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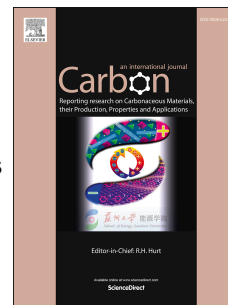
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# Journal Pre-proof

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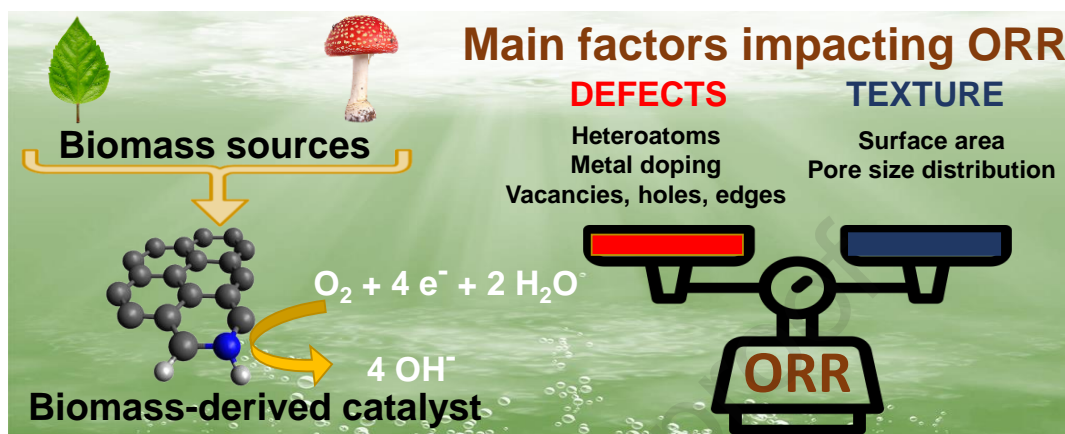
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## Graphical abstract



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# Recent progress in the development of efficient biomass-based ORR electrocatalysts

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**Abstract**

Platinum is considered the reference catalyst in many electrochemical devices such as electrolyzers or fuel cells. Nevertheless, the large-scale commercialization of these Pt-based devices is limited by the prohibitive cost of platinum as well as its quantity and availability. Regardless of its price and scarcity, it is well known that the oxygen reduction reaction (ORR) with Pt in acidic media is slow compared to that in alkaline media. Due to the lower overpotentials in the latter case, the possibility of using Pt-free catalysts opens the door to new catalyst research. Among them, the development of carbon-based catalysts, either metal-free or with non-precious metals, from the conversion of biomass precursors by various synthetic processes has recently become a challenging goal, as biomass represents an eco-friendly source of carbon. The surface chemistry, textural properties and structure of carbonaceous materials make it complex to identify the origin of ORR catalytic activities. This review provides a critical discussion of the influence of the physicochemical and electrochemical properties of biomass-derived, carbon-based electrocatalysts for the ORR reported over the past decade.

**Keywords:** Oxygen reduction reaction; Biomass-derived carbon-based electrocatalysts; Metal-free catalysts; Non-precious metal catalysts; Pt-free electrocatalysts

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**70 Abbreviations**

71

72  $A_{BET}$ , BET area

73 BDS, benzyl disulfide

74 BET, Brunauer–Emmett–Teller

75  $C_{O_2}^b$ , concentration of O<sub>2</sub> in the bulk of the electrolyte

76 CTAB, Cetyltrimethylammonium bromide

77 CV, Cyclic Voltammetry

78 DFT, Density Functional Theory

79 DMF, Dimethylformamide

80  $D_{O_2}$ , diffusion coefficient of O<sub>2</sub> in the electrolyte81  $E_{ad}$ , adsorption energy of HO<sub>2</sub><sup>•</sup>82  $E_{ONSET}$ , onset potential83  $E_{1/2}$ , half-wave potential

84 HTC, Hydrothermal Carbonization

85 ICP, Inductively Coupled Plasma

86  $j_k$ , kinetic current density87  $j_l$ , limiting current density

88 KL, Koutecky-Levich

89 LSV, Linear Sweep Voltammetry

90 MOF, Metal-Organic Framework

91  $n$ , number of transferred electrons

92 NPMC, Non-precious metal-doped carbon material

93 OER, Oxygen Evolution Reaction

94 OMC, Ordered Mesoporous Carbon

95 OMS, Ordered Mesoporous Silica

96 ORR, Oxygen Reduction Reaction

97 PEMFC, Proton Exchange Membrane Fuel Cell

98 Pt/C, Platinum on Carbon

99 RDE, Rotating Disk Electrode

- 100 RHE, Reversible Hydrogen Electrode  
101 RRDE, Rotating Ring Disk Electrode  
102 SAC, Single-atom catalyst  
103  $\omega$ , angular velocity  
104  $\nu$ , kinematic viscosity  
105  
106

Journal Pre-proof



## 107 **1. Introduction**

108 Excessive consumption of fossil resources, particularly to produce energy through the  
109 combustion of fossil fuels, leads to a significant increase in the amount of greenhouse gases,  
110 which are harmful to the planet, and is therefore at the heart of society's concerns about the  
111 acceleration of global warming. In order to reduce its impact, the Paris Agreement has set a  
112 maximum threshold of 1.5 °C increase in average temperature by the end of the 21<sup>st</sup> century  
113 [1]. To reach this target, it is imperative to change the current energy system by encouraging  
114 the development of new renewable energy sources.

115 Among possible renewable energy vectors, hydrogen is proposed as one of the most  
116 attractive alternatives to replace fossil fuels, as it can be used in fuel cells to produce electricity  
117 with water as the only byproduct. The most mature fuel cells that consumes hydrogen at the  
118 anode and oxygen at the cathode is the Proton Exchange Membrane Fuel Cell (PEMFC). This  
119 electrochemical device is a very promising because of the absence of polluting emissions and  
120 the high energy efficiency for energy production compared to combustion engines in vehicles  
121 that emit harmful exhaust gases (carbon monoxide, nitrogen dioxide, unburnt hydrocarbons,  
122 soot, heavy metals, etc.) [2]. Metal-air batteries emerge as other electrochemical systems being  
123 also widely studied to meet our growing energy needs. These systems generate electricity  
124 through electrochemical reactions on electrodes, which consist of a pure metal anode (e.g.  
125 lithium and sodium) and an ambient air cathode, which must exhibit efficient performance for  
126 the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR). The cathode  
127 electrode of metal-air batteries has significant drawbacks, such as large overpotentials for both  
128 reactions, high cost, and poor stability, which still need to be overcome to achieve greater  
129 efficiency in power generation [3,4].

130 The development of such technologies on a large scale is still limited due to the low kinetics  
131 and high overpotential of the ORR, which takes place at the cathode electrode of fuel cells and

132 metal-air batteries [5–7]. The sluggish kinetics of the ORR makes it necessary to use  
133 electrocatalysts to reduce the high overpotential of this reaction. Platinum is widely used  
134 because of its excellent performance as an ORR electrocatalyst, but its prohibitive price and  
135 low availability on Earth are a real bottleneck for fuel cell development [8]. To solve this  
136 problem, the design of low-cost electrocatalysts for ORR in alkaline and acidic media, with  
137 performance and stability close to that of platinum, is highly anticipated. Several strategies have  
138 been explored to replace platinum by designing: (i) metal-free carbon catalysts doped with  
139 heteroatoms, and (ii) non-precious metal electrocatalysts supported on carbon materials.

140 Biomass is the richest “green” source of carbon in nature, and it can be classified into three  
141 families: plant biomass (phytomass), animal biomass (zoomass) and microorganisms [5,9].  
142 Every year, about 140 billion tons of biomass are generated worldwide and can be an  
143 environmental problem, especially in developed countries where most of biomass residues from  
144 agriculture are left in the fields to decompose [10,11]. To valorize biomass, one can first use it  
145 to produce energy, biofuels or biomaterials rich in heteroatoms (N, S, P, etc.) and metals (Fe,  
146 Cu, Mn, etc.) [12–14]. One can also use it for the production of carbonaceous materials that can  
147 be applied as electrocatalysts or as supports of metal active phases for ORR electrocatalysts  
148 [5,15–17]. Nevertheless, biomass precursors have inherently poor electrochemical properties,  
149 and therefore they must be modified or doped accordingly. The resulting materials can then  
150 exhibit unique textural properties, depending on the method of synthesis and the parameters  
151 used during the transformation of the biomass into carbonaceous materials (also known as  
152 chars) [10]. These chars have been shown to be of great interest in many applications such as  
153 energy storage and conversion (supercapacitors, batteries, fuel cells ...) [16].

154 Many interesting review articles have been published in recent years, providing important  
155 information on biomass-derived carbon-based electrocatalysts, with or without metals  
156 [5,15,18–20]. However, most of these papers focus on metal-free or metal-doped carbonaceous

157 catalysts from biomass by studying the influence of porosity or the influence of the chemical  
158 composition of these materials but rarely both combined. In this review, we propose to study  
159 both the impact of surface chemistry and textural properties on the ORR performance of several  
160 recently synthesized metal-doped and metal-free carbonaceous catalysts derived from biomass.  
161 The objective of the present paper is thus to provide a comprehensive overview of the  
162 performance of different ORR electrocatalysts based on biomass precursors synthesized during  
163 the past decade, with particular attention to the textural properties and chemical compositions  
164 of the carbon materials, including the identification of active sites. Below, the simplified  
165 mechanism of ORR on the surface of a carbon-based electrocatalyst in acidic or alkaline  
166 medium is first discussed, followed by a brief description of the most common biomass  
167 precursors and the synthesis strategies of biomass-based carbon materials. Next, a comparative  
168 study of heteroatom-doped carbon catalysts and non-precious metal-containing catalysts is  
169 discussed in detail, focusing on the effect of the biomass precursor and the consequences on  
170 ORR performance as a function of the textural properties and surface chemistry of the active  
171 sites.

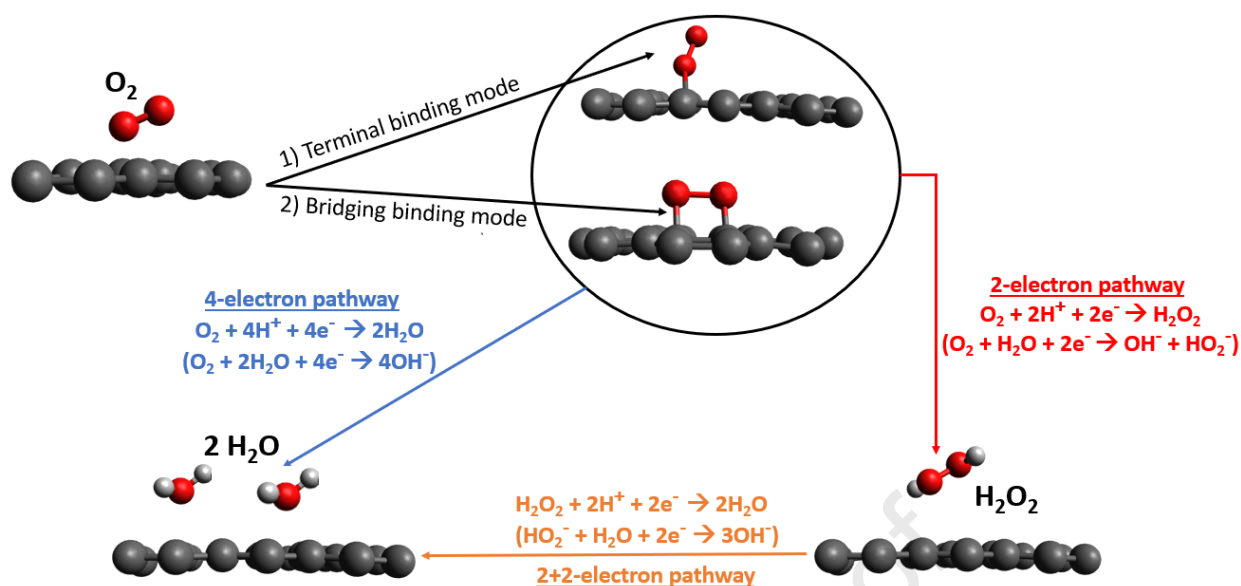
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## 173 **2. Mechanism and kinetics of ORR**

174 The mechanisms governing the oxygen reduction reaction (ORR) are based on a complex  
175 sequence of intermediate reactions. The most general and widely accepted mechanism in acidic  
176 medium (Figure 1) is that proposed by Wroblowa et al. [21]. Although it gives a simplistic view  
177 of the ORR, it is well known that it is highly dependent on the nature of the electrocatalysts and  
178 the working conditions.

179

180



181  
182

183 **Figure 1.** Simplified ORR mechanism on a carbon surface through three different pathways in  
184 acidic medium. The chemical reactions for ORR in alkaline medium are shown in brackets.

185 In general, the first step in the ORR in acidic medium is the chemisorption of O<sub>2</sub> molecules  
186 on the catalyst surface. They are then either reduced directly to water *via* the 4-electron pathway  
187 ( $O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$ ) or reduced to H<sub>2</sub>O<sub>2</sub> *via* the 2-electron pathway ( $O_2 + 2 H^+ +$   
188  $2 e^- \rightarrow H_2O_2$ ). In the latter case, some materials may cause a further reduction of H<sub>2</sub>O<sub>2</sub> to  
189 water molecules, leading to the 2+2-electron pathway ( $H_2O_2 + 2 H^+ + 2 e^- \rightarrow 2 H_2O$ ).

190 Another important issue is the method to be used to assess the catalytic activity for the ORR.  
191 Generally, the evaluation of the ORR performance of electrocatalysts is performed in a 3-  
192 electrode cell consisting of a working electrode, on which the electrocatalyst is deposited, a  
193 reference electrode and a counter electrode. The electrolytes used to study the oxygen reduction  
194 reaction can be alkaline (0.1 M KOH is the most commonly used) or acidic (typically 0.5 M  
195 H<sub>2</sub>SO<sub>4</sub> or 0.1 M HClO<sub>4</sub>) depending on the medium in which the electrocatalyst is to be  
196 characterized [2]. The influence of pH on the ORR activity of metal-free carbon-based catalysts  
197 has been studied previously. Experimental results showed that the ORR performance is worse  
198 in acidic than in alkaline media. According to DFT studies, this is due to a higher stabilization

199 of ORR intermediates in a protic environment, which leads to a higher energy requirement to  
200 complete the subsequent ORR steps and, consequently, to a lower catalytic activity [15]. The  
201 lack of protons in alkaline media leads to a lower stability of ORR intermediates and easy  
202 continuation of ORR mechanisms. It is worth noting that the ORR mechanisms in alkaline  
203 media are similar to those in acidic media (Figure 1). Nevertheless,  $\text{H}_2\text{O}_2$  is converted into  $\text{HO}_2^-$   
204 *via* equation (X1).



206 The 4-electron pathway, the 2-electron pathway and the 2+2-electrons pathway are given in  
207 equations X2, X3 and X4, respectively.



211 Regardless of the medium in which the ORR occurs, the 4-electron pathway is generally  
212 preferred to the 2-electron or 2+2-electron pathway because of the absence of intermediate  
213 species ( $\text{H}_2\text{O}_2$  or  $\text{HO}_2^-$ ). The latter may indeed participate in undesirable reactions and  
214 accelerate the aging of certain electrochemical systems [22].

215 Cyclic voltammetry (CV) is often used to qualitatively evaluate the ORR electrocatalytic  
216 activity of materials by studying the position of the reduction peak in the cathodic scan in an  
217  $\text{O}_2$ -saturated electrolyte. However, this route is insufficient to obtain accurate results due to the  
218 lack of quantitative parameters to compare different materials. At the same time, linear sweep  
219 voltammetry (LSV) with rotating disk electrodes (RDEs) aims to quantitatively study the  
220 kinetics of ORR by measuring several indicators such as onset potential, half-wave potential,  
221 limiting current density, or number of electrons transferred during the ORR process [23]. Figure  
222 2 shows a typical linear sweep voltammetry (LSV) curve measured in a 3-electrode cell with

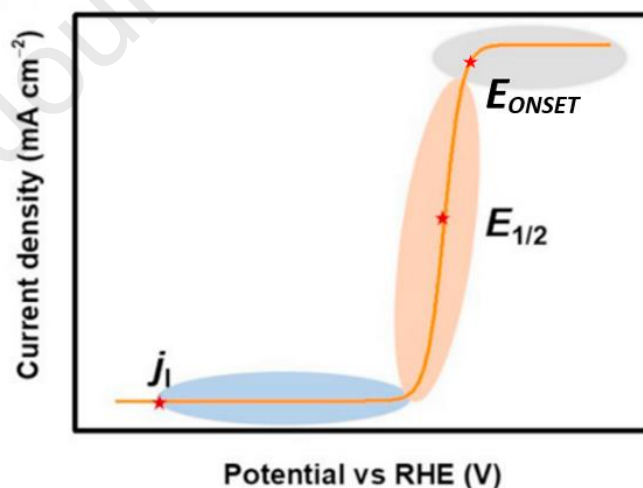
223 the presence of an electrocatalyst for ORR [24]. However, the definition and methods of  
224 determining these indicators differ among authors, and are generally not well explained or  
225 standardized. According to various publications in the literature, the most common definitions  
226 and determination methods for these indicators are as follows:

- 227 • The onset potential,  $E_{ONSET}$ , is the potential at which  $O_2$  reduction begins, accompanied by  
228 an increase in current density. Some authors measure this potential at 5% of the limiting  
229 current density [25,26], while others take it at a fixed value of current density (*e.g.*, - 0.1 mA  
230  $cm^{-2}$ ) [27–29]. This parameter reveals important information about the kinetics of the ORR  
231 and is the most reported in the literature. In general, the standard catalyst used as a reference  
232 material in ORR is a commercial platinum-based electrocatalyst, with a 20 wt.% Pt loading  
233 supported on carbon black, here simply referred to as Pt/C. The measured onset potential for  
234 the commercial Pt/C is equal to or greater than 0.96 V vs. RHE in 0.1 M KOH solution,  
235 which may change slightly depending on the parameters used in the electrochemical  
236 measurements.
- 237 • The half-wave potential,  $E_{1/2}$ , is the potential corresponding to half the limiting current  
238 density.  $E_{1/2}$  is then calculated as the intermediate value between the onset potential and the  
239 potential at which the diffusion-limited current is reached. For the commercial Pt/C, the half-  
240 wave potential is about 0.85 V vs. RHE in 0.1 M KOH solution.
- 241 • The limiting current density,  $j_l$ , is the measured current density at which the ORR is limited  
242 by mass transfer. This corresponds to the case where every molecule of  $O_2$  arriving at the  
243 surface of the electrocatalyst is immediately reduced, and the current limitation comes solely  
244 from the diffusion of  $O_2$  from the bulk of the electrolyte to the electrode surface and the  
245 number of electrons transferred.

