Supporting Information

© Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2012

Renewable Nitrogen-Doped Hydrothermal Carbons Derived from Microalgae

Camillo Falco,[a] Marta Sevilla,[a,b] Robin J. White,[a] Regina Rothe,[a] and Maria-Magdalena Titirici[a]

cssc_201200022_sm_miscellaneous_information.pdf
Figure S1. TGA analysis of the microalgae-derived HTC carbons with and without glucose addition (10ºC/min – 1000ºC under N₂ 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 cm\(^{-1}\) stand out in the raw algae spectrum. The first one, centred at ca. 1640 cm\(^{-1}\), is the Amide I band of proteins and is ascribable to C=O stretching vibration in peptide linkages. However, the broad peak profile suggests the presence of side contributions at ca. 1740 and 1620 cm\(^{-1}\) corresponding to C=O stretching of ester carbonyl from lipids and C=C stretching vibration of olefinic and aromatic compounds respectively. The second intense band at ca. 1530 cm\(^{-1}\) (Amide II) arises mainly from in-plane N-H bending vibration. The broad absorption band at ca. 1030 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 cm\(^{-1}\) and 3110 - 3670 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.\(^1,2\)

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 loose 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 cm\(^{-1}\) indicating that C=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 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 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.\(^3\) 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 cm\(^{-1}\) region arising from C-H out of plane bending vibrations of aromatic structures,\(^4\) which confirms that increasing HTC temperature leads to a higher extent of aromatization.