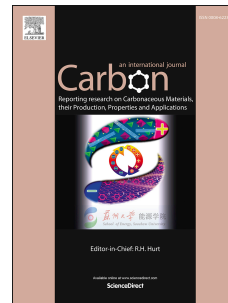# Journal Pre-proof

Metal-free heteroatom-doped carbon-based catalysts for ORR. A critical assessment about the role of heteroatoms

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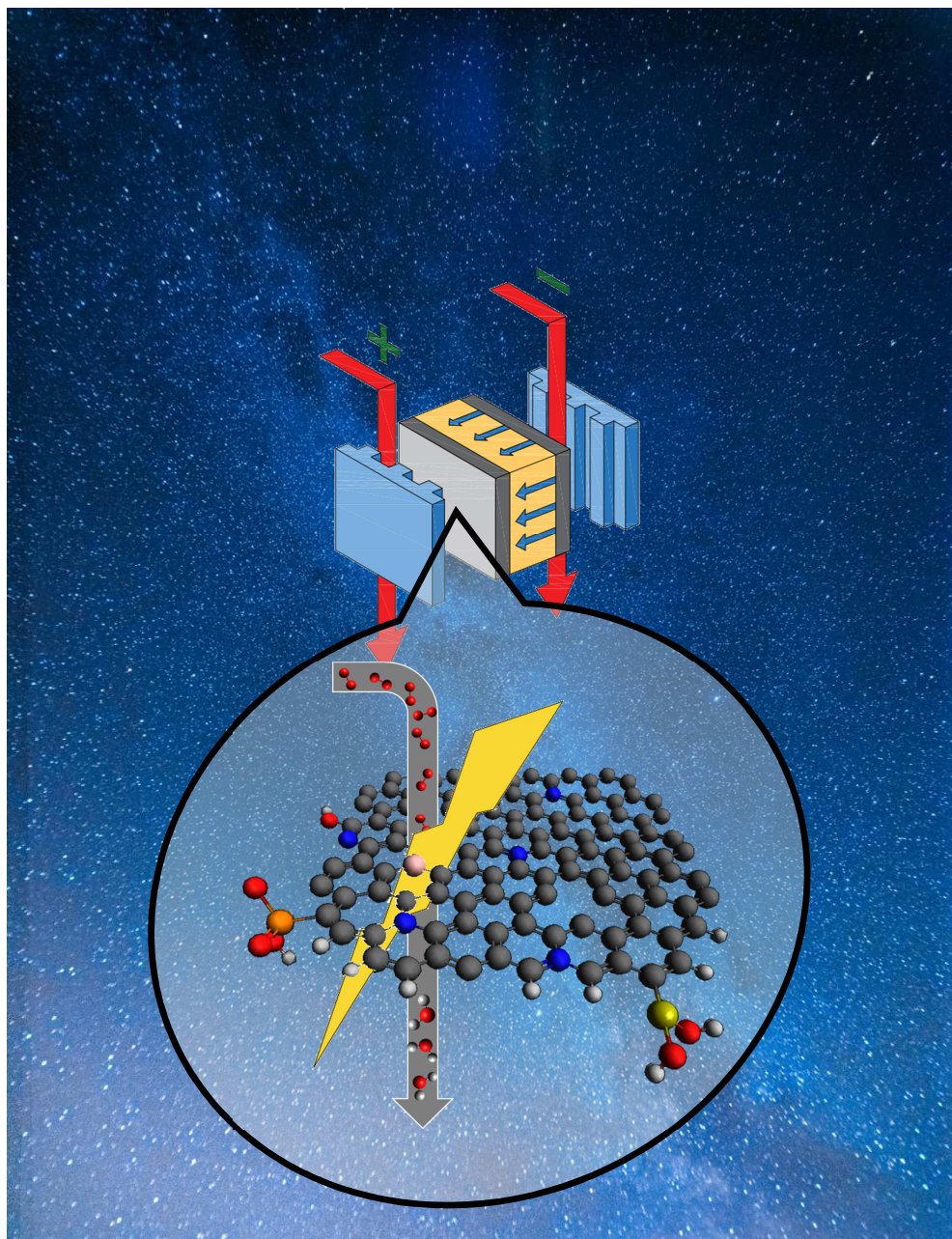
Metal-free Heteroatom-doped Carbon-based catalysts for ORR. A critical assessment about the role of heteroatoms

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Abstract

Metal-free carbon-based catalysts have gained much attention during last years because of their interesting properties towards oxygen reduction reaction. Intrinsic parameters of carbon materials such as porosity, structural order, conductivity and defects have proved to have a strong influence in the catalytic activity of these materials. However, the highest differences in catalytic activity are obtained via doping with heteroatoms, being nitrogen the most remarkable in terms of activity and selectivity. One of the most challenging goals of the scientific community is to unravel the role of the functional groups in order to design an optimized material. However, the complexity of isolating one specific functionality, the difficult unambiguous characterization of the species and the influence of the intrinsic properties of the carbon materials, make the identification of the active sites a complex and controversial issue. This review presents a critical assessment about the role of heteroatoms on ORR from the analysis of the literature that combine both experimental work and computational modelling.

Content

1 Introduction

Combustion of fossil fuels satisfies most of global energy demand, it is the main responsible for the global warming and, most likely, for the climate change that we are already experiencing [1–4]. To try to solve this problem and maintain the global temperature change below 1.5ºC [1,5], a fast decrease in fossil fuels utilization and the massive implementation of renewable energies is mandatory. One option to achieve this objective is the "power to gas" technology in which the exceeding renewable energy is converted into a fuel gas that can be used upon demand or employed in vehicles [6,7]. One of the most promising alternatives is the synthesis of H_2 from water electrolysis that could be used in transportation or the electric grid, being an example of hydrogen economy. H_2 would be used as fuel in fuel cells due to their high efficiency towards energy generation and low pollutant production [8,9].

Among fuel cells, polymer electrolyte membrane fuel cells (PEMFC) are one of the most auspicious alternatives towards the replacement for the current combustion engines in transportation applications due to their highly efficient energy production from green fuels (H_2), the non-pollutant products generation and because they do not need recharging of both oxidant and fuel [10–13].
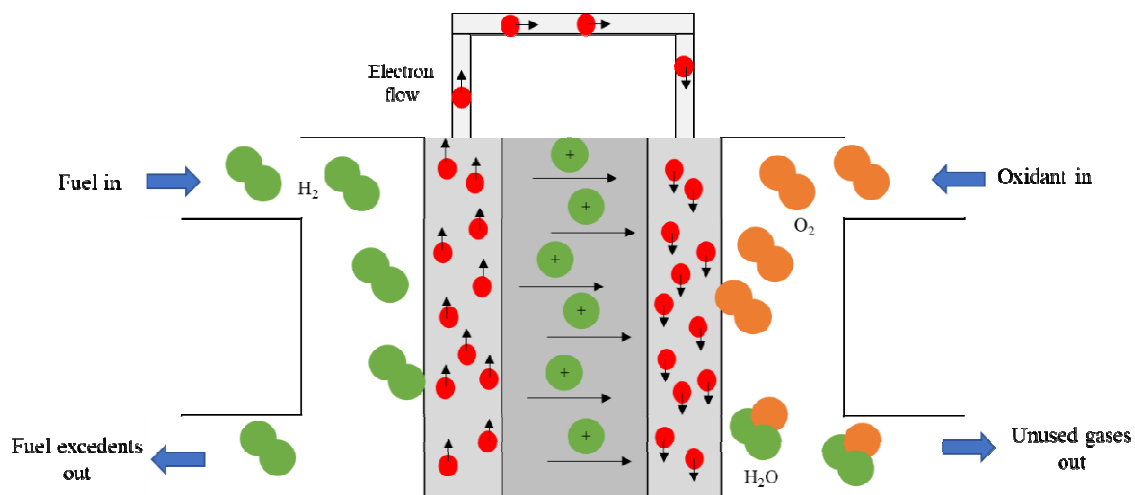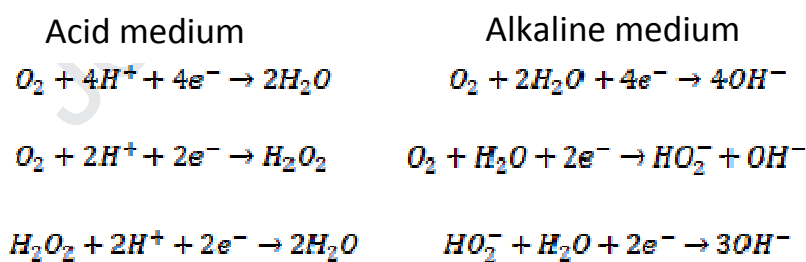
Figure 1: Schematic illustration of Polymer Electrolyte Membrane Fuel Cells (PEMFC) working in acid conditions.

Figure 1 includes a scheme for a PEMFC, showing hydrogen oxidation in the anode and oxygen reduction in the cathode. Both anode and cathode electrodes require a catalyst for hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR), respectively. Of particular interest in the scientific community is the ORR since it exhibits large limitations in terms of high overpotential, low limiting current and the high cost of the electrodes.

ORR is not only an important reaction for FCs, but it is also relevant for other devices or applications, such as metal-air batteries, hydrogen peroxide production, etc. On the one hand, metal-air batteries are electrochemical devices that generate electricity through redox reactions between metal and oxygen [14,15]. In contrast to other batteries, metal-air family has higher energy density because the oxygen is not stored [14,15]. Even though the use of oxygen is considered as the main advantage of these devices, the oxygen electrode is also the most complicated and, sometimes, expensive component of metal-air batteries [14,15]. On the other hand, hydrogen peroxide (H_2O_2) production is a very attractive topic for different applications[16,17]. H_2O_2 is a versatile and multifunctional chemical whose interesting properties are due to its oxidizing

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power. The production of this chemical exceeds 4 million tonnes per year and the industry around this compound generates almost 4 billion dollars [16]. The industrial synthesis of hydrogen peroxide is based on the anthraquinone process, a multistep and very energetic process. In this context, one of the most challenging targets on this topic focuses on the synthesis of hydrogen peroxide through the electrochemical reduction of oxygen molecules, which is a process safer, greener and works under ambient pressure and temperature.

It is widely known that the ORR mechanism depends on the electrolyte (acidic or alkaline) and the selectivity of the catalyst. ORR can occur through (i) a four electrons pathway, what is the most desired reaction since it involves higher energy production, and (ii) via two electrons pathway, which leads to H_2O_2 or HO_2^- production (acidic or alkaline electrolyte, respectively). Nevertheless, the H_2O_2 and HO_2^- species can be further reduced to H_2O and OH^- species, thus giving rise to the so-called 2+2 electrons mechanism.

<table>
<tr><td align="center">Acid medium</td><td align="center">Alkaline medium</td></tr>
<tr><td>$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$</td><td>$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$</td></tr>
<tr><td>$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$</td><td>$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$</td></tr>
<tr><td>$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$</td><td>$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$</td></tr>
</table>

Unfortunately, the most active and selective catalyst to water formation is based on platinum nanoparticles supported on carbon materials [18,19]. Apart from its high cost and low terrestrial abundance, commercial catalysts also exhibit low durability, Pt dissolution and CO deactivation which make impossible the large-scale commercialization [18,19]. Pt-loading on the anode electrode is close to 0.05 mg·cm^{-2},

whereas the Pt amount on the cathode electrode is almost ten times higher due to the lower oxygen reduction reaction rate [20]. This means that almost 90% of the platinum in the fuel cells is located in the cathode electrode. Consequently, the search for new cathode catalysts becomes into a scientific and technologic hot-topic as deduced from the strong increase in research publications since the last 15 years [21]. The studies found in the literature can be classified into two groups: (i) the development of non-precious metal-based catalysts and (ii) metal-free based catalysts.

Regarding the first group, even though the amount of noble metal, such as platinum, has been reduced because of the use of non-precious metal catalysts, metals can lixiviate and agglomerate, producing the loss of efficiency during time [22]. Nevertheless, the research on this kind of materials has reached significant progress in the development of new highly efficient devices and interesting reviews can be found about this topic [22–29].