- 246 • The number of transferred electrons can be defined as the number of electrons produced per  
 247 molecule of O<sub>2</sub> reduced during the ORR process. Over the years, this parameter has been  
 248 calculated by the Koutecky-Levich (KL) theory using Equation (1):

$$249 \quad \frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_l} = \frac{1}{j_k} + \frac{1}{0.62 n F D_{O_2}^{2/3} C_{O_2}^b \nu^{-1/6}} \omega^{-1/2} \quad (1)$$

250 where  $j$  is the current density (A cm<sup>-2</sup>) obtained after the normalization of the current  
 251 measured during the experiment (A) by the geometric area of the electrode (cm<sup>2</sup>),  $j_k$  is the  
 252 kinetic current density (A cm<sup>-2</sup>),  $j_l$  is the limiting current density (A cm<sup>-2</sup>),  $\omega$  is the angular  
 253 velocity of the rotating electrode (rad s<sup>-1</sup>),  $n$  is the number of transferred electrons,  $F$  is the  
 254 Faraday constant (96 486.4 C mol<sup>-1</sup>),  $D_{O_2}$  is the diffusion coefficient of O<sub>2</sub> in the electrolyte  
 255 (cm<sup>2</sup> s<sup>-1</sup>),  $C_{O_2}^b$  is the concentration of O<sub>2</sub> in the bulk of the electrolyte (mol cm<sup>-3</sup>), and  $\nu$  is the  
 256 kinematic viscosity of the electrolyte used (cm<sup>2</sup> s<sup>-1</sup>). The inverse of the current ( $1/j$ ) is then  
 257 plotted against the inverse of the square root of the rotation speed ( $\omega^{-1/2}$ ) to determine the  
 258 number of electrons transferred ( $n$ ) at different potentials [5,30].



259 **Figure 2.** Schematic illustration of a linear sweep voltammetry (LSV) curve during ORR  
 260 (Adapted from Ref. [24], Copyright 2021, with permission from Elsevier).  
 261

262 However, a recent publication has shown that the KL method is not accurate when using  
 263 porous materials such as carbons [31]. This is because the KL theory was developed for a flat

264 surface and does not take into account the internal porosity. In this case, the use of the rotating  
 265 ring disk electrode (RRDE) is more rigorous since the latter uses a second working electrode to  
 266 quantify the amount of H<sub>2</sub>O<sub>2</sub> generated during the ORR. The number of transferred electrons,  
 267  $n$ , is determined by measuring the currents produced on the disk (with the formation of H<sub>2</sub>O<sub>2</sub>  
 268 or HO<sub>2</sub><sup>-</sup> in acidic and alkaline medium, respectively) and the current of the second working  
 269 electrode with the oxidation of H<sub>2</sub>O<sub>2</sub> or HO<sub>2</sub><sup>-</sup>, again depending on the medium, to O<sub>2</sub> by  
 270 applying a sufficiently positive potential on the ring, typically between 1.2 and 1.6 V vs. a  
 271 reversible hydrogen electrode (RHE) (Equation (2)) [32]. This second working electrode is  
 272 often based on a platinum ring, although gold has proven to produce even better results [33].

$$273 \quad n = \frac{4I_d}{I_d + \frac{I_r}{N}} \quad (2)$$

274 In Equation (2),  $I_r$  (A) and  $I_d$  (A) are the measured currents at the ring and disk, respectively,  
 275 and  $N$  is the RRDE collection efficiency (determined experimentally). The rate of H<sub>2</sub>O<sub>2</sub> or HO<sub>2</sub><sup>-</sup>  
 276 (%) produced during the ORR process can also be calculated using Equation (3):

$$277 \quad \text{H}_2\text{O}_2 \text{ (\%)} = 200 \frac{NI_r}{I_d N + I_r} \quad (3)$$

278

### 279 **3. Presentation of biomass and synthesis of an efficient electrocatalyst**

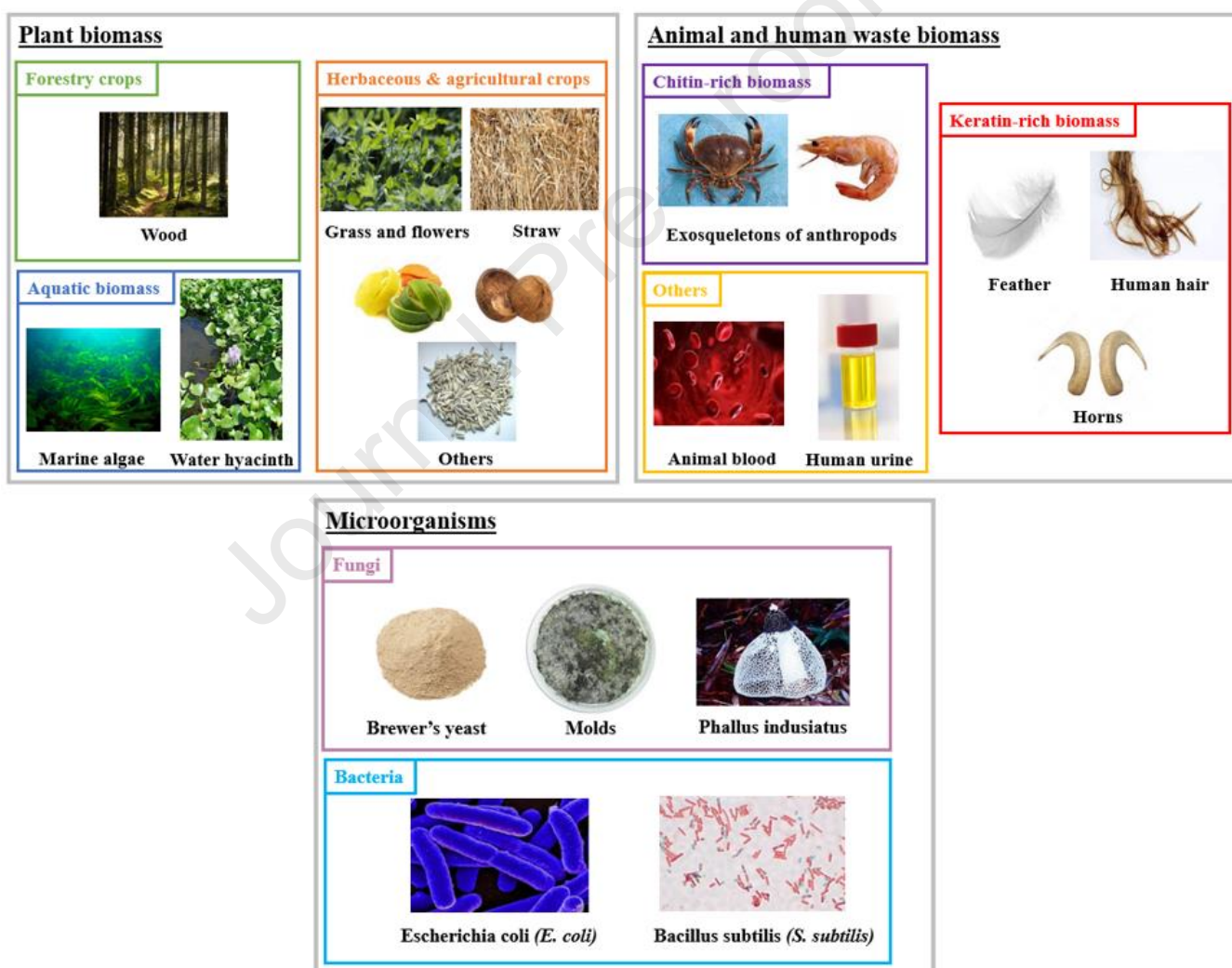
#### 280 *3.1. Brief presentation of some biomasses*

281 Biomass is the only component in nature that can be considered a green, inexpensive and  
 282 abundant source of carbon. Furthermore, the unique properties of biomass make it an attractive  
 283 precursor for the production of carbon materials with a variety of properties. The properties of  
 284 these biomass-derived carbon materials depend on the nature, morphology, structure, textural  
 285 properties, chemical composition, thermal history, etc., of the pristine precursor. This makes  
 286 biomass and biomass-derived carbon chemistry a complex branch of science in which great



287 efforts have been made to advance the understanding of these materials in multiple applications,  
 288 such as energy storage, sensing, environmental field or electrocatalysis, among others.

289 As mentioned above, biomass resources can be classified into three main categories [9,34];  
 290 (i) plant biomass (algae [35], seaweed [36,37], water hyacinth [38], alfalfa [39], seeds [40],  
 291 straws [41,42], bagasse [43], etc.), (ii) animal and human waste biomass (bone [44,45], blood  
 292 [25,46,47], urine [48], hair [49], tannery waste [50], etc.), and (iii) microorganisms (fungi [51–  
 293 53], and bacteria [54–57]), as shown in Figure 3.



294

295 **Figure 3.** Presentation of some biomass sources used as catalyst precursors.

296 *3.1.1. Biomass of plant origin*

297 Cellulose, with the chemical formula  $(C_6H_{10}O_5)_n$ , is one of the main constituents of the cell  
298 wall of many plants and is composed of several glucose units, the number of which depends on  
299 its precursor. In general, cellulose is in the form of microfibrils with a parallel arrangement of  
300 linear  $\beta$ -(poly-1,4-D-glucose) chains (Figure 4a). A collection of these microfibrils is called  
301 cellulose fiber. Cellulose can also be synthesized by bacteria with a higher degree of  
302 crystallinity and purity compared to that found naturally in plants, due to the absence of other  
303 molecules that induce modifications and reduce the purity of plant cellulose [5,17,20,58,59].

304 The second most abundant biomass resource in nature is hemicellulose, which belongs to  
305 the same polysaccharide family as cellulose. This polymer is composed of several sugar-based  
306 units that consist of five-membered carbon heterocycles (xylose and arabinose), six-membered  
307 carbon heterocycles (galactose and mannose) and seven-membered carbon heterocycles (4-O  
308 methylglucuronic acid). These units are linked together through hydrogen bonds to form  
309 hemicellulose (Figure 4b) [60]. The third most abundant plant biomass is lignin. Lignin is a  
310 three-dimensional non-carbohydrate polymer composed of three phenylpropanoic alcohols  
311 (coumaryl alcohol, coniferyl alcohol, sinapyl alcohol) that acts as a cement between cellulose  
312 fibers, and making wood a cellulose-reinforced, lignin-matrix biocomposite to a first  
313 approximation (Figure 4c) [20,61]. Finally, tannins are considered the fourth most common  
314 plant biomass in nature. Tannins belong to the polyphenol family and are found in the vacuoles  
315 and cell walls of plants, and are used as a chemical defense against several microorganisms,  
316 insects and fungi [5,20,58,62]. Since the proportions of these different polymers vary from plant  
317 to plant, the production of carbons from biomass results in a wide range of materials with  
318 diverse physicochemical characteristics. However, carbohydrates and polysaccharides are  
319 composed solely of carbon, oxygen and hydrogen atoms, which makes them unattractive  
320 precursors of carbonaceous materials for obtaining highly efficient ORR electrocatalysts,  
321 because the homogeneous distribution of charge density through the carbon layers is not

322 disrupted so that it can create active sites. To increase the catalytic properties of the resulting  
323 carbon materials, the introduction of heteroatoms is mandatory, as shown in the following  
324 references [5,63–65]. The introduction of N, P and S atoms indeed leads to a significant increase  
325 in the catalytic activity of glucose and lignin-derived carbon materials.

326 Other biomolecules of great interest for the production of carbons from biomass are  
327 carbohydrates. Carbohydrates are sugars that can be divided into three groups: (i)  
328 monosaccharides, which are composed of 3 to 7 carbon atoms (such as ribose with 5 carbon  
329 atoms or glucose with 6 carbon atoms), (ii) oligosaccharides, which are formed by 2 to 9  
330 monosaccharides connected by glycosidic bonds (such as sucrose or maltose), and (iii)  
331 polysaccharides, which are macromolecules consisting of 10 or more monosaccharide units  
332 (such as starch) [66].

333 Agricultural biomass wastes and residues (crop leaves, roots, nut shells, fruit peels ...) are  
334 therefore often useful as carbon precursors, as they are particularly rich in cellulose,  
335 hemicellulose and lignin [11]. Moreover, the forestry industry also generates significant  
336 amounts of biomass waste (sawdust, branches, etc.) that can be used to produce biomass-based  
337 carbon materials.

### 338 3.1.2. Biomass of animal and human origin

339 Animal and human biomass is mostly composed of proteins and minerals. Proteins are the  
340 most common animal biomass used to produce carbon materials. Proteins are macromolecules  
341 with a wide variety of polypeptides that are involved in multiple functions in living cells. One  
342 of the most interesting features of proteins for obtaining carbon materials is that they are based  
343 on nitrogen-rich compounds (from amino acid groups) and, therefore, they are interesting  
344 candidates for the preparation of nitrogen-doped carbon-based electrocatalysts [5].

345 Another important biomass precursor in the animal kingdom is chitin. With the formula  
346  $(C_8H_{13}O_5N)_n$ , chitin is an amino-polysaccharide biopolymer found in fungi and the

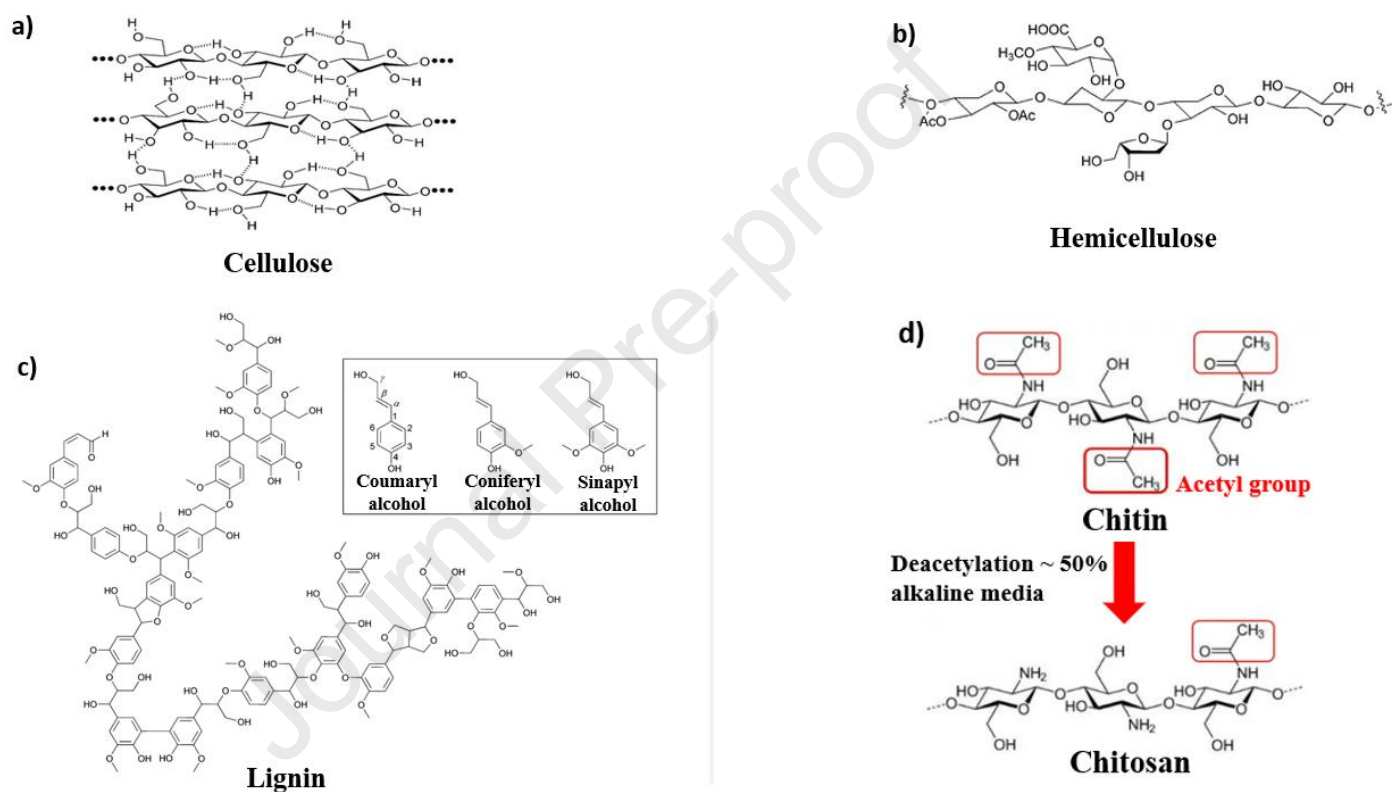
347 exoskeletons of arthropods as ordered crystalline microfibrils (Figure 4d) [67]. Chitosan is a  
348 semi-crystalline polymer obtained when the deacetylation of chitin (removal of its acetyl group  
349  $-\text{CO}-\text{CH}_3$ ) approaches about 50% in alkaline medium (Figure 4d). Chitosan has unique  
350 complexing and chelating properties that will promote the incorporation of dopants into the  
351 resultant carbon material due to the presence of amino, hydroxyl and acetamido groups [68].  
352 Keratin is also a promising precursor for the preparation of carbon materials derived from  
353 animal biomass. Keratin is a nitrogen- and sulfur-rich fibrous protein that is the main  
354 component forming the outermost layers of the vertebrates epidermis [69]. Keratin occurs  
355 primarily in two forms:  $\alpha$  or  $\beta$ . The former is found in soft tissues (human hair, sheep wool, etc.)  
356 while the latter is found in hard tissues (bird feathers, horns, hooves, etc.). Generally, keratin  
357 extraction is performed by acid, alkali or even enzyme hydrolysis of biomass precursors [70].

