



Article Hydrothermal Carbon/Carbon Nanotube Composites as Electrocatalysts for the Oxygen Reduction Reaction

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Abstract: The oxygen reduction reaction is an essential reaction in several energy conversion devices such as fuel cells and batteries. So far, the best performance is obtained by using platinum-based electrocatalysts, which make the devices really expensive, and thus, new and more affordable materials should be designed. Biomass-derived carbons were prepared by hydrothermal carbonization in the presence of carbon nanotubes with different oxygen surface functionalities to evaluate their effect on the final properties. Additionally, nitrogen functional groups were also introduced by ball milling the carbon composite together with melamine. The oxygen groups on the surface of the carbon nanotubes favor their dispersion into the precursor mixture and the formation of a more homogenous carbon structure with higher mechanical strength. This type of structure partially avoids the crushing of the nanotubes and the carbon spheres during the ball milling, resulting in a carbon composite with enhanced electrical conductivity. Undoped and N-doped composites were used as electrocatalysts for the oxygen reduction reaction. The onset potential increases by 20% due to the incorporation of carbon nanotubes (CNTs) and nitrogen, which increases the number of active sites and improves the chemical reactivity, while the limiting current density increases by 47% due to the higher electrical conductivity.

Keywords: carbon nanotubes; hydrothermal carbons; nitrogen functionalization; oxygen reduction reaction; electrocatalysis

1. Introduction

In the last decades, researchers have focused on developing new innovative materials to enhance the performance of environmentally friendly energy conversion devices. In this context, fuel cells are considered an interesting alternative towards greener electrical energy conversion due to their high efficiency and low emission of pollutants [1,2]. However, the overall performance of these devices is limited by the sluggish kinetics of the oxygen reduction reaction (ORR) that takes place at the cathode [1,3]. Currently, the most efficient electrocatalyst towards the ORR is based on platinum [3,4], which is a scarce and expensive noble metal that extremely pushes up the cost of the fuel cell [5]. Consequently, extensive research efforts have been made to develop non-noble metal catalysts, or metal-free catalysts, exhibiting good catalytic activity towards ORR and excellent durability [1,3,4,6–8].

Carbon materials are a promising alternative to Pt-based electrocatalysts. Carbon nanotubes, carbon nanofibers, activated carbons, carbon xerogels, and graphene-based materials have been

widely studied as electrocatalysts [6,9–15]. Among them, activated carbons are interesting materials, as they can be obtained by low-cost and environmentally friendly routes [16]. In fact, the use of hydrothermal processes to prepare carbon materials from biomass has emerged recently as an interesting strategy [12,17–20]. Biomass is an abundant, low-cost, and environmental-friendly source [21], which makes hydrothermal carbons (HTCs) good candidates to replace Pt-based electrocatalysts [2,8,22]. HTCs are commonly made up of spherical particles, which size can be controlled by modifying the synthesis conditions: concentration and the type of saccharide precursor and temperature and time of the hydrothermal treatment [20]. Nevertheless, the chemical properties of HTCs need to be modified in order to approach the outstanding electrochemical performance of Pt-electrocatalyst reference materials [23,24]. These modifications can be achieved by the incorporation of heteroatoms like nitrogen, sulfur, phosphorus, or boron and/or advanced carbon materials like graphene oxide or carbon nanotubes (CNTs) [9,12,13,17,25–28]. Nitrogen is the most promising heteroatom for ORR, as pyridinic nitrogen favors the bonding of oxygen to the adjacent carbon, while the presence of quaternary nitrogen favors oxygen dissociation [7,29]. Therefore, the appropriate nitrogen functionalities seem to be essential to improve the electroactivity of the carbon materials towards the ORR. On the other hand, the use of CNT to prepare carbon composites is an interesting solution to stabilize the surface chemistry, to increase the graphitic domains and to accelerate electron transfer [30–32]. A recent publication has shown the benefits of adding CNT during the polymerization of glucose, ascertaining the optimum dose of CNT to maximize the performance of the composites in supercapacitor applications [31]. In the same line, carbide-derived carbons, graphene, chitosan, carbonized metal-organic frameworks (MOF), and activated carbons have been combined with CNT to obtained composites with improved performance towards the ORR [5,10,11,30,33–35]. Nonetheless, most of these carbon composites contain also metals to enhance the electroactivity of the carbons, which may somewhat hinder the real effects of the CNT on the properties of the composites.

