

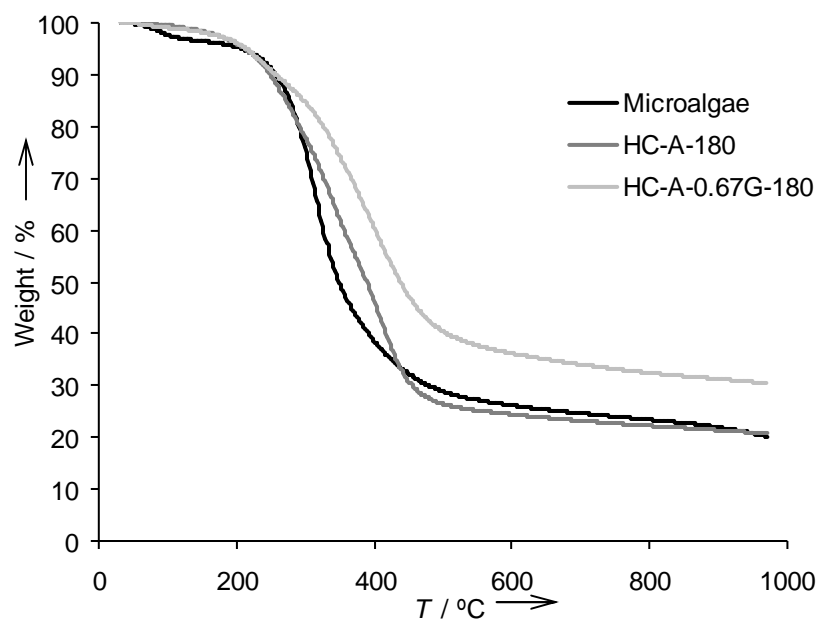
## Supporting Information

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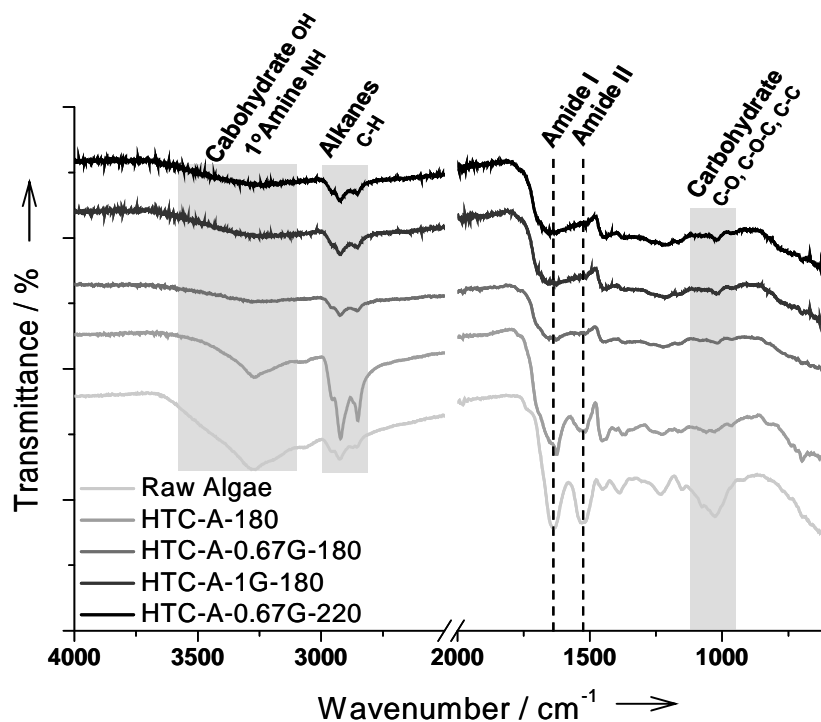
### **Renewable Nitrogen-Doped Hydrothermal Carbons Derived from Microalgae**

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**Figure S1.** TGA analysis of the microalgae-derived HTC carbons with and without glucose addition (10°C/min – 1000°C under N<sub>2</sub> atmosphere).



**Figure S2.** FTIR spectra of raw microalgae and microalgae-derived HTC carbons with and without glucose addition and at different HTC temperatures.

The characterization of the chemical structure of the N-doped materials was completed by the performance of FTIR measurements. Two intense bands in the region  $1500 - 1750 \text{ cm}^{-1}$  stand out in the raw algae spectrum. The first one, centred at ca.  $1640 \text{ cm}^{-1}$ , is the Amide I band of proteins and is ascribable to  $\text{C}=\text{O}$  stretching vibration in peptide linkages. However, the broad peak profile suggests the presence of side contributions at ca.  $1740$  and  $1620 \text{ cm}^{-1}$  corresponding to  $\text{C}=\text{O}$  stretching of ester carbonyl from lipids and  $\text{C}=\text{C}$  stretching vibration of olefinic and aromatic compounds respectively. The second intense band at ca.  $1530 \text{ cm}^{-1}$  (Amide II) arises mainly from in-plane N-H bending vibration. The broad absorption band at ca.  $1030 \text{ cm}^{-1}$  (Carbohydrate I) can be attributed to the carbohydrate fraction, in particular to the presence of C-O, C-O-C and C-C species. The higher wavenumber absorption bands at  $2845 - 2960 \text{ cm}^{-1}$  and  $3110 - 3670 \text{ cm}^{-1}$  are assigned respectively to the stretching vibrations of C-H in alkanes present in the lipid fraction, and carbohydrate O-H or primary amines N-H.<sup>1,2</sup>

The IR spectrum of HTC treated algae (HC-A-180) confirms the findings obtained from solid state NMR analysis. The Amide I and II bands lose most of their intensity indicating the depletion of the polypeptide chains. In particular, the Amide I band is now sharper and shifted to ca.  $1620 \text{ cm}^{-1}$  indicating that  $\text{C}=\text{C}$  species belonging to aromatic/olefinic structures are now relatively more abundant. In agreement with the elemental analysis and NMR measurements, the absorption bands corresponding to alkanes increase dramatically, confirming that the microalgae-derived HTC product has a strong hydrocarbon character. The carbohydrate band disappearance coupled to the reduced intensity of the  $3110 - 3670 \text{ cm}^{-1}$  peak suggests that the sugar fraction originally present in the raw algae has fully reacted. These evidences are also valid for the samples where glucose was added (i.e. HC-A-0.67G-180, HC-A-1G-180 and HC-A-0.67G-220). However, one main difference stands out: the intensity of the alkanes absorption band decreases significantly, suggesting that the glucose addition drastically reduces the hydrocarbon character of the microalgae derived HTC product presumably due to a dilution effect. Furthermore, the intensity decrease of the Amide I and II bands is even more pronounced. The  $1500 - 1750 \text{ cm}^{-1}$  range is now characterized by one broad peak indicating the heterogeneity of the species contributing to its intensity. N-containing heterocyclic aromatic structures, such as the pyrroles identified by NRM, absorb within this wavenumber range.<sup>3</sup> The incorporation of N into pyrroles and other N-containing

heterocyclic aromatic structures (pyridine, quaternary-N) has been confirmed by XPS analysis, as described in the paper. On the other hand, the spectrum of HC-A-0.67G-220 shows more defined features in the 690-820  $\text{cm}^{-1}$  region arising from C-H out of plane bending vibrations of aromatic structures,<sup>4</sup> which confirms that increasing HTC temperature leads to a higher extent of aromatization.

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