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Renewable Microalgae-derived Nitrogen Doped Hydrothermal Carbons

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Nitrogen-doped carbon materials were synthesised via an effective, sustainable and green one-step route based on the hydrothermal carbonization of microalgae with high nitrogen dopant content (ca. 11 wt%). The addition of the monosaccharide glucose to the reaction mixture was found to be advantageous, enhancing both the fixation of nitrogen in the synthesized HTC carbons, resulting in materials possessing nitrogen content in excess of 7 wt %, and promisingly reaction yield. Increasing the amount of glucose leads to a higher N retention in the HTC carbons, which suggests co-condensation of the microalgae and glucose-derived degradation/hydrolysis products via Maillard-type cascade reactions, yielding N-containing aromatic heterocycles (e.g. pyrrole) as confirmed by Solid State ^{13}C NMR, XPS and FTIR. Additionally, increasing the HTC processing temperature leads to a further aromatization of the HTC carbon chemical structure and the formation of increasingly more condensed N-containing functional motifs (i.e. pyridinic-N and quaternary-N).

Introduction

The incorporation of nitrogen atoms within the molecular framework of carbon materials has raised great interest in the materials science research community due to several beneficial effects on material physicochemical properties. The presence of structural nitrogen atoms within the graphitic / aromatic structure of carbon materials contributes with additional electrons to the material conduction band, resulting in improved thermal / oxidation stability and higher electrical conductivity.[1,2] Both features are crucial for successful application in for example the oxygen reduction reaction in fuel cell electrocatalysis,[3] electrodes in electrochemical double layer capacitors[4] and anode materials in lithium ion batteries.[5] Furthermore, due to the electron-rich nature of nitrogen atoms, N-containing surface functionalities have demonstrated to be beneficial to carbon material adsorption properties, especially in the field of CO_2 capture (electron acceptor).[6,7]

N-doped carbons are commonly synthesised via the pyrolysis of N-containing precursors (e.g. amino sugars, melamine, N-containing polymers),[7,8] or post-synthesis functionalization of carbon materials (e.g. treatment with melamine and/or urea and ammonia treatment).[9] Recently the hydrothermal carbonisation (HTC) of appropriate biomass has proven to be an effective alternative synthesis pathway for the production of homogeneously N-doped carbonaceous materials, whose chemical structure can be tuned according to processing conditions. N-containing monosaccharides/polysaccharides or a mixture of amino acids (e.g. proteins) and sugars have so far been successfully used as N-doped carbon precursors.[10-14] Based on these evidences, HTC of protein-rich biomasses has a high potential to become a green, economic and sustainable synthetic route to CO_2-negative and highly functionalized carbon material.

Aquatic microalgae biomass is primarily composed of proteins, carbohydrates, fats and nucleic acids in varying proportions depending on the species.[15] In particular, the microalgae *Spirulina Platensis,* used in this work, contains a relatively high protein fraction and as a consequence, they exhibit a high nitrogen content (Figure 1; Table 1). Furthermore, microalgae are characterized by very high photosynthesis efficiency and are considered a fast growing biomass, commonly doubling their biomass within a 24 h growth window.[16-18] They have a harvesting cycle of 1 - 10 days allowing a much higher turn-over than typical annual crop production cycles. They also grow in adverse conditions and extreme environments (i.e. very alkaline water); therefore their cultivation does not compete for spaces employed in traditional food production.[18,19] As a result of all these logistical advantages, microalgae are generating great interest with regard to their application in developing biorefinery schemes. In particular, their utilisation as a biofuel precursor is being intensively investigated since higher oil quantities (up to 80% by weight) than conventional crops (e.g. rapeseed,

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soybeans or jatropha) are possible.[15-19] These characteristics make microalgae also attractive precursors for the production of carbon materials. In spite of that, there are only two reports regarding the direct use of algae/microalgae with this aim. Thus, Raymundo-Piñero et al. produced oxygen-rich nanotextured carbons with moderate surface areas but with a tuned porosity advantageous for supercapacitor applications by direct carbonization of different brown and red seaweeds at temperatures in the 600 – 900 ºC.[20] More recently, Heilmann et al. performed the HTC treatment of algae/microalgae for the generation of chars with high heats of combustion.[21] However, there are no literature reports pertaining to the exploitation of the high nitrogen content of some microalgae to produce N-doped carbon materials. Herein, we report on the sustainable and economic synthesis of N-doped carbon materials from microalgae, providing a detailed characterization of the chemical composition and structure of the produced materials. The effects of glucose addition to the reaction mixture were also studied in order to establish potential advantages provided by the reactions between the monosaccharides and the microalgae protein (amino) functions.