Most of these published works are mainly focused on the preparation and application of carbon composites bearing CNT. However, little attention has been paid to the surface chemistry of the CNT, which can modify the final textural and chemical properties of the hydrothermal carbons, and hence, the effectiveness of the subsequent stages used to incorporate heteroatoms or metals. Accordingly, this work aims to study the isolated role of CNT during the hydrothermal carbonization of glucose by evaluating the modifications caused by the incorporation of CNT into the structure and electrochemical performance of the hydrothermal carbon/carbon nanotube composites. The composites were prepared by hydrothermal carbonization of glucose in the presence of multiwalled CNT and oxidized CNT. An attempt has been made to evaluate the effect of the surface chemistry of CNT in the polymerization of glucose and in the final properties of the composites. Besides, nitrogen functionalities were incorporated into the as-prepared composites. The effect of the structure of the composites, due to the presence of the CNT, on the functionalization process and on the nature of the nitrogen functionalities, has also been assessed. Electrochemical measurements were performed to fully characterize the electrocatalytic activity of the composites towards the oxygen reduction reaction. Interesting results regarding the electrochemical performance of the composites are detailed, showing the advantage of adding CNT during the hydrothermal polymerization of glucose to convert biomass into a high-value carbon composite.

2. Materials and Methods

2.1. Chemicals and Materials

The reagents used for the synthesis of the carbon materials were: D-glucose (Merck), multiwalled carbon nanotubes (Nanocyl NC3100 series, with average diameter of 9.5 nm, average length of 1.5 μ m, and carbon purity higher than 95%), distilled water (from a Panice reverse osmosis water system), nitric acid (Fluka \geq 65%), and melamine (Sigma-Aldrich, \geq 99%). The reagents used for the preparation

of the electrode were: ultrapure water (Millipore), absolute ethanol (VWR Chemicals, \geq 99.5%), and

Nafion[®] (Sigma Aldrich, solution of 5 wt.% in a mixture of water (15–20%) and aliphatic alcohols).

2.2. Materials Preparation

The glucose-derived carbon/CNT composite (CG/CNT) was synthesized by hydrothermal polymerization of glucose in the presence of CNT. Briefly, glucose (15.0 wt.%) and CNT (0.3 wt.%) were dispersed in distilled water (84.7 wt.%) in an unsealed Teflon lined reactor chamber under sonication for 30 min at room temperature. After sonication, the Teflon lined reactor chamber was introduced into a stainless steel autoclave, sealed, and heated at 180 °C for 12 h. The autoclave was then cooled down naturally to room temperature, and the organic polymer obtained was filtered and washed with abundant distilled water. Finally, the sample was dried at 80 °C for 24 h and carbonized at 700 °C under a nitrogen flow of 150 cm³ min⁻¹. The carbonization process was performed in a vertical furnace using a heating rate of 10 °C min⁻¹ and 2 h as the residence time. In order to evaluate the effect of the surface chemistry of CNT on the polymerization of glucose, oxidized CNT were also employed to prepare the composite CG/CNT_{oxi}, following the methodology described above for sample CG/CNT. The oxidation of CNT was performed by the typical liquid-phase oxidation method. Briefly, 1 g of CNT was boiled with 75 mL of a 7 mol L^{-1} solution of nitric acid for 3 h. The oxidized material was then washed with abundant distilled water until neutral pH was reached and then dried at 80 °C for 24 h. The prepared materials (CG/CNT and CG/CNT_{oxi}) were functionalized with nitrogen by ball milling the carbon composite (60 wt.%) with melamine (40 wt.%). The ball milling process was performed in an enclosed flask with two zirconia balls at a 15 Hz frequency during 4 h using a Retsch MM200 mixer mill. Then, the samples were treated in a vertical furnace at 700 °C for 2 h under a nitrogen flow of 150 cm³ min⁻¹ to force the decomposition of melamine. The heating rate was fixed at 10 °C min⁻¹. Functionalized samples were labeled N-CG/CNT and N-CG/CNT_{oxi}. Additionally, a sample composed only by glucose (CG) was also prepared following the methodology described above for sample CG/CNT without the addition of CNT.