### 358 *3.1.3. Microorganisms*

359 Microorganisms are mainly divided into three families: fungi, bacteria and viruses. Among  
360 them, bacteria and fungi have attracted attention due to their rapid reproduction and special  
361 physicochemical properties [9]. They can be used as precursors and doping sources for the  
362 synthesis of carbon doped with one or more heteroatoms after decomposition and carbonization  
363 of proteins, phospholipids and metal salts [56,71]. Some metals such as iron can also be  
364 introduced into the carbon matrix originating from microorganisms [54,56].

365 Bacteria are considered the most common living organisms in natural environments.  
366 Typically, bacteria are grown in culture broths and then harvested after centrifugation, washing  
367 and drying [9]. During the transformation into carbonaceous material, the decomposition of  
368 polysaccharides, lipids and phospholipids present in bacteria allows the introduction of  
369 heteroatoms in the carbon skeleton such as nitrogen [54–56], phosphorus [54–56] or sulfur  
370 [54,56], which lead to the creation of numerous defects and active sites favorable to applications  
371 as catalysts.

372 Fungi are heterotrophic microorganisms that possess nuclei and cell walls. The main  
 373 component of these walls is chitin [9,72], unlike plants where the main component is cellulose.  
 374 Fungi can be divided into three types: molds [73], yeasts [74] and mushrooms [51–53]. They  
 375 are distinguished by their differences in morphology and chemical composition of the cell wall.  
 376 All fungi are rich in proteins and chitin, which will be used to obtain heteroatom doped-carbon  
 377 materials, useful for application in electrocatalysis as in the case of bacteria [9].

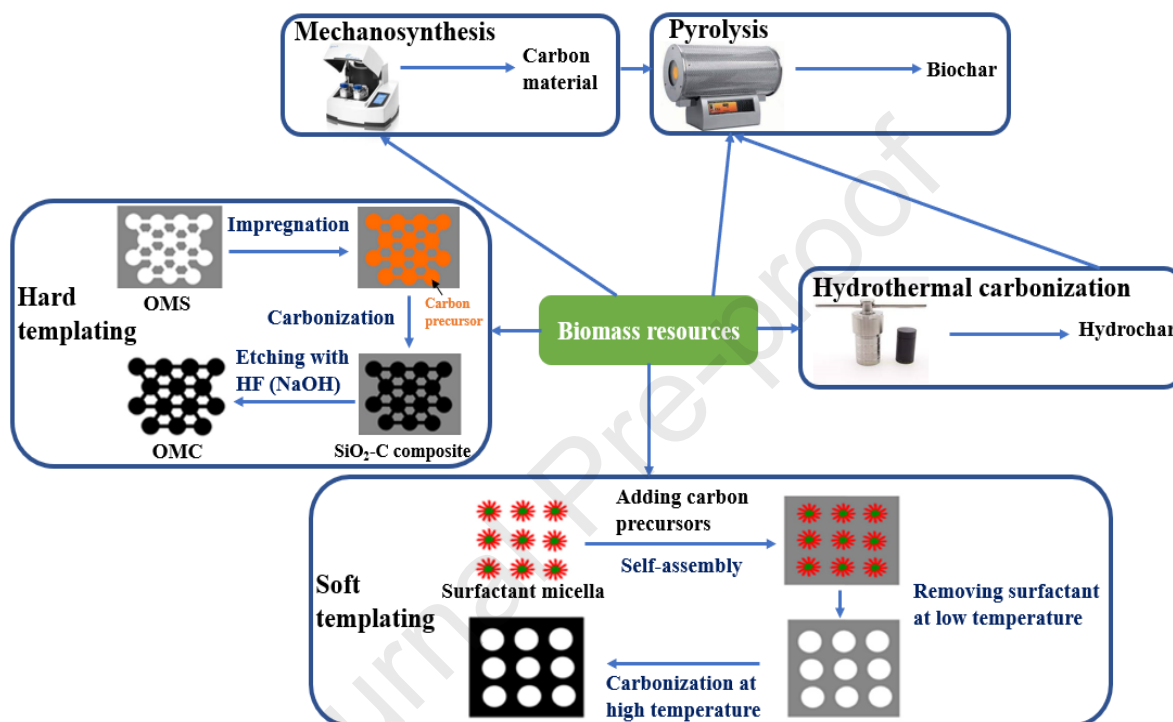


378  
 379 **Figure 4.** Chemical structure of: a) cellulose; b) hemicellulose; c) lignin; and d) chitin and  
 380 chitosan.

### 381 3.2. Synthesis of carbon materials from biomass

382 Obtaining carbon materials from biomass depends on the multiple parameters of their  
 383 possible synthesis methods, a summary of which is shown in Figure 5. The following is a brief  
 384 overview of the most widely used and efficient techniques for the production of carbons from  
 385 biomass. It should be emphasized that it is almost impossible to obtain undoped carbon

386 materials derived from biomass, as biomass is intrinsically rich in heteroatoms. It is possible to  
 387 classify the different forms of heteroatom doping of the final products as: (i) intrinsic doping  
 388 with heteroatoms coming from the constituent elements of the biomass precursor, or (ii)  
 389 extrinsic doping where the heteroatoms have been intentionally introduced during the synthesis  
 390 of the carbonaceous material.



391  
 392 **Figure 5.** Conversion of biomass precursors into porous carbon materials by different synthesis  
 393 routes. Hard-templating and soft-templating thumbnails (OMS and OMC standing for ordered  
 394 mesoporous silica and carbon, respectively) are reprinted from Ref. [75], Copyright 2014, with  
 395 permission from Elsevier.

### 396 3.2.1. Pyrolysis

397 Pyrolysis involves subjecting a carbonaceous precursor, *i.e.*, biomass in the present case, to  
 398 thermal treatment at temperatures typically between 350 °C and 1000 °C, with a heating ramp  
 399 of generally less than 10 °C min<sup>-1</sup>, in an inert atmosphere, typically N<sub>2</sub> or Ar. The heating rate  
 400 has a significant influence on the yield of carbon materials obtained from biomass. A high  
 401 heating rate will lead to a low yield due to high volatilization of the precursor and bio-oils are



402 often obtained as the final product. In contrast, a high yield of carbon material (also called char)  
403 can be obtained by using low heating rates [20].

404 The high temperatures of pyrolysis promote reactions in the precursor, such as condensation,  
405 crosslinking, isomerization and dehydration reactions, which convert it into a carbon material.  
406 In addition, various volatile compounds are released from the thermal decomposition of the  
407 biomass. At low temperatures, the resulting material is mainly in the form of carbonaceous  
408 materials with a high heteroatom content. This high degree of doping decreases when the  
409 temperature of the thermal treatment increases, accompanied by a reorganization of the carbon  
410 towards a less disordered state with a corresponding increase of the electrical conductivity [20],  
411 but never going spontaneously to graphitization when the precursor is biomass. The presence  
412 of certain metals, including Fe, Co, Ni and Mn, strongly influence the texture of the resulting  
413 carbons, since these metals promote graphitization through the 2 to 5 electrons in the *d* atomic  
414 orbitals that can induce strong bonds between the metal and the carbon-based materials [76].  
415 Two possible mechanisms have been proposed for this catalysis process: (1) the dissolution-  
416 precipitation mechanism where the amorphous carbon is first dissolved in metal particles and  
417 then precipitates into graphitic carbon, and (2) the formation-decomposition mechanism of  
418 intermediate carbides where the carbon interacts with the metal to produce metal carbides.  
419 Then, the metal atoms in the metal carbide moieties are volatilized at high temperature, leaving  
420 the graphitic carbon [10].

421 Activation is known as a process for improving or modulating the porosity and texture of  
422 carbon materials by the action of an activating agent. This method can be used during the  
423 pyrolysis of biomass to improve the textural properties of the resulting carbons. Physical  
424 activation is defined as a controlled gasification of the material by the action of an oxidizing  
425 gas with respect to carbon at the considered temperature, such as oxygen but especially water  
426 vapor and carbon dioxide, used as reactive gases after a first step of pyrolysis under inert gas

427 [77]. On the other hand, chemical activation corresponds to the chemical attack by reagents in  
428 the molten phase, such as  $ZnCl_2$ , KOH or NaOH [10,20,78]. Chemical activation is often  
429 performed by impregnation or simple physical mixing of the biomass precursor with the  
430 reagent. Then, a heat treatment is carried out. After cooling, the material is cleaned of excess  
431 chemical agent by washing with water, and then filtered and dried [79]. Both chemical and  
432 physical agents selectively attack the carbon material, generating a well-developed  
433 micro/mesoporosity in the pristine carbon [80].

434 Furthermore, not only the activation of carbonaceous materials may be relevant, but also the  
435 introduction of heteroatom precursors that can lead to the functionalization of biomass-derived  
436 carbons. To achieve this goal, it is useful for the pyrolysis of the biomass precursor to occur in  
437 the presence of one or more heteroatom sources (rich in nitrogen, sulfur, boron or/and  
438 phosphorus) to allow the introduction of additional elements into the carbonaceous backbone  
439 to change the electron and spin density around the surrounding carbon atoms. It is also common  
440 to use a stream of  $NH_3$  during pyrolysis to both add nitrogen to the material and create  
441 micropores by reaction with carbon at high temperature, since ammonia acts as both an  
442 activating and N-doping agent [5].

### 443 3.2.2. *Hydrothermal carbonization at low temperature*

444 Hydrothermal carbonization (HTC) is based on the reaction of a biomass precursor with  
445 water in an autoclave at a temperature generally between 100 and 200 °C and under a self-  
446 generated moderate pressure. The addition of an acid to the water accelerates the hydrolysis  
447 and separation of the biomass components. The transformation of these components into gas  
448 creates a large amount of micropores in the final carbonaceous material, usually called  
449 hydrochar. In addition, the aqueous medium and low temperatures involved promote the  
450 formation of a hydrochar with a large amount of oxygen functional groups, which decrease the  
451 electrical conductivity of the material but improve its hydrophilicity [81]. The properties of



452 hydrochar depend not only on the HTC conditions, which are quite versatile since it is possible  
453 to vary the temperature, time, pressure, pH, concentration and nature of various additives, but  
454 also of course on the nature of the biomass itself. Falco et al. [82] proposed the hydrothermal  
455 carbonization of glucose and raw straw, leading to the production of monodisperse spherical  
456 particles in the case of the pure carbohydrate. For the lignocellulosic biomass, composed of a  
457 mix of biopolymers, a fibrous structure close to the initial structure of raw straw with some  
458 particles was obtained.

459 However, hydrochars generally have a much lower carbon content than carbon materials  
460 obtained directly by conventional pyrolysis due to the higher level of dehydration that takes  
461 place during pyrolysis. Moreover, the specific surface area and thus the pore volume are higher  
462 for carbonaceous materials obtained by pyrolysis than for hydrochars. This observation has  
463 been attributed to the residual presence of decomposition products on the surface of hydrochars,  
464 which implies pore blockage [83].

### 465 3.2.3. *Mechanosynthesis*

466 The aforementioned procedures for the preparation of carbon materials involve thermal  
467 treatments, which increases the cost of these methodologies. To overcome this limitation,  
468 mechanosynthesis has been proposed as a promising alternative to produce carbon-based  
469 materials by using mechanical forces to provide the energy needed to convert biomass into  
470 carbons. Mechanosynthesis is an advanced milling technique that consists of a solid-state  
471 powder processing technique [84]. In order to achieve reproducibility of the different syntheses,  
472 the use of ball mills is preferred as it provides control over the parameters (grinding speed and  
473 time) compared to the manual grinding with a mortar and pestle that is highly dependent on the  
474 user. During the rotation of the ball mill, collisions of the balls with the powders, through  
475 mechanical forces, induce bond cleavages and surface defects, leading to chemical modification  
476 of the reagents [85]. This is a new synthesis route for the preparation of carbonaceous materials,

477 whereas it has been widely used in recent years to obtain metal alloys and oxides.[86] Recent  
478 studies [87,88] have proven that the use of mechanosynthesis leads to carbon materials with  
479 high yield without the use of toxic and polluting solvents. Nevertheless, despite the high energy  
480 input of mechanosynthesis, a second pyrolysis step may be recommended for special  
481 applications in order to increase the degree of graphitization of the resulting carbon and thus  
482 the electrical conductivity of the material.

#### 483 3.2.4. *Template methods*

484 One of the main limitations of pyrolysis and hydrothermal carbonization is the lack of control  
485 over the textural properties of the resulting carbon materials. In order to prepare carbon  
486 materials with controlled structures and porosities, the use of templates during thermal  
487 treatments is the most common methodology. Template methodologies can be classified into  
488 two different groups: hard-templating and soft-templating [89,90]. They are not strictly  
489 speaking methods for producing carbon materials but for modulating the textural properties of  
490 the resulting carbons. Templates can be used in pyrolysis, hydrothermal treatments and so on.  
491 Nevertheless, this section will explain the different types of templates and the advantages and  
492 disadvantages of their use.

493 The hard-template method is based on the replication of a well-structured material with a  
494 defined pore structure (such as mesoporous silicas [20,75,80], MOFs [78,91,92], zeolites  
495 [75,93], metal oxides [20] etc.). The carbon precursor is introduced into the pores of the  
496 template through chemical [94] or electrochemical [95] methods, and then heat treatment is  
497 applied. In hard-template methods, the template material is thermodynamically stable at high  
498 temperature and the carbon material is produced with the reverse structure of the template.  
499 Finally, the template can be removed, if required, using chemicals (*e.g.*, HF or NaOH). The  
500 main limitation of this method is indeed the use of such toxic chemicals for template removal,  
501 which limits the environmental friendliness of this type of carbon material production [20].

502 To avoid the major limitation of hard-template methods, soft-templating is proposed to  
503 overcome the use of hazardous chemicals. The soft-template method is based on the self-  
504 assembly of carbon precursors with amphiphilic molecules such as surfactants (*e.g.*,  
505 cetyltrimethylammonium bromide, CTAB [96]) or block copolymers (*e.g.*, Pluronic® F127  
506 [87,88,97]) in a suitable solvent. Typically, the carbon precursor positions itself around the  
507 micelles spontaneously formed by the organic agents in the solution. The soft template is then  
508 removed during pyrolysis, leading to a developed but highly controlled porosity in the resulting  
509 carbon materials [20]. Other synthesis routes for the preparation of carbon materials exist, such  
510 as laser-induced carbonization [98] or microwave-assisted carbonization [99,100], which are  
511 notably used for the rapid heating of biomass, but they have not been widely discussed in the  
512 literature and only a few works can be found on these methods.

513

#### 514 **4. Biomass-derived carbon materials used in ORR**

##### 515 *4.1. Metal-free, heteroatom-doped carbon materials*

516 Biomass-derived carbon, whether intentionally doped or not, have been presented as one of  
517 the most promising alternatives as electrode materials in many applications, such as metal-air  
518 batteries [101], supercapacitors [79,102] or fuel cells [15]. The carbon precursor, the  
519 preparation method or the use of functionalization routes make biomass-derived carbons  
520 catalytically active materials or metal catalyst supports for ORR. Interestingly, heteroatoms,  
521 such as phosphorus, boron, and in particular nitrogen, play a prominent role in enhancing the  
522 ORR properties of carbon materials because they have an electron-withdrawal effect on the  
523 adjacent carbon atoms. This creates a positive electron density in the carbon network, which  
524 acts as an active site where dioxygen molecules are attracted, chemisorbed and then reduced  
525 [103–105]. In addition, heteroatoms can also serve as anchor points for various metals that can

526 also behave as active sites for the ORR. Since the strength of the metal-heteroatom bond is  
527 often much higher than the metal-carbon interaction, the activity and stability of heteroatom-  
528 based electrocatalysts are much higher than those of electrocatalysts that do not have such  
529 defects [19].