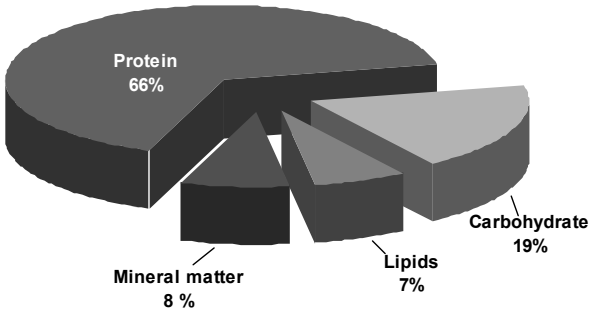

Figure 1. Blue-green Spirulina Platensis microalgae composition (wt%) .

Results and Discussion

Structural characterization of the N-doped materials

SEM image analysis of the raw microalgae shows the typical morphology of spray dried *Spirulina Platensis* composed of globular particles with an average size of several micrometers (e,g. 10 - 100 µm; Figure 2a) and a surface characterized by concave bottomlands and relatively smooth texture (Figure 2b). As a consequence of HTC treatment at temperatures higher than 180 ºC, particle disruption takes places and irregular agglomerates showing a high degree of surface roughness are formed (Figures 2c and d). Spherical microparticles, characteristic of HTC products derived from carbohydrates, are identified to a minor extent (image not shown) probably due to the low content of carbohydrates characterizing this microalgae species (Figure 1). Interestingly, microalgae-derived HTC carbon obtained at higher temperatures (i.e. 200-220 ºC), show a softer consistency similar to the one observed for pitch, indicating the formation of aromatic structures of low melting point probably generated from the lipid fraction. On the other hand, when the microalgae substrate is hydrothermally processed in the presence of glucose, the resulting HTC carbon is composed mostly of spheroidal particles, morphology typically observed for pure glucose-derived HTC material (Figures 2e and 2f). However, in this case the particles have a larger average diameter (> 2 µm) and a rough surface (Figure 2f). Nonetheless, these materials are non-porous (S_{BET} ~ 6 m^2 g^{-1}), as usually observed for HTC carbon materials.

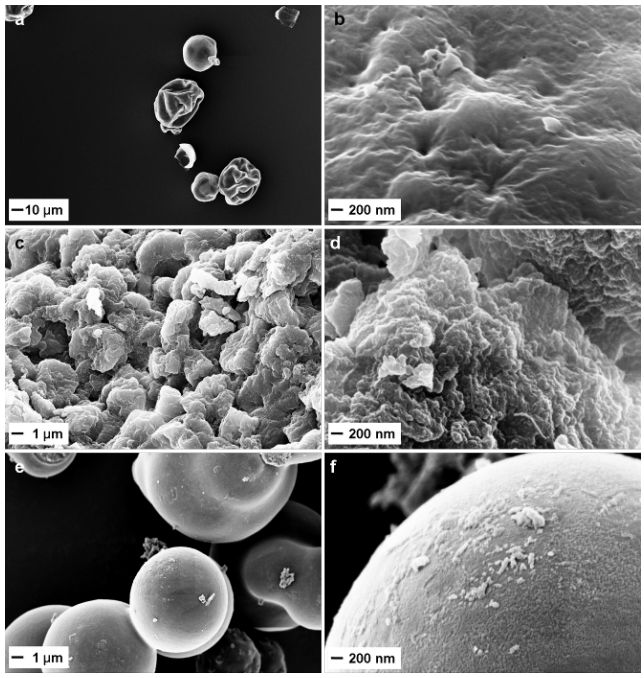

Figure 2. SEM images of raw microalgae (a and b), microalgae derived HTC product (200 ºC) (c and d)), and HTC carbon derived from a mixture of glucose and microalgae (220 ºC) (e and f).

Chemical characterisation of the N-doped materials

The elemental composition of raw microalgae and microalgae-derived HTC products is indicated in Table 1. The samples have been labelled as HC-A-T for the microalgae-derived HTC carbons and HC-A-xG-T for the microalgae/glucose-derived HTC carbons, x being the glucose to microalgae mass ratio (x = 0.33, 0.67 and 1) and T the HTC temperature in ºC (180 – 240) (Table 1). The elemental analysis data of raw microalgae reveals the relatively high N content (i.e. 11.4 wt%) arising from the relatively high protein fraction of this microalgae species (Table 1; Figure 1). Although nitrogen is mainly contained in the polypeptide backbone chains constituting the proteins, minor quantities may also be present in the amino-acids R groups and in the carbohydrate fraction. HTC treatment of the microalgae leads to a major decrease of the heteroatoms fractions (i.e. N and O) coupled to an increase of the carbon content, as evidenced by the elemental analysis (Table 1). Although the increase of the HTC temperature leads to a carbon enrichment of the products,

they still exhibit relatively high H content (Table 1), which underlines their prevalent hydrocarbon nature compared to saccharide-derived HTC carbons (64 – 73 wt% C and 4.0 – 4.6 wt% H).[22,23] The abundance of alkyl chains in the microalgae-derived HTC products is probed by NMR and FTIR, as will be shown later. They probably derive from the lipid fraction and lead to the observed pitch-like appearance for the samples synthesized at higher temperatures due to cracking reactions.