2.3. Physicochemical Characterization

The textural properties of all samples were determined by nitrogen adsorption-desorption isotherms performed at -196 °C. Before the analysis, the samples were degassed under vacuum at 150 °C overnight. The isotherms were obtained in a Quantachrome Autosorb iQ automated gas sorption analyzer. The specific surface area (S_{BET}) was estimated by applying the Brunauer–Emmett–Teller (BET) equation to the nitrogen adsorption branch of the isotherm. The micropore volume (V_{micro}) and the external surface area (S_{ext}) were determined by applying the t-plot method. The morphology of the composites was studied using a scanning electron microscope (Quanta FEG 400, FEI Company, Hillsboro, OR, USA). The composites were previously attached to an aluminum pin using conductive double-sided adhesive tape. A secondary electron detector Everhart-Thornley and an accelerating voltage of 15 kV were used in all the analyses. In addition, the surface chemistry of the HTC composites was evaluated by Fourier transform infrared spectroscopy (FTIR). FTIR spectra were recorded using a JASCO FT/IR 6800 spectrometer at a maximum resolution of 4 cm⁻¹ over a range between 4000 and 400 cm⁻¹. The spectra were collected in attenuated total reflectance (ATR) mode over 256 scans. Raman spectra were measured directly on the carbon materials using a Jobin-Yvon XPLORA apparatus (Horiba Scientific, Kyoto, Japan) with a monochromatic wavelength laser of 532 nm. The chemical composition was determined by Elemental Analysis performed in a Vario Micro Cube analyzer from Elementar. This technique involves the combustion of the sample at a temperature close to 1000 °C in an oxygen-rich atmosphere. Analysis of the combustion products allows determining the contents of C, H, N, and S, while oxygen content is determined by the difference. The nitrogen surface functionalities of the N-doped composites were analyzed in a Kratos AXIS Ultra HSA X-ray photoelectron spectrometer (XPS). VISION and CASAXPS software were used for data acquisition and data analysis, respectively. The XPS measurements were performed with a monochromatic Al Ka

X-ray source (1486.7 eV), operating at 15 kV in hybrid mode, with a pass energy of 40 eV for regions of interest and 80 eV for the survey. The C 1s peak position was fixed at 284.6 eV and used as a reference to locate the other peaks. The fitting of the XPS in the N 1s region was performed by least squares using Shirley line as the background and Gaussian–Lorentzian peak shape. The electrical conductivity was measured by the four-point probe method applied to a disc-shaped piece of 1 cm diameter made of each carbon sample. The disc-shaped pieces were prepared by pressing at 8 t in a mold for 60 s. The four points were placed in contact with the carbon surface, and a potential between 0 and 2 V was applied. The current response was measured using a SourceMeter[®] unit instrument (Keithley 2400) and recorded with LabView software. A linear relationship between the potential applied and the current measured was obtained, following the Ohm Law, from which the resistivity of the samples, and in turn, the electrical conductivity, can be calculated.

2.4. Electrode Preparation

Each sample (1 mg) was first dispersed in 450 μ L of a solution containing 20% of Nafion[®] and 80% of a liquid solution composed of ultrapure water and ethanol (1:1.5, v:v). The suspension was sonicated for 30 min until a homogeneous dispersion was obtained. Finally, the dispersion was deposited on a glassy carbon rotating ring-disk electrode (electrode from Metrohm that consists of a 5 mm disc of glassy carbon with a concentric platinum ring at a distance of 375 μ m) to have a mass loading of 0.1 mg cm⁻².

2.5. Electrochemical Measurements

The electrochemical measurements were performed on a PGSTAT 302N potentiostat/galvanostat (Metrohm) by using a three-electrode cell configuration, which involves a beaker-type cell with three electrodes (working, counter, and reference) immersed in 0.1 mol L⁻¹ KOH electrolyte solution. The rotating ring-disk electrode with the sample deposited on it was used as a working electrode, while an Ag/AgCl (KCl 3 mol L^{-1}) and a glassy carbon rod were used as reference and counter electrode, respectively. Initially, nitrogen gas was bubbled through the electrolyte for 30 min to remove all oxygen in the electrolyte solution. Cyclic voltammetry (CV) experiments were performed by changing the scan rates from 5 to 100 mV s⁻¹ using a voltage window of 1.2 V (from 0.2 to -1.0 V vs the reference electrode). Linear sweep voltammetry (LSV) measurements were also performed in the same potential range at a scan rate of 5 mV s⁻¹ with a disk rotation speed range from 400 to 3000 rpm. After the measurements with the electrolyte saturated in nitrogen, the electrolyte was saturated with oxygen for 30 min. Then, the CV and LSV experiments described above were performed to evaluate the performance of the materials towards the ORR. The current density measured at the ring and disk was calculated by subtracting the current obtained from the electrolyte saturated with N_2 from the current measured in the O₂-saturated electrolyte. The onset potential (*E*onset) was determined from the LSV curve recorded at 1600 rpm for a current density of -0.1 mA cm⁻² and converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation (Equation (S12) in the supporting information). The percentage of hydrogen peroxide (H₂O₂) produced during the ORR, and the number of electrons transferred were calculated from the current measured at the ring and disk following the Equations (S11) and (S7) shown in the supporting information. The chronoamperometric response was measured by applying 0.4 V vs RHE for 10000 s to compare the stability of the different electrocatalysts.

