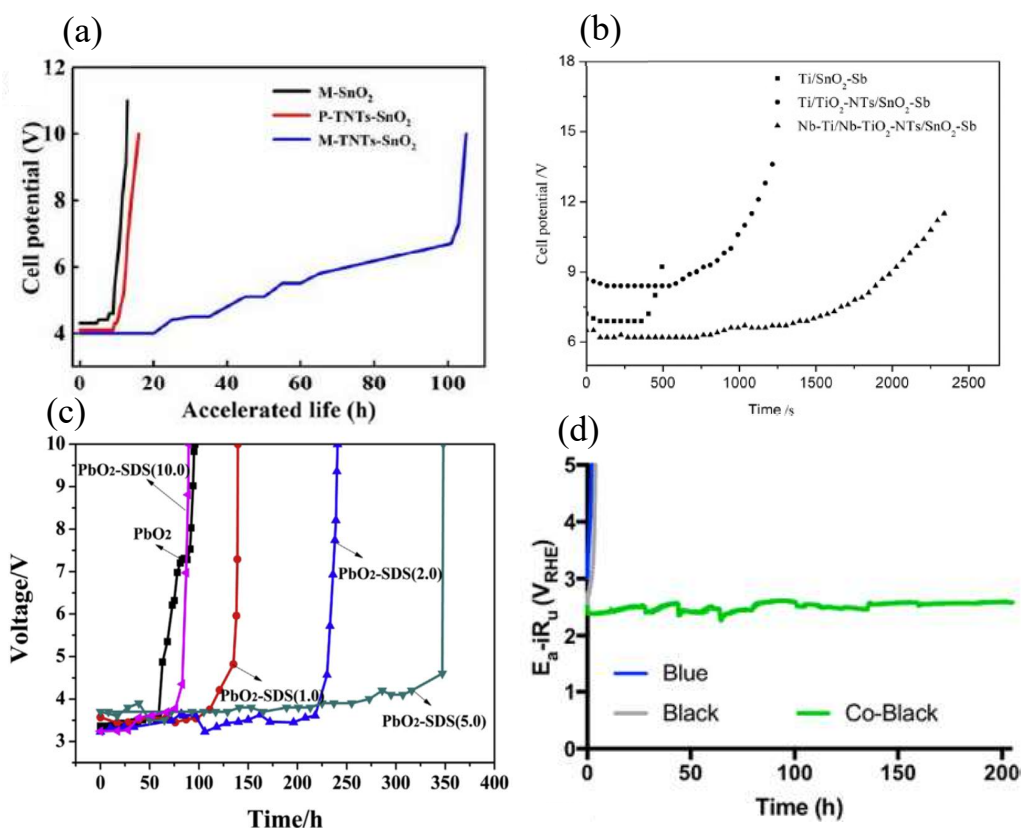
2019 The anode surface modification was the more common way for improving electrode stability. Li et al. used  
2020 sodium dodecyl sulfate (SDS) to modify PbO<sub>2</sub> electrode by electro-deposition method, showing that SDS  
2021 could obviously refine the coating particles, increase the OEP and accelerate charge transfer [440]. The  
2022 modified PbO<sub>2</sub> electrode had a better electro-catalytic performance and stability. The accelerated service  
2023 life could reach 348 h, which was almost 3.6 times longer than that of PbO<sub>2</sub> electrode (96 h) under the same  
2024 condition (Fig. 26c) [440]. Zhang et al. (2014) employed CNT to modify Ti/SnO<sub>2</sub>-Sb using a pulse  
2025 electrodeposition method [241]. The modified electrode had a smaller crystallite particles, a higher OEP  
2026 and its service lifetime was 4.8-time longer than that of the Ti/SnO<sub>2</sub>-Sb electrode [241]. It was reported that  
2027 cobalt-doped Black TNT array anode had a longer lifetime (200 h) when compared with Blue-TNT (2.3 h)  
2028 at 10 mA cm<sup>-2</sup> in 30 mM NaClO<sub>4</sub> (Fig. 26d) [441].

2029 Up to now, many efforts on electrode fabrications have been made to make anodes with low cost, strong  
2030 stability, long service lifetime and enhanced electrocatalytic activity. However, they are usually designed  
2031 for small electrochemical devices to treat wastewater. Scale-up has not always been faced in the right way,



2032 the full applications for industrial use, demonstration or even pilot scale applications are still very limited.  
 2033 This is probably due to the economic difficulties, immature electrode fabrication and lifetime duration as  
 2034 well as reliable reactor design. Thus, there is an urgent need to develop them at industrial scale to meet the  
 2035 practical demand [12].

2036



2037

2038 **Figure 26.** (a) variation of cell voltage during accelerated life tests, [235]. Copyright (2020) Elsevier; (b)  
 2039 Accelerated service life tests on different electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with a current density of 1 A  
 2040 cm<sup>-2</sup> at 25 °C, [439]. Copyright (2017) Elsevier; (c) Accelerated life test of the different PbO<sub>2</sub> electrodes  
 2041 (H<sub>2</sub>SO<sub>4</sub>: 3 M; current density: 500 mA cm<sup>-2</sup>, [440], Copyright (2017) Elsevier and (d) Comparison of the  
 2042 anodic stability of the NTA electrodes in 30 mM KClO<sub>4</sub> at a current density of 10 mA cm<sup>-2</sup>. [441],

2043

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2044

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2053

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