530 In general, defects located in the carbon matrix allow to generate active sites for the ORR,  
531 especially due to the presence of heteroatoms from the biomass precursor. Nevertheless, it  
532 should not be overlooked that the introduction of these heteroatoms also induces point defects  
533 that may also be responsible for the improved ORR performance of these electrocatalysts [63].  
534 Whatever the nature of the heteroatoms concerned, it is possible to perform a mono-doping  
535 with a single heteroatom or a multi-doping in order to play on the synergy between several  
536 kinds of heteroatoms to increase the performances of the ORR [106]. From a theoretical and  
537 experimental points of view, the defects induced have been shown to be responsible for the high  
538 catalytic performance of different heteroatom-doped carbon materials. Among them, the role  
539 of pentagons and carbenes should be noted [107].

540 Textural properties should not be forgotten when considering active sites in carbon materials  
541 as it has been also shown that the higher the textural properties, the higher the catalytic activity  
542 towards the ORR. This is particularly notable when carbon materials have ultramicropores  
543 (pore width < 0.7 nm), which can act as “nano-reactors” that enhance the kinetics of this  
544 reaction [108,109]. Through mathematical modeling of the ORR in porous carbon materials,  
545 Gabe et al. [110] highlighted the importance of microporosity in facilitating the access of O<sub>2</sub> to  
546 active sites. In addition, they demonstrated that pore size distribution is of paramount  
547 importance by showing that narrow pores increase the residence time of the H<sub>2</sub>O<sub>2</sub> molecules  
548 produced *via* the 2-electron pathway. This large residence time increases the chances of further  
549 reduction of H<sub>2</sub>O<sub>2</sub> to water molecules *via* the 2+2-electron pathway.

550 The specific surface area of the synthesized biomass-based carbon material thus has a  
551 significant effect on the catalysis of the ORR by providing greater accessibility to the active  
552 sites. Usually, the specific area of a sample is determined by the well-known Brunauer–  
553 Emmett–Teller (BET) method, which consists in determining the nitrogen adsorption isotherms  
554 at  $-196^{\circ}\text{C}$  and/or  $\text{CO}_2$  at  $0^{\circ}\text{C}$ . The analysis of these isotherms then gives access to the textural  
555 properties of the material. The higher the available surface area, the greater the exposure of the  
556 active sites, resulting in improved catalytic performances in the ORR. Li et al. [111] prepared  
557 a biomass-derived N-doped carbon material by a two-step pyrolysis at  $500^{\circ}\text{C}$  of *Scindapsus*-  
558 type aquatic plant under  $\text{N}_2$  flow and then at  $800^{\circ}\text{C}$  under  $\text{NH}_3$ . The resulting carbon material  
559 had a specific BET area of  $1599\text{ m}^2\text{ g}^{-1}$  with an interconnected porous architecture favoring the  
560 transport of molecules to the active sites. This resulted in an excellent  $E_{\text{ONSET}}$  of  $0.995\text{ V}$  vs.  
561 RHE and an  $E_{1/2}$  of  $0.825\text{ V}$  vs. RHE.

562 The porosity of carbon materials is not only due to the inherent characteristics of the  
563 precursors, but can also be modulated by the activation process, as discussed in Section 3.2.  
564 The use of chemical or physical agents in the thermal treatment of biomass precursor allows  
565 the generation of nanopores after the volatilization of several gases ( $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ , etc.)  
566 during pyrolysis, which has led to improved ORR activities in different carbon materials. Zhou  
567 et al. [112] thus obtained a biochar with a high specific area of  $1969\text{ m}^2\text{ g}^{-1}$  after immersing  
568 eggplant pieces in a  $0.5\text{ M}$  KOH solution for 24 hours, followed by pyrolysis at  $800^{\circ}\text{C}$ . Then,  
569 the material was washed to remove excess KOH and the powder was ball-milled and  
570 subsequently heat-treated at  $1000^{\circ}\text{C}$  in the presence of  $\text{NH}_3$ . The same synthesis was performed  
571 without KOH activation for comparison and the resulting surface specific area was  $289\text{ m}^2\text{ g}^{-1}$   
572 lower, resulting in a decrease in  $E_{\text{ONSET}}$  and  $E_{1/2}$  of  $90\text{ mV}$  and  $200\text{ mV}$ , respectively. Other  
573 authors also used KOH [113–115] or  $\text{KHCO}_3$  [115] as chemical activating agents to modify the  
574 textural properties and induce changes in microporosity to increase the electrocatalytic activity

575 in ORR of their biomass-based materials. Therefore, the specific surface area and the presence  
576 of different types of pores are important factors that influence the mass transport of O<sub>2</sub> to the  
577 active sites of the electrocatalyst and thus the kinetics of the ORR. Mesopores and macropores  
578 provide transport channels for dioxygen molecules to the active sites in the micropores and help  
579 the transport of water produced in the micropores to the bulk of the electrolyte.

580 However, having a large surface area does not always mean exhibiting excellent ORR  
581 activity. For example, He et al. [116] obtained an N, S co-doped carbon material with a specific  
582 surface area of 1689 m<sup>2</sup> g<sup>-1</sup> by a first pyrolysis at 800 °C of mulberry leaves as precursor in the  
583 presence of KOH, followed by a second pyrolysis in the presence of thiourea at the same  
584 temperature. However, they only obtained an onset potential of 0.86 V vs. RHE in alkaline  
585 medium. This proves that the specific surface area is important to provide good accessibility to  
586 the active sites but the nature and density of these sites are also relevant to induce the  
587 chemisorption and reduction of oxygen.

588 Nevertheless, this review article does not focus only on the textural properties of carbon  
589 materials and the consequences on catalytic activity for the ORR. If readers are interested in  
590 more information, we encourage them to read the works of Radovic [107,117] for an in-depth  
591 understanding of point defects and textural properties. In the following, we discuss the influence  
592 of biomass precursors and heteroatom composition on catalytic activity for the ORR.

#### 593 *4.1.1. Single heteroatom-doped carbon materials*

594

##### 595 *4.1.1.1. Nitrogen-doped carbon materials*

596 As commented above, carbonaceous materials produced from biomass are inherently rich in  
597 heteroatoms. This results in a change in electron density near the carbon atoms, which facilitates  
598 O<sub>2</sub> adsorption and charge transfer and thus improves ORR performance [63,118]. One of the  
599 origins of the controversy over N-doped carbon materials is the relationship between total  
600 nitrogen content and ORR activity. For many years, some authors [119,120] indeed directly

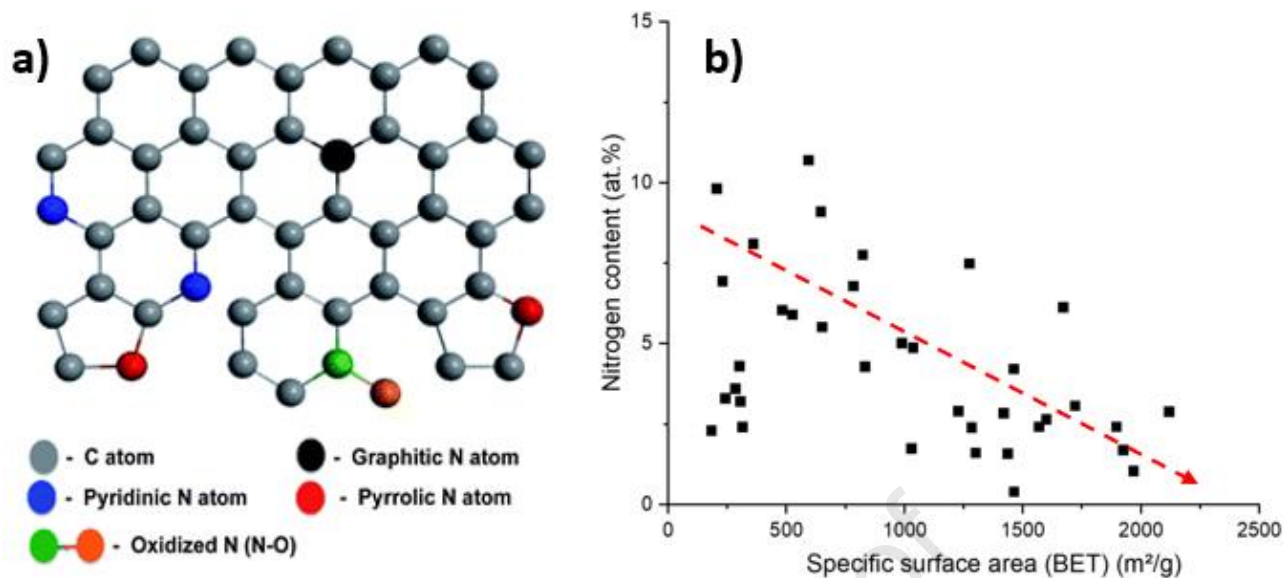
601 linked the catalytic activity towards ORR to the nitrogen content. Nevertheless, this claim has  
602 been shown to be wrong because it is not only the N content that is relevant for ORR in N-  
603 doped carbon materials, but more importantly the type of nitrogen. Zhang et al. [121] thus  
604 reported the synthesis of a char obtained by mechanochemical synthesis of coconut shell powder,  
605 melamine and  $\text{KHCO}_3$  activator (introduced with a mass ratio of 1:3:3) followed by pyrolysis  
606 at 800 °C. With a high nitrogen content (11.51 at.%) in their material, they obtained an  $E_{\text{ONSET}}$   
607 of 0.95 V vs. RHE and an  $E_{1/2}$  of 0.77 V vs. RHE. Meanwhile, Wang et al. [122] produced a  
608 biochar from coconut palm with only 2.84 at.% nitrogen but with better electrocatalytic  
609 performance ( $E_{\text{ONSET}} = 1.01$  V vs. RHE;  $E_{1/2} = 0.87$  V vs. RHE). This means that it is not the N  
610 content that determines the ORR performance, but rather the nature of the nitrogen species that  
611 must be additionally obviously accessible by the  $\text{O}_2$  molecule in order to trigger the ORR  
612 process.

613 The specific positions of the nitrogen atoms [123] (Figure 6a) in the carbon matrix appear to  
614 play an important role in the catalytic activity towards the ORR. A general agreement seems to  
615 be found after years of great controversy. For example, Zhang et al. [124] produced a nitrogen-  
616 rich (4.26 at.%) carbonaceous material from Yuba with the majority in the form of graphitic N  
617 (3.23 at.%), which shows a comparable electrocatalytic performance to commercial Pt/C with  
618 an  $E_{\text{ONSET}}$  of 0.97 V vs. RHE and an  $E_{1/2}$  of 0.86 V vs. RHE. The high proportion of graphitic  
619 N in the material is reported to be the main reason for this high catalytic activity observed for  
620 the ORR. The high catalytic performance of graphitic N was further confirmed by selective  
621 doping of a carbon material [125,126]. The selective doping with a single species (i.e., graphitic  
622 N) allowed the evaluation of the catalytic performance of such a functional group. Carbon  
623 materials selectively doped with graphitic N showed similar catalytic performance to Pt/C  
624 electrocatalysts, confirming the highly catalytic efficiency of this functionality towards the  
625 ORR. In the work of Liu et al. [127], the proportion of pyridinic N and graphitic N is more than

626 50% of the total N content (7.76 at.%) detected in their carbonaceous material from water  
627 lettuce, which could explain an  $E_{ONSET}$  equal to 1.00 V vs. RHE recorded for their catalyst.  
628 Some other studies [111,128–133] have also shown that graphitic nitrogen (also called  
629 quaternary) and pyridinic nitrogen are considered as the most active nitrogen species to provide  
630 high catalytic performance for ORR activity compared to other nitrogen functionalities.  
631 Nevertheless, some authors [134–137] have reported that pyrrolic nitrogen atoms or N-C-O  
632 species have notable ORR catalytic activity.

633 The textural properties and degree of nitrogen functionalization have been shown to be very  
634 important for the preparation of highly active N-doped carbon-based ORR electrocatalysts.  
635 However, high degrees of functionalization often lead to a significant decrease in the porous  
636 texture of carbon materials [138]. Figure 6b shows a graphical representation of nitrogen  
637 content versus BET area for several biomass-derived N-doped carbon catalysts reported in the  
638 literature [40,41,43,51,52,92,111–113,115,122,124,127,129–132,136,137,139–156]. This  
639 graph indicates that the highest textural properties are observed in carbon materials with the  
640 lowest degree of functionalization, and therefore, if a high nitrogen content is required, the  
641 textural properties will likely be diminished. This was also observed in the work of Lin et al.  
642 [157]. These authors increased the specific surface area of their N-doped carbon material by  
643 increasing the proportion of KOH in the activation step: with the resulting increase in surface  
644 area, the nitrogen content was significantly reduced. However, as discussed above, both  
645 parameters are important for good catalytic properties in ORR. It is therefore imperative to find  
646 the right balance between these two parameters to create a high-performance catalyst.

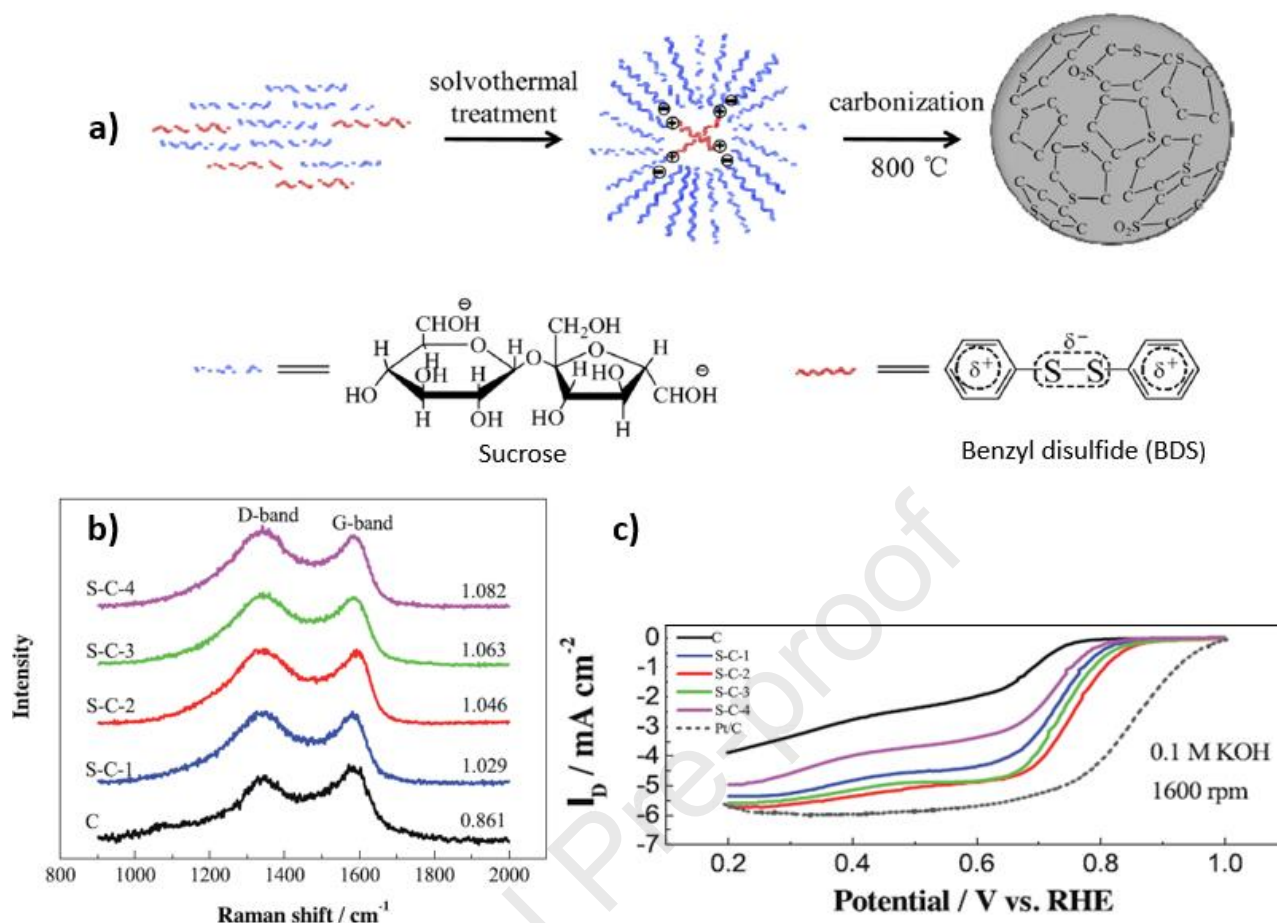




647  
 648 **Figure 6.** a) Possible positions of nitrogen atoms in the carbon backbone (Reprinted from Ref.  
 649 [123] with permission from the Royal Society of Chemistry); b) Nitrogen content vs. specific  
 650 BET area of different biomass-based N-doped carbon catalysts from the literature  
 651 [40,41,43,51,52,92,111–113,115,122,124,127,129–132,136,137,139–156].