When glucose is added to the reaction mixture (i.e. samples labelled HC-A-xG-T), beneficial effects are observed with regard to HTC yield and N content. Both quantities are appreciably higher (yield ~ 30 – 50 % and N content ~ 7- 8 wt%) as compared to samples prepared from pure microalgae. These findings are even more glaring when analyzed in terms of nitrogen and carbon efficiencies, respectively defined as the % of N or C contained in the microalgae/glucose mixture which is retained in the HTC product (Figure 3). Thus, for HTC carbon obtained from a mixture of glucose and microalgae, the amount of recovered nitrogen is much higher (as high as *ca.* 6 times) than when no glucose was added (only 11-13 %). This finding suggests that when microalgae are the sole carbon precursor, most of the nitrogen is lost in the form of liquid or volatile decomposition products. Conversely when glucose is added, a larger fraction of nitrogen (> 24 %) is fixated in the synthesized HTC carbons presumably via co-condensation reactions involving the microalgae-derived and the monosaccharide-derived degradation / hydrolysis products (i.e. Maillard reactions). This speculation is strongly supported by the evidence that the sample showing the highest N-efficiency (~ 60 %) is the one with the highest glucose to microalgae mass ratio (HC-A-1G-180; Figure 3).

Table 1. Elemental composition and HTC yield of raw microalgae and microalgae derived HTC carbons.

Sample	Yield (%)[a]	N (wt%)	C (wt%)	O (wt%)	H (wt%)
Raw Microalgae	-	11.4	48.0	33.7	7.0
HC-A-180	18.0	6.8	65.7	18.0	8.4
HC-A-200	20.0	6.7	67.9	15.8	8.8
HC-A-220	23.0	6.4	70.3	13.2	9.5
HC-A-0.33G-180	26.0	7.9	66.8	17.2	7.5
HC-A-1G-180	47.5	7.1	67.4	18.5	6.3
HC-A-0.67G-180	32.0	7.3	65.9	19.3	6.9
HC-A-0.67G-200	31.0	7.5	70.2	14.8	6.9
HC-A-0.67G-220	29.0	7.5	72.9	11.5	7.6
HC-A-0.67G-240	28.0	7.3	72.7	11.7	7.5

[a] Yield is defined as: g of HTC material per 100 g of starting mixture.

To a lesser degree, the same trend is also observed for C-efficiency. The reaction between glucose-derived and microalgae-derived degradation / hydrolysis products may also play a major role in this case, leading to a higher carbon recovery from the microalgae fraction. However, it must be taken into account that glucose has a higher C-efficiency when treated under hydrothermal conditions (≈ 70 %). Therefore, the increased C-efficiency for the samples where glucose was added can also be partially due to the formation of a relatively high amount of HTC carbon solely from glucose. Additionally, TGA investigations reveal that the carbonisation yield and the decomposition temperature of HC-A-xG-T samples are higher than for the HC-A-T sample series (Figure S1 ESI), suggesting a higher thermal stability in the former case probably due to a higher degree of aromatization of the carbonaceous structure. Furthermore, the TGA results highlight potential advantages of the HTC treatment over the direct solid state pyrolysis of microalgae. First of all, HTC allows the dissolution and partial removal of the mineral matter contained in the microalgae (mineral matter content of HTC carbons ~ 4 %), whereas the solid state pyrolysis process leads to its accumulation in the solid product (~ 40 % as deduced from Figure S1 ESI, taking into account that the mineral matter content of raw microalgae is 8 %; Figure 1), requiring thus an additional acid washing step to purify the sample. Furthermore, the yield of the dry pyrolysis process is only 12 %, therefore most of the nitrogen and carbon contained in the microalgae are lost as volatiles, highlighting the unfeasibility of that process as a viable synthetic route.