3. Results and Discussion

3.1. Textural, Morphological, and Chemical Properties

The changes in the textural properties due to the presence of CNT during the polymerization of glucose were evaluated by nitrogen adsorption at -196 °C. The shape of the isotherms is displayed in Figure 1, while the textural parameters are shown in Table 1. Sample CG exhibited a type I isotherm characteristic of exclusively microporous materials. The incorporation of CNT and oxidized CNT

 (CNT_{oxi}) during the polymerization of glucose resulted in composites with different porous structures $(CG/CNT \text{ and } CG/CNT_{oxi})$. The specific surface area of the composite CG/CNT was quite similar to that of the sample CG (Table 1), but interesting differences in the isotherm shape at medium and high relative pressure were observed (Figure 1b). The volume of nitrogen adsorbed remained constant at low-medium relative pressures (from 0.1 to 0.5), and then, abruptly increased at high relative pressure, which is characteristic of macroporous adsorbents. Besides, the isotherm of this composite exhibited a hysteresis loop at medium-high pressures produced by capillary condensation, which could be attributed to materials with mesopores corresponding to interparticle spaces, like carbon nanotubes (Figure S1).



Figure 1. N₂ adsorption–desorption isotherms of carbonized glucose and undoped and N-doped carbon composites prepared by introducing a carbon nanotube (CNT; **a**) and oxidized CNT (**b**). Filled symbols: adsorption; open symbols: desorption.

Sample	$S_{\rm BET}$ (m ² g ⁻¹)	$V_{\rm micro}~({ m cm}^3~{ m g}^{-1})$	S_{ext} (m ² g ⁻¹)
CG	574	0.22	15
CG/CNT	545	0.21	21
CG/CNT _{oxi}	489	0.20	37
N-CG/CNT	387	0.16	44
N-CG/CNT _{oxi}	451	0.19	57

Table 1. Textural properties of carbonized glucose and undoped and N-doped carbon composites.

On the other hand, the specific surface area of the composite CG/CNT_{oxi} was 15% and 10% lower than that of the sample CG and composite CG/CNT (Table 1), respectively. This result suggests that the presence of CNT_{oxi} had an effect on the polymerization of glucose or the carbonization process, resulting in a material with lower microporosity. The shape of the isotherm at medium-high relative pressure, assigned to the presence of CNT, was similar to that of the composite CG/CNT, indicating that the oxidation of the CNT did not alter the volume of pores of the composites. In fact, it was observed that CNT_{oxi} exhibited similar pore volume as the non-oxidized CNT (Figure S1). On the other hand, the external surface areas were also modified due to the presence of CNT and CNT_{oxi} during the polymerization of glucose. The external surface area of CNT and CNT_{oxi} was much higher than that of sample CG (Table S1), and hence, the composite exhibited a larger external surface area than sample CG, demonstrating the presence of CNT inside the structure. However, although the same amount of CNT and CNT_{oxi} was introduced for the preparation of the composites, differences in the external surface area were observed. This result indicates that the presence of CNT_{oxi} during the hydrothermal process modified the polymerization reaction, resulting in a material with a higher external surface area. So, to better understand the morphological changes resulting from the incorporation of CNT and CNT_{oxi} during the polymerization of glucose, the samples were examined by scanning electron microscopy

(SEM). Sample CG was composed of spheres of 0.69 \pm 0.09 μ m diameter (Figure 2a), which is a typical morphology of hydrothermal carbons [20,23]. The presence of CNT gave rise to an inhomogeneous material with two different carbon sphere size distributions (0.24 \pm 0.03 μ m and 0.40 \pm 0.05 μ m), while the incorporation of CNT_{oxi} resulted in a homogenous material with carbon spheres of 0.25 \pm 0.04 μ m.



Figure 2. SEM micrographs of carbonized glucose (**a**) and carbon composites prepared by introducing CNT (**b**) and oxidized CNT (**c**).