#### 652 4.1.1.2. Sulfur-doped carbon materials

653 The introduction of other heteroatoms, such as sulfur, into biomass-derived carbon materials  
 654 has also been studied due to the larger size of the sulfur atom, which not only induces changes  
 655 in the electron density along the carbon layers, but also create additional defects in the carbon  
 656 matrix. Sulfur-doped carbon spheres (4.04 at.% S) were obtained after solvothermal synthesis  
 657 of sucrose with benzyl disulfide (BDS) and subsequent pyrolysis at 800 °C [158] (Figure 7a).  
 658 The authors investigated the effect on the ORR performance of the S content by changing the  
 659 sucrose/BDS molar ratio. The better catalytic performance was not attributed to the S content,  
 660 but to the defects that were generated as a result of the addition of sulfur species during the heat  
 661 treatment. High-temperature treatment indeed leads to the formation of S-based volatiles,  
 662 resulting in a greater contribution of defects in the carbon material.



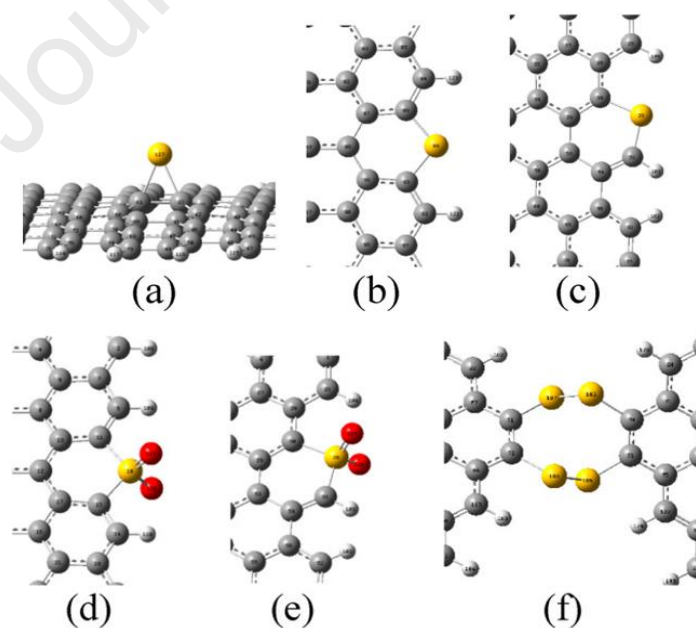
663

664 **Figure 7.** a) Schematic illustration of the preparation of S-doped carbon spheres; b) Raman  
 665 spectra of as-prepared S-doped carbon spheres (S-C-1, S-C-2, S-C-3, S-C-4 refer to samples  
 666 obtained with sucrose:BDS molar ratios of 10:1, 6:1, 4:1 and 1:1, respectively). The ratio of D-  
 667 band to G-band ( $I_D/I_G$ ) is given for each sample; c) Linear sweep voltammograms (LSVs) on  
 668 the rotating ring-disk electrode for the as-prepared carbon spheres with and without S doping,  
 669 and the commercial Pt/C catalyst in O<sub>2</sub>-saturated 0.1 M KOH solution at 1600 rpm (Reprinted  
 670 from Ref. [158], Copyright 2015, with permission from Elsevier).

671 To support this hypothesis, Raman spectroscopy was used as it provides valuable  
 672 information about the structural order. With this technique, two characteristic peaks are  
 673 observed in the spectra: the G-band and D-band, which are associated with stretching vibrations  
 674 of the sp<sup>2</sup>-hybridized C atoms and the defects in the carbon structure, respectively. The higher  
 675 the  $I_D/I_G$  intensity ratio, the greater the presence of defects in general [159]. The sulfur-doped

676 samples showed a higher  $I_D/I_G$  ratio compared to pristine carbon (Figure 7b), suggesting that  
677 sulfur-doping has introduced additional defects. In addition, the S-doped carbon materials  
678 exhibited higher ORR catalytic performance than undoped carbon, indicating the importance  
679 of defects from the insertion of sulfur into the carbon backbone (Figure 7c).

680 Zhang et al. [160] performed DFT calculations to understand the nature of the active sites in  
681 sulfur-doped graphene. For the study, different clusters of sulfur-doped graphene were chosen:  
682 sulfur adsorbed on the graphene layer (Figure 8a), S-substitution at zigzag (Figure 8b) and  
683 armchair (Figure 8c) edges,  $\text{SO}_2$ -substitution at zigzag (Figure 8d) and armchair (Figure 8e)  
684 edges, and two pieces of graphene connected by sulfur ring clusters (Figure 8f). Based on the  
685 formation energy, sulfur adsorption on the graphene surface was found to be the most stable  
686 configuration and the presence of Stone-Walker defects enhance the sulfur doping. Moreover,  
687 the authors found that the active sites of these S-doped clusters are localized on the carbon  
688 atoms located at the zigzag edges or near the  $-\text{SO}_2$  species. The electrocatalytic activity for ORR  
689 was attributed to the high spin and charge densities generated by these active sites.



690  
691 **Figure 8.** Illustration of several possible sulfur-doped graphene clusters: (a) sulfur adsorbed on  
692 the graphene layer; S-substitution at (b) zigzag, and (c) and armchair edges;  $\text{SO}_2$ -substitution

693 at (d) zigzag, and (e) armchair edges; and (f) two pieces of graphene connected by sulfur ring  
694 clusters (f). Carbon, hydrogen, sulfur, and oxygen atoms are shown in gray, white, yellow and  
695 red, respectively (Reprinted with permission from Ref. [160], Copyright 2014, with permission  
696 from American Chemical Society).

697

#### 698 4.1.1.3. Phosphorus-doped carbon materials

699 Heteroatoms less electronegative than carbon, such as phosphorus, have also been used to  
700 facilitate the adsorption and reduction of the dioxygen molecule in carbon materials. The  
701 creation of a positive charge on the phosphorus facilitates the chemisorption of O<sub>2</sub> directly onto  
702 the heteroatom and not onto neighboring carbon atoms as was the case with nitrogen doping.  
703 For instance, effective doping of hollow carbon spheres with homogeneously distributed  
704 phosphorus on the surface (1.59 at.%) and in the bulk (1.61 at.%) of the material was prepared  
705 by Wu et al. [161] using tetraphenylphosphonium bromide as the phosphorus source and  
706 glucose as the carbon source. They also used an anionic surfactant (sodium dodecyl sulfate) to  
707 control the morphology and porosity of the final material obtained by hydrothermal synthesis  
708 followed by pyrolysis at 800 °C. They attributed the high ORR performance ( $E_{ONSET} = 0.90$  V  
709 vs. RHE) to the phosphorus species, proposed as active sites, and/or to the modified electronic  
710 density induced by the phosphorus species. The introduction of phosphorus into the carbon  
711 matrix induces changes in the carbon atoms located near the P heteroatom, which might lead to  
712 improved catalytic activity. DFT simulations were performed to study the influence of  
713 phosphorus atoms on the ORR activity of P-doped carbon materials [162]. The presence of  
714 phosphorus promotes O<sub>2</sub> chemisorption on the surface of P-doped graphene and CNTs. O<sub>2</sub>  
715 molecules bind in a bridging bond mode configuration on P atoms, forming two P-O bonds.  
716 Subsequently, oxygen reduction occurs through dissociation of the dioxygen molecules into  
717 two oxygen atoms or through hydrogenation with the formation of OOH species [162,163].

718 Although the origin of the catalytic activity of N-doped carbon materials seems clearer, the  
 719 identification of the active sites in other heteroatom-doped carbons is controversial. Few  
 720 researchers directly attribute catalytic activity to heteroatoms, but others link it to defects  
 721 generated after volatilization of these species. Further understanding of this topic must be  
 722 addressed in the coming years for the design of advanced metal-free carbon-based  
 723 electrocatalysts. Table 1 reports the synthesis procedure, physicochemical properties and ORR  
 724 performance obtained from some metal-free and single heteroatom-doped carbons derived from  
 725 biomass.

726

727 **Table 1.** Metal-free and single heteroatom-doped carbon electrocatalysts for ORR.

728 Electrochemical data were obtained in 0.1 M KOH electrolyte.

Biomass source	Other sources	Synthesis method	Doping atoms (at.%)	Specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	Total pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	$E_{\text{ONSET}}$ (V vs. RHE)	$E_{1/2}$ (V vs. RHE)	$j_l$ ( $\text{mA cm}^{-2}$ ) at 1600 rpm	Number of transferred electrons $n$	Ref.
Scindapsus	$\text{NH}_3$	Pyrolysis	N: 2.65	1599	--	0.995	0.825	--	3.9	[111]
Eggplant	KOH $\text{NH}_3$	Activation, ball-milling, pyrolysis	N: 1.04	1969	--	0.93	0.83	5.5 at 0.2 V vs. RHE	3.87	[112]
Plum blossom	KOH Melamine	Carbonization, activation, pyrolysis	N: 2.89	2119	0.76	0.91	0.82	5.96 at 0.2 V vs. RHE	3.83	[113]
Papaya skin	Melamine $\text{KHCO}_3$	Pyrolysis, ball-milling, pyrolysis, activation	N: 6.13	1671	--	1.00	0.85	5.84 at 0.2 V vs. RHE	3.96	[115]
Coconut mesocarp	Melamine $\text{KHCO}_3$	Ball-milling, activation, pyrolysis	N: 11.55	1676	0.72	0.95	0.77	5.05 at 0.2 V vs. RHE	~4	[121]
Coconut palm leaves	Melamine KOH $\text{KHCO}_3$	Pyrolysis, functionalization, activation	N: 2.84	1419	0.94	1.01	0.87	5.5 at 0.2V vs. RHE	3.96	[122]
Glucose	Zeolitic imidazolate framework (ZIF-7)	Immersion, pyrolysis	N: 6.79	783	0.56	0.86	0.70	--	3.68	[92]
Corn starch	Urea	Immersion, pyrolysis	N: 2.42	1569	3.65	0.93	0.81	--	3.54-3.7	[129]

Yuba	ZnCl <sub>2</sub>	Immersion, pyrolysis	N: 4.26	832	--	0.97	0.86	5.09 at 0.6 V vs. RHE	3.81	[124]
Water lettuces	NH <sub>3</sub>	Freeze-drying, pyrolysis	N: 7.76	823	0.57	1.00	0.89	--	3.82-3.98	[127]
Shrimp shells	--	HTC, Silica templating, pyrolysis	N: 8.1	360	--	0.91	0.75	5.3 at 0.6 V vs. RHE	3.75-3.95	[131]
Soybean dregs	Urea	Calcination urea, pyrolysis	N: 6.04	483	1.57	0.90	0.77	--	3.31-3.63	[132]
Chicken feathers	KOH	Activation, pyrolysis	N: 4.3	301	--	0.96	--	--	--	[136]
Chicken feathers	KOH	Carbonization, activation, pyrolysis	N: 2.3	183	0.24	0.98	--	--	~4	[137]
Glucose	CNTs Urea	Immersion, pyrolysis	N: 10.7	594	0.58	0.95	0.82	--	3.9	[139]
Bacterial cellulose	Urea	Immersion, freeze-drying, pyrolysis	N: 9.82	206	--	0.93	0.80	5.0 at 0.4 V vs. RHE	3.6-4.0	[140]
<i>Typha orientalis</i>	NH <sub>3</sub>	HTC, freeze-drying, pyrolysis	N: 9.1	898	0.36	0.93	0.78	4.8 at 0.2 V vs. RHE	3.85-3.96	[141]
Silk cocoons	ZnCl <sub>2</sub>	Boiling, carbonization, activation	N: 7.49	1274	0.6	0.99	0.83	--	3.72-3.96	[142]
Bacterial cellulose	Polypyrrole	Polymerization, lyophilization, pyrolysis	N: 6.94	230	--	0.93	--	5.7 at 0.2 V vs. RHE	~4	[143]
Soybean	Na <sub>2</sub> CO <sub>3</sub> CaCl <sub>2</sub>	Immersion, boiling, coagulation, freeze-drying, pyrolysis	N: 5.52	652	0.68	0.94	0.81	4.41 at 0.4 V vs. RHE	3.48-3.84	[144]
Beancurd	NaCl Urea Na <sub>2</sub> CO <sub>3</sub>	Immersion, lyophilization, pyrolysis, immersion, pyrolysis	N: 5.02	988	0.69	0.96	0.81	--	3.9	[145]
Glucose	Dicyandiamide ZnCl <sub>2</sub>	HTC, activation	N: 4.88	1036	0.53	0.92	--	2.67 at 0.5 V vs. RHE	3.5-3.9	[146]
Corn straw	KOH	Carbonization, activation	N: 4.21	1461	0.92	0.81	--	--	--	[41]
Dandelion seeds	ZnCl <sub>2</sub>	Activation, pyrolysis	N: 2.9	1228	0.67	0.83	0.75	4.98 at 0.1 V vs. RHE	3.7-4.0	[40]
Glucose	NH <sub>3</sub>	HTC, pyrolysis	N: 2.61	2589	1.71	0.84	0.76	--	3.60-3.77	[148]

Enoki mushrooms ( <i>Flammulina velutipes</i> )	CNTs	Ball-milling, pyrolysis	N: 3.2	305	0.35	0.94	0.81	3.98 at 0.5 V vs. RHE	3.9	[52]
Pomelo peels	--	HTC, pyrolysis	N: 2.41	314	0.22	0.88	--	--	3.52	[150]
Bagasse	NH <sub>3</sub>	Boiling, freeze-drying, pyrolysis	N: 2.4	1284	--	0.88	0.77	5.21 at 0.1 V vs. RHE	3.8	[43]
Grape skins	--	Fermentation, HTC, pyrolysis	N: 1.74	1029	0.52	0.96	--	6.93 at 0 V vs. RHE	3.8-4.0	[152]
Ginkgo leaves	NH <sub>3</sub>	Pyrolysis, pyrolysis	N: 1.59	1436	--	--	0.81	--	3.7	[153]
Alder wood	NaOH Dicyandiamide	Activation, immersion, pyrolysis	N: 1.7	1924	1.6	0.93	0.8	--	~4	[154]
Poplar catkins	ZnCl <sub>2</sub>	Activation, pyrolysis	N: 0.4	1463	1.31	0.82	0.76	--	~4	[155]
Lotus roots	K <sub>2</sub> CO <sub>3</sub>	Carbonization, ball-milling, activation	N: 1.61	1301	0.74	0.84	0.76	4.4 at 0.2 V vs. RHE	~4	[156]
Sucrose	Benzyl disulfide	HTC, pyrolysis	S: 4.0	561	0.18	0.88	0.77	5.06 at 0.5 V vs. RHE	3.81	[158]
Glucose	C <sub>24</sub> H <sub>20</sub> P(Br), sodium dodecyl sulfate	HTC, soft-templating, pyrolysis	P: 1.61	654	0.36	0.90	--	--	3.86	[161]

729

730 *4.1.2. Multi-doped carbon materials*

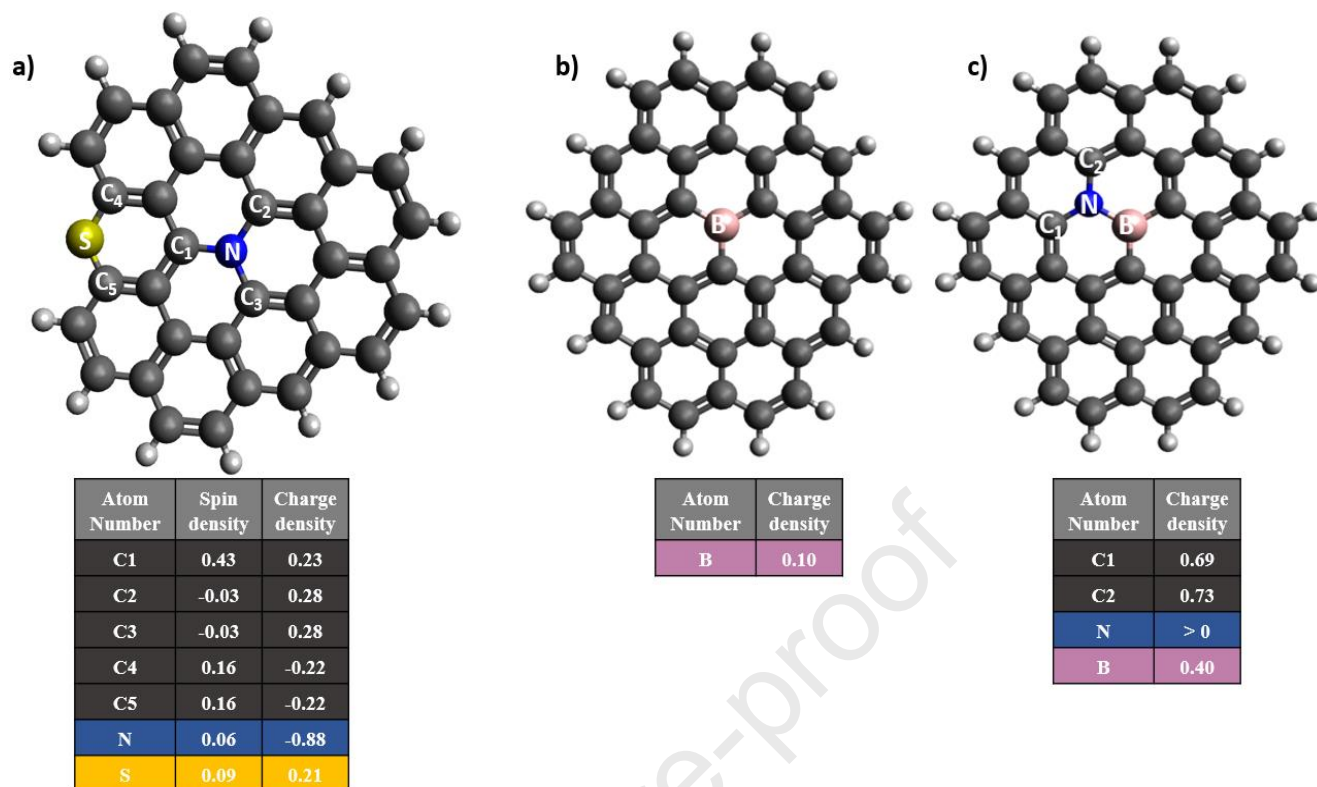
731 The purpose of doping with several heteroatoms is the creation of a synergistic effect in the  
732 electron density of the carbon material to improve the catalytic activity for ORR, due to the  
733 presence of different active sites or the coexistence of different moieties. Co-doping and multi-  
734 doping of porous carbonaceous materials are very common in the literature as they allow  
735 maximizing the effects produced by each heteroatom in the carbon structure [106]. This multi-  
736 doping can be obtained from two alternative strategies: (i) the use of biomass precursors  
737 containing different heteroatoms; or (ii) the introduction of external sources of heteroatoms into  
738 the biomass precursors.