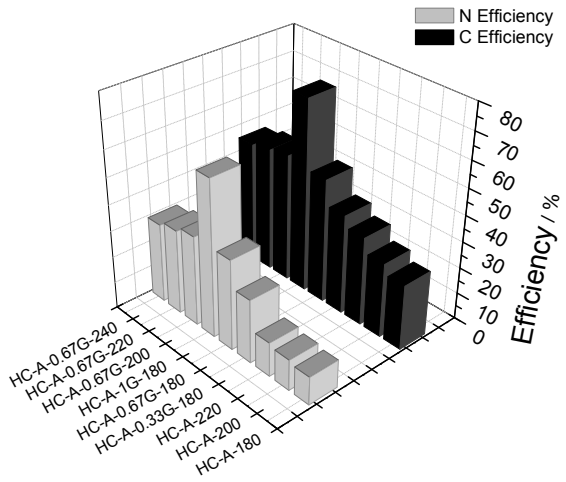

Figure 3. Nitrogen and carbon efficiencies for microalgae-derived HTC materials. N efficiency was determined as the amount of N in the HTC product [(wt% N in HTC) * (yield)] divided by the amount of N in the starting mixture [(wt% N in algae * wt % algae in starting mixture)], and C efficiency was determined as the amount of C in the HTC product [(wt% C in HTC) * (yield)] divided by the amount of C in the starting mixture [(wt% C in algae * wt% algae in starting mixture + wt% C in glucose * wt% glucose in starting mixture)].

It is worth noting that when HC-A-0.67G-180 is further pyrolyzed at 700 ºC, the C content increases to 76.5 wt% with a slight decrease of the nitrogen fraction (i.e. 6.1 wt%), demonstrating that “nitrogen” in HC-A-0.67G-180 is present as relative stable species (e.g. pyrrole) in the carbonaceous material framework. To confirm this observation and provide more insight into the chemical structure of the presented microalgae-derived

HTC carbons, solid state ^{13}C and ^{15}N CP MAS NMR, XPS and FTIR measurements were performed. The corresponding solid state ^{13}C NMR spectra are shown in Figure 4a. The main difference observed between raw microalgae and HTC microalgae (HC-A-180) lies in the amide (δ = 170 - 175 ppm) and –NH-substituted α-carbons (δ = 50 - 60 ppm)[24] peaks, together with the carbohydrate fraction (δ = 55 - 105 ppm). A major decrease in the relative intensities of the aforementioned resonances is observed, indicating the loss of N-functionalities and depletion of the sugar fraction during HTC. On the other hand, except for a minor relative intensity increase and broadening of the aromatic-C peak (i.e. δ = 125 - 129 ppm), ascribable to olefinic, arene or N-containing heterocyclic aromatic structures,[25] no major concomitant peak formation is observed ($\delta \approx$ 105 – 155 ppm) upon HTC treatment of the microalgae. In accordance with the elemental analysis, the main resonances characterizing the ^{13}C spectrum are within the aliphatic region ($\delta \approx$ 0 - 45 ppm), indicating that the microalgae-derived HTC product is mostly composed of alkyl chains and therefore characterized by a strong hydrocarbon character. Considering the low yield of HTC-A-180 (i.e. 18%), the presence of such structures can be mostly attributed to the fatty acids alkyl chains that have been incorporated within the microalgae derived HTC product.

When glucose was added to the reaction mixture (i.e. HC-A-xG-T sample series), the same changes were observed in the ^{13}C solid state NMR spectra with notably one major difference; the aromatic-C peak is relatively more intense and characterised by two distinct shoulders at δ = 110 – 118 ppm and 148 - 151 ppm, attributed respectively to the furan β- and α-carbons generated from glucose-derived HTC.[26] In accordance with this finding, an increase of these latter resonances can be seen with the addition of a higher amount of glucose (i.e. HC-A-1.5G-180), presumably caused by a larger “furan” material content. On the other hand, increasing the HTC processing temperature (e.g. HC-A-0.67G-220) causes the loss of these “furan” shoulders, since under these more severe conditions such species are converted into more thermally stable extended aromatic/“arene”-like structures.[26,27] It should be pointed out that the increase in the relative intensity of the aromatic-C resonance may also partially arise from the formation of N-containing heterocyclic aromatic structures resonating within this range.[28]

To obtain a more detailed and direct characterization of the nitrogen species, solid state ^{15}N CP MAS NMR experiments were also performed (Figure 4b). Unfortunately, these experiments suffer from reduced sensitivity owing to two main reasons: i) the low natural isotopic abundance of ^{15}N allows detecting only the most abundant species within the sample and ii) only N species with protons in their closest proximities can be observed due to unfavourable magnetization transfer between the protons and the ^{15}N nuclei. The spectrum of raw microalgae is characterised by one single sharp and intense peak at δ = 260 ppm, ascribable to amide groups. This finding confirms that the largest fraction of nitrogen in the raw microalgae is contained in the polypeptide chains. No major changes are observed in the case of HTC treated microalgae (HC-A-180), except for a decrease of the peak intensity, indicated by a higher peak to noise ratio. It can be deduced then that the relatively low fraction of nitrogen left after HTC ($\approx$ 10%; Figure 2) is still conserved as amide bonds, which have not been fully hydrolyzed probably due to the limited solubility of the raw microalgae in water. On the other hand, for HTC carbons obtained from a mixture of microalgae and glucose, the amide peak intensity is even more reduced, indicating an enhanced extent of hydrolysis, and a second broad peak observed at δ = 200 – 250 ppm corresponding to pyrrolic-N.[28] These species are usually formed from the reaction between carbohydrates and amines via the Maillard reaction under HTC conditions.[28] However, the possibility of more condensed N-containing aromatic structures (e.g. pyridine, quaternary nitrogen species) being formed during the conversion of microalgae/glucose mixtures into HTC cannot be discounted based on these results, since as previously suggested, non-protonated nitrogen species cannot be detected during ^{15}N CP experiments.