The second and probably more innovative alternative consists on the use of metal-free catalysts based on heteroatom-doped carbon materials, which is a specific section of the wide field of defects in carbon materials. Due to the lack of metals, the development of these catalysts could significantly decrease the cost of the cathode. The strong research activity on carbon materials as electrocatalysts for ORR started around 12 years ago being the paper published by Dai et al. in 2009 [30], the one that reported, for nitrogen-doped carbon nanotubes, catalytic activities close to platinum-based catalysts. Since then, huge efforts are in progress with the aim of improving the performance of carbon-based catalysts. However, a large number of works on this topic sometimes are contradictory and have provoked a huge controversy about the nature of the active sites and the reaction mechanism. This is due to the complexity of carbon materials in which surface chemistry, porosity and structure are three important factors that, in general,

determine their performance. Many times, interpretation of results focuses only on one of these factors and omit others that can have an important contribution. Furthermore, metal impurities can also be responsible for contradictory results since low amounts of metal impurities can significantly improve the catalytic activity of the carbon materials [31]. Thus, high purity carbon materials are necessary to get specific information of metal-free carbon based catalysts.

In this sense, this review provides a comprehensive summary of the most relevant studies in ORR catalysis by non-doped and heteroatom-doped carbon materials. We essentially focus on heteroatom-doped carbon materials which is a small part of the wide and complex field of defects in carbon materials. We have to note that in the last few years a significant number of interesting reviews have been published that focus on carbon-based metal-free catalysts that present important information from both experimental and theoretical points of view [32–37]. In this review we have tried to deepen into the origin of the active sites as well as the contribution of each heteroatom functionality considering the fundamentals of Carbon Science. Therefore, we try to provide information about the relevance of surface chemistry but without omitting the role of porosity and structure of carbon materials in the ORR catalytic activity, pointing out and analysing the contribution that each functionality plays in the catalysis of ORR in carbon-based metal-free catalysts. This article provides a discussion over ORR from experimental and computational chemistry literature.

At this moment, to our opinion, it is important to clarify that when we refer to structure and surface chemistry, we include defects since they are the responsible for many of the properties of the carbon materials. The relevance of defects is well-known and is a subject of deep analysis in solid state physics and chemistry disciplines. Thus, we have to consider that heteroatom doping, vacancies or unsaturated carbon atoms (different

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kind of point defects), and other structural defects (i.e, topological defects such as Stone-Wales defect, pentagons, heptagons, etc), are very often found in carbon materials. A control over the nature and amount of the defects will determine the properties of the carbon material including catalytic and electrocatalytic activities. This makes defects engineering a fascinating area of research that will be an essential area of research in the future. Some interesting examples on this issue can be found in the following references [38–43].

2 General view of oxygen reduction reaction mechanism on carbon-based catalysts

The mechanism through which ORR proceeds is much more complicated than the simplistic view of a 2 or 4 electron routes. ORR involves multiple elementary steps, such as O_2 adsorption, electron and proton transfer and products desorption. Figure 2 summarizes the possible ORR mechanisms catalysed by non-doped and heteroatom-doped carbon materials that the authors deduce from the analysis of the different publications presented in this review. In addition, Table 1 classifies the proposed mechanisms according to the dioxygen binding mode and the number of transferred electrons.
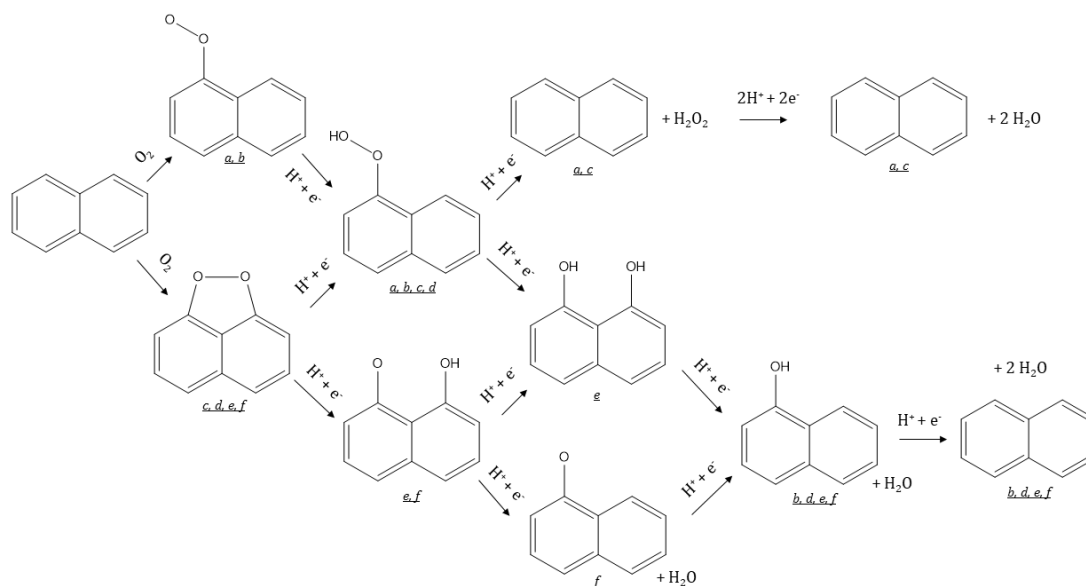
Figure 2: Summary of the most proposed mechanisms for the catalysis of ORR by carbon-based catalysts.

The first stage of the oxygen reduction reaction consists on the adsorption of the dioxygen molecule on the surface of the catalyst. This might occur via terminal or bridging binding modes, which means that the oxygen molecule would be adsorbed through one or two carbon atoms, respectively. The dissociative mechanism involves a rupture of the oxygen-oxygen bond, whereas the associative mechanism keeps the oxygen-oxygen bond.

Table 1: Representation of the adsorption mode, electron pathway and mechanisms of the different proposed ORR path in Figure 2.

Route	Adsorption mode	Electrons pathway	Mechanism
A	Terminal	2	Associative
B	Terminal	4	Dissociative
C	Bridging	2	Associative
D	Bridging	4	Associative
E	Bridging	4	Dissociative
F	Bridging	4	Dissociative

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If the oxygen is adsorbed through one active site (or terminal binding mode), the first electron-proton pair supply involves the formation of a C-O-O-H type intermediate. Then, the next electron-proton supply may involve the rupture of the C-O bond, leading to H_2O_2 generation (route *a*) or the rupture between both oxygen atoms (route *b*), which results in the formation of one water molecule and one oxygen atom bonded to the carbon surface. Route *b* is followed by subsequent reduction stages up to the generation of the second water molecule.

On the other hand, if the chemisorption happens via two active sites (or bridging binding mode), four different ORR mechanisms have been proposed. First, the rupture of one C-O bond along with the first electron-proton pair supply would lead to the formation of a C-O-O-H type intermediate. From this point, the possibilities are the same as in route *a* and *b*, being the difference just the initial chemisorption mode. The second possibility involves the rupture of the O-O bond (routes *e* and *f*), where both configurations lead to 4 electrons processes and the generation of water molecules.

3 Metal-free Carbon-based catalysts

Properties and applications of carbon materials are mostly determined by their structure, porosity and surface chemistry. These three factors can have a wide range of variation making Carbon Science a very complex and rich subject. In the specific case of ORR, the main factor that causes the highest differences in catalytic activity is the doping with heteroatoms different to oxygen, being the most remarkable the effect of N functional groups. However, the effect of porosity and structure should not be omitted since they have a very important contribution to the overall performance of the material:

microporosity can act as nanoreactors and, since this is an electron transfer process, the electrical conductivity of the carbon material (determined by the structure) is essential for the reaction to take place. Other type of defects such as unsaturated carbon atoms, vacancies or additional structural defects play also a relevant role.

According to the above considerations, the review has been structured by explaining in a first section the "non-doped carbon materials" in which we will take into account the effect of porosity and structure and will make some brief comments about the effect of the oxygen groups (which are naturally found in the carbon materials). The next sections will collect the most important results about heteroatom-doped carbon materials, specifically N, P, B and S. Since the most studied and the most remarkable results are found for N-doped carbon materials, most of the review is focused on this heteroatom.

3.1 Non-doped Carbon Materials

The effect of porosity has often been obviated in the discussion of the catalytic activity of carbon-based catalysts; however, some studies have demonstrated the important role that porosity plays in the ORR catalysis. This aspect was highlighted by Appleby et al. when they reported ORR kinetic studies on a series of carbon materials in alkaline electrolyte [44], by demonstrating that the catalytic activity towards ORR increases linearly with BET surface area for carbon blacks [44]. However, this trend was not observed in activated carbons whose porosity is much more complex than for carbon blacks [44]. In this sense, Gabe et al. [45] reported, via mathematical modelling and experimental results, the influence of microporosity in the oxygen reduction reaction catalysis. The authors found that microporosity is certainly correlated to a high activity in the ORR and the shape of the ORR curves depends on the micropore size

distribution, being the H_2O_2 reduction favoured in the narrow micropores (size below 0.7 nm) [45]. Liu et al. [46] studied the effect of micro and mesoporosity on carbon-based catalysts. They concluded that the microporosity is the responsible for the catalytic activity, but mesopores are also necessary to facilitate the accessibility to active sites within the microporosity [46]. The crucial role that mesopores play for achieving an adequate oxygen mass transfer to the micropores was supported and pointed out by Bandosz et al. [47]. In addition, the authors also concluded that strong adsorption of dioxygen molecule takes place in hydrophobic ultramicropores (pores of size below 0.7 nm) [47] and have recently proposed that the ultramicropores can be the active sites for this reaction [48].

The structure of the carbon materials also has an important effect on the oxygen reduction reaction catalysis, since carbon nanotubes (CNTs) exhibit higher catalytic activity than graphite/graphene-based electrodes [49,50]. The small number of graphene layers and the curvature of CNTs, especially for those CNTs of smaller diameter, can be the responsible for such an increase in ORR activity. Moreover, the selectivity of the ORR also differs in CNT, promoting a 4e- reaction path [50]. The origin of the effect of curvature mainly comes from the change of the hybridization of the carbon atoms that affects the electronic structure [51]. The well-conjugated structure of a graphene layer impedes the change from sp^2 to sp^3 and, consequently the oxygen chemisorption, which should be mainly restricted to the edge of the layers. However, the use of CNTs makes possible the control over the degree of the sp^3 hybridization [51]. An interesting example can be found in the computational study done with silicon-doped graphene and silicon-doped CNT; the oxygen adsorption energy and the free energy of the rate-determining step in ORR is lower when the oxygen chemisorption takes place inside the CNT (negative curvature) [52]. Furthermore, density functional theory simulations

reveal the importance of the length of the nanotubes in the oxygen adsorption energy; the higher the length of the CNTs, the lower the chemisorption energy of oxygen molecules in the basal plane of the carbon nanotubes [53].

According to the literature, edge chemistry also influences the catalytic activity towards ORR. Deng et al. [54] investigated the electrocatalytic activity towards ORR of graphene layers obtained with different size, taking into account that the smaller the size of the graphene layer, the higher the amount of edge-type carbon atoms. Interestingly, the smallest the graphene size reported, the higher the catalytic activity towards ORR, which points out the crucial role that edge chemistry plays in electrocatalysts [54]. Theoretical calculations indicate that catalytic activity in those materials is due to zigzag edge sites [54]. Chen et al. [55] reported the doping of sulphur and reduction of graphene oxides by hydrothermal method. The S-doping induce the formation of abundant edge sites and defects in the graphene-based materials leading to higher catalytic activity towards ORR. The authors proposed the asymmetric spin densities and the higher edge plane defects as responsible for the high oxygen reduction catalysis [55]. In fact, it has been proposed that the reactivity towards electron transfer of the edges is at least two times higher than that for the basal plane of a graphene layer [56]. This higher reactivity is not only observed in the catalytic activity towards ORR but also in other reactions like electro-oxidation of ascorbic acid (AA) and beta-nicotinamide adenine dinucleotide (NADH), among others [57].

Structural defects engineering is recently gaining more attention. In most carbon-based catalysts, structural defects (such as pentagon or heptagon carbon rings, vacancies, defects at edges and 1D defects) are intrinsically present. Jia et al.[58] reported a synthetic strategy for specific carbon defects; pristine HOPG was etched by argon plasma to form uniform grooves. The obtained sample (Ar-HOPG) was washed,

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followed by annealing at 700 °C in an ammonia flow. The resultant N-doped highly oriented pyrolytic graphitic (N-HOPG) was annealed at 1150°C under nitrogen atmosphere to obtain HOPG with a high number of vacancies and topological defects (D-HOPG). X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy indicated the complete removal of nitrogen in D-HOPG and an increase in defects during the heat treatment. From X-ray absorption near-edge structure, positron annihilation, high-angle annular dark-field scanning transmission electron microscopy and density functional theory (DFT) calculations, the authors confirm that the increase in the number of structural defects occurs because of the reconstruction of the edge carbon lattice from N-HOPG, specifically, through the conversion of pyridinic nitrogen species into pentagons [58]. Interestingly, D-HOPG shows the highest catalytic activity towards ORR, with an onset potential of 0.81 V vs RHE in acidic electrolyte, whereas N-HOPG shows an onset potential of 0.76 V vs RHE. Work function measurements suggest that pentagons have the highest electron-donating capability and hence the highest ability for charge transfer with oxygen. This was confirmed by the higher catalytic activity of the defect-containing carbon materials compared to pyridinic-containing ones. Recent works also corroborate the highly efficient catalysis of pentagon containing defects through experimental and computational approaches [43,59,60].

