

Induction of Thermal and Fluorescence effects on Hydrothermal Char during Raman Spectroscopy

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Abstract

We have determined the change in temperature that our carbon samples undergo during Raman spectroscopy and developed a technique to counteract them. By producing Potassium Bromide pellets of our char samples we increase their thermal conductivity. We have determined that the characteristic D and G band of carbonaceous materials is an incorrect interpretation for hydrothermal chars, and is resultant from these thermal changes in the material. By applying our own fitting method to the new Raman spectra obtained using KBr pellets we characterize hydrothermal chars produced at reaction times ranging from 4 hours to 24 hours based on furan/arene sub-groups.

Keywords

Carbon, Char, Raman

Introduction

Hydrothermal chars(hydrochars)[1] are carbonaceous solids derived from the thermal degradation of biomass under liquid water conditions[2]. The resulting material is oxygen rich, aromatic, and possesses carboxylic acid sites [3, 4]. These materials have been linked to a variety of applications, such as gas storage[5], metal adsorption[6] and soil amendment[7]. Hydrothermal carbonization is advantageous as a one-step method for producing materials with range of properties [8, 9], chemistry [10, 11] and potential applications [12, 13].

Raman Spectroscopy of hydrochars

NMR and IR spectra are two common methods for analyzing carbonaceous solids [6, 14-16]. NMR analysis of carbonaceous solids has been used to identify carbon types among aliphatic, aromatic and carbonyl categories. It also allows for nuclei based correlations and other powerful tools for assigning structures. In a previous work, we developed a fitting method, which can be used to elucidate the structure of hydrothermal char using Raman spectroscopy [17].

Table 1 is a summary of the peak locations of vibrational modes present in CHO hydrochars based on our DFT study. These methods allow for characterization of the furan versus arene content of char on a bulk basis. In this work we will explore the effects of Raman laser power on the hydrochar, how these effects can be mitigated and examine the Raman spectra of hydrochar using these modified methods.

Band	Range (cm ⁻¹)
Carbonyl band	1650-1750
G _R band	1600-1630
G band	1570-1610
G _L band	1510-1560
Aliphatic mode	1450-1470
Kekulé/furan band	1405-1465
Methyl band	1385-1405
D band	1340-1380
Ether	1020-1150
Breathing modeR	1190-1270
C-H wagging on rings	1140-1190
Breathing model	990-1070

In this work, we show that the Raman spectra of glucose char samples from the same batch produce imply different structures depending on the power of the laser. Figure 1 shows the Raman spectra of two hydrochar samples that have been conducted at 0.13mW and 1.3mW. The blue curve represents the spectrum collected at 1.3mW, at this power we see a traditional hydrochar spectra as previously reported in previous literature [18, 19]. The red curve represents the spectrum collected at 0.13mW. The spectra shows 3 relatively sharp peaks at 1290 cm⁻¹, 1450 cm⁻¹ and 1575 cm⁻¹ respectively. Based on the fitting of Brown et al the peak at 1575cm⁻¹ can be attributed to 2 bands, a 'G band' at 1575cm⁻¹ and band 1544cm⁻¹ attributed to asymmetric breathing modes. The D/G ratio of this Raman spectra is 0.505, the Kekulé/D ratio is 0.588 and the Kekulé/G ratio is 0.298. These factors imply a molecule that possesses a combination of arenes and furans that are mostly unfused. That is, individual aromatics linked by aliphatic groups.

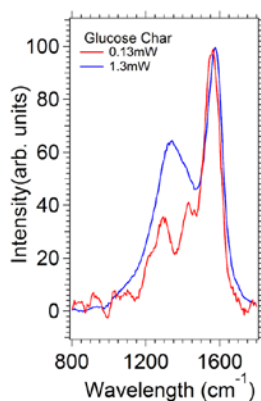


Figure 1: Raman spectra of glucose hydrochar 180 °C 24 hour reaction time. 532nm wavelength.

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