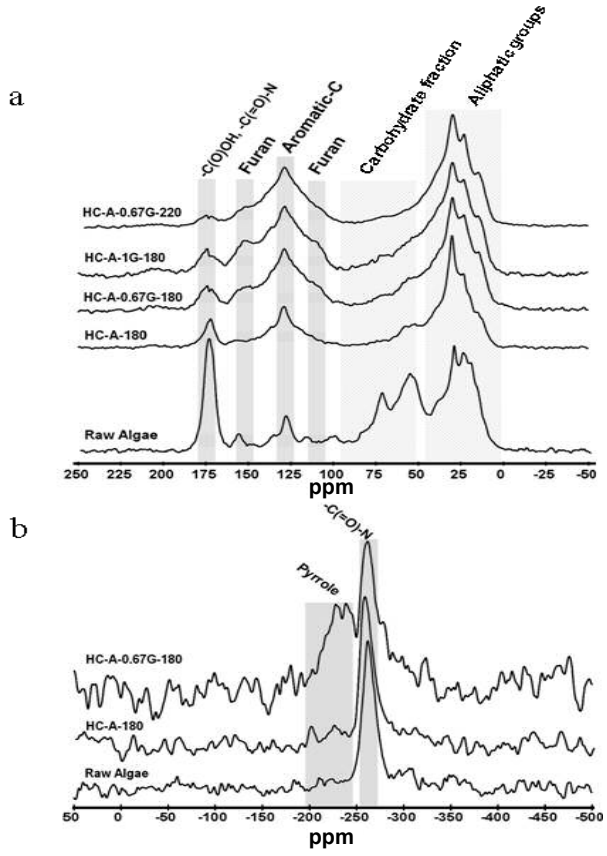

Figure 4. Solid state ^{13}C (a) and ^{15}N (b) CP MAS NMR spectra of raw microalgae and microalgae-derived HTC materials with and without glucose addition and at different HTC temperatures.

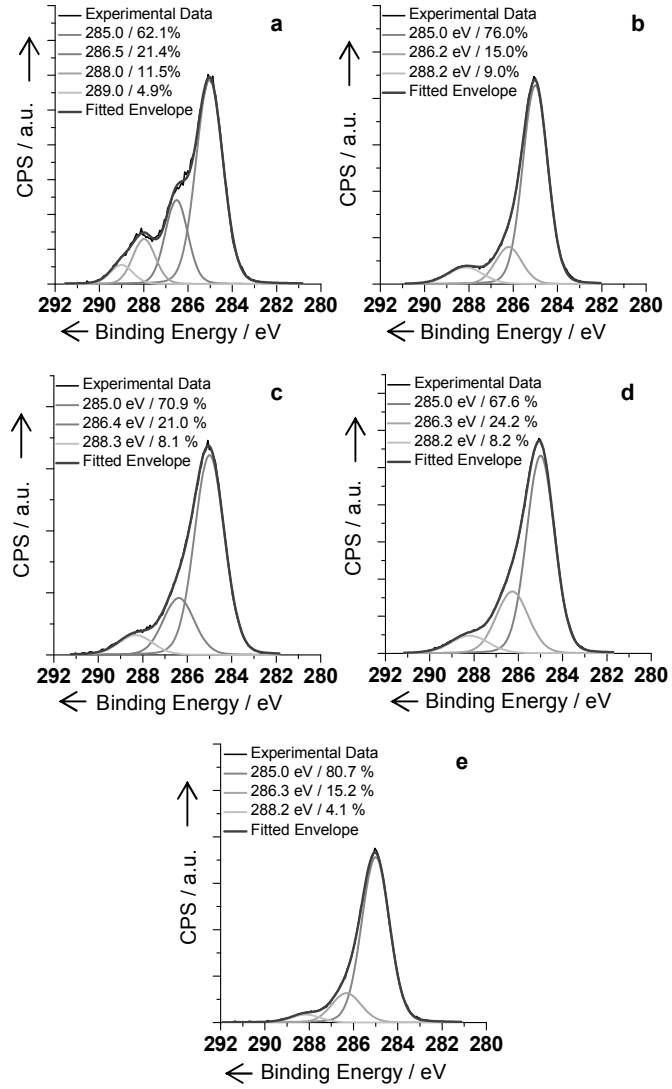

Figure 5. High resolution XPS analysis of the C 1(s) photoelectron envelopes for raw microalgae (a), HC-A-180 (b), HC-A-0.67G-180 (c), HC-A-1G-180 (d) and HC-A-0.67G-220 (e).