In addition to pentagons or heptagons formation, carbene-like zigzag sites and carbyne-like armchair sites formation at graphene edges are possible mechanisms for nascent site deactivation [61]. Radovic et al. proposed that, under air atmosphere, part of zigzag and armchair edges must be carbenes, carbynes or H-deficient free radicals [62], and those should not be dismissed as possible active centres towards oxygen reduction reaction. The main consequence of the presence of these defects is the observed ferromagnetism of carbon materials, which can be interpreted considering the presence of carbene

structures at the zigzag edge [62]. Furthermore, the presence of carbene leads to different oxygen chemisorption structures. Thus, the oxygen molecule can be adsorbed through a double C-O bond in one single carbon atom and in a C-O-O configuration, being the first more favourable than the second (Figure 3A) [63,64]. It does not only reveal a new chemisorption configuration for oxygen molecules but can also explain the oxygen reduction reaction [64], the oxidation of the carbon materials through carbon dioxide formation [63] and the creation of oxygen functional groups in the basal plane of carbon-based catalysts [65]. This approach is in agreement with experimental studies in which it was demonstrated a correlation between ORR catalytic activity of non-doped carbon materials and the O_2 carbon gasification reactivity [50].

Therefore, the presence of structural defects (in their multiple possibilities) is necessary to explain the catalytic activity of non-doped carbon-based catalysts for oxygen reduction reaction. Nevertheless, defects contribution can only be positive if the conductivity of the catalysts is high enough to provide electrons to the active sites [66]. Once the introduction of defects leads to a conductivity lower than 70 $S \cdot m^{-1}$, the positive effect of such defects is overshadowed by the low resistance towards electron transfer [66].

Oxygen functional groups are naturally found in carbon materials and can be created on the carbon surface through different well-known methodologies being even possible to tailor the nature of the functional groups. This means that pure carbon materials cannot be prepared. However, their influence towards ORR does not seem to be important or, at least, they are not the main factor responsible for the activity found for the best reported metal-free carbon-based catalysts. In the 1990s, several studies focused on the effect of oxygen functional groups in glassy carbon. The oxidation of carbon electrodes like glassy carbon led to a slight improvement of the catalytic activity [67–69];

however, such activity was very different from that of the platinum commercial catalysts. The authors attributed this behavior to the presence of aryloxy radicals on the carbon surface. Such aryloxy radicals would be responsible for the increased paramagnetism, which accompanies chemical and electrochemical oxidation of carbon materials [67–69]. These paramagnetic centers may reduce HO_2^- into OH^- resulting in a higher number of transferred electrons during the reduction of dioxygen molecules [67–69]. However, this enhancement was also attributed to the influence of the surface area in ORR catalysis, which also changes with the pretreatment [69] and could also explain the higher number of transferred electrons during ORR. Nevertheless, a more recent work points out the beneficial role that epoxy and ether-groups play in the selectivity towards hydrogen peroxide formation [70]. Other work has proven that the oxygen functional groups do not produce an important enhancement of the ORR catalytic activity [71] and that it is significantly increased if another heteroatom like nitrogen is added to the carbon material [71]. Despite the low activity that oxygen functional groups show by themselves, they can generate a significant synergistic effect with other functional groups, as we will discuss in the next section.

3.2 Heteroatom-doped carbon materials

By doping carbon with more electronegative atoms such as nitrogen, a positive charge density is created on adjacent carbon atoms, which facilitates oxygen adsorption and charge transfer, resulting in enhanced ORR activity [30]. The opposite strategy has also been studied, and it has been reported that the doping with a less electronegative atom, such as boron or phosphorus, can also facilitate the oxygen molecule adsorption and reduction [72].

In this section, we will discuss about heteroatom-doped carbon materials paying attention to the proposed nature of the active sites and the reaction mechanisms through which oxygen reduction reaction occurs. Since a large piece of work deals about N-doped carbon materials due to their remarkable performance, we will dedicate more space to this heteroatom.

3.2.1 Nitrogen-doped carbon materials

The introduction of nitrogen atoms into the carbon matrix is the most studied doping method for ORR. Nevertheless, despite the promising possibilities of N-doped carbon materials, there are only few studies that report highly efficient electrocatalysts towards ORR and most of them in alkaline electrolyte. In most of the cases, the catalytic activity of the reported N-doped carbon materials is far from platinum-based catalysts, although the characterization of the materials very often describes similar N functionalities as for the best N-containing carbon electrocatalyst. These results have led to a huge controversy about the nature of the active sites generated by the nitrogen heteroatoms in the carbon framework. The huge controversy and debate about the nature of the active sites lie in the difficulty to isolate one specific nitrogen species in a carbon material. The isolation of one nitrogen species incorporated in the carbon material structure is not straightforward. Even though it was possible, the lack of control over other important properties (such as structural order, morphology, defects and porosity, among others), that may have a strong influence in the performance of metal-free carbon-based catalysts (see Section 3.1), makes difficult to deepen into the knowledge of this topic.

In 2009, Dai et al. [30] showed the high activity towards ORR in alkaline medium of vertically aligned N-doped carbon nanotubes (VA-NCNT), reaching a platinum-like performance (Figure 3B). The reaction pathway was determined to be 2 + 2, where O_2 is

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first reduced to HO_2^- and, then, converted to OH^-. In addition to carbon nanotubes, graphene and graphene-based electrodes have been the most studied carbon materials for nitrogen doping since their well-defined structure provides an excellent model to understand the effect of different nitrogen functionalities on ORR catalysis. Qu et al. [73] demonstrated the remarkable catalytic activity of N-doped graphene obtained via chemical vapor deposition (CVD) (Figure 3C). Although the onset potential is still lower than the commercial platinum-based catalysts, the current density is three times higher. Moreover, the differences in both onset potential and current density compared with the pristine graphene reveals the role of nitrogen functionalities. Sheng et al. [74] reported a route of synthesis of N-doped graphene through the thermal annealing at different temperatures (700-1000 ºC) of graphite oxide using melamine as nitrogen source. By controlling the temperature of the treatment, the nitrogen atomic percentage was 10.1 % at 700 ºC. Higher temperatures lead to a decrease in both nitrogen and oxygen contents. The improved catalytic activity was attributed to the incorporation of the nitrogen atoms into the graphene layers that modify the electronic structure of the adjacent carbon atoms [74]. In addition to the CVD methodology [73,75–77], other studies have reported improved catalytic activity of graphene-based materials via nitrogen doping through arc-discharge [78], thermal annealing of graphitic carbon with NH_3 [79] and urea [80], among others.
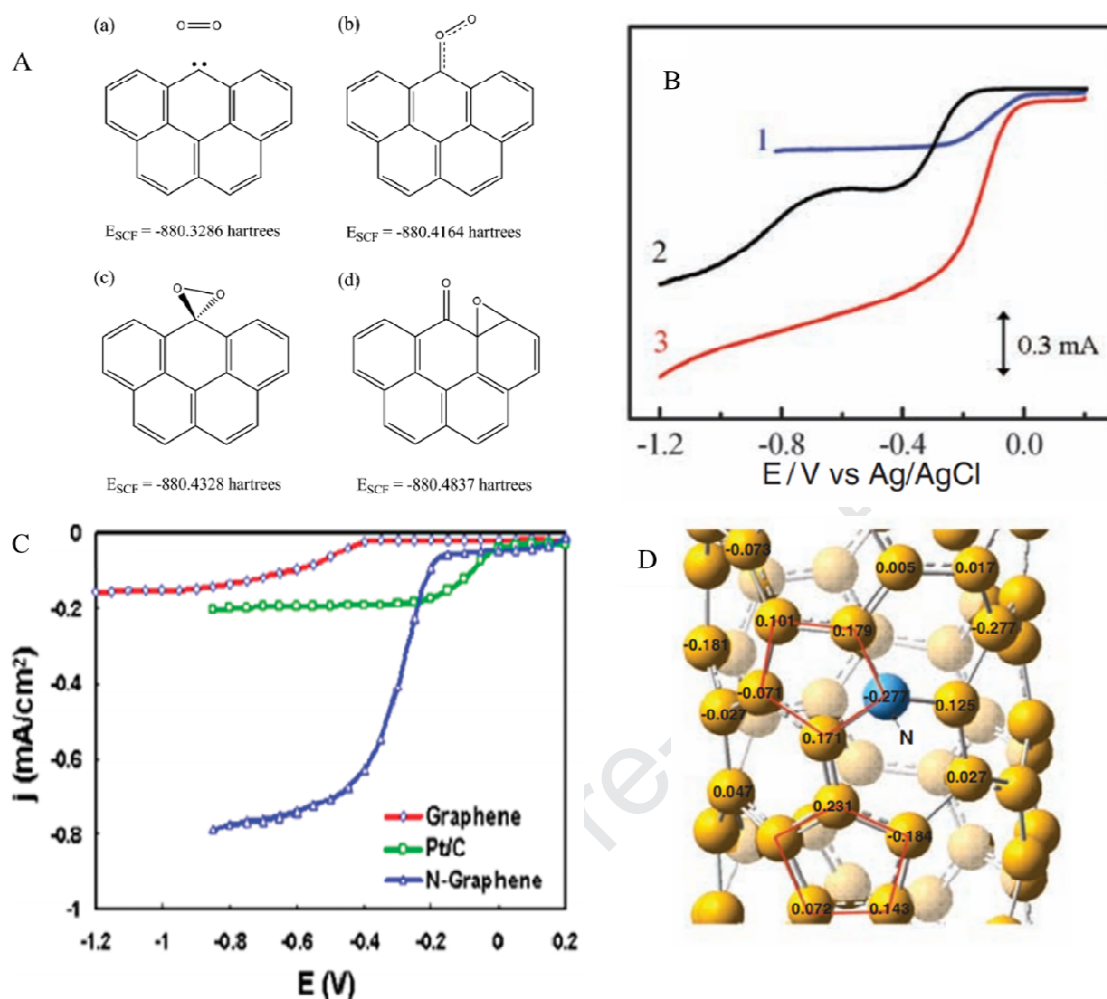
Figure 3: (A) Selected thermodynamically stable graphene clusters (C19H10) that illustrate a likely path for the formation of an epoxide-type functionality on the graphene basal plane subsequent to O_2 chemisorption on a carbene-type edge site (Reprinted with permission from Ref. 63, Copyright 2009, American Chemical Society). (B) RRDE voltammograms for oxygen reduction in air-saturated 0.1 M KOH at the Pt-C (curve 1), VA-CCNT (curve 2), and VA-NCNT (curve 3) electrodes (From Ref. 30.Reprinted with permission from AAAS). (C) RRDE voltammograms for the ORR in air-saturated 0.1 M KOH at the graphene electrode (red line), Pt/C (green line) and N-graphene electrode (blue line). Electrode rotating rate: 1000 rpm. Scan rate: 0.01 V/s. (Reprinted with permission from Ref. 73, Copyright 2010, American Chemical Society). (D) Calculated charge density distribution for the NCNTs of Figure 3B (From Ref. 30. Reprinted with permission from AAAS).

Although N-doped carbon nanotubes and graphene-based electrocatalysts are the simplest demonstration of the positive effect of nitrogen atoms in the enhancement of ORR catalytic activity of carbon materials, the most extended routes of synthesis of N-doped carbon materials are the carbonization of nitrogen-based precursors, such as polymers or ionic liquids and the direct reaction between carbon materials and nitrogen precursors [81–85]. These methods of synthesis do not permit a precise control of

properties such as morphology, structural order, porosity, electrical conductivity, etc., what makes difficult to unravel the role of the N species on ORR catalytic activity. For this reason, several studies have tried to overcome these limitations using templates such as SiO_2[83,86–89] or TiO_2[90,91]. The nitrogen-containing carbon precursor is deposited within the porous structure of the template via chemical or electrochemical synthesis. Once the precursor is deposited into the porosity, a heat treatment is performed to generate the ordered porous N-doped carbon materials.