739 *4.1.2.1. Nitrogen and sulfur co-doped carbon materials*

740 One of the most interesting performances of co-doped carbon materials is achieved by the  
741 introduction of nitrogen and sulfur together. The work of Li et al. [164] showed a synergistic  
742 effect by the introduction of pyridinic and graphitic nitrogen species along with thiophene  
743 species into the carbon backbone. The authors attributed the coexistence of the two N and S  
744 heteroatoms as the responsible for the improved catalytic properties towards the ORR.  
745 Nevertheless, they also mentioned the presence of intrinsic defects in the carbon matrix that  
746 could explain this increase in ORR performance. In this sense, Radovic et al. [165]  
747 demonstrated that the presence of nitrogen and point defects in the vicinity can also improve  
748 the catalytic activity. Indeed, carbenes, carbynes or even H-deficient free radicals can be part  
749 of zigzag and armchair edges of graphene and catalyze the reduction of oxygen. Gao et al.  
750 directly carbonized sweet potato vine [166] and honeysuckle [167] at 800 °C to produce  
751 nitrogen- and sulfur-doped carbon materials. The biochar obtained from honeysuckle contained  
752 a higher proportion of N-pyridinic and S-thiophene species and, according to the authors'  
753 hypothesis, had better catalytic properties for the ORR compared to that obtained from sweet  
754 potato vine alone. Similarly, Amiin et al. [168] attributed the ORR catalytic activity of their  
755 N, S-co-doped carbon material from the pyrolysis of graphene oxide with sheep horn due to the  
756 presence of a significant amount of graphitic N and pyridinic N with sulfur incorporated at the  
757 defect sites and edges in the form of thiophene species. The same conclusion was drawn by  
758 Zhang et al. [169] for their N,S-doped carbon material obtained from rapeseed. Density  
759 functional theory (DFT) has been applied by Liang et al. [170] to dual-doped nitrogen and sulfur  
760 carbon materials. It showed the presence of a large number of active carbon atoms due to the  
761 synergistic effect of S- and N-doping that introduces asymmetrical charge and spin densities,  
762 resulting in higher ORR performance (Figure 9a). The same kind of effect was also observed  
763 with B- and B,N-doping (Figure 9b, 9c).





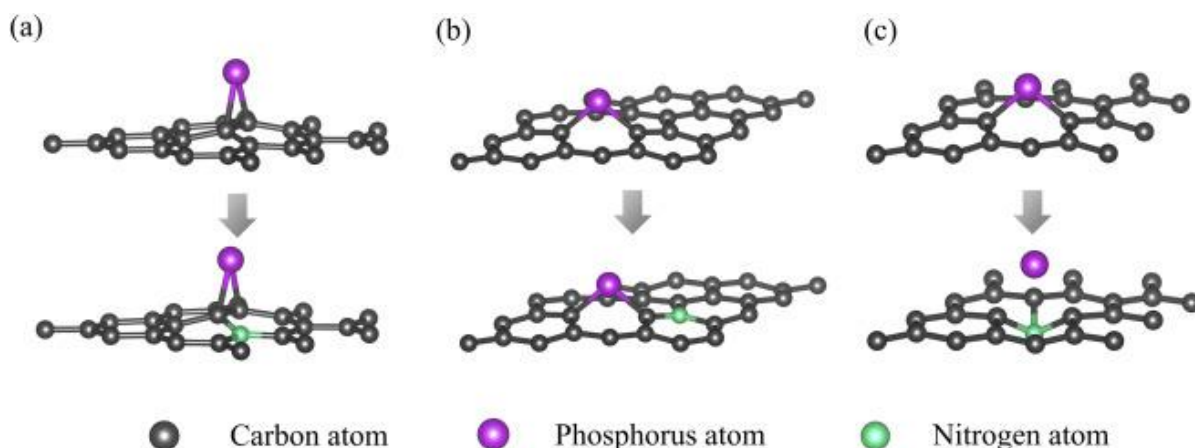
764  
 765 **Figure 9.** (a) Spin and charge density of the carbon network (C, black) in which nitrogen (N,  
 766 blue) and sulfur (S, yellow) are incorporated (Adapted from Ref. [170], Copyright 2012, with  
 767 permission from John Wiley and Sons); (b) Charge distribution of boron-doped graphene and  
 768 (c) B-doped graphene containing one graphitic nitrogen (Adapted from Ref. [171], Copyright  
 769 2019, with permission from Elsevier).

770 Most biomass precursors do not contain multiple heteroatoms in their chemical composition.  
 771 Therefore, external functionalization of biomass-derived carbon materials is a common strategy  
 772 to increase the catalytic activity towards the ORR. For example, Shen et al. [172] obtained an  
 773 onset potential of about 1.00 V vs. RHE in alkaline medium using S-containing lignin from  
 774 sugarcane residues with melamine and urea (external sources of nitrogen) initially dispersed in  
 775 dimethylformamide (DMF). The mixture was pyrolyzed at 1000 °C and the resulting carbon  
 776 materials showed a nitrogen content of 4.18 at.% (2.7 at.% of graphitic N) in the final product.  
 777 However, the authors did not attribute the highly efficient catalysis to the presence of S  
 778 moieties, but only to the graphitic N and total pore volume (1.40 cm<sup>3</sup> g<sup>-1</sup>). There are multiple

779 routes to produce an N, S-doped carbon material. Other examples of preparing such materials  
780 are the simultaneous use of two heteroatom-containing precursors in the thermal treatment, such  
781 as methylene blue [173] or thiourea [116,174,175], both rich in N and S.

#### 782 4.1.2.2. Nitrogen and phosphorus co-doped carbon materials

783 Co-doping carbon materials with nitrogen and phosphorus is another popular option for  
784 scientists because the synergy between these two heteroatoms provides high-performance  
785 electrocatalysts for ORR. For example, Wei et al. [55] synthesized an N, P-doped carbon  
786 material from the direct pyrolysis of *Escherichia coli* (*E. coli*) bacteria at 1000 °C for 2 h in an  
787 N<sub>2</sub> atmosphere. The authors attributed the very efficient electrochemical performance of their  
788 material in alkaline media ( $E_{ONSET} = 0.87$  V vs. RHE,  $j_l = 6.21$  mA cm<sup>-2</sup> at 0.1 V vs. RHE) to  
789 the presence of a large proportion of pyridinic N, graphitic N and P-C bonds, highlighting a  
790 synergistic effect between N and P. Gao et al. [176] have identified by DFT simulation and  
791 experimentally verified that the active sites in N- and P-co-doped carbon materials are located  
792 at the edges of graphene layers, specifically near the oxidized P sites in the vicinity of graphitic  
793 nitrogen. The order of introduction of the N and P dopants appears to be of paramount  
794 importance according to Zhao et al. [177] When phosphorus is introduced first into the carbon  
795 lattice, it is either bound with a bridging mode configuration (outside mode, Figure 10a) or in  
796 substitution of a carbon atom in the matrix (inside mode, Figure 10b) causing the distortion of  
797 the 2D structure of the catalyst. The authors pointed out that if P is introduced by the inside  
798 mode, when N is subsequently introduced, it can replace P atoms in the carbon matrix (see  
799 Figure 10c), leading to a higher number of graphitic N atoms in the carbon material, known to  
800 be highly active sites for the ORR. The authors also demonstrated by DFT studies that the  
801 formation of graphitic N around phosphorus functionalities is thermodynamically favored.



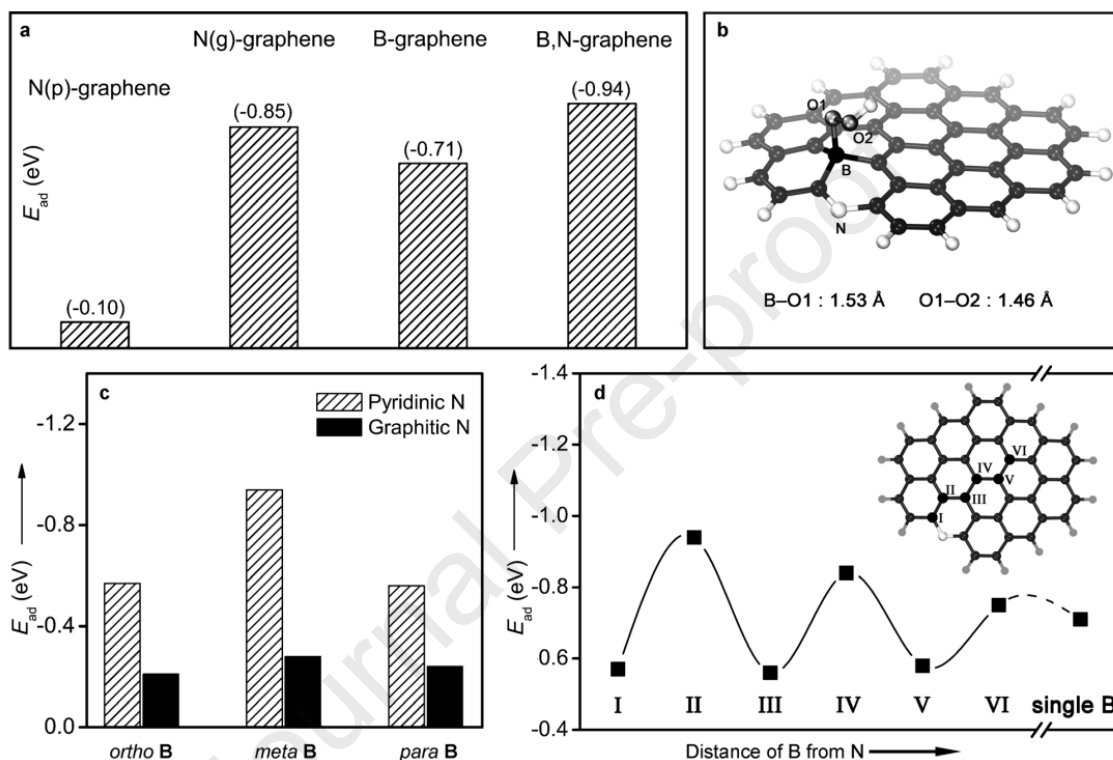
802

803 **Figure 10.** Representations of different doping modes when phosphorus is introduced first, and  
 804 then nitrogen. (a) Outside mode; (b) inside mode; and (c) self-sacrifice mode (Reprinted from  
 805 Ref. [177], Copyright 2018, with permission from Elsevier).

#### 806 4.1.2.3. Nitrogen and boron co-doped carbon materials

807 Cao et al. [178] reported the synthesis of B,N-doped *Platanus*-based carbon material by  
 808 impregnation of *Platanus* fruit hair in a solution of urea and boric acid (4:1:1 mass ratio),  
 809 followed by pyrolysis at 900 °C under N<sub>2</sub>. The authors attributed the effective ORR  
 810 performance of the resulting carbon materials to the synergistic effect of N and B. The boron  
 811 atom in B-C-N configuration retains a more positive charge density compared to the B-C  
 812 configuration, resulting in a better adsorption step that subsequently leads to a better ORR  
 813 performance. Zhang et al. [179] showed in their DFT calculations that the synergy between  
 814 boron and nitrogen in an N, B-co-doped sample leads to a lower adsorption energy of the OOH·  
 815 intermediate formed during ORR, compared to carbons doped only with nitrogen or boron  
 816 (Figure 11a). Indeed, an increase of the charge density of the boron is observed when nitrogen  
 817 surrounds it. They also showed that the ORR is particularly enhanced when the B-C-N  
 818 functionalities are located at graphene edges. Based on the adsorption energies of the OOH·  
 819 intermediate on N, B-doped carbon catalysts, they revealed that oxygen chemisorption and  
 820 reduction occur at the boron atom (Figure 11b). More precisely, the synergy between the boron  
 821 atoms located in the meta position with respect to the pyridine nitrogen leads to a lower

822 adsorption energy of the intermediate on the boron atom (Figure 11c, 11d), and this combination  
 823 is believed to be responsible for the observed enhanced ORR catalytic activities. Moreover, a  
 824 theoretical study by Larijani and Khorshidian [171] confirmed the positive synergy of a co-  
 825 doped B, N carbon material with an increase in the charge density of the boron atom surrounded  
 826 by a nitrogen atom (see again Figure 9b, 9c).



827  
 828 **Figure 11.** a) Adsorption energies of  $\text{HO}_2^*$  ( $E_{ad}$ ) on N- and/or B-doped graphene. N(p) and N(g)  
 829 indicate pyridinic and graphitic N bonding, respectively; b) Optimized configuration of  $\text{HO}_2^*$   
 830 adsorbed on B,N-graphene; c)  $E_{ad}$  on various B,N-graphene models with pyridinic or graphitic  
 831 N groups; d)  $E_{ad}$  on various B, N-graphene models with B active sites as a function of the  
 832 distance to a pyridinic N atom (sites I–VI marked in inset). Reprinted from Ref [179], Copyright  
 833 2013, with permission from John Wiley and Sons.

#### 834 4.1.2.4. Nitrogen and fluorine co-doped carbon materials

835 More recently, nitrogen and fluorine co-doping of carbon materials from biomass precursors  
 836 has resulted in good catalytic performance for ORR due to the combined effect of these two

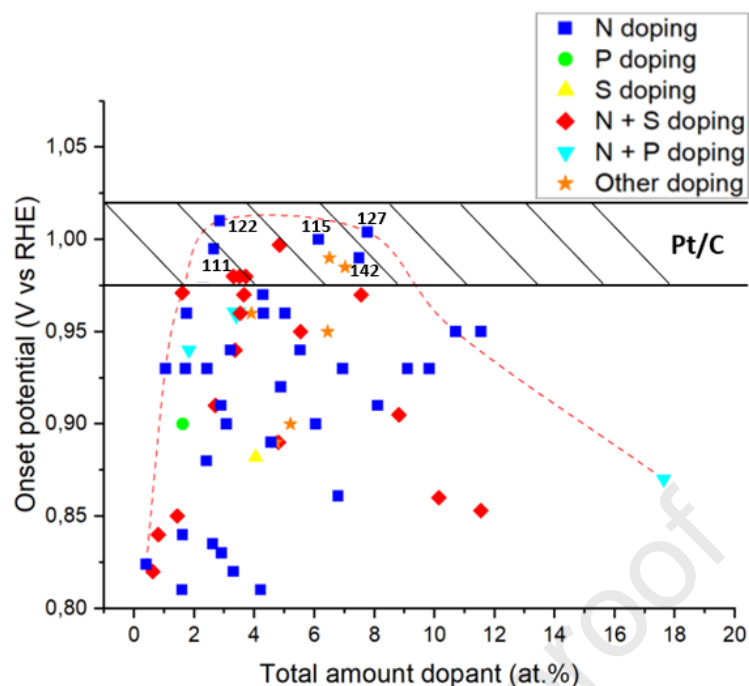
837 heteroatoms [39,180]. In a study of Zhou et al., fluorine doping has been shown to increase the  
838 surface wettability of carbonaceous materials by organic electrolytes [181], resulting in  
839 improved transport of electrolyte and O<sub>2</sub> to the micropores where the active sites are located.  
840 In addition, fluorine is the most electronegative element, which leads to polarization of C-F  
841 bonds and induces a delocalization of charge density near these carbon atoms. A DFT study by  
842 Peera et al. [182] showed that the presence of pyridinic N and graphitic N atoms in N, F-co-  
843 doped carbon nanofibers promotes the formation of semi-ionic C-F bonds and thus increases  
844 the catalytic activity in ORR.

#### 845 4.1.2.5. Tri- and tetra-doped carbon materials

846 Carbon materials can be doped with more than two different kinds of heteroatoms to further  
847 enhance the catalytic properties of the pristine material. Although there are few reports  
848 concerning multi-doping [183–185], some works are worth mentioning. Sadeghassani et al.  
849 [183] obtained an N, S, P, B-doped carbon material with an onset potential of 0.90 V vs. RHE  
850 and a number of transferred electrons  $n$  of 4.0 using garlic and graphene as precursors. Although  
851 the value of  $n$  is similar to that of the commercial Pt/C, the  $E_{ONSET}$  is still quite far from it. The  
852 same observation can be made from the work of Wang et al. [54]. These authors synthesized a  
853 tri-doped (N, S and P) carbon material using *E. coli* bacteria and reduced graphene oxide with  
854 an  $E_{ONSET} = 0.88$  V vs. RHE, far from that of Pt/C ( $E_{ONSET} = 0.97$  V vs. RHE), and a number of  
855 transferred electrons  $n$  of 3.95, similar to commercial Pt/C. This result can be explained by a  
856 possible overestimation of  $n$  when applying the Koutecky-Levich theory for porous materials  
857 [33]. Huang et al. [185] showed through a DFT computational study that the presence of several  
858 heteroatoms (N, P and S) in the carbon backbone allows to decrease the energy barrier of the  
859 ORR steps, leading to an improved catalytic activity due to the synergistic effect between all  
860 these species. Nevertheless, it should be pointed out that specific studies still must be conducted  
861 to account for the ORR behavior of each multi-doped carbon material, and that no general rule  
862 is found to explain which combination provides the best ORR catalytic performance.