The chemical nature of the surface functional groups was characterised by high resolution XPS analysis of the C 1(s) and N 1(s) photoelectron envelopes (Figures 5 and 6 respectively). This surface analysis was complemented by FTIR (described in detail in the SI). The deconvolution of the C 1(s) envelope of raw microalgae, (Figure 5a), shows three main peaks at 285.0 eV (C-C/-CH_x), 286.5 eV (C-O-H (hydroxyl), C-O-C (ether) and C-N (amine)) and 288.0 eV (C=O (carbonyl) and N-C=O (amide)), with a minor contribution at 289.0 eV (O=C-O (acid or ester)). The relatively high intensity of the 286.5 and 288.0 eV peaks underlines the presence of a considerable amount of heteroatom containing species (i.e. O and N) in the raw microalgae, which are part of the protein and sugar fractions. In the case of microalgae-derived HTC carbon (i.e. HC-A-180; Figure 5b), the contribution of these two peaks to the overall C 1s envelope is highly reduced indicating that during HTC a large fraction of the N and O containing species are depleted. This finding is in agreement with the elemental analysis and solid state NMR analysis, as well as FTIR measurements (Figure S2 ESI). Interestingly, for the HTC carbons obtained from a mixture of glucose and microalgae (Figures 5c and d), only the 288.3 eV peak exhibits a reduced intensity. Conversely, the 286.3 - 286.4 eV peak is still very prominent. These findings can be respectively correlated to the progressive hydrolysis of the protein content during HTC and the formation of aromatic heterocycles (e.g. furan, pyrrole, pyridine) formed during the HTC process. As previously observed with elemental analysis, increasing the HTC temperature leads to a higher degree of carbonisation (i.e. carbon enrichment), as indicated by the reduced relative intensities of the 286.3 and 288.2 eV peaks for HC-A-0.67G-220 (Figure 5e).

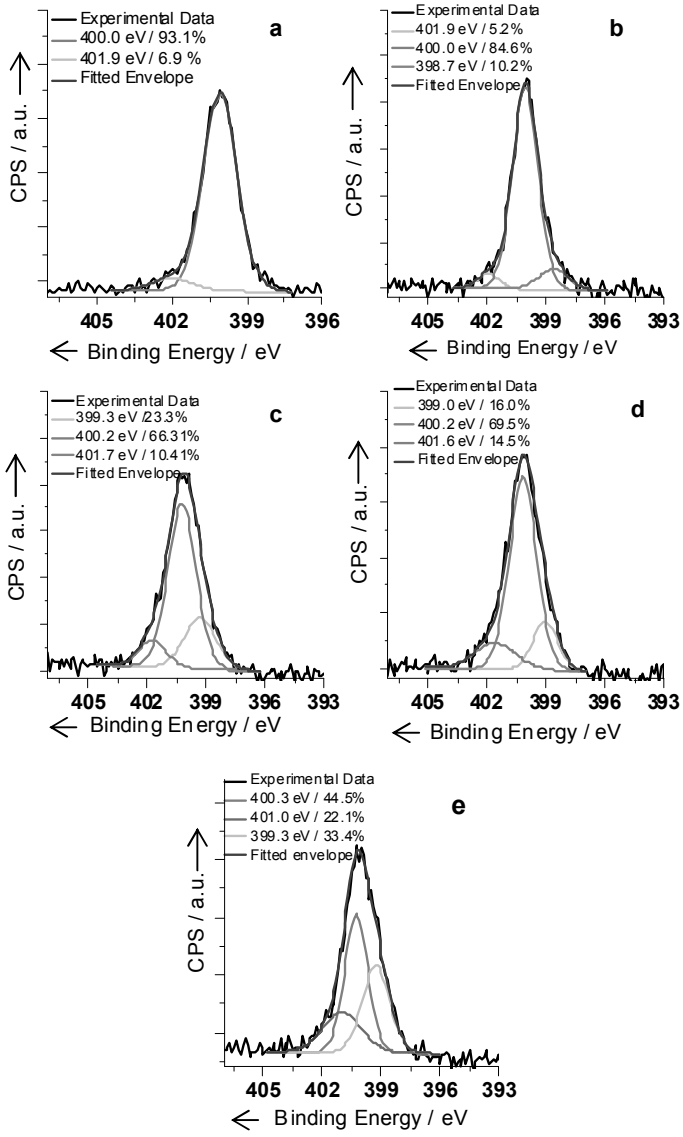

Figure 6. High resolution XPS analysis of the N 1(s) photoelectron envelopes for raw microalgae (a), HC-A-180 (b), HC-A-0.67G-180 (c), HC-A-1G-180 (d) and HC-A-0.67G-220 (e).

