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Synchrotron based NEXAFS study on nitrogen doped hydrothermal carbon: Insights into surface functionalities and formation mechanisms

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ABSTRACT

Synchrotron-based Near-Edge X-ray Absorption Fine Structure (NEXAFS) studies have been conducted on two hydrothermally produced carbon (HTC) structures and their main surface structural features are reported. The two HTCs were produced respectively from sucrose, and sucrose with added $(NH_4)_2SO_4$, under subcritical water conditions. The NEXAFS carbon K-edge spectra reveal the presence of C═C, C–O–C (furan), C═O and C–OH functionalities on the surface of the sucrose derived HTC. For the nitrogen-doped HTC, the carbon K-edge spectra indicate an increase in C═C and C–OH functionalities, as well as the inclusion of C═N and C–N functionalities. Additionally, the nitrogen K-edge for the doped hydrothermal carbon displayed characteristic peaks for pyridinic, pyrrolic and tertiary amine nitrogen surface groups. Furthermore, a mechanistic pathway to inclusion of nitrogen atoms in the HTC-SAS structure is postulated.

1. Introduction

Heteroatom doped carbon materials have found a large number of applications in several domains, such as renewable fuels, catalysts, gas sensors, filtration media, energy storage materials and water adsorption [1–3]. Many of these doped materials have been proven to have significant advantages and enhanced properties over their pure carbon counterparts in identical applications [4,5]. For this reason, a wide range of heteroatoms have been doped into carbon materials using a number of different approaches, such as electric arc, pyrolysis, pre- and post-treatments and hydrothermal carbonization [3,5–8]. Among these techniques, hydrothermal carbonization has been rapidly gaining interest as an alternative to high temperature synthesis methods.

The hydrothermal carbonization process allows the synthesis of a range of functionalized carbon-based materials, including doped materials, at relatively lower temperatures (~200 °C); a lower energy investment compared to existing thermal processes. This process also allows the tuning of functionalities, size and morphology of the carbon product via modification of the reaction conditions (e.g., temperature, reaction time, pH, etc.) [8,9]. The most interesting point of this approach is undoubtedly the possibility of converting waste biomass into doped-carbonaceous materials [10,11]. These carbons are commonly referred to as hydrothermal carbons (HTC) or hydrochar.

The chemical structure of HTC was initially examined in various studies via X-ray photoelectron spectroscopy (XPS), Fourier transform infra-red spectroscopy (FTIR) and X-ray diffraction (XRD). These studies lead to the initial conclusion that HTC consisted of a condensed polyaromatic structure littered with various oxygen functionalities [12]. Unfortunately [13], examining the structure of HTC, like most amorphous carbons, is inherently difficult using these techniques. This is due to the typically poor response when using these analysis techniques on HTC. Additionally, XPS analysis is limited to the surface and provides no information about the bulk carbon structure of HTC.

It was for these reasons that the previous conclusion on the structure of HTC was proven to be inaccurate through the use of advanced solid state NMR techniques, which do not suffer from the same response problems [14–18]. Solid state NMR revealed that the chemical structure of HTC is vastly different from the carbon structures produced from other heat treatment techniques (e.g., pyrolysis). In HTC, the main structural motif consists of interlinked

Abbreviations: HTC, hydrothermal carbon; NEXAFS, Near Edge X-Ray Absorption Fine Structure; XPS, X-Ray photoelectron spectroscopy.

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furan rings, in contrast to the arene/graphite structures that form during other synthetic approaches. Upon the addition of nitrogen, the HTC polyfuran network becomes increasingly condensed through the incorporation of five and six membered *N*-hetero-aromatic structures, although the main furan structure is still present [18]. These structural details and the discovery of the predominate furan structural motif was only possible through solid state NMR techniques, which allowed for the study of connectivities between several functional groups contained in the structure [15,16,18].

Although solid state NMR has provided arguably most significant insights into the bulk structure of doped HTC, no structural information can be extracted about HTC surfaces, which is where the HTC growth reactions occur. Furthermore, structural insights into HTC surfaces is crucial in applications that impinge predominantly on surface properties (e.g., catalysis and charge storage processes in electrochemical capacitors) [19].

For this reason, the synchrotron-based Near Edge X-ray Adsorption Fine Structure (NEXAFS) technique constitutes a complementary and crucially important spectroscopic technique to interrogate the surface structural make up of amorphous carbons [20,21]. Critically, energy differences between the resonant X-ray excitations of core-level (1s) electrons to unoccupied orbitals or continuum levels (either π^* or σ^*) are resolvable using NEXAFS, making it possible to examine low-atomic number elements [22,23]. These excitations observed in K-edge spectra of low-atomic number elements are directly related to the chemical environment of the absorber, including its oxidation state [22–25]. As a result, previous NEXAFS studies have been able to successfully determine the bonding configuration and hybridization of several types of atoms in the near-surface region for many materials similar to HTC, including biochar, polymers and soil organic matter [22–25]. In this work, NEXAFS has been utilized for the first time to examine the carbon surface of HTC produced from sucrose that has been doped with nitrogen.