In any case, N-doped carbon materials with excellent performance, and prepared through conventional synthesis methods without the use of templates, have been published. For example, in 2011, Yang et al. [92] synthesised highly efficient catalysts through the heat treatment of the most familiar nucleobases (adenine, guanine, cytosine, thymine and uracil) mixed with 1-ethyl-3-methylimidazolium dicyanamide at 1000ºC. The obtained samples show almost platinum-like performance with high onset potential. Men et al. [93] synthesised hierarchical N-doped porous graphene/carbon composites (NPGC) from glucose after pyrolysis at 950 ºC. NPGC exhibits a high onset potential (0.91 V vs RHE) with a number of electrons close to four, which means a direct oxygen reduction towards water production.

In spite of the fact that most of the research on this topic focuses on the synthesis of the most active N-doped carbon material through very different strategies that seem to follow a trial and error methodology, we can find studies, with increasing number in recent years, that try to deepen into the nature of the active sites in N-doped carbon materials and the reasons why N atoms provoke such improvement. Obviously, this knowledge is essential to define the guiding principles for the design and nanoscale engineering of advanced metal-free carbon-based catalysts for ORR.

Undoubtedly, not only experimental results but also computational studies are necessary to get the most accurate view on this complex topic. For example, Gong et al. reported that the high electron affinity of the nitrogen atom can produce a positive charge density into the adjacent carbon atom, which would provide an easier oxygen adsorption (Figure 3D) [30]. The high activity of N-doped carbon nanotubes was supported by Hu et al. [94]. They proposed that N-doping can reduce the bandgap between the HOMO and the LUMO through the increase of the energy level of the HOMO, which facilitates the electron transfer to the adsorbed oxygen. Moreover, it has been demonstrated through DFT calculations that the positive charge density of the adjacent carbon atoms to the nitrogen heteroatom facilitates the oxygen chemisorption and, then, reduction [30,94,95]. All these works permit to conclude that the catalytic active sites are not nitrogen atoms themselves but the neighbour carbon atoms where oxygen molecule is attracted, chemisorbed and then reduced.

Nevertheless, the identification of the nitrogen species that create the most active catalytic sites is still under debate. In fact, almost all nitrogen functionalities have been proposed as responsible for the excellent catalytic activity of N-doped carbon materials. Some authors directly attribute the high catalytic activity of N-doped carbon materials to the nitrogen content, which is considered as the key in understanding the catalysis of ORR [96–98]. However, more recent studies are in disagreement with that conclusion [99–101] since specific functionalities seem to be the responsible for the highest activities. Thus, an extended analysis and discussion about the nature of the active sites is necessary to get a better understanding of N-doped carbon materials as electrocatalysts towards ORR. In the next sections, we discuss about the role of different N functionalities in the catalytic activity as deduced from the abundant available literature.

3.2.1.1 Pyridinic Nitrogen species

Among all nitrogen species, pyridinic nitrogen is the most reported as responsible for the high activity of N-doped carbon materials. For example, Rao et al. [102] prepared vertically aligned N-doped carbon nanotubes with a variety of polymer precursors. The enhancement in the catalytic activity of the materials was attributed to the increase in the atomic percentage of pyridinic nitrogen species since the higher the pyridinic atomic percentage, the higher the catalytic activity towards ORR.

Similarly, Miao et al. [103] prepared nitrogen-doped reduced graphene oxide materials by hydrothermal method, followed by an annealing treatment. The different treatment temperatures enable to tailor the content of the nitrogen species. The pyridinic nitrogen content increased with the annealing temperature (from 600 to 800ºC) as well as the catalytic performance, which suggested that pyridinic nitrogen species are the active centres in these N-doped carbon materials. Ensafi et al. [104] reported the higher catalytic activity of pyridine functionalized reduced graphene oxide (Py-EGO), obtained by a filtration method, compared with nitrogen-doped reduced graphene oxide (NrGO) samples prepared by hydrothermal method in presence of ammonia. Py-EGO exhibited higher content in pyridine functional groups and higher catalytic activity than NrGO sample. Chang et al. [105] supported the key role of pyridinic nitrogen species towards ORR catalysis through the catalytic test of pyridinic N-rich doped graphene nanoplatelets and its counterpart without pyridine moieties. The N-rich samples showed superior activity towards ORR than without the pyridinic moieties, which highlighted the crucial role of the pyridinic functional groups. Furthermore, Lv et al.[106] reported the selective formation of pyridinic nitrogen-doped hydrogen-substituted graphidyne (HsGDY) and that these species resulted in highly active catalysts towards ORR.
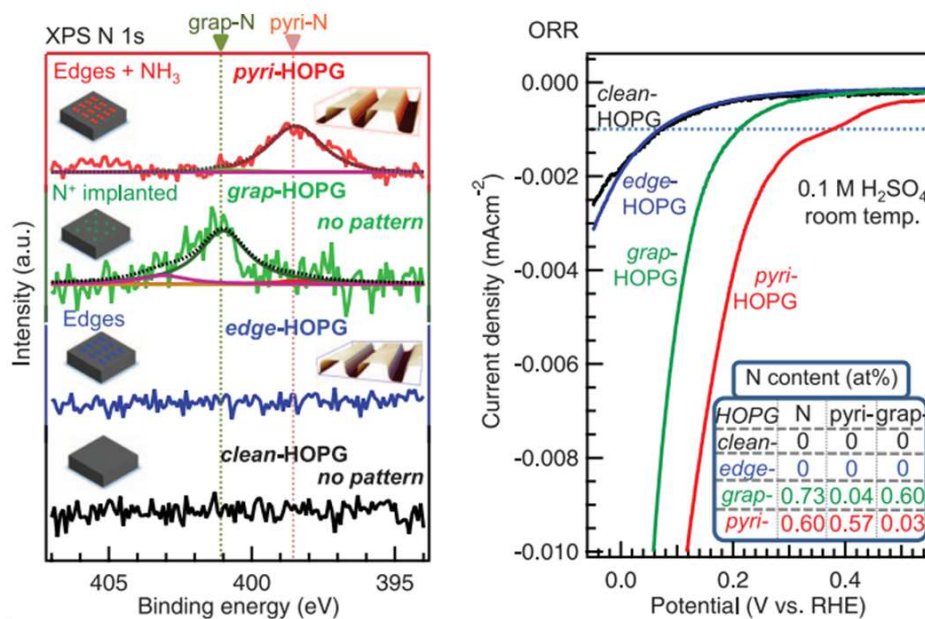
Figure 4: N1s spectra and ORR results of clean-HOPG, edge-HOPG, grap-HOPG and pyri-HOPG (From Ref. 107. Reprinted with permission from AAAS).

An interesting approach is the study by Guo et al. [107]. The authors characterized the ORR active sites in N-doped carbon materials obtained by well-controlled N doping of highly oriented pyrolytic graphite (*clean*-HOPG) (Figure 4). For this purpose, *clean*-HOPG samples were bombarded with an Ar^+ ion beam through a thin metallic mask to create a material with a high concentration of carbon edge-sites (*edge*-HOPG). This *edge*-HOPG was exposed to NH_3 at 973 K, creating *pyri*-HOPG sample which contained pyridinic species as determined by XPS. Additionally, *clean*-HOPG were cleaned by annealing at 1073K under ultra-high vacuum (UHV) for 15 min and then, nitrogen doping was carried out by mild bombardment with a nitrogen ion beam at 600 K. The obtained sample, named as *grap*-HOPG, exhibited only the presence of quaternary nitrogen species. The materials were evaluated as catalysts for ORR in acidic electrolyte. *pyri*-HOPG was the sample with highest activity towards ORR, although an improvement in the catalytic activity of *grap*-HOPG was also observed in acidic electrolyte. Interestingly, the post-ORR XPS analysis demonstrated the transformation of pyridinic species into pyridonic nitrogen functionalities. The authors use the

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differences in the composition after ORR to suggest that the carbon atom next to pyridinic N is responsible for the ORR catalysis and not the pyridinic N themselves.

In the same context, three N-doped multilayer graphene materials were obtained from graphene oxide using different nitrogen sources and doping methods [108]. XPS of the samples after ORR showed an increase in the OH amount of the adjacent carbon atom and, consequently, the generation of pyridonic-like nitrogen functionalities during the ORR catalysis (Figure 5A). This was attributed to the formation of an intermediate step for the oxygen reduction reaction in the carbon material containing pyridinic nitrogen, where the dioxygen would react through the adjacent carbon atom to pyridine species via terminal binding mode, thereby creating N-C-O species during the oxygen reduction reaction [108].
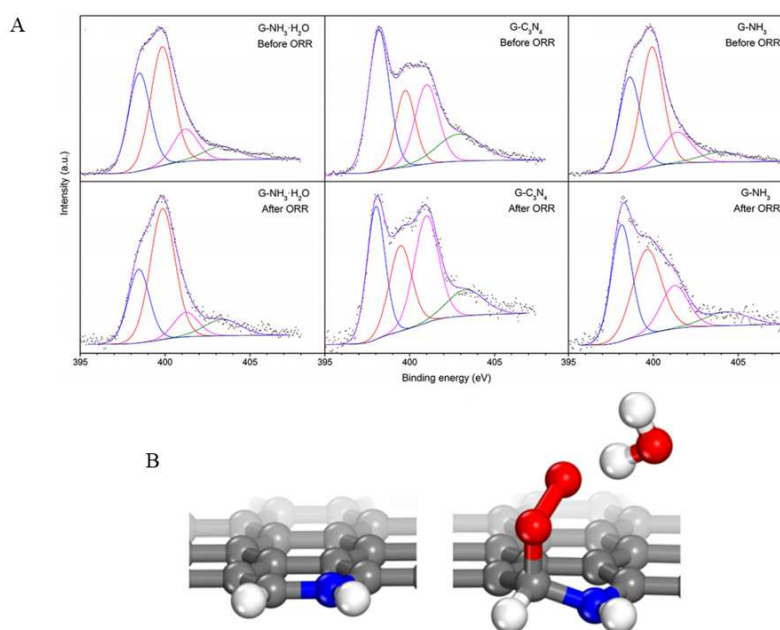

Figure 5: (A) N1s spectra of the three multilayer graphene samples before and after ORR (Reprinted with permission from Ref. 108, Copyright 2014, American Chemical Society), and (B) geometric detail of the surface model of pyridine functional group in armchair position before and after the O_2 chemisorption (Reprinted from Ref. 119. Copyright 2016, with permission from Elsevier).

However, these interesting observations might arise an important question; are pyridinic species the responsible for the creation of the active sites towards ORR or the pyridonic-type nitrogen groups formed during the initial stages of ORR? The next section evaluates the N-C-O species as active sites. However, before that discussion, an extended evaluation of the ORR mechanism along with the most relevant studies in computational chemistry concerning pyridine species, is presented below.