863 Figure 12 shows  $E_{ONSET}$  as a function of the total amount of heteroatoms in catalysts obtained  
864 from biomass, and which are reported in the literature [37,40,41,43,48–52,92,111–  
865 113,115,116,121,122,124,127–132,136,137,139–156,158,161,166–169,172–175,180,183–  
866 186,186–196]. On the one hand, a large dispersion of  $E_{ONSET}$  values is observed as a function  
867 of the dopant content in the electrocatalyst, which could be explained by the influence of the  
868 textural properties and the location of these heteroatoms in the carbon skeleton; this location  
869 indeed varies the catalytic activity towards the ORR. The N-doped carbon samples with the  
870 best results in terms of  $E_{ONSET}$  (i.e., with values closest to those of Pt/C) reported here were  
871 obtained from plant biomass precursors, either in the presence of melamine with chemical  
872 activation during the synthesis process, or in the presence of an  $NH_3$  stream during the pyrolysis  
873 of the samples, or from N-rich animal biomass precursors (silk cocoons). It is interesting to note  
874 that all the final products present relatively large specific surface areas (for most of them,  $A_{BET}$   
875  $> 1000 \text{ m}^2 \text{ g}^{-1}$ ) favoring the contact of the  $O_2$ -saturated electrolyte with the material and thus  
876 facilitating the interaction between oxygen and active sites with important proportions of  
877 pyridinic N and graphitic N (the proportion of both types of N representing at least 58 % of the  
878 total N introduced in the carbonaceous materials). On the other hand, it is imperative to adapt  
879 or to adjust the amount of dopant that one wishes to introduce into the material to have an  
880 effective electrocatalyst for the ORR. While a minimum of active sites is required to be able to  
881 reduce the dioxygen molecules (as seen at the lowest doping level), the addition of an excess  
882 of dopant (at about 8 at.%) negatively affects the catalytic activity, as evidenced by the drop in  
883 the onset potential; this drop is a consequence of a decrease in the electrical conductivity or  
884 porosity of the carbonaceous material [138,197]. Therefore, it is important to control the doping  
885 level during the development of an electrocatalyst, and some of the metal-free electrocatalysts  
886 shown in Figure 12 have an onset potential equal to or close to that of commercial Pt/C-based  
887 electrocatalysts reported in literature.





888

References	Carbon precursors	N-doping agent	Activation	$E_{ONSET}$	$A_{BET}$	N-content	N-pyridinic	N-graphitic
142	Silk cocoons	X	ZnCl <sub>2</sub>	0.99	1274	7.49	0.91	4.04
111	<i>Scindapsus</i>	NH <sub>3</sub> flux	X	0.995	1599	2.65	1.07	0.58
127	Water lettuces	NH <sub>3</sub> flux	X	1.00	823	7.76	2.63	1.99
115	Papaya skins	Melamine	KHCO <sub>3</sub>	1.00	1671	6.13	2.38	1.65
122	Coconut palm leaves	Melamine	KHCO <sub>3</sub> +KOH	1.01	1419	2.84	0.64	1.01

889

890 **Figure 12.** Onset potential measured in alkaline medium as a function of total amount of dopant  
 891 in biomass-derived, heteroatom-doped carbon catalysts from the literature [37,40,41,43,48–  
 892 52,92,111–113,115,116,121,122,124,127–132,136,137,139–156,158,161,166–169,172–  
 893 175,180,183–186,186–196].

894 The electrocatalysts are separated into several families in the figure: mono-doping with N, P  
 895 or S, co-doping with N + S or N + P, and all others: co-doping with other heteroatoms or multi-  
 896 doping. The N-doped carbon materials obtained with the closest  $E_{ONSET}$  to that of Pt/C have  
 897 been reported in the table along with the biomass precursor, the nitrogen external source and  
 898 the activation used during the synthesis procedure (if any), the BET area, and the total nitrogen,  
 899 pyridinic N and graphitic N contents. Different types of biomass-derived multi-doped carbon  
 900 electrocatalysts have been reported in Table 2 along with the results obtained in ORR.

901 **Table 2.** Metal-free and multi-doped carbon electrocatalysts for ORR. Electrochemical data  
 902 were obtained in 0.1 M KOH electrolyte.

Biomass source	Other sources	Synthesis method	Doping atoms (at.%)	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	$E_{ONSET}$ (V vs. RHE)	$E_{1/2}$ (V vs. RHE)	$j_l$ (mA cm <sup>-2</sup> ) at 1600 rpm	Number of transferred electrons $n$	Ref.
Sweet potato vine	--	Pyrolysis	N: 1.2 S: 0.23	885	0.52	0.85	0.65	--	~4	[166]
Honey-suckles	--	Pyrolysis	N: 1.95 S: 0.75	803	0.49	0.91	0.77	--	3.6	[167]
Sheep horns	Graphene oxide	Ball milling, pyrolysis	N: 3.14 S: 0.22	320	--	--	0.78	5.41 at 0.1 V vs. RHE	3.52-3.83	[168]
Rapeseed meal	ZnCl <sub>2</sub>	Carbonization, activation	N: 3.0 S: 0.5	1564	0.8	0.98	0.76	--	3.5-3.9	[169]
Bagasse lignin	Melamine Urea	Immersion, pyrolysis	N: 4.18 S: 0.65	1208	1.4	1.00	0.86	4.67 at 0.1 V vs. RHE	~4	[172]
Poplar catkins	--	Immersion, pyrolysis, activation under CO <sub>2</sub>	N: 0.27 S: 0.35	604	0.35	0.82	0.76	4.6 at 0.2 V vs. RHE	3.9-4.0	[173]
Mulberry leaves	KOH Thiourea	Activation, freeze-drying, pyrolysis	N: 8.17 S: 1.97	1689	1.01	0.86	--	--	3.7-3.9	[116]
Silk cocoon ( <i>Astridia velutina</i> )	KOH Thiourea	Activation, pyrolysis	N: 9.75 S: 1.79	377	--	0.85	0.72	4.5 at 0 V vs. RHE	~4	[174]
<i>Allium cepa</i>	Thiourea KOH	Immersion, activation, pyrolysis	N: 5.32 S: 2.23	1859	--	0.97	0.82	5.63 at 0.2 V vs. RHE	3.95	[175]
Keratin	KOH NH <sub>3</sub>	Carbonization, activation, pyrolysis	N: 1.5 S: 0.1	1799	1.01	0.97	0.84	--	3.8	[186]
Alkaline lignin	Urea	Pyrolysis	N: 2.98 S: 0.67	1209	0.74	0.97	0.83	--	3.8	[188]
Lotus seedpods	Melamine Phytic acid	Carbonization, pyrolysis	N: 15.95 P: 1.68	270	--	0.87	--	--	3.6-4.0	[191]



<i>E. coli</i>	Graphene oxide	Culture bacteria, impregnation, lyophilization, pyrolysis	N: 2.42 P: 1.25 S: 0.42	288	--	0.88	--	--	3.95	[54]
Lignin	Urea Melamine ZnCl <sub>2</sub> NaCl <sub>2</sub>	Immersion, freeze-drying, pyrolysis	N: 3.35 S: 0.8 Cl: 0.59	1290	2.81	0.89	0.79	6.93 at 0.1 V vs. RHE	3.93	[184]
Spinach leaves	ZnCl <sub>2</sub>	Activation, pyrolysis	N: 5.43 P: 0.71 S: 0.30	1145	--	0.95	0.82	5.19 at 0.5 V vs. RHE	3.81	[185]

903

904 *4.2. Non-precious metal-doped carbon materials (NPMCs)*

905 Besides metal-free carbon-based electrocatalysts, non-precious metal-containing carbon-  
906 based electrocatalysts are a promising alternative to replace platinum-based electrodes in the  
907 cathode electrode of fuel cells. Non-precious metal atoms are considered to be highly effective  
908 active sites for ORR. However, the stability of these species needs to be improved. In this sense,  
909 metal-N bonds are highly recommendable to create robust and efficient ORR electrocatalysts  
910 based on non-precious metals, since nitrogen species are known as excellent anchoring points  
911 to provide stability to metal active sites [91,198]. In this section, the influence of the presence  
912 of one or more metals in the heteroatom-rich carbon backbone on the ORR catalytic properties  
913 of these materials is discussed. Table 3 provides a concise summary of some non-precious  
914 metal-doped carbon catalysts derived from biomass along with their ORR properties in alkaline  
915 media.

916

917

918

919 **Table 3.** Non-precious metal-doped carbon electrocatalysts for ORR. Electrochemical data  
 920 were obtained in 0.1 M KOH electrolyte.

Biomass source	Other sources	Synthesis method	Doping atoms (at.%)	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	$E_{ONSET}$ (V vs. RHE)	$E_{1/2}$ (V vs. RHE)	$j_l$ (mA cm <sup>-2</sup> ) at 1600 rpm	Number of transferred electrons $n$	Ref.
Cellulose	KOH FeCl <sub>3</sub> NH <sub>3</sub>	HTC, activation, microwave radiation, oxidation, microwave ammoxidation	N: 1.5 wt.% (EA) Fe: --	1261	1.03	0.91	0.81	--	3.9	[99]
Sugarcane	KOH FeCl <sub>3</sub> CoCl <sub>2</sub> NH <sub>3</sub>	HTC, impregnation, activation, microwave ammoxidation	N : 1.5 Fe : --	857	0.66	0.91	0.81	--	3.8-3.9	[100]
Wood briquettes	FeCl <sub>3</sub> H <sub>3</sub> PO <sub>4</sub>	Impregnation, pyrolysis	N: 3.84 P: 0.57 Fe: 0.53	1608	0.73	1.10	0.89	--	3.88	[199]
Brewer's yeast powder	FeCl <sub>3</sub> Liquid NH <sub>3</sub> NH <sub>3</sub>	HTC, pyrolysis	N: 3.9 P: 0.46 Fe: 0.8	290	--	0.99	0.86	5.64 at 0.2 V vs. RHE	3.86-3.93	[74]
Douglas fir sawdust	Melamine Fe(NO <sub>3</sub> ) <sub>3</sub> solution	HTC, pyrolysis	N: 2.9 Fe: <0.6	765	--	0.91	0.78	5.86 at 0.5 V vs. RHE	3.4-3.8	[200]
Glucose	Melamine FeSO <sub>4</sub> ·7H <sub>2</sub> O	Pyrolysis	N: 5.21 Fe: 0.48	393	0.99	0.87	--	5.21 at 0.5 V vs. RHE	3.77	[201]
Wheat flour	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	Silica templating, pyrolysis, immersion, pyrolysis	N: 3.78 Fe: 0.25	365	0.55	0.98	0.86	--	3.96	[202]
Soybean straw	Melamine Magnesium oxide Ferric nitrate	Pyrolysis	N: 5.56 Fe: 0.4	521	2.2	0.99	0.85	--	3.94	[42]
Starch	Graphene oxide FeCl <sub>3</sub> KSCN	HTC, impregnation, pyrolysis	N: 2.22 S: 0.56 Fe: 0.31	750	--	0.95	0.83	--	3.96	[203]
Shrimp shells	Phosphoric acid	HTC, pyrolysis	N: 2.51 P: 1.42 Fe: 0.32	857	0.55	0.96	0.82	4.47 at 0.2 V vs. RHE	3.78	[204]

<i>Agaricus bisporus</i>	(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> ZnCl <sub>2</sub> FeCl <sub>3</sub> •6H <sub>2</sub> O	HTC, activation, pyrolysis	N: 2.36 P: 0.46 Fe: 0.76	1646	0.901	0.97	0.82	4.47 at 0.3 V vs. RHE	3.91	[53]
<i>Shewanella oneidensis</i> MR-1	--	Culture and fixation bacteria, pyrolysis	N: 2.26 S: 0.1 P: 0.46 Fe: 0.18	142	--	0.98	0.83	--	3.9	[56]
Vitamin B <sub>2</sub>	NaCl Co(OAc) <sub>2</sub> •4 H <sub>2</sub> O	Lyophilization, pyrolysis	N: 4.6 Co: 0.6	513	0.32	0.97	0.86	--	3.98	[205]
Root nodules	ZnCl <sub>2</sub>	Carbonization, activation, pyrolysis	N: 1.45 S: 0.36 Mo: 0.05 Fe: 0.106 wt.%	1838	1.19	0.97	0.87	5.23 at 0.2 V vs. RHE	3.63-3.99	[206]
Pig blood	Zn(NO <sub>3</sub> ) <sub>2</sub> •6 H <sub>2</sub> O NH <sub>3</sub>	Purification of blood, HTC, pyrolysis	N: 6 wt.% Fe: 1.3 wt.% Zn: 0.2 wt.%	1260	2.94	1.00	0.87	--	~4	[207]

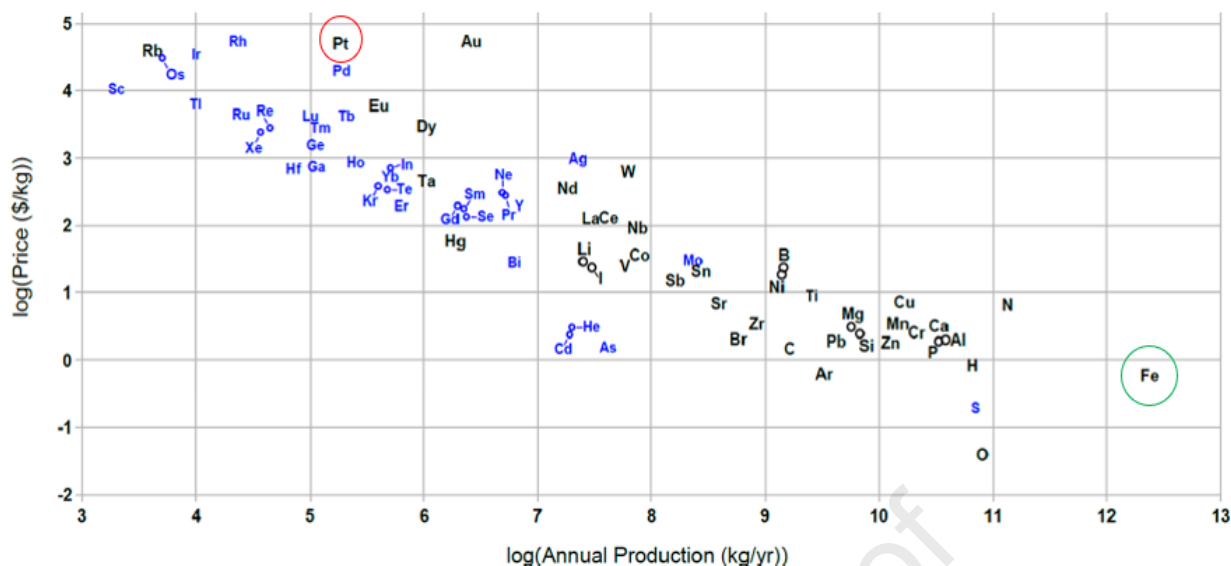
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922 Non-precious metal-based active sites can be found in multiple forms, such as nanoparticles,  
923 clusters or even single-atom arrangement. Single-atom catalysts (SACs) are noteworthy  
924 because full atomic exposure is achieved if the metal is atomically dispersed in the carbon  
925 material, exposing the greatest number of the active sites [208,209]. In 1964, Jasinski [210] first  
926 showed that a transition metal in a porphyrin (cobalt phthalocyanine in the study) could exhibit  
927 ORR catalytic activity in alkaline media through the formation of metal complexes in which  
928 the central metal atoms binds to four nitrogen atoms. Nevertheless, these compounds have  
929 relatively poor stability in acidic media where the metals are leached by the electrolyte at low  
930 pH, leading to a degradation of the catalytic properties of the material. In order to increase the  
931 catalytic stability of these single atoms, it is recommended to introduce the metal atoms into a  
932 well-structured and stable support, especially N-doped carbon materials. Heat treatment of  
933 metal porphyrin can produce metal and N-co-doped carbon materials with improved ORR  
934 activity [91]. Since the discovery of the high activity of SACs, the development of carbon-based

935 electrocatalysts that contain nitrogen and metals (denoted M-N-C) has become a challenging  
936 goal of the scientific community. These catalysts can be obtained by using metal-containing  
937 macrocycles instead, as was the case for Jasinski [210], or from less expensive compounds that  
938 are intrinsically metal-rich in nature [211], such as biomass containing metal impurities.