In order to obtain a more detailed analysis of surface N-species and in particular to ascertain the presence of non-

protonated N-containing aromatic heterocycles, an analysis of the N 1s XPS envelope was carried out (Figure 6). However, this technique suffers from a sensitivity limitation arising from the fact that several N-species overlap over a very narrow binding energy range (i.e. pyrrole ≈ 400.2 eV, amide ≈ 399.9 eV, amine ≈ 399.3 eV, pyridine ≈ 398.9 eV).[29] As a consequence, it allows discerning which one is the most abundant species, but in the case of very broad N 1(s) envelopes, spotting the overlap of minor contributions is a hard task. The N 1(s) envelope of raw microalgae is characterized by one single peak at *ca.* 400.0 eV, ascribable to amide bonds present in the proteins polypeptide chains (Figure 6a). In the case of HTC treated microalgae (Figure 6b), the most intense peak remains the one at 400.0 eV, indicating the relatively low fraction of nitrogen remaining in the HTC product is present as "amide" in accordance with NMR (Figure 4b) and FTIR results (Figure S2 ESI). However, as described earlier, it is not possible to discard the possibility of a pyrrole contribution (i.e. 400.2 eV) generated from the reaction between the hydrolyzed amino acids (i.e. free amines) and the carbohydrate fraction originally present in the raw microalgae. Furthermore, two other less significant contributions can be observed at *ca*. 401.9 and 398.7 eV, respectively assigned to quaternary-N and pyridinic-N species that have been formed during the carbonization process.

The addition of glucose has the effect of broadening and slightly shifting the N 1(s) envelope profile of microalgae-derived HTC carbons to higher binding energy values (Figures 6c and d). The most intense peak, at 400.2 eV, can be assigned to pyrrolic-N. The other two, as previously seen, are attributed to quaternary-N (401.0 – 401.7 eV) and pyridinic-N species (399.0 – 399.3 eV). The relative intensity of these latter peaks is higher than in HC-A-180, suggesting a higher extent of formation of such species when glucose is added. These results further demonstrate the incorporation of N as aromatic heterocycles when glucose is present, as suggested based on FTIR (Figure S2 ESI) and NMR results. It should be mentioned that for the peak at 399.0 - 399.3 eV, there is also the possibility of amine groups contribution (399.3 eV). However, these N-moieties were not detected with ^{15}N solid state NMR, so therefore may only be present in minimal quantities at the material surface. When the HTC temperature is raised (i.e. HC-A-0.67G-220, Figure 6e), an increase of the side peaks contributions (401.0 and 399.3 eV) takes place, which suggests the conversion of pyrrolic-N into more stable N-groups, (i.e. quaternary- and pyridinic-N), as occurs during a pyrolysis process of N-containing carbonaceous substances.[30]

The combination of the results obtained from elemental analysis, solid state NMR, FTIR and XPS allows depicting the most likely scenario for the HTC of algae and resultant synthesis of N-doped carbon materials. When treated under hydrothermal conditions, the polypeptide chains constituting the protein fraction are hydrolyzed into their amino acid building blocks. If the raw algae are the only carbon precursor, then most of the amino acids remain in solution and therefore large part of the nitrogen is lost in the liquid phase. The resulting solid product is mainly characterized by alkyl chains derived from the fatty acids constituent and therefore has a prevalent hydrocarbon character. On the contrary, when glucose is present, Maillard-type cascade reactions involving the amino groups in amino acids and the carbonyl moieties present in carbohydrates and their derivatives (e.g. HMF), allows fixating a higher amount of nitrogen in the synthesized hydrothermal carbon. Furthermore, the glucose degradation products (e.g. levulinic acid and formic acid) presumably enhance the amide bonds hydrolysis by lowering the solution pH and acting as an *in-situ* catalyst. This may also be an additional factor leading to higher HTC yields for the samples synthesized upon glucose addition. These reactions patterns have already been reported for the reaction of model molecules, i.e. carbohydrates (glucose) and amino acids/proteins (i.e. glycine or albumine) under hydrothermal conditions and have been observed to produce a carbon material containing N-heterocyclic aromatic structures, such as pyrrole, pyridine and quaternary-N species.[11,14] We have shown that such N-containing moieties are also present in the HTC carbons derived from the mixture of a protein-rich biomass (i.e. microalgae) and glucose, confirming the similarity of the reaction mechanisms to the model compounds. What is more, depending on the HTC temperature, the N-species distribution can be tuned. More severe processing conditions (i.e. higher temperature) favour the incorporation of nitrogen into more stable aromatic structures (e.g. pyridine and quaternary-N species) as a result of a higher extent of carbonization.