The terminal binding mode is the most widely accepted ORR scheme for pyridinic species. This means that molecular O_2 is adsorbed in a C-O-O configuration. However, the associative or dissociative mechanisms are still under a huge controversy for this active site. While some authors demonstrate almost 4 (or 2+2) electrons pathway for pyridine containing carbon materials [98,109,110], other works reported high selectivity towards hydrogen peroxide [111–115]. In acidic electrolyte, the hydrogen peroxide formation for pyridinic species was strongly demonstrated by Y. Sun et al. [113]. The pyrolysis of CMK-3 and polyethylimine (PEI) produced a pyridine-rich nitrogen carbon material, which reached more than 95% of selectivity towards H_2O_2 formation during the oxygen reduction reaction. Otherwise, 4 (or 2+2) transferred electrons pathway predominates in alkaline solution [98,109,110]. Therefore, the employed electrolyte plays a key role in the selectivity of pyridine rich carbon materials. A detailed mechanism was proposed for 2 and 2+2 electrons pathway in carbon materials containing armchair-type pyridinic species (Figure 6) [107] in which the electrolyte may determine the pathway followed during the reaction. The porosity is another factor that must not be discarded for having a strong influence in the number of transferred electrons (see section 3.1).
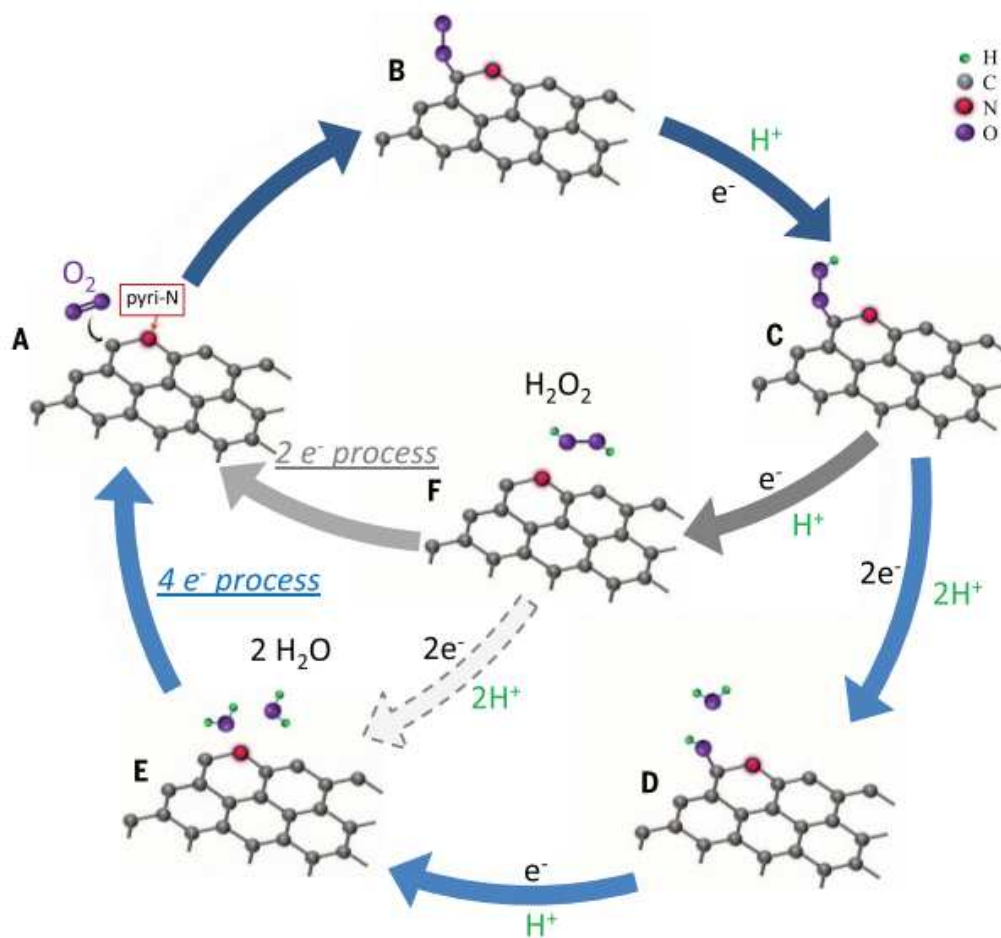
Figure 6: Schematic pathway for ORR on pyridinic nitrogen species in armchair position (From Ref. 107. Reprinted with permission from AAAS).

Pyridinic nitrogen species have not only been the most evaluated in ORR from an experimental point of view, but also from a computational chemistry approach. DFT calculations showed that pyridinic-N in armchair position enhances the adsorption of molecular dioxygen on the adjacent carbon atom because of the positive charge density and high spin density created in the carbon atom by the high electronegativity of the nitrogen atom and the consequent electron-withdrawal effect [75]. However, the evaluation of the pyridinic-N in zigzag position revealed poor catalytic activity [116], even lower than pristine carbon materials [117]. The adjacent carbon atoms in a zigzag position needs very high energy to change its hybridization [117]. Indeed, Huang et al. [118] reported that for a given zigzag edge site, the presence of a pyridine group is not

favourable for the ORR. To get further insights into this matter, Ferre-Vilaplana et al. [119] evaluated and compared the oxygen chemisorption step for pyridine groups with different structure and location in the graphene layer. Interestingly, the chemisorption of molecular oxygen in the carbon atom adjacent to the pyridinic nitrogen at armchair position is the most favourable compared to a carbon atom adjacent to a pyridine located in a zigzag position. The results obtained confirm the formation of N-C-O-O groups via O_2 adsorption in the carbon atom adjacent to pyridine species at armchair position (Figure 5B).

All these studies show the role that the position of the functionality, and consequently the local structure of the material, plays towards the ORR. This also allows us to understand the variety of results found since the concentration of zigzag or armchair pyridine groups will be very much dependent on the preparation method and precursors used. In addition, this discussion arises the important question of analysing the catalyst after use or, ideally, under operando conditions.

3.2.1.2 *Pyridonic-type Nitrogen species*

The evaluation of N-C-O species as active sites in N-doped carbon materials is strongly related with the presence of pyridinic nitrogen since, as we commented above, the adjacent carbon atom to the pyridinic nitrogen seems to react with dioxygen creating N-C-O species as an intermediate of the oxygen reduction, which are also detected in post-reaction materials. Thus, the question is whether the catalytic activity comes from the pyridines or directly from the pyridone-type nitrogen species, which may favour a stronger chemisorption of the dioxygen molecule on the carbon atom. In the following, several examples are presented that propose that the catalytic activity is due to these species.

Polyaniline (PANI) was heat-treated under two different conditions; inert and slightly oxidant atmosphere up to 800ºC (PANI_N2_800 and PANI_O2_800, respectively) [120]. From XPS and TPD analysis, it is observed that the heat treatment in an oxidant atmosphere leads to a higher contribution of pyridonic-type nitrogen species (N-C-O moieties), what also results in an enhancement of the catalytic activity of PANI_O2_800 compared to its counterpart in inert atmosphere [120]. This suggested that N-C-O species are not only intermediate functional groups formed during the oxygen reduction of carbon-containing pyridines, but also they can be catalytic active sites.

The high catalytic activity of N-C-O species was supported by Li et al. [121]. They present a synthesis of N- and O- co-doped carbon nanowebs through activation with KOH after the pyrolysis of a polypyrrole nanoweb. The synergistic effect between the O (from KOH activation) and N groups (from the PPy precursor) creates highly active pyridonic groups on the carbon matrix. The obtained co-doped materials exhibit higher intrinsic ORR activity than the materials without the incorporation of oxygen groups. Furthermore, Silva et al. [122] reported the synthesis of N- and O- doped carbon materials obtained via the pyrolysis of PANI/SBA-15 composite. The high catalytic activity of these materials was attributed to the synergistic effect of the O (from the Silica) and N species (from polyaniline).

In spite of the low popularity of pyridone-type species as active sites for ORR, the discovery of N-C-O as intermediate of the oxygen reduction reaction has produced an increase in the number of publications related with N- and O- co-doped carbon materials for ORR electrocatalysis [71,123–125].

The structure of the pyridone group responsible for the catalytic activity is very much related to the discussion included in the previous section. Only pyridone groups at

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armchair position would be responsible for the catalytic activity. Thus, armchair edge sites would be preferable for creating the highest concentration of active sites.

DFT simulations also evaluated the ORR catalytic behaviour of these pyridone-type species in which the obtained results suggest that they exhibit higher performance than non-doped carbon materials [117]. The electron withdrawal effect that both oxygen and nitrogen heteroatoms provoke in the adjacent carbon atoms seems to create a positive charge density that acts as active sites, in which the dioxygen molecule would be attracted [120].

3.2.1.3 *Pyrrolic Nitrogen species*

Pyrrolic N atoms are incorporated into five-membered heterocyclic rings and are bonded to two carbon atoms. Such nitrogen species are not very common in carbon materials because pyrrolic species have a low stability, what makes that the concentration of this functionality is low after a carbonization or heat treatment [126]. For instance, Lin et al. [127] demonstrated that the carbonization of polypyrrole produced a decrease in pyrrol groups from 100% (in the pristine polymer) to 0 % at 1000ºC.

However, there are some studies that attribute the catalytic activity of N-containing carbon materials to the presence of this species.

Li et al. propose the transformation of pyridinic species into pyrrolic functional groups at high temperature [128]. Such increase in pyrrolic species was considered as responsible for the observed high catalytic activity of these N-doped carbon materials. Unni et al. [129] observed a relationship between the pyrrolic content and the catalytic activity in nitrogen-doped graphene. The authors propose that the high pyrrolic nitrogen

content along with the high surface area, result in the efficient ORR catalysis of the N-doped carbon materials obtained by heat treatment of graphene oxide with adsorbed pyrrole monomers at different temperatures (800-1000ºC). Li et al.[130] reported the synthesis of N-containing carbon materials supported on SBA-15 template with different N species. The highest catalytic activity towards ORR was obtained by the N-doped carbon materials which exhibited the highest pyrrolic and pyridinic contents. Likewise, Feng et al. [131] reported the synthesis of pyridinic and pyrrolic nitrogen-doped carbon using SBA-15 as template. The obtained materials exhibited comparable catalytic activity as platinum-based catalyst.

Based on high-resolution XPS and experimental ORR activities of N-doped carbon black materials, Liu et al. [132] proposed an order of the activity of the nitrogen functionalities as follows: pyridinic nitrogen > pyrrolic nitrogen > graphitic or quaternary nitrogen > oxidized nitrogen > pristine carbon material, pointing out the high activity of pyrrolic nitrogen as well as by pyridinic nitrogen [132].

It has been proposed that pyrrole-based nitrogen-doped carbon materials induce a 4 electrons pathway through a bridging binding mode in the vicinities of the nitrogen functionality [133]. Then, the posterior reduction stages lead to the cleavage of the O-O bond as a result of the formation of two C-O-H intermediates, which leads to the final formation of two water molecules [133].

It must be noted that the identification of pyrrole groups is done using XPS and the differentiation among pyrrole and pyridone functional groups is very difficult since both of them appear at similar binding energies. In fact, sometimes we can find in the literature on N-doped carbon materials that the 400.5 eV peak is only assigned to pyrrol groups although it could also correspond to pyridone species. Then, taking into account the low thermal stability of pyrrol groups, the difficulty of an straightforward

identification (which can be confused with pyridone) and that pyridone groups can generate high catalytic activity (see section 3.2.1.2), we can understand that pyrrol groups are mainly considered as inactive by most of the scientific community [99,116,117,134–137].

3.2.1.4 *Quaternary Nitrogen species*

Quaternary (or graphitic) nitrogen species are considered as functionalities responsible for the formation of high catalytic activity sites. However, most of the studies that can be found in the literature do not distinguish between basal or edge-type quaternary nitrogen species and just conclude that those nitrogen species are responsible for the highly effective catalysis of oxygen reduction. Nevertheless, they have important structural differences that result in very different behaviour in ORR. This aspect was studied in detail by the evaluation of the free energies of the oxygen reduction steps [138]. Not only the position of the quaternary nitrogen plays a key role in the oxygen reduction energies, but also in the selectivity [138].

There are few studies that explicitly mention basal-type quaternary nitrogen as the responsible for the catalytic activity. For example, Gong et. al. [30] explained the highly efficient catalysis of N-doped carbon nanotubes to the presence of basal-type quaternary nitrogen. The basal-type N atom in the graphene layer can provide electrons to the π system what results in an increase of the nucleophile character of the adjacent carbon atom, which enhances the O_2 adsorption and, then, the ORR [30].

However, experimental and computational studies contradict the previous argument. Flyagina et al. [139] evaluated by DFT the variation of energy for the oxygen adsorption on a basal-type quaternary nitrogen and it was observed that the energy gradually increases from a distance of 2.8 A to 1.6 A when the oxygen molecule is

approaching to the carbon matrix, which points out the high energetic cost of the oxygen chemisorption in the adjacent carbon atom to a basal-type quaternary nitrogen species. This conclusion was also supported by Ikeda et al. [116]. The chemisorption of the oxygen molecule on the sites created by basal-type quaternary species is the least favourable chemisorption configuration from a thermodynamic point of view.

It seems that oxygen molecule chemisorption on the sites formed by basal type quaternary N is not favourable considering the difficulties in changing the hybridization of the carbon atoms in the graphene layers.