2. Experimental

2.1. Material synthesis

Two 350 mL deionized water solutions, the first containing 23.94 g of sucrose (Sigma Aldrich; 99%) and the second containing 23.94 g of sucrose plus 9.25 g of solid ammonium sulfate ($(NH_4)_2SO_4$; Sigma Aldrich; 99%) (1:2 equivalent ratios of sucrose:NH_4^+), were sealed into separate poly(tetrafluroethylene)-lined reactors for hydro-thermal synthesis at 200 °C over 4 h. After reaction, the reactors were left to cool naturally in the oven before filtering of the resultant suspension. The obtained solid black powder (HTC) was washed using acetone in a Soxhlet extractor at a cycle rate of one cycle per 30 min for 24 h. The washing procedure was used to remove any non-chemically bound residues that had dried on the HTCs surface from the liquid solution. The solid product remaining after washing was denoted here as HC-S for the sample derived from sucrose, and HC-SAS for the sample derived from sucrose doped with $(NH_4)_2SO_4$. Analysis of the liquid solution produced under hydrothermal carbonization has been reported in a previous study [8].

2.2. NEXAFS spectroscopy

2.2.1. Reference materials

Reference compounds for NEXAFS were chosen based on functional group similarities to HTCs. The compounds examined were polyvinylpyrrolidone (Sigma Aldrich; average MW 10,000; >99%), 2-picolinic acid (Sigma Aldrich; >99%), urea (Sigma Aldrich; >99%), oxalic acid (Sigma Aldrich; >99%), ammonium sulfate ($(NH_4)_2SO_4$; Sigma Aldrich; >99%), and ammonium phosphate ($(NH_4)_3PO_4$; Sigma Aldrich; >99%). Highly orientated pyrolytic graphite (HOPG) was also measured concurrently with carbon K-edge scans for energy correction. The reference materials, HC-S and HC-SAS samples were pressed into individual indium foil (3 mm × 10 mm) and mounted onto the gold plate of a Prevac drain current-only sample holder using carbon tape.

2.2.2. NEXAFS method

The NEXAFS spectroscopy measurements were performed in the ultrahigh vacuum (UHV) end station attached to the Soft X-ray Spectroscopy Beamline at the Australian Synchrotron [26]. Nearly perfectly linearly polarized photons ($P \approx 1$) from an APPLE II elliptical polarized undulator X-ray source with high spectral resolution ($E/^\circ E \leq 104$) were focused to a beam size of ~100 μm^2 onto samples within an UHV chamber. Photon flux at the carbon edge was ~5×10^{10} photons/s per 200 mA of ring current. The UHV chamber, which has a base pressure lower than 2×10^{-10} mbar, was equipped with a channeltron detector that measured X-ray adsorption via partial electron yield at the magic angle of 54.7° to obtain the optimum response. This was measured between the surface plane of the sample and the direction vector of the incident linearly polarized light beam.

The recorded signal was normalized to the incident photon flux using the stable monitor method, in which the sample signal is compared consecutively to clean reference samples and the time variation in flux is measured via a gold mesh [27]. The normalized spectra were scaled by setting the pre-edge signal (280 eV for carbon and 380 eV for nitrogen) to zero and the post edge (320 eV for carbon, 415 eV for nitrogen) to 1. The photon energy was calibrated by measuring the NEXAFS spectrum of HOPG simultaneously to the sample signal and normalizing to the excitation peak at 291.65 eV.

To allow for the effects of synchrotron radiation beam damage on the HTCs, a sequence of scans was initially measured on the same spot until significant changes were observed in the carbon and nitrogen K-edge spectra. The scan time was subsequently restricted to an appropriate interval below this (~0.5 s per 0.1 eV step) in which beam damage during a single scan was negligible.

2.2.3. NEXAFS analysis and peak fitting

Post analysis treatment of the data and peak fitting was performed using the Athena package in Demeter Version 0.9.24 [28]. The location of the peaks for both the carbon K-edge and nitrogen K-edge NEXAFS spectra for HC-S and HC-SAS was based on the analysis of reference samples with similar functionalities that were analyzed concurrently, previous work on HC-S and HC-SAS [8,14] and literature sources that are referenced for each peak position throughout the results. The carbon K-edge of both the HC-S and HC-SAS spectra were deconvoluted using the arctangent function for the ionization step at 290.0 eV and a series of nine Gaussian peaks representing the main $C1s \rightarrow \pi^*$/$C1s \rightarrow \sigma^*$ transitions at 284.8, 285.8, 286.5, 287.3, 288.2, 289.3, 291.9, 296.9 and 300.6 eV and 284.8, 285.9, 286.6, 287.5, 288.2, 289.4, 291.4, 296.0 and 300.6 eV, respectively. The nitrogen K-edge spectra for HC-SAS was deconvoluted using two arctangent functions at 403.9 and 406.4 eV, and a series of eight Gaussian peaks at 399.3, 400.5, 401.4, 402.3, 403.3, 405.7, 408.4 and 411.8 eV. The full width half maximum (FWHM) for the fitted Gaussian peaks before the ionization step on the carbon (290.6 eV) and nitrogen (406.2 eV) K-edges was constrained to ~0.5 eV, while the FWHM of peaks after this step were not constrained since peaks after the ionization step tend to be very broad and overlap [17,26,27]. Through use of peak fitting, a number of addition peaks are identified in the spectra of HC-S and HC-SAS.