Conclusion

In this work we have demonstrated that HTC of microalgae (*Spirulina Platensis*) is a straightforward, effective and sustainable method for the synthesis of N-doped carbon materials (up to ~ 8 wt%). The N-content of the raw algae is efficiently retained in the synthesized HTC products. In this regard, the addition of glucose to the initial HTC reaction mixture is highly beneficial as it enhances fixation and incorporation of N, as well as overall carbon yield in these algae-derived HTC carbons. This higher N efficiency is attributed to glucose performing a double role, namely acting as a in-situ hydrolysis and co-condensation reaction reagent. In the former case, the HTC degradation products of glucose (e.g. levulinic acid and formic acid) favour the hydrolysis of the polypeptide amide bonds by lowering the reaction mixture pH. For the latter role, the presence of carbonyl

functional groups (i.e. a reducing sugar) in the monosaccharides and their derivatives (e.g. HMF) is fundamental, since these moieties react with the amino groups of the amino acids presumably via Maillard-type cascade reactions yielding stable N-containing heterocycles (e.g. pyrrole, pyridine and quaternary-N species), as proved by solid state NMR, XPS and FTIR. The stability of these species is further supported by the evidence that pyrolysis at 700 ^{o}C of the algae-derived HTC carbons causes negligible loss of the N-content.

Overall this work further strengthens the position of the hydrothermal method for biomass conversion, particularly within the concept of a holistic bio-refinery concept, since it demonstrates how this thermochemical processing technique allows to effectively synthesise a range of functional carbonaceous materials with several potential end-applications from importantly, as demonstrated here, inexpensive and fast-growing biomass, microalgae.

Experimental Section

Material Synthesis. N-doped carbon materials were obtained by hydrothermal carbonization of microalgae (*Spirulina Platensis*) and a mixture microalgae/glucose as follows. First, microalgae or a mixture microalgae/glucose were dispersed in water (15 wt% microalgae, 0 – 15 wt% glucose) and stirred for 18 h. The dispersion was then sealed in a glass vial inside a typical PTFE-lined autoclave system and heat-treated at 180 – 240 ºC for 24 h. After the reaction, the autoclave was cooled down in a water bath at room temperature. The solid products were separated by filtration, washed with distilled water and finally dried at 80 ºC under vacuum overnight.

Characterisation. Elemental Analysis (EA) was performed using an Elementar vario MICRO cube. SEM images were acquired on a LEO 1550/LEO GmbH Oberkochen equipped with an Everhard Thornley secondary electron and in-lens detectors. Fourier transform infrared (FTIR) spectra of the materials were recorded in ATR geometry on a Varian 1000 FTIR spectrometer, Scimitar Series (FTS1000). X-ray photoelectron spectroscopy (XPS) was carried out by means of a Thermo Scientific K-Alpha ESCA instrument using monochromatic Al-Kα radiation (hν = 1486.6 eV). Binding energies for the high-resolution spectra were calibrated by setting C 1s at 285.0 eV. ^{13}C and ^{15}N solid-state MAS NMR spectra were acquired on a Bruker Avance 300 MHz (7 T) spectrometer using respectively 4 and 7 mm zirconia rotors as sample holders, spinning at MAS rate nMAS = 14 kHz and 5 kHz. For ^{13}C experiments, the chemical shift reference was tetramethylsilane (TMS; d =0 ppm).^{1}H t_1 relaxation time was set to 3 s. Proton-to-carbon CP MAS was used to enhance carbon sensitivity with a cross-polarisation time equal to 1 ms. N {^{1}H} CP MAS experiments were done using a recycle delay of 3 s and a contact time of 2 ms, TPPM decoupling was applied during signal acquisition, and the number of transients was 7200. ^{15}N chemical shift were referenced to labelled glycine at -348 ppm on the nitromethane scale (CH_3NO_2; δ = 0 ppm).

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Keywords: hydrothermal synthesis · biomass · N doping · carbon · green chemistry

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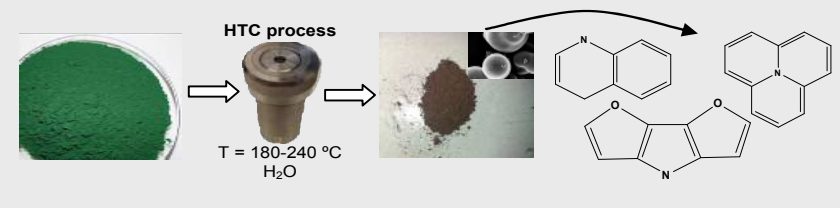

HTC of microalgae/glucose: a green, sustainable and economical synthesis route of N-doped carbons with nitrogen contents in the 7– 8 wt %. The nitrogen is stored in stable heterocyclic aromatic structures, such as pyrrole, pyridine and quaternary-N species, as proved by solid state NMR, XPS and FTIR, which further translates in the preservation of the N in the structure of the material when pyrolyzed.

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