Edge-type graphitic nitrogen and pyridine are the most proposed functionalities in the literature as responsible for the most active sites in N-doped carbon materials. Basal-type quaternary nitrogen is located inside the graphene layer what promotes a variation of charge density inside the graphene layer. However, as it was explained previously, this configuration does not permit the adsorption of the oxygen molecule in the neighbour carbon atoms [116,117,138,140]. However, the introduction of the nitrogen species close to the edge, facilitates an electron withdrawal effect at the edge carbon atoms [116,117,138,140] being this critical to understand the catalytic activity.
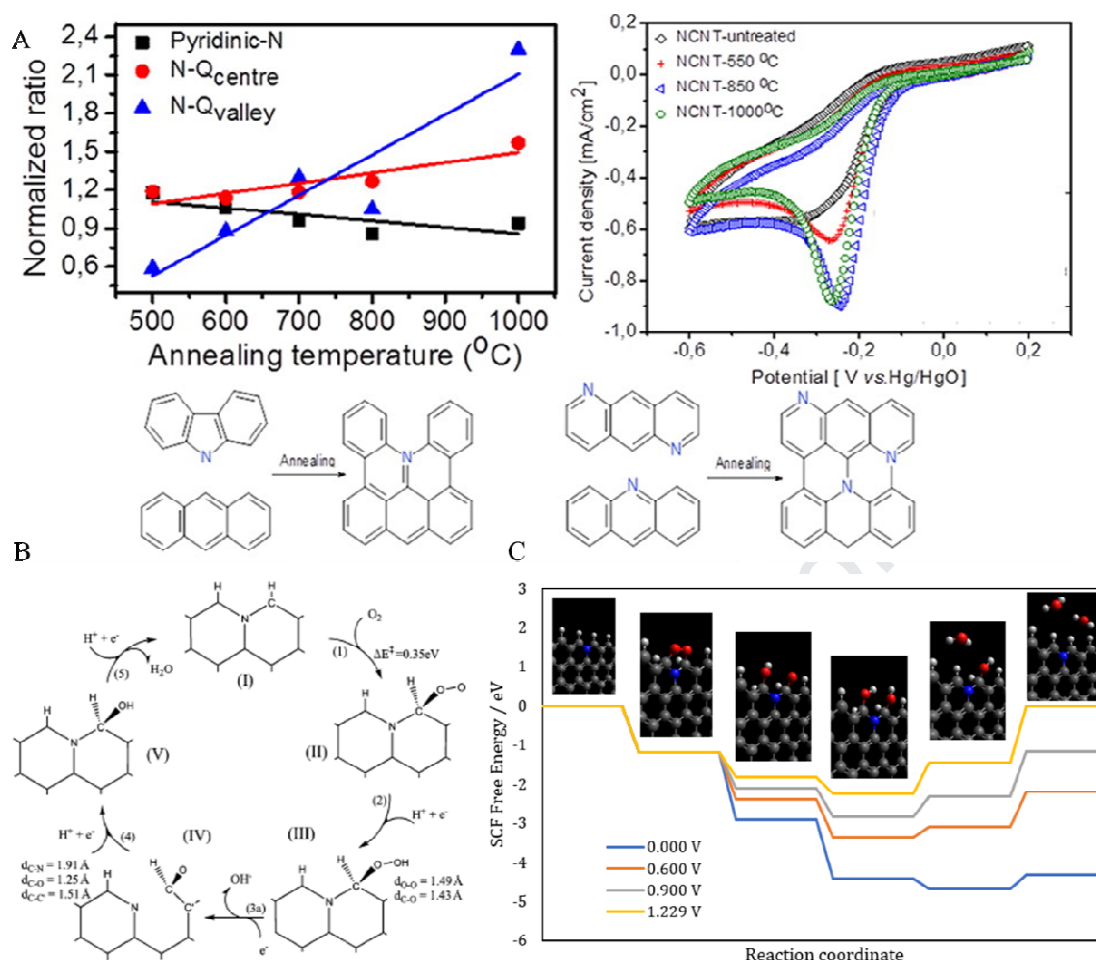
32

Figure 7: (A) Normalized ratio of nitrogen functionalities vs annealing temperature, background-corrected cyclic voltammograms in O_2-saturated 1 M KOH for undoped CNTs and nitrogen-doped CNTs annealed at high temperatures and proposed condensation reactions by annealing from pyrrolic-N to N-Qvalley and from pyridinic-N to N-Qvalley and N-Qcenter) (Reprinted with permission from Ref. 141. Copyright 2012 American Chemical Society). (B) Proposed ORR catalytic cycle for edge-type quaternary structure via C-O-O (Reproduced from Ref. 140 with permission from The Royal Society of Chemistry). (C) SCF energy diagram and proposed mechanism for ORR of edge-type quaternary nitrogen via C-O-O-C. White represents hydrogen, grey represents carbon, blue represents nitrogen and red represents oxygen (Reproduced from Ref. 117 with permission from The Royal Society of Chemistry).

The highly effective catalysis produced by edge-type quaternary nitrogen species was proposed by Sharifi et al from their study with N-doped CNT after annealing at different temperatures [141]. The authors proposed that annealing at high temperatures of N-doped CNT results in the transformation of pyrrolic and pyridinic nitrogen into edge-type quaternary functional groups due to condensation reactions (N-Qvalley from pyrrolic and N-Qvalley and NQ-centre from pyridinic groups, in Figure 7A). The edge-type groups (N-Qvalley) are the responsible for the high catalytic activity observed with

increasing the heat treatment temperature (Figure 7A). This N-functional groups transformation by thermal treatment is widely known since the influential work by J. R. Pels et. al. in 1995 [142].

Recently, it has been reported that the heat treatment at high temperatures of PANI results in the conversion of both pyridines and pyridones species into quaternary nitrogen species [143]. Interestingly, the higher the temperature used during the heat treatment, the higher the catalytic activity of the obtained samples. Indeed, the highest treatment temperature results in almost platinum-like performance in alkaline electrolyte for a N-doped carbon material with approximately 90 at% of quaternary-type nitrogen species obtained from such transformation. The authors attributed the high catalytic activity to the increase in the amount of edge-type quaternary nitrogen species.

The ORR mechanism for carbon materials containing edge-type quaternary nitrogen functional groups, is still under controversy. The nitrogen heteroatom, due to its higher electronegativity, promotes an electron withdrawal in the adjacent carbon atoms. Thus, a positive charge density is created in these edge-type carbon atoms, where the dioxygen molecule can be attracted and chemisorbed. There are two possible chemisorption configurations: through one or two carbon atoms, which lead to a different oxygen reduction path. Kim et al. [140] reported that the chemisorption through one carbon atom results in the oxygen molecule reduction through a 4 electrons pathway, which involves one ring-opening via cleavage of a N-C bond in order to facilitate the oxygen reduction (Figure 7B). This chemisorption mode can be favoured by the presence of defects in the vicinities of the edge-type quaternary nitrogen [64].

However, the chemisorption through two carbon atoms seems to be the most accepted and proposed mode in the literature [51,116,117,138,143,144]. Once the dioxygen is adsorbed via a C-O-O-C configuration, the introduction of the first electron-proton pair

(i.e., the first reduction stage) leads to the dissociation of the O-O bond and the formation of one hydrogen bond between both oxygen atoms [117]. This mechanism also results in a 4 electrons pathway with the formation of two water molecules (Figure 7C) [117], but without ring-opening.

The chemical state of the quaternary N species after reaction should be evaluated to get a more precise information about the nature of the active sites.

3.2.2 Phosphorus-doped carbon materials

Phosphorus atom has the same electron configuration of valence electrons as nitrogen but its electronegativity is lower than nitrogen and carbon atoms. In addition, this element can use the 3d orbitals for bonding. Phosphorus doping in carbon materials was very much studied because it inhibits the carbon-oxygen reaction [145,146], being important for oxidation protection [147,148] and fire retardant [149]. Phosphorous functional groups result in an effective modification of electrical properties and chemical reactivity of carbon materials, giving rise to numerous applications that are being developed recently, especially in catalysis [149,150] due to their strong acid properties.

In the field of ORR catalysis, the research on phosphorus doped carbon materials is not as abundant as with nitrogen because the improvement of the catalytic activity is not so remarkable. Nevertheless, we can find some studies about P-doped carbon materials as electrocatalysts for ORR [150].

In 2011, Liu et al. [151] reported the synthesis of phosphorus-doped graphite materials and their evaluation towards ORR. P-doped graphite was prepared by pyrolysis of toluene and triphenylphosphine (TPP) at 1000ºC. For comparison purposes, carbon materials without phosphorus were synthesized by the same methodology using only

toluene. The introduction of phosphorus in the carbon framework was confirmed by XPS and the evaluation of their catalytic activity pointed out the beneficial effect of the phosphorus atoms. This effect was also observed by Guo et al. [152]. They compared P-doped carbon nanotubes (P-CNT) and pristine carbon nanotubes (CNT). P-CNT showed an improved onset potential and larger current density (Figure 8A). Yang et al. [153] attribute the higher catalytic performance of their P-doped ordered mesoporous carbon to covalently bound P atoms in the carbon framework.

The beneficial effect of phosphorus was also associated with the formation of defects in the carbon structure after P doping [154]; those defects may increase the electron delocalization due to the good electron-donating properties of the phosphorus atom favouring ORR [155].

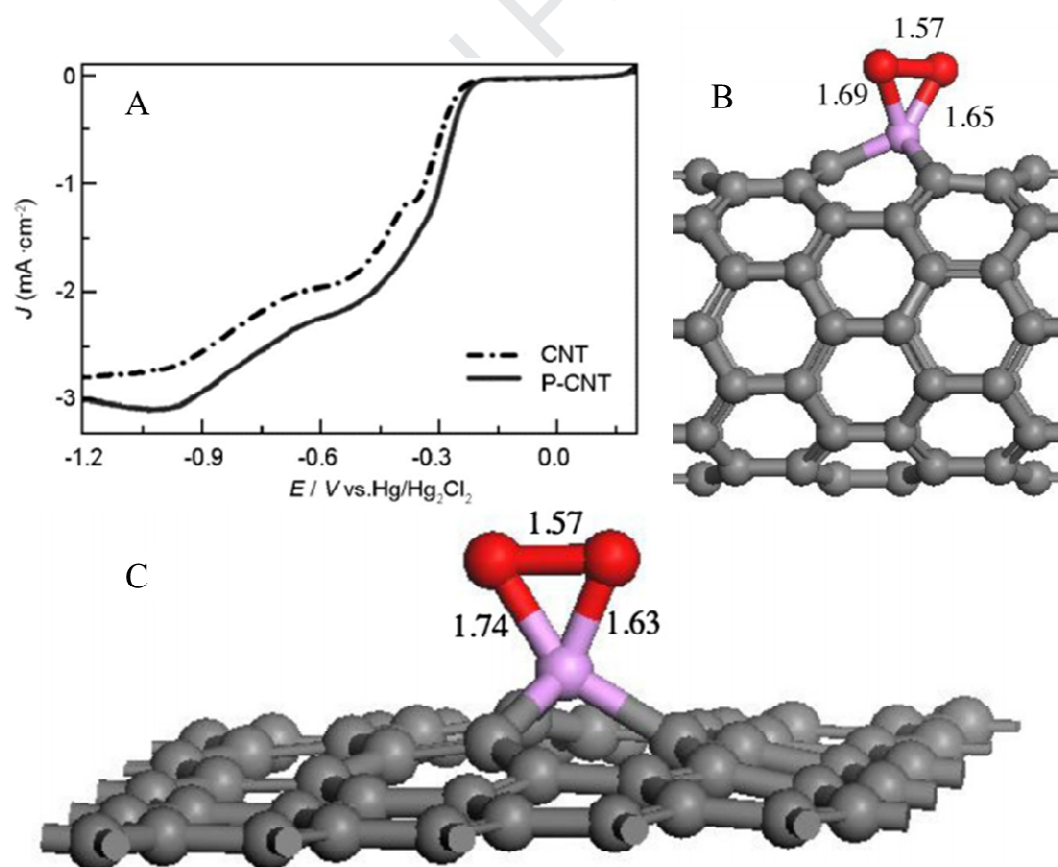**Figure 8**: (A) LSV curves of PCNT and CNT at a scan rate of 5 mV·$^{-1}$ and a rotation rate of 1600 rpm in O$_2$-saturated 0.1 M KOH solution (Reprinted from Ref. 152. Copyright 2016, with permission from Elsevier). (B) Optimized geometrical structure of O$_2$ adsorption on P-doped graphene. (Reprinted from

Ref. 156. Copyright 2013, with permission from Elsevier) (C) Optimized geometrical structure of O_2 adsorption on P-doped CNT. (Reprinted from Ref. 156. Copyright 2013, with permission from Elsevier)

To get further insights into the nature of the active sites and to understand if phosphorus atoms play a direct role in the ORR catalysis, these phosphorus functional groups were evaluated through DFT simulations [156]. The binding of oxygen molecule in P-doped graphene and carbon nanotubes is favoured when P is present. The oxygen molecules are directly bonded via bridging binding mode configuration to the phosphorus atom, thereby forming two P-O bonds (Figure 8B and C) [156]. After oxygen molecule chemisorption the reduction may occur through dissociation of dioxygen molecule into two oxygen atoms or the hydrogenation to form OOH species, being the second the most favourable pathway [157]. However, these theoretical studies do not take into account that P may induce the formation of defects that may be essential to understand the catalytic activity as suggested by other authors [154,155].