It can be deduced from the SEM images that the chemical surface properties of the CNT had a noticeable effect on the formation of the carbon spheres. The growth mechanism of the spheres involves a complex set of simultaneous chemical reactions (isomerization, dehydration, condensation, or addition) that takes place during the polymerization of glucose [19,20]. Initially, the dehydration of glucose is promoted, giving rise to anions that react with each other via polymerization reactions [16]. Then, the aromatization of these molecules occurs, resulting in condensed furan rings bridged by aliphatic regions. These reactions proceed until the polymerized intermediates achieve a critical concentration, which produces the nucleation and growth of the particles forming a spherical-shaped structure [19,23]. The presence of CNT during the polymerization of glucose results in materials with smaller spheres, which suggests that CNT may promote the formation of nucleation points leading to a large number of small spherical particles, and hence, to a larger external surface area (Table 1) [31]. Besides, the oxygen groups on the surface of CNT_{oxi} also favor the dispersion of the CNT into the precursor mixture, and hence, the appearance of the nucleation points is more homogeneous. The assistance of CNT during the polymerization of glucose could be confirmed by FTIR spectroscopy (Figure 3a). The polymerized glucose obtained prior to carbonization (sample G) presented four main bands of interest: (i) an intense peak at 3400 cm⁻¹, which is attributed to O-H stretching vibration, (ii) a double-peak at 1600–1700 cm⁻¹, which is assigned to carbonyl groups, (iii) some peaks in the absorption region of 1200 cm⁻¹ ascribed to C-O-C stretching groups, and (iv) some peaks in the absorption band ca. 800 cm⁻¹ attributed to C-O-H bonds. These results demonstrated that the organic spheres obtained from the hydrothermal process exhibit a large amount of oxygen functional groups. The intensity of these peaks decreased by introducing CNT, being almost negligible for the composite prepared with CNT_{oxi}, especially the band assigned to -OH groups. These results suggest that the incorporation of CNT_{oxi} gives rise to materials with a lower concentration of oxygen functional groups (sample G/CNT_{oxi}), indicating a higher degree of polymerization compared to the sample that bears the pristine CNT (sample G/CNT) and the polymerized glucose (sample G).

These changes in the morphology due to the presence of CNT and CNT_{oxi} may also modify the effect of the ball milling process employed to incorporate nitrogen functionalities, as observed from the textural properties. The functionalization of CG/CNT with melamine gave rise to a material (N-CG/CNT) with a lower volume adsorbed at high relative pressure (Figure 1), which lost 29% of its BET surface area due to the functionalization process (Table 1). However, sample N-CG/CNT_{oxi} remained almost identical to CG/CNT_{oxi}, as only a decrease of 8% was observed in the BET surface area. This difference could be due to the final morphology of the composites that could give rise to a different behavior during the ball milling process. Some of the CNT and carbon spheres were crushed due to the ball milling (Figure S2), especially in the composite N-CG/CNT, which explains the significant loss in microporosity mentioned above. Besides, the thermal treatment applied to decompose melamine after ball milling seems to rearrange (or merge) the particles. These effects were less evident in the case of N-CG/CNT_{oxi}, although some loss of sphericity and some merged particles were also observed (Figure S2b). These differences between the N-doped composites might be due to the more heterogeneous structure obtained by the incorporation of CNT_{oxi} that probably resulted in a carbon structure with higher mechanical strength, and hence, the textural and morphological properties suffer fewer modifications during the functionalization process.



Figure 3. (a) FTIR spectra of hydrothermal glucose prepared without CNT (G) and in the presence of CNT (G/CNT) and CNT_{oxi} (G/CNT_{oxi}) and (b) Raman spectra of carbonized glucose and undoped and N-doped carbon composites prepared by introducing CNT and oxidized CNT.

As stated above, the surface chemistry of the CNT affected the polymerization of glucose, as the incorporation of CNT_{oxi} results in a material with a higher degree of polymerization. This modification in the polymerization reaction also resulted in differences in the ordering of the final carbon structure, which was evaluated by Raman spectroscopy. Figure 3b shows the Raman spectra for all undoped and doped carbons. The samples show a band at 1580 cm⁻¹ ascribed to the graphitic domains (G band) and a second broad band centered at 1350 cm⁻¹ (D band), which indicates disordered structures of turbostratic carbon layers. The intensity of both bands increased due to the addition of CNT and after the incorporation of nitrogen functionalities, especially for those samples prepared with oxidized CNT, suggesting a higher degree of ordering. The Raman spectra were further analyzed considering the splitting of the Raman features commonly employed for disordered carbonaceous materials [36]. The integrated areas of the main D and G bands were obtained from the deconvolution as a measure of relative disorder in carbon materials. The A_D/A_G ratio calculated from the integration of the peaks of the different spectra decreases by introducing CNT during the polymerization of glucose, especially by using CNT_{oxi} (Table S2). In addition, the relative decrease in the A_D/A_G ratio indicates the existence of a more ordered structure after the doping process. It should be highlighted that the A_D/A_G ratio usually increases after nitrogen functionalization due to the nitrogen replacing the carbon atoms, which increases the number of defects [15]. However, the degree of disorder of these samples is quite high, and hence, the Raman spectrum of N-CG/CNT_{oxi} is still attributed to a disordered carbonaceous material with a large number of defects.