939 Iron is the most widely used and the cheapest transition metal (Figure 13) for the production  
940 of non-precious metal carbon catalysts for ORR [212]. It has been repeatedly observed that the  
941 introduction of iron into the carbon backbone promotes graphitization of the carbon material  
942 upon pyrolysis at high temperature, which allows for an increase in the electrical conductivity  
943 of the sample and facilitates electron transport [213–216]. Nevertheless, the iron doping level  
944 of the carbon-based catalyst does not correlate linearly with the catalytic activity in ORR.  
945 Therefore, it is important to select not only the right doping level but also the type of Fe species  
946 to have optimal catalytic activity in ORR. Indeed, Kuo et al. [99] developed an N- and Fe-doped  
947 catalyst by hydrothermal synthesis of cellulose at 180 °C for 16 hours, and then the resulting  
948 solid was mixed with FeCl<sub>3</sub> in different proportions, followed by two microwave irradiations  
949 (the first under inert gas and the second under NH<sub>3</sub> flow). They observed a similar onset  
950 potential and half-wave potential for 1 wt.% and 5 wt.% iron doping in the N-doped carbon  
951 material ( $E_{ONSET} = 0.91$  V vs. RHE;  $E_{1/2} = 0.81$  V vs. RHE), but a lower limiting current density  
952 was observed in the second case (3.2 mA cm<sup>-2</sup> and 1.4 mA cm<sup>-2</sup>, respectively).

953



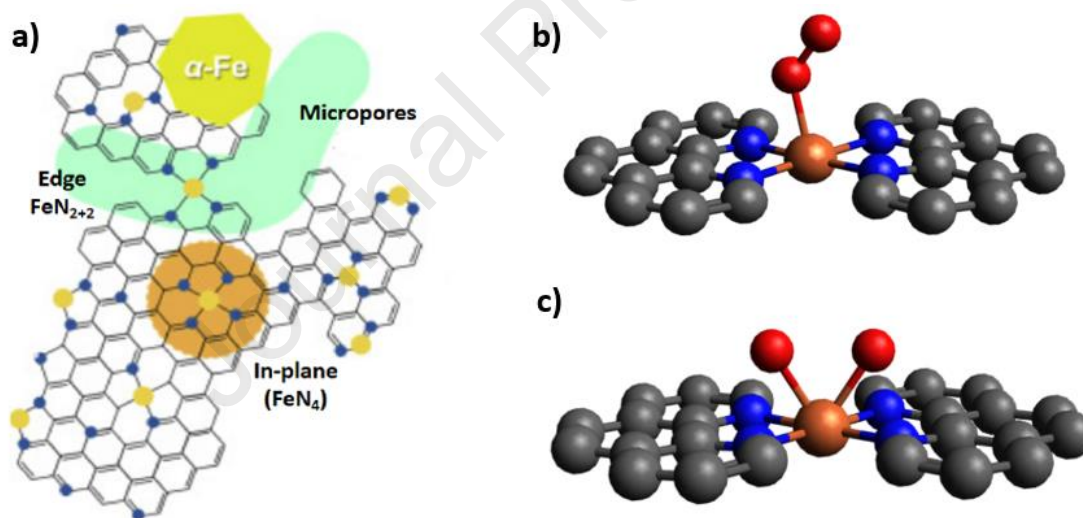
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955 **Figure 13.** Price of different elements as a function of their annual production (adapted with  
 956 permission from Ref. [212]. Copyright 2016 American Chemical Society).

957 Excessive iron doping in a carbon catalyst doped with heteroatoms does not always lead to  
 958 better performance in terms of onset potential and half-wave potential, since Fe nanoparticles  
 959 can: (i) block the porosity where most of the active sites are located; or (ii) lead to agglomeration  
 960 that decreases the ORR activity [198,199,217]. Other authors [199] have shown that increasing  
 961 the level of Fe doping in a N, P-co-doped carbon catalyst improves the onset potential and half-  
 962 wave potential to an optimized value of 1.86 wt.%. The authors attributed this optimum to a  
 963 homogeneous dispersion of the iron in the carbon lattice. Above 1.86 wt.% Fe, a slight decrease  
 964 in electrocatalytic activity is observed, attributed to agglomeration of iron particles and thus to  
 965 a decrease in the number of active sites. The same trend was also observed by Wang et al. [74]  
 966 for their N, P and Fe-tri-doped carbon catalyst prepared by using brewer's yeast powder,  
 967 ammonium hydroxide and iron chloride as precursors.

968 Nevertheless, as with nitrogen, it is not the total iron content that is critical to the ORR  
 969 catalytic activity but the type of iron species. The work of Kramm et al. [218] highlighted the  
 970 possible presence of several iron species in Fe-N-C type catalysts using  $^{57}\text{Fe}$  Mössbauer  
 971 spectroscopy, including  $\text{FeN}_4$  sites with iron ions in a different spin state,  $\text{Fe}_x\text{N}$  sites (with  $x \leq$

972 2.1), and iron nitrides with a stoichiometry between those of  $\text{Fe}_x\text{N}$  and  $\text{FeN}_4$  sites. This study  
973 showed that  $\text{FeN}_4$  species with ferrous ions in a high spin state and a low spin state present high  
974 catalytic activity in ORR with improved stability in acidic media. The two active sites that are  
975 predominantly present in Fe-N-C type electrocatalysts are the  $\text{Fe-N}_4$  "in-plane" sites located in  
976 the middle of the planes, and the  $\text{Fe-N}_{2+2}$  "edge" sites present in the micropores (Figure 14a)  
977 [219]. For example, by  $^{57}\text{Fe}$  Mössbauer spectroscopy, Pérez-Rodríguez et al. [220] detected in  
978 their carbonaceous material  $\text{FeN}_4$  groups with ferrous ions in a low spin state that are associated  
979 with the good performance observed in ORR in alkaline medium ( $E_{1/2} = 0.78$  V vs. RHE). In  
980 general,  $\text{O}_2$  molecules are directly chemisorbed onto iron (the center of the  $\text{FeN}_4$  active site) in  
981 two possible ways: end-on configuration (Figure 14b) or side-on configuration (Figure 14c)  
982 before being reduced into hydroxide peroxide or/and water [221].



983  
984 **Figure 14.** a) Schematic representation of the different sites present in a Fe-N-C material  
985 (adapted from Ref. [219], Copyright 2020, with permission from Elsevier). Optimized  
986 geometries of  $\text{O}_2$  adsorbed on  $\text{FeN}_4$  clusters: b) end-on and c) side-on configurations (adapted  
987 from Ref. [221], Copyright 2013, with permission from Royal Society of Chemistry).

988 In addition to nitrogen, other heteroatoms such as phosphorus can be introduced into the  
989 carbon material to serve as metal anchors and thus increase the synergies between the different

990 functionalities present in the material by increasing the number and type of active sites. Qin et  
991 al. [222] found Fe<sub>2</sub>P species in biomass-derived carbon materials after hydrothermal synthesis  
992 using potassium ferricyanide and egg yolks, followed by pyrolysis at 1000 °C for 2h under NH<sub>3</sub>  
993 flow. The authors attributed the high catalytic performance towards the ORR to the presence of  
994 these iron-phosphorus species. Similarly, Li et al. [204] showed the importance of incorporating  
995 phosphorus into the N, P and Fe tri-doped carbon material (P/Fe/N-SS) derived from shrimp  
996 shells, H<sub>3</sub>PO<sub>4</sub> and FeCl<sub>3</sub> as sources of nitrogen, phosphorus, and iron respectively. The authors  
997 performed the same synthesis without the addition of phosphorus (Fe/N-SS) and observed a  
998 decrease in  $E_{ONSET}$  and  $E_{1/2}$  by 5 mV and 4 mV, respectively. The authors attributed the observed  
999 differences in catalytic activity in ORR to the presence of FeP species detected by XPS in the  
1000 P/Fe/N-SS tri-doped sample. Other works have also proved the catalytic activity of iron-  
1001 phosphorus species in the ORR [199,223]. As in the case of metal-free catalysts, multi-doping  
1002 with heteroatoms can be achieved to create synergistic effects. A tetra-doped (N, S, P and Fe)  
1003 porous carbon material was obtained by Guo et al. [56] following the decomposition of  
1004 *Shewanella oneidensis* MR-1 bacteria by direct pyrolysis. The authors obtained excellent  
1005 electrochemical performance ( $E_{ONSET} = 0.98$  V vs. RHE;  $E_{1/2} = 0.83$  V vs. RHE), comparable  
1006 to Pt/C. According to the characterization, this was attributed to a synergy between the different  
1007 heteroatoms along with the porous structure of their material.

1008 Another relevant metallic arrangement that has not been mentioned previously is the core-  
1009 shell encapsulation of metal nanoparticles by graphene-like carbon layers. Although not in  
1010 direct contact with the electrolyte and dioxygen molecules, it has been shown that metal entities  
1011 encapsulated in graphene sheets can improve ORR performances [213]. In the work of Hu et  
1012 al. [224], encapsulation of iron carbide Fe<sub>3</sub>C nanoparticles in N-doped graphitic layers showed  
1013 improved catalytic properties in ORR and stability in both acidic and alkaline media, a rare fact  
1014 attributed to the synergy between the protective graphenic layers and the carbides nanoparticles.

1015 These nanoparticles allow an activity of the graphenic layers of the shell surrounding the core  
1016 particle, in terms of induced changes in the electron density of the carbon atoms of the graphene-  
1017 like layers that promote the ORR. This observation was also made by Wang et al. [225] where  
1018 the authors attributed the ORR performance of N- and Fe-doped carbon materials to the  
1019 presence of these Fe<sub>3</sub>C nanoparticles. Other researchers [35,200,201] have also observed an  
1020 enhancement of the catalytic activity of their material by these core-shell nanoparticles in  
1021 carbon materials. The chemistry behind this behavior was explained by DFT calculations [226].  
1022 A metallic iron nanoparticle encapsulated under the N-doped carbon layers provides a large  
1023 number of electrons to the carbon shells, which are then used in the active sites of the carbon  
1024 layers to chemisorb and reduce dioxygen molecules. This core-shell conformation is not only  
1025 effective when iron carbides are used, but also works with Fe<sub>3</sub>O<sub>4</sub> [42,202,227]. In addition,  
1026 other metals such as Co [227], Ni [227], etc. can also produce core-shell metal configurations  
1027 in which improved catalytic activity is observed.

1028 Other metals for ORR electrocatalysis such as Co [115,205,217,228–230], Mo [231], and  
1029 Mn [232] have emerged as excellent active sites in biomass-derived carbon materials to further  
1030 improve the catalytic activity for oxygen reduction. These metals exhibited excellent catalytic  
1031 activities, similar or better than those of Fe-based electrocatalysts, but it should be noted that  
1032 the cost of these metal is higher than that of Fe. Liu et al. [229] produced a Co, N-co-doped  
1033 carbon material from corn stover with an  $E_{1/2}$  of 0.743 V vs. RHE in alkaline medium, close to  
1034 that of Pt/C 20 wt.% ( $E_{1/2} = 0.793$  V vs. RHE), mainly attributed to the proportion of graphitic  
1035 N, pyridinic N, and Co embedded in the carbon matrix. DFT calculations showed that single  
1036 Co atoms bonded to two, three or four nitrogen atoms (CoN<sub>2</sub> [233], CoN<sub>3</sub> [234], or CoN<sub>4</sub> [235])  
1037 provide excellent ORR activity ( $E_{ONSET} \leq 0.95$  V vs. RHE in alkaline medium), and that the  
1038 most important parameter on ORR activity is the valence electron occupancy of Co *d*-orbitals.  
1039 Nevertheless, Co nanoparticles were also found to be effective in the reduction of dioxygen



1040 molecules [236]. As mentioned above, highly efficient biomass-derived electrocatalysts can  
1041 also be based on Mo, Mn, Ni, Cu, etc. A more in-depth explanation of the effect of each metal  
1042 and the origin of catalytic activity in ORR performance can be found in the literature [237–  
1043 241].

1044 Another promising alternative is the use of two or more metals to induce synergistic effects  
1045 that could enhance the ORR performance, similar to the multi-doping of carbon materials. Kuo  
1046 et al. [100] obtained two Fe-Co, N-doped carbon material from sugarcane and palm kernel shell  
1047 by hydrothermal synthesis and microwave ammoxidation. They obtained for both kinds of  
1048 materials an  $E_{ONSET}$  of about 0.90 V vs. RHE and  $E_{1/2}$  of 0.80 V vs. RHE in alkaline medium,  
1049 and their performance was attributed to the FeCo/N species embedded in the porous carbon  
1050 material. On the other hand, Hao et al. [206] obtained a carbon material from plant root nodules,  
1051 intrinsically doped with N, S, Fe and Mo since these heteroatoms were initially present in the  
1052 starting biomass precursor. The metals in the roots were indeed taken up from the soil by the  
1053 plant for growth and contributed to the catalytic performances in ORR although they were only  
1054 present in trace amounts (0.05 wt.% Mo and 0.1 wt.% Fe, measured by ICP).

## 1055 **5. Conclusion and perspectives**

1056 The valorization of biomass as carbon-based catalysts materials has been reported as a  
1057 promising alternative to platinum based-electrocatalysts for the oxygen reduction reaction  
1058 (ORR), mainly in alkaline media where overpotentials and kinetics are favorable. In fact,  
1059 biomass resources are considered the main green source of carbon precursors with a wide  
1060 variety of properties and applications. All carbon materials have intrinsic characteristics that  
1061 affect ORR catalytic activity. Textural properties appear to be of paramount importance to  
1062 ensure the accessibility of the dioxygen molecules from the electrolyte to the active sites, which  
1063 seem to be located in the microporosity of carbon materials. Nevertheless, other parameters  
1064 such as defects have proven to be of great interest by acting as active sites where oxygen

1065 molecules are chemisorbed and reduced. Therefore, the design of an advanced electrocatalyst  
1066 requires the creation of well-developed porosity in carbon materials, whether the active sites  
1067 are based on metals or heteroatoms. In this review, the ORR performance in alkaline medium  
1068 of recent bio-based carbon electrocatalysts has been reported and compared to understand better  
1069 the influence of different physicochemical properties on the ORR.

1070 Biomass-derived carbon materials are inherently rich in heteroatoms, which are a different  
1071 form of defects in the carbon structure. These heteroatoms cause significant changes in the  
1072 electron density distribution in the carbon matrix, localizing charges in the carbon atoms  
1073 adjacent to the heteroatoms. This localized charge density can act as an active site, where  
1074 oxygen molecules can be easily chemisorbed and reduced, resulting in improved catalytic  
1075 performance compared to the homogenous charge distribution of undoped carbon materials.  
1076 Among all heteroatoms, nitrogen-based functionalities have been reported to be the most  
1077 influential species in ORR, both theoretically and experimentally. In particular, pyridinic N and  
1078 graphitic N are proposed as the most active functionalities for the ORR of biomass-derived  
1079 carbons. The introduction of other heteroatoms, such as sulfur, phosphorus or boron into carbon  
1080 materials have also shown positive effects, but the origin of the catalytic activity is still under  
1081 debate. The literature proposes two main hypotheses: (i) the heteroatoms are intrinsic active  
1082 sites; or (ii) the defects produced by the introduction of these heteroatoms are the ones that truly  
1083 behave as active sites towards the ORR. The identification of active sites and the origin of  
1084 catalytic activity in heteroatom-doped carbon materials have become one of the most  
1085 challenging goals in materials science.

1086 Electrocatalysts based on non-precious metals have also been extensively studied in the  
1087 literature, as different metals have been shown to catalyze the ORR as efficiently as platinum-  
1088 based electrodes, especially in alkaline media. This effect is particularly noticeable in  
1089 carbonaceous materials containing both nitrogen and metal. The role of the N species is to act

1090 as anchor points where the metal species are attached. At the same time, the metal atoms are  
1091 responsible for the reduction of dioxygen molecules. The combination of metal atoms and N  
1092 species often leads to highly efficient ORR performance with improved stability. The most  
1093 interesting metal-containing electrocatalysts are based on Fe and Co, which exhibit excellent  
1094 ORR performances at a competitive cost. Another important discussion about metal-containing  
1095 electrocatalysts derived from biomass concerns the origin of the catalytic activity. Metals can  
1096 be found in multiple configurations (surface nanoparticles, clusters and single atoms, and  
1097 encapsulated nanoparticles), and all are proposed to be responsible for high catalytic behaviors.  
1098 Future research on the precise role of metal configuration and species as well as different co-  
1099 doping materials should be considered for the preparation of excellent biomass-derived  
1100 materials for the ORR.

1101 Most researchers are currently focusing their work on evaluating the ORR behavior of  
1102 carbon materials in alkaline media. Yet, it is widely known that the most optimized fuel cell  
1103 stations are based on proton-exchange membranes, which means that the cathode electrode is  
1104 immersed in an acidic medium. The catalytic activity of most carbon-based electrocatalysts in  
1105 an alkaline medium is significantly higher than that obtained in an acidic environment. Pending  
1106 significant improvement of anion-exchange membranes, future research should therefore also  
1107 focus on the development of stable and efficient electrocatalysts in acidic media, including  
1108 finding strategies to minimize the problems of carbon corrosion and leaching of the non-  
1109 precious metals involved.

1110 Biomass-derived nanomaterials have attracted increasing interest and rapid development in  
1111 the future is possible, especially for energy conversion applications, given the renewable, very  
1112 abundant and inexpensive aspects of biomass, which can compete with conventional chemical  
1113 precursors often derived from the oil industry. Moreover, these bio-based porous carbon  
1114 materials can be used in other applications such as supercapacitors, CO<sub>2</sub> capture or other

1115 catalytic reactions. Therefore, the search for synthesis protocols using "green precursors" such  
1116 as biomass should be privileged in order to meet the energy needs of society in a sustainable  
1117 way.

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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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