Although phosphorus doping does not seem to produce an important improvement in the ORR catalytic activity, making scarce the number of studies, the co-doping with another heteroatom (especially with N) has gained much attention in recent years. This is because the change in the local electronic properties of co-doped carbon materials may increase the catalytic activity towards oxygen evolution reaction (OER), what is useful for the design of bifunctional catalysts in reversible fuel cells [158,159].

In this sense, J. Zhang et al. [160] developed an approach to prepare 3D mesoporous carbon materials with nitrogen and phosphorus functional groups by pyrolysis of P-containing polyaniline obtained from polymerization of aniline in the presence of phytic acid. The obtained material does not only show excellent catalytic activity towards ORR but also for OER. The authors, on the basis of DFT simulations, associate this activity to a synergistic effect between both functional groups in the carbon framework. This synergistic effect was also proposed by Borghei et al. [161]. They reported an

electroactive material obtained from nitrogen and phosphorus containing activated carbons. The activation was carried out using phosphoric acid at 550ºC and then the materials were treated with urea as a nitrogen source. Despite the low content of nitrogen, the ORR activity significantly increased after urea treatment. This beneficial effect was not only observed in carbon-based catalysts, but also in P-doped polyaniline [162]. Besides the synergistic effect, the observed catalytic activity of carbon-based catalysts was also attributed to the large fraction of mesopores and the large proportion of graphitic and pyridinic nitrogen [161]. Phosphorus atoms do not only directly lead to a beneficial effect for ORR catalysis because of the formation of P species, but it may also promote structural order as it has been observed in polyacrylonitrile carbon fibers preparation in presence of small amounts of phosphoric acid [163]; such increase in structural order should result in an improvement in electrical conductivity which is a key parameter for improving the ORR (see Section 3.1).

Concerning the active sites of P and N co-doped carbon materials, Li et al.[164] proposed via DFT simulations that quaternary nitrogen along with phosphorus groups are responsible for the enhancement in the catalytic activity. Moreover, it was demonstrated that the most favourable co-doping route begins with first the introduction of phosphorus and, then, the introduction of nitrogen atoms [165]. This was explained considering that the presence of P produces local structural changes and promotes the formation of quaternary N species, being one possible mechanism the substitution of P by N atoms in the carbon framework acting as "self-sacrifice" agent [165].

3.2.3 Boron-doped carbon materials

Boron-doped carbon materials can be another promising alternative for metal-free carbon-based catalysts. Similar to the phosphorus atoms, boron has lower electronegativity than nitrogen and carbon atoms and it was extensively studied in $C-O_2$ reaction inhibition [166,167]. Some experimental studies have reported that B-doped carbon materials can have an ORR catalytic activity close to that for commercial catalysts based on platinum nanoparticles [168,169]. The high activity of such carbon-based catalysts is attributed to the electron-deficient character of the boron atoms. DFT simulations revealed that the higher electronegativity of the adjacent carbon atoms to the boron induces a positive charge into the heteroatom. Such positive charge density favours the chemisorption of the dioxygen molecule. In contrast to the N-doped carbon materials, where the oxygen is chemisorbed on the adjacent carbon atoms to the nitrogen, for the B-doped carbon, O_2 is adsorbed on the boron itself [72], similar to what happens with phosphorus atom. However, this will occur in borinine type species, whereas in substitutional B atoms in ortho position with respect to the H-saturated edge site, oxygen molecule chemisorption is favoured in the two neighbour carbon atoms [64]. Like in the case of phosphorus, it cannot be discarded that the presence of B may induce the creation of defects which are the responsible for the improvement in catalytic activity [154].

In any case, we cannot find many studies on B-doped carbon materials for ORR that suggest that promising materials based on only this specific heteroatom can be designed. However, we can find a significant piece of work on co-doping carbon materials with B and another more electronegative heteroatom, mainly N.

Zao et al. [170] reported two different routes of synthesis of B- and N- co-doped carbon nanotubes via chemical vapour deposition. The first method is based on the sequential doping of boron and nitrogen using triphenylborane in the CVD and then, the heat

treatment in NH$_3$ to dope with nitrogen. As a consequence, the nitrogen and boron species are separated between them. On the other hand, the simultaneous doping with boron and nitrogen during the CVD leads to the creation of N-B-C moieties [170]. Experimental and theoretical results suggest that the N-B-C species do not enhance the catalytic activity, whereas the separated functionalities can improve the catalytic activity towards ORR (Figure 9A) [170]. On the other hand, the synergistic effect between B and N was reported by Zheng et al. [171] since B and N co-doped graphene exhibited higher catalytic activity than the B-doped carbon and N-doped carbon materials. In this case, boron atom in meta position with respect to pyridinic nitrogen atoms was proposed as active centres for ORR [171]. Interestingly, Gong et al. [172] reported B- N- co-doped carbon materials with high catalytic performance, even higher than Pt/commercial catalysts. In order to get a better understanding, the authors evaluated through DFT calculations five possible B-N configurations; (i) one BN pair in the basal plane of the graphene layer, (ii) one BN located at the edges, (iii) three BN pairs at the edge, (iv) a long line of BN pairs at the nanoribbon edges and (v) the interface between BN and graphene domains (Figure 9B). The oxygen chemisorption in the configuration (i) is unfavourable thermodynamically, whereas the chemisorption in BN located at the edges of the graphene layer becomes energetically favourable, which can improve the catalytic activity for ORR [172]. The comparative study on the B- and N- doped carbon materials reveals that the co-doping route plays a more dominant role in enhancing the ORR behaviour than the single doping methods [172].
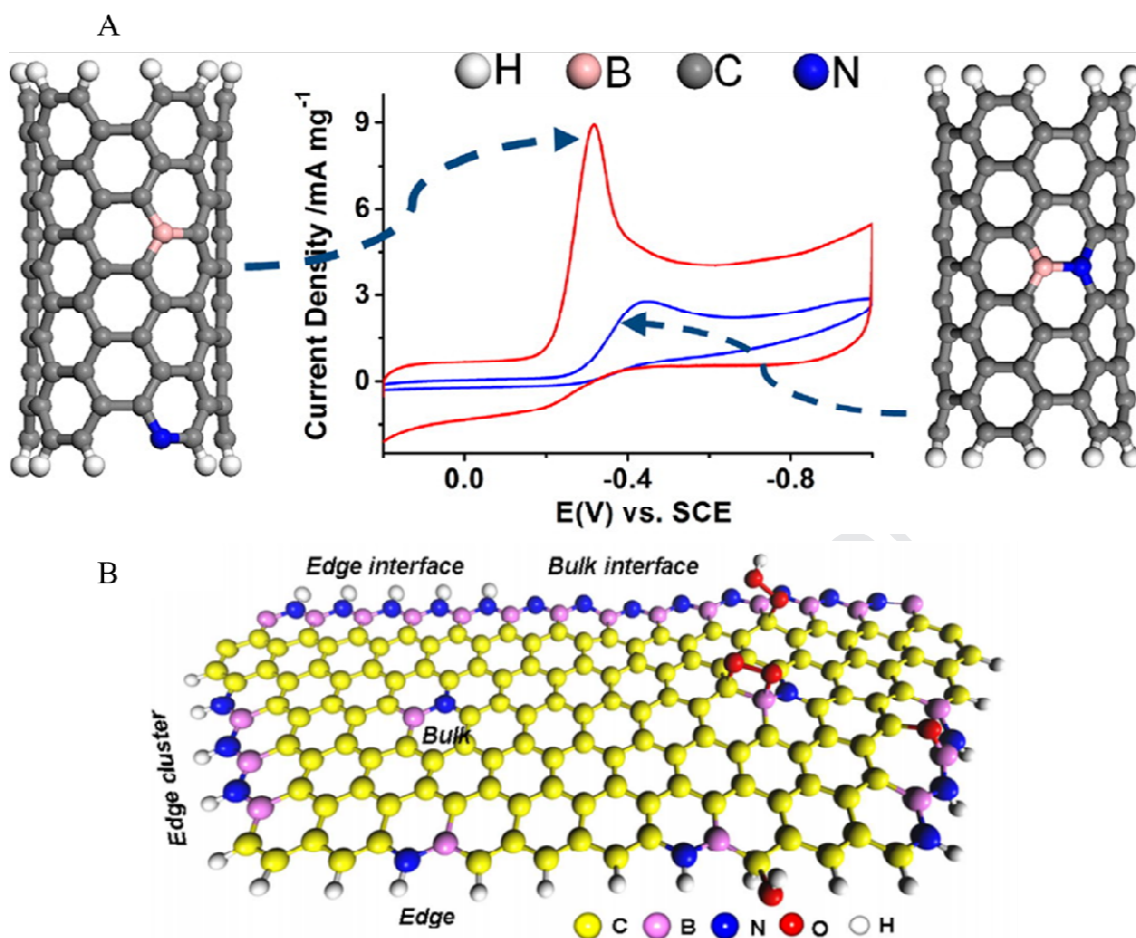
A

B

Figure 9: (A) Illustrative of different N-B moieties configurations and their catalytic activity towards ORR (Reprinted with permission from Ref. 170. Copyright 2013 American Chemical Society). (B) Schematic representation of structural models along with some selected intermediate states (Reprinted with permission from Ref. 172. Copyright 2015 American Chemical Society).

In the search for deepening into the reasons of their high catalytic activity, Ozaki et al. reported several studies focusing on this topic. In 2006, the authors showed that the simultaneous doping of boron and nitrogen in the carbon material is an effective way to improve the catalytic activity [173]. They reported that the ORR has a good correlation with the surface concentration of the B-N-C moieties and edge-type nitrogen [174]. In 2010, they deepened into the role of both heteroatoms in the ORR catalysis. By DFT simulations, they confirmed the effectivity of co-doping carbon-based catalysts with boron and nitrogen through the evaluation of the O_2 chemisorption and subsequent reduction steps onto multiple B-N- functional groups [175]. Interestingly, the strong attractive interatomic interaction between both heteroatoms helps nitrogen to occupy

specific sites, which are the most adequate for enhancing the catalytic activity [175]. Furthermore, B-N species reduce the free energy of oxygen molecule adsorption, which suggests an enhancement of the catalytic activity [175]. More recently, they studied the ORR mechanism of carbon materials containing B-N species, proposing a 2+2 electrons pathway for these species, where the oxygen is first reduced to hydrogen peroxide and, then, by the action of the B-N moieties, the hydrogen peroxide is reduced to water molecules [176].

3.2.4 Sulfur-doped carbon materials

Different types of sulfur functionalities can be found on the carbon surface and can be classified, according to the number of carbon atoms bonded to them, as sulphides or sulfoxides (two carbon atoms) and thiols or thioquinones (one carbon atom). Disulfides can be also found. The most common S-functionalities are thiols and sulfoxides [177].

Sulfur doping in carbon materials has gained attention due to the interesting properties induced by the sulfur atoms. S-doped carbon materials play an important role in gas adsorption [178], electrochemical capacitors [179], rechargeable batteries [180], photoactivity [181] and electronic properties [182].

Sulfur-doping has been proposed as a strategy for improving the ORR catalysis although there are no a large number of studies that focus on only sulfur doping and the reasons for such improvement are not clear. For example, Yang et al. [183] suggest that S-doping increases the amount of edge sites and structural disorder of graphene and attribute the improvement in ORR catalytic activity to spin density changes originated by sulfur doping. Other authors consider that the presence of sulfur in the carbon

framework is the responsible for the formation of defects that are the responsible for the increased ORR activity [154].

Wang et al. [184] reported the synthesis of ordered mesoporous carbons (OMC) using sucrose as carbon source. In order to dope OMC samples with sulfur, the same procedure was done but with the addition of benzyl disulphide, resulting in OMC-S materials. From XPS analysis, two oxidation states of sulfur atoms were detected, that is, sulphide groups and oxidized sulfur groups. The ratio of both species varies depending on the amount of benzyl disulphide used in the synthesis and the higher the amount of benzyl disulphide used, the higher the contribution of sulphide groups. Interestingly, all samples show identical onset potential in the oxygen reduction reaction; however, the limiting current density increases with the amount of sulphide species. Park et al. [185] reported the synthesis of sulfur-doped graphene through the heat treatment of the pristine graphene in presence of CS_2. XPS analysis showed the selective formation of thiophene groups. Once again, the higher the sulfur content, the higher the limiting current density, with no changes in the onset potential of these materials. These observations are in agreement with the effect of sulfur in increasing the concentration of defects similar in catalytic activity to those of the pristine material, but not in the formation of new active sites with higher activity.