Regarding the chemical composition, all samples were mainly composed of carbon (Table 2), with some contribution of hydrogen and oxygen. The differences in the amount of oxygen between CNT and CNT_{oxi} demonstrated that the CNT have been successfully oxidized. On the other hand, carbonized glucose (sample CG) exhibited a percentage of oxygen around 4.1%, which is within the

range typically observed in HTC carbon materials [23,31]. The amount of oxygen decreased due to the presence of CNT and CNT_{oxi}, which is in agreement with the hypothesis mentioned above about the higher degree of polymerization of these samples after the hydrothermal synthesis, as observed by FTIR. On the other hand, the amount of oxygen in the N-doped composites was doubled due to the ball milling process. This phenomenon may be due to the defects created, which then react with air, incorporating oxygen into the carbon structure [24]. Besides, the ball milling process allows the successful introduction of nitrogen, the incorporation of this heteroatom in the composite N-CG/CNT being higher. This effect is due to the lower degree of polymerization of the composite CG/CNT that allows a higher degree of functionalization.

Sample	C (wt.%)	H (wt.%)	O (wt.%)	N (wt.%)	<i>K</i> (S m ⁻¹)
CG	93.9	2.0	4.1	0.0	11
CG/CNT	94.3	2.1	3.6	0.0	150
CG/CNT _{oxi}	94.6	2.1	3.3	0.0	400
N-CG/CNT	85.1	1.7	6.4	6.8	280
N-CG/CNT _{oxi}	86.5	1.7	6.2	5.6	714
CNT	99.5	0.1	0.4	0.0	2500
CNT _{oxi}	95.3	0.9	3.8	0.0	1900

Table 2. Chemical composition and electrical conductivity of carbonized glucose, undoped and N-doped carbon composites, carbon nanotubes, and oxidized carbon nanotubes.

All these differences in the textural, morphological, and chemical properties result in materials with different electrical conductivities, as shown in Table 2. Carbon nanotubes exhibited a high electrical conductivity, which decreased up to 24% due to the presence of oxygen functionalities (CNT_{oxi}). On the other hand, the electrical conductivity of carbonized glucose was significantly low, but it could be increased up to 150 and 400 S m⁻¹ due to the incorporation of CNT and CNT_{oxi}, respectively. It should be highlighted that the composite CG/CNT_{oxi} exhibited a higher electrical conductivity than CG/CNT, despite CNT_{oxi} having lower conductivity than the pristine CNT. It is well-known that oxygen functional groups decrease the electrical conductivity but increase the wettability of carbon materials [37]. In this case, CNT_{oxi} was used to assist the polymerization of glucose, so after the hydrothermal process and subsequent carbonization, the oxygen functional groups were no longer on the surface of the CNT_{oxi}. Consequently, both composites (CG/CNT and CG/CNT_{oxi}) exhibited similar chemical composition, as shown in Table 2. However, the use of CNT_{oxi} favored the formation of a more homogeneous structure with a larger degree of ordering and higher mechanical strength that partially prevents the crushing of the CNT and the carbon spheres, and hence, leads to a carbon structure with enhanced electrical conductivity. Besides, the addition of nitrogen functionalities also improves the electrical conductivity of the composites up to 87% and 78% for N-CG/CNT and N-CG/CNT_{oxi}, respectively. In this case, the increase is very similar for both composites, despite sample N-CG/CNT bearing a higher amount of nitrogen. This difference could be due to the type of nitrogen functional groups that have been identified by XPS (Figure 4). The high-resolution XPS spectra in the N 1s region were deconvoluted into the three main nitrogen contributions: pyridinic nitrogen (398.4 \pm 0.1 eV), pyrrolic nitrogen ($400.1 \pm 0.1 \text{ eV}$) and quaternary nitrogen ($401.3 \pm 0.1 \text{ eV}$). The proportion of pyridinic nitrogen in the composite N-CG/CNT_{oxi} was slightly lower, while the contribution of the peak attributed to quaternary nitrogen was 30% higher in comparison with N-CG/CNT. These quaternary groups may create donor electronic states near the Fermi level, enhancing the electrical conductivity [37]. Therefore, both the amount and type of nitrogen functional group are essential to increase the electrical conductivity of carbon materials.



Figure 4. XPS spectra of N1s for N-doped composites N-CG/CNT (a) and N-CG/CNT_{oxi} (b).

3.2. Electrochemical Measurements

The electrochemical activity of the carbon composites towards the oxygen reduction reaction (ORR) was determined by cyclic voltammetry (CV) in a rotating ring-disk electrode (RRDE). Featureless cyclic voltammograms were obtained from the measurement performed with the electrolyte saturated with N_2 , demonstrating that the samples did not present any electrocatalytic activity under these conditions (Figure S3). Nonetheless, well-defined cathodic peaks were detected from the measurement performed with the electrolyte saturated with O_2 , which indicates that all materials were electrochemically active towards the ORR (Figure S3). Similar results were observed for the N-doped composites (Figure S4). However, significant differences in the electroactivity could be found due to their distinct physico-chemical properties. Therefore, the performance of the carbon composites as electrocatalysts for the ORR was evaluated by linear sweep voltammetry (LSV) to elucidate the relationship between the electroactivity and the physico-chemical properties. The LSV recorded at 1600 rpm and the number of electrons transferred are plotted in Figure 5.

Two crucial parameters can be obtained from the LSV: the onset potential (V) and the limiting current density $(mA cm^{-2})$, their values being shown in Table 3. The onset potential increases by the formation of the composite (3%) and the incorporation of nitrogen (7%), probably due to the higher amount of active sites provided by the CNT and the nitrogen functionalities. Similar results were obtained for the composites prepared with CNT_{oxi} (Figure 5b), increasing 6% the onset potential due to the introduction of CNT_{oxi} and 13% more due to the nitrogen functionalities. So, the most remarkable enhancement was observed for the N-doped composite $N-CG/CNT_{oxi}$, shifting the onset potential from 0.66 (sample CG) to 0.79 V. This value is similar to those previously reported for biomass-derived carbons [24,38]. The limiting current density also followed the same trend. However, in this case, the increase could be attributed to the higher electrical conductivity of the samples, as a direct relationship has been found between the limiting current density and the electrical conductivity (Figure S5). These results demonstrate the importance of incorporating CNT into the hydrothermal carbon structures, especially CNT_{oxi}, and introducing nitrogen functionalities. Besides, the measurements performed using an RRDE allow evaluating the efficiency of the oxygen reduction process by calculating the production of sub-products during the reaction (Table 3), which is related to the mechanism of the reaction. Sample CG produced a considerable amount of sub-products that decreased due to the presence of CNT, and the drop was even more significant upon the incorporation of nitrogen functional groups. These results were correlated with the number of electrons transferred, a number of electrons transferred close to 4 indicating that the oxygen reduction was accomplished in a single step, while a number close to 2 corresponded to the production of sub-products. So, from the values shown in Figure 5c,d, it could be concluded that the incorporation of CNT and CNT_{oxi} did not seem to produce any significant effect on the reaction mechanism, as the values obtained were quite similar to those

of the carbonized glucose (CG). However, the introduction of nitrogen functionalities results in a noticeable improvement in the efficiency of the oxygen reduction, as the N-doped composites shift the mechanism of the reaction towards the four-electron pathway (number of electrons transferred = 3.3, measured at -0.2 V). This value is higher than those previously shown for HTC [24,38]. This effect is due to the presence of nitrogen into the carbon structure that improves its electronic structure and chemical reactivity [15].



Figure 5. Linear sweep voltammograms (LSV) and the number of electrons transferred measured at 1600 rpm for the carbonized glucose and the undoped and N-doped carbon composites prepared by introducing CNT (**a**,**c**) and oxidized CNT (**b**,**d**).

Table 3. Electrochemical parameters obtained from linear sweep voltammetry measurement	s.

Sample	Eonset (V) ¹	$J_{\rm L}$ (mA cm ⁻²)	H ₂ O ₂ (%) ²	$J_{\rm k}$ (mA cm ⁻²) 3
CG	0.66	1.7	75	1.3
CG/CNT	0.68	1.8	67	2.0
CG/CNT _{oxi}	0.70	2.1	67	3.1
N-CG/CNT	0.73	2.0	43	2.3
N-CG/CNT _{oxi}	0.79	2.5	36	5.7

 1 Onset potential measured at -0.1 mA cm $^{-2}.$ 2 Production of hydrogen peroxide at 0.2 V vs RHE. 3 Kinetic current density measured at 0.4 V vs RHE.

Another important parameter that is commonly used to evaluate the activity of the electrocatalysts towards the ORR is the kinetic current density (J_k), which is calculated from the Koutecký–Levich equation (Equation (S13) shown in the supporting information). The J_k value calculated for N-CG/CNT_{oxi} was higher than that of composite N-CG/CNT (Table 3) despite both having a similar nitrogen content, which suggests that the presence of nitrogen was not enough to enhance the reaction. This difference in the J_k values of the N-doped samples could be due to the type of nitrogen functionalities or to the modification produced by the incorporation of oxidized CNT. The comparison between composite N-CG/CNT and CG/CNT_{oxi} (composites with similar onset potential and J_L) revealed that, in these samples, the improvement in the J_k value was due to the modification of the

physico-chemical properties produced by the introduction of CNT_{oxi} during the polymerization of the glucose, as CG/CNT_{oxi} exhibited a higher J_k value than N-CG/CNT. The long-term stability was another critical parameter to assess the performance of carbon materials as electrocatalysts towards the ORR. Therefore, the durability of all the samples was tested by chronoamperometry performed at 0.4 V vs RHE for 10000 s (Figure 6). It can be observed that the carbonized glucose sample lost 53% of its initial current density, which was already the lowest current density registered (Table 3). Nonetheless, the stability was highly increased by introducing CNT and CNT_{oxi} (13% and 27% more retention than CG, respectively) and was even further increased by the introduction of nitrogen. In fact, the N-doped composites exhibited a current density retention of more than 80%, especially composite N-CG/CNT_{oxi}. Therefore, taking into account all the important electrochemical parameters, composite N-CG/CNT_{oxi} exhibited the highest electrocatalytic performance, which could be attributed to its high external surface area, its higher electrical conductivity, and the larger number of active sites offered by the quaternary and pyridinic nitrogen functional groups.



Figure 6. Chronoamperometry experiments measured at 0.4 V vs RHE for 10000 s for the carbonized glucose and the undoped and N-doped carbon composites prepared by introducing CNT (**a**) and oxidized CNT (**b**).

4. Conclusions

Biomass-derived carbon composites were prepared by hydrothermal carbonization in the presence of CNT and oxidized CNT (CNT_{oxi}) to evaluate the effect of the different oxygen functional groups on the hydrothermal polymerization of glucose and on the final physico-chemical properties. The presence of CNT during the polymerization of glucose promoted the formation of nucleation points that led to a large number of small spherical particles. The incorporation of CNT_{oxi} also favored the dispersion of the CNT into the precursor mixture, giving rise to a more homogenous carbon structure with a large number of small spheres (64% smaller than those of sample CG). Besides, the presence of CNT_{oxi} results in materials with a lower concentration of oxygen functional groups, suggesting a higher degree of polymerization compared to the sample that bears the pristine CNT. The efficiency of the ball milling employed to functionalize the composites was also modified due to these features provided by the CNT_{oxi} . The composite with the more homogeneous structure (CG/CNT_{oxi}) exhibited higher mechanical strength, and henceforth, the textural and morphological properties suffered fewer modifications during the functionalization process. In fact, a decrease of only 8% was observed in the BET surface area of sample N-CG/CNT_{oxi}, while this value rose to 29% for the composite N-CG/CNT. On the other hand, the ball milling process doubled the amount of oxygen and allows the successful introduction of nitrogen. However, differences between the incorporation of these heteroatoms were observed due to the final degree of polymerization of the samples. Lower incorporation of oxygen and nitrogen was detected for the composite with a higher degree of polymerization (N-CG/CNT_{oxi}). Besides, the textural, morphological, and chemical properties obtained for the composite N-CG/CNT_{oxi} resulted in a material with enhanced electrical conductivity (from 11 to 714 S m⁻¹). Regarding the electrochemical performance, the onset potential increased by 20% due to the presence of CNT and nitrogen functional groups that act as active sites; the limiting current density increased linearly with the electrical conductivity, being improved by 47%; the production of sub-products decreased from 75% to 36% due to the incorporation of nitrogen, which shifted the mechanism of the reaction to the four-electron pathway; the kinetic current density increased from 1.3 to 3.1 mA cm⁻² due to the addition of CNT_{oxi} during the polymerization of glucose and up to 5.7 mA cm⁻² due to the presence of nitrogen functionalities; and the stability improved due to the nitrogen content, retaining almost 90% of the initial current density after 10000 s. Therefore, considering all the important electrochemical parameters, sample N-CG/CNT_{oxi} exhibited the highest electrocatalytic performance, which could be attributed to its high external surface area, its higher electrical conductivity, and the large number of active sites offered by the CNT and the nitrogen functional groups.

Supplementary Materials: The following are available online at http://www.mdpi.com/2504-477X/4/1/20/s1, Figure S1: N₂ adsorption-desorption isotherms of carbon nanotubes and oxidized carbon nanotubes, Table S1: Textural properties of carbon nanotubes and oxidized carbon nanotubes, Figure S2: SEM micrographs of N-doped composites with carbon nanotubes and with oxidized carbon nanotubes, Table S2: Integrated areas of the peaks D and G obtained by Raman spectroscopy, Figure S3: Cyclic Voltammograms measured at a scan rate of 5 mV s⁻¹ in an electrolyte saturated with N₂ and O₂ for carbonized glucose (a), composite CG/CNT (b) and composite CG/CNT_{oxi} (c), Figure S4: Cyclic Voltammograms measured at a scan rate of 5 mV s⁻¹ in an electrolyte saturated with N₂ and O₂ for N-doped composites prepared with CNT (a) and CNT_{oxi} (b), Figure S5: Relationship between the limiting current density and electrical conductivity, Equations (S1)-(S14) to calculate the electrochemical parameters.

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