Seredych et al.[186] analysed sulfur doped reduced graphite oxide (RGOS). To introduce sulfur atoms into the RGO, the material was heated at 800ºC in hydrogen sulphide (1000 ppm of H_2S in a nitrogen atmosphere), resulting in sulfur-doped reduced graphite oxide. The authors attributed the good performance of the RGOS to the presence of both sulfur and oxygen atoms, and that similar atomic amount is the most adequate to optimize the synergistic effects on ORR. Other factors such as porosity and induced hydrophobicity by sulfur are positively contributing to the improvement of the

catalytic activity for ORR. Thus, the presence of both S and O containing functionalities can be the responsible for the formation of higher effective active sites. This investigation is in agreement with a previous study by Liang et al. [187], where a similar effect was observed in carbon materials co-doped with sulfur and nitrogen heteroatoms.

In order to demonstrate the positive effect of sulfur atoms towards ORR catalysis, Poh et al. [188] reported sulfur doping of graphene during thermal exfoliation of graphite oxides. Three different sulfur precursors (H_2S, CS_2 and SO_2) were used. The physical and chemical properties of these materials pointed out that all undoped graphene possessed a higher number of defects with respect to their sulfur-doped counterparts, which is in disagreement with the large part of the already commented works. Interestingly, the oxidation state of the sulfur atom was similar for all materials and it was associated with the presence of oxidized sulfur groups (in form of $-SO_3H$), regardless the sulfur precursor and the method used to generate the graphene. The formation of active sites with higher activity due to the presence of these sulfur groups was confirmed since all sulfur-doped carbon materials exhibited higher onset potential than their undoped counterparts.
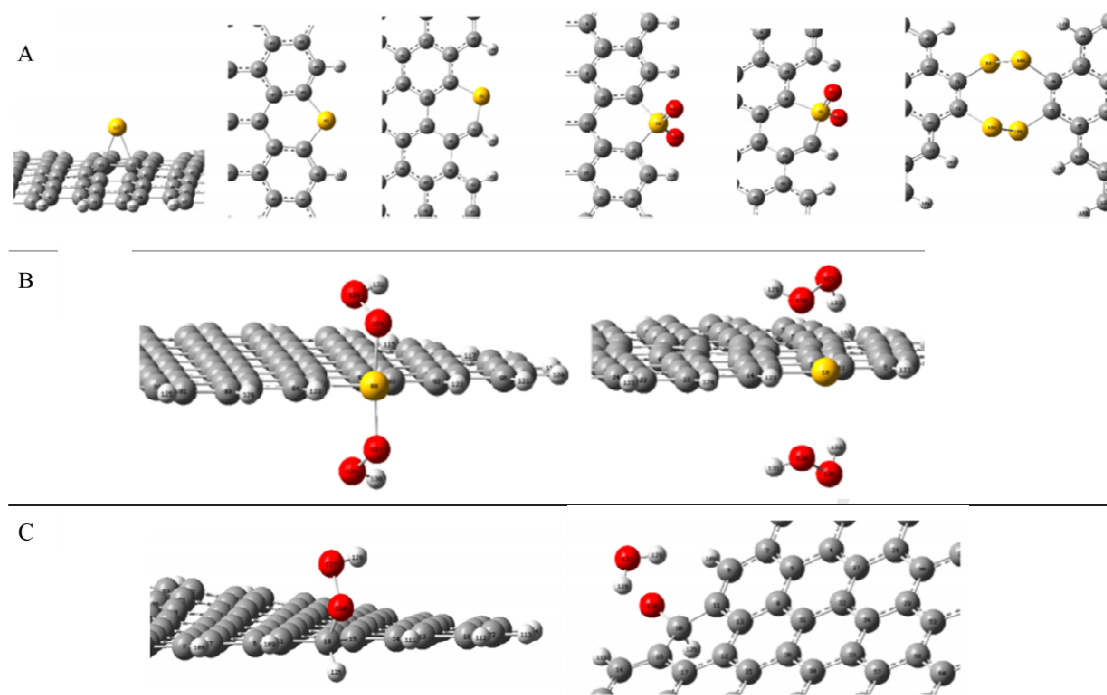
Figure 30: (A) Illustration of several possible sulfur-doped graphene clusters. (Reprinted with permission from Ref. 189. Copyright 2014 American Chemical Society) (B) 2 electron pathway process on the sulfur-doped graphene cluster where sulfur species acts as active sites. (Reprinted with permission from Ref. 189. Copyright 2014 American Chemical Society) (C) 4 electrons pathway on the sulfur-doped graphene cluster where a carbon atom as active sites (Reprinted with permission from Ref. 189. Copyright 2014 American Chemical Society).

Concerning computational chemistry, DFT calculations were carried out by Zhang et al. [189] with the aim of understanding the reaction mechanism and the nature of the active sites of sulfur-doped graphene. For that purpose, four sulfur doping structures were proposed: adsorbed S on the graphene layer, S substitution at edge sites, SO_2 substitution at edge sites and sulfur-ring clusters connecting two pieces of graphene (Figure 10A). The formation energies of these configurations highlight that surface sulfur chemisorption is the most stable configuration, that sulfur atoms at zigzag edge sites have lower formation energy than sulfur substitution at armchair positions and that the presence of Stone-Walker defects facilitate sulfur doping. Regarding the active sites towards ORR in these materials, the authors conclude that spin and charge densities determine the catalytic activity. Substitutional S itself or carbon atoms located at the zigzag edges or close to $-SO_2$ species, can be active sites for ORR.

Two electron transfer pathway proceeds on the substitutional sulfur atom being the catalytic active site (Figure 10B), while four-electron transfer takes place on the carbon atoms with high positive spin or charge density (Figure 10C). $-SO_2$ functionalities gives rise to the highest positive charge and spin densities for the neighbor carbon atoms, in which the most favorable is the four electrons mechanism. The authors also conclude that the Stone–Wales defects facilitate sulfur doing in graphene and improve the catalytic activity of sulfur-doped graphene.

In summary, sulfur doping can improve the catalytic activity of carbon materials either through the increase in the amount of defects that can act as catalytic sites or by activating the neighbour carbon atoms, because of the increase in charge or spin densities, induced by sulfur species. In this case, oxidized sulfur is the functionality which produces the strongest activation and the preferred to design the highest activity material.

4   Short overview, future research and perspectives

Metal-free carbon-based materials have received great attention during last years because of their promising performance as electrocatalysts in oxygen reduction reaction. Intrinsic properties of non-doped carbon materials, such as porosity and defects, have demonstrated to play an important role. Indeed, defects seem to be one of the most challenging targets, in which a large number of studies have demonstrated its relevance in many applications including ORR electrocatalysis, and makes necessary a strong research effort on defects engineering. Among the different defects, one of the most relevant in the enhancement of the catalytic activity of metal-free carbon materials is the presence of heteroatoms in the carbon structure, and among them nitrogen heteroatoms are the most influential.

The synthesis and properties of nitrogen containing carbon materials is well known in Carbon Science and these materials were/are very much studied in different applications like in catalysis or adsorption processes. The testing of N-doped carbon materials in ORR showed that they had a promising catalytic activity and this experimental observation has resulted in a high number of publications reporting activities that, in some cases, are close to that for Pt-containing catalysts. Taking into account the different nature of the N-functionalities that can be encountered in the carbon materials and the additional factors such as structure, porosity, defects, etc., that increase the complexity of the system under study, it can be understood that all nitrogen functional groups have been proposed in the literature as active sites towards ORR. However, the important piece of work done on this topic during nearly the last fifteen years has helped to get important information about the nature of the active sites. In the previous sections, we have tried to discuss about the effect of specific N-functional groups on the catalytic activity of carbon materials towards ORR.

Interestingly, from the combination of experimental studies on materials with a detailed characterization and computational work, important conclusions have been obtained that are already accepted by the scientific community. Thus, two functionalities are mostly accepted as the responsible for the formation of the higher activity active sites in N-doped carbon materials: pyridines and quaternary-type nitrogen functional groups.

Although this can be assumed as a general conclusion, it is very important to take into account that the structure of those functional groups determines the catalytic activity. Quaternary nitrogen species located in the basal plane of a graphene layer hardly contribute to an improvement of the catalytic activity; however, if the same heteroatom is located close to the edge, a completely different effect is observed. The high electronegativity of the nitrogen atom promotes an electron withdrawal of the two

adjacent edge-type carbon atoms, which results in a positively charged density and, therefore, easier oxygen molecule chemisorption. Position of pyridine species is also decisive since zigzag position does not produce catalytic active sites in the neighbour carbon atoms. Both adjacent carbon atoms are not located in an edge position what makes difficult the change of their hybridization state and, then, the oxygen molecule chemisorption. However, if pyridines are located in armchair position, one adjacent carbon atom is located in the edge and oxygen molecule can be easily adsorbed.

Analysis of samples after ORR has shown that the nature of the functionalities changes and pyridones are detected in the studies published to the moment. This means that pyridines in armchair position can produce pyridone groups and, consequently, the observed catalytic activity could be due to the pyridone species instead of pyridines. Although both of them are related, the reaction mechanism could be different depending on the species which is really participating at the reaction conditions. This means that higher attention should be paid to the state of the material at reaction conditions, making necessary characterization of the materials as close as possible to the operando conditions, being these measurements one of the hot topics for the future research.

Finally, the outstanding catalytic properties of N-doped carbon materials are usually measured in alkaline electrolytes, being much lower in acidic conditions. The technology for polymer electrolyte membrane fuel cells is well developed for acidic conditions in which well-performing membranes are available. This means that it is mandatory to understand the reasons why the catalytic activity is so strongly dependent on the electrolyte, in order to design, if possible, a material that may work adequately in acidic conditions. This is the second aspect that requires a strong research in the future. Other important factor that must be handled is the practical application of these carbon-based catalysts, since they are often tested in rotating (ring) disk electrode (RRDE), but

not in devices close to the final application. RRDE is very useful to evaluate the activity of the catalysts; however, different problems may arise in FCs that may result in the inapplicability of the material. Therefore, the use and study of such catalysts in Fuel Cell stations is one of the next challenges.

Phosphorus, boron and sulfur-doped carbon materials have also demonstrated efficiency towards ORR although the improvement seems to be below that from nitrogen. Of particular interest is the origin of this performance, which is unclear. There are mainly two theories for explaining the results observed: the creation of defects induced by the heteroatoms doping and the change in the electronic properties of the neighbourhoods of the heteroatom. A deeper investigation is still necessary to understand the effect of these heteroatoms. However, it seems that the presence of these heteroatoms can improve the performance of nitrogen species. Thus, co-doping could be a very attractive methodology to enhance the catalytic activity not only for ORR catalysis, but also to design bifunctional catalysts that can be efficient for ORR and OER.

It is interesting to highlight that introducing a more electronegative heteroatom than carbon seems to be an attractive methodology to enhance the activity of carbon-based ORR catalysts, especially by using nitrogen. On the other hand, the introduction of less electronegative heteroatoms has also been proposed as a profitable route to increase the catalytic activity of these materials. However, the most successful heteroatom, nitrogen, is the one that presents similar atomic size and electronic configuration. This means that the introduction of nitrogen creates stable species in the carbon matrix, what is a key parameter to produce stable active sites. Nitrogen can also produce stable species with other heteroatoms, such as phosphorus or boron. Therefore, the combination of nitrogen with other heteroatoms can be a very attractive option for the design of advanced carbon catalysts.

Besides the co-doping with two functionalities, other interesting alternative is the combination of additional defects and heteroatoms, in which the beneficial effect of both approaches can work together towards the enhancement of the catalytic activity of carbon-based metal-free ORR catalysts.

Furthermore, special attention must be focused in metal impurities, which can significantly improve the ORR performance of carbon catalysts although with very low concentration of metals [31] and this can be an important source of error when reporting data for metal-free carbon based catalysts. However, this can also be an opportunity since controlled loading of very small amounts of non-precious metals can be a direction for further improvement of heteroatom doped carbon materials.

Oxygen reduction reaction is only the guiding principle of metal-free carbon-based catalysts, but there are also many other applications in which these catalysts can have, or can be designed to reach, high performance. The knowledge about reactions such as hydrogen evolution reaction (HER), oxygen evolution reaction (OER), hydrogen peroxide reduction reaction (H_2O_2RR) or, even, carbon dioxide reduction reaction (CO_2RR), among others, is still under development. The understanding in the catalysis of these reactions by defect-engineered carbon materials can be an important contribution to the energetic transition from fossil fuels to carbon free energy sources.

5 Acknowledgements

6 References

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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: