

Carbon Nanoparticles Prepared from Household Waste

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The presented paper is concerning the influence of the coffee cake carbonisation condition on the carbon structure and surface chemical composition. For these the results of some additional measurements, i.e. thermogravimetry, FTIR, etc. are reported, to expose the type of carbon surface groups created by carbonisation.

Keywords: Coffee, Carbonization.

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1. INTRODUCTION

Carbon nanomaterials [1] are of significant interest due to their unique properties at the nanoscale and therefore gained much focus on their production procedure and reduction of the price production. The carbonaceous nanoparticles [2], like nanotubes, fullerenes, graphenes, etc have found a wide variety of application that includes: pharmacy, biology, environmental and material science etc. Such nanoparticles are met high demands. There has been considerable interest in carbons made through various carbonization methods [3], mainly because they are easy to prepare.

Herein the effectiveness of granular carbon preparation from household waste (coffee cake) was investigated.

2. MATERIALS AND METHOD

Colombian blend coffee roasted at 180-190 °C for 10 min [4] purchased from Starbucks ® was milled in household coffee grinder and used for espresso coffee drink preparation. Prior carbonization the spent coffee ground was washed with DI water and dried in oven for 8 h at 80 °C.

The rapid carbonization of the Colombian blend roasted coffee ground was performed in a bench-top muffler in air. Six samples were prepared with different conditions as follows. The dried spent coffee was divided into portions 2 g each. For each run, 2 g of coffee cake was placed in a ceramic evaporation bowl and heated in muffler at heating rate of 10°C/min for 200, 300, 350, 400 and 500 °C correspondingly when heating was stopped and samples were slowly cooled outside of the muffler. The other portion of coffee residues was left intact.

Fourier transmission infrared (FTIR) spectra were recorded for samples stirred with dried KBr using a Thermo Nicolet FTIR spectrometer.

Thermogravimetric experiments were carried out by a MOM Derivatograph, in the temperature range of 25-950 °C at heating rate 10 °C/min at air in order to determine the pyrolysis behaviour of spent coffee. Thermal transitions were monitored using a Mettler Toledo,

DSC-1. Samples were sealed in alumina pans and run from -20 to 550 °C at scan rates of 10 °C min⁻¹. The changes in enthalpy were calculated using Mettler Toledo Stare® software. TEM and XRD experiments were conducted using JEOL transmission electron microscope operating at 200 kV and DRON-2 diffractometer using CuKα radiation correspondingly.

3. RESULTS AND DISCUSSION

The composition of roast coffee is highly complex, but carbohydrates are the bulk constituent of roast coffee, largely present as complex polysaccharides [5]. A full assignment of the FTIR spectra (not shown here) of coffee cake is a challenging problem and will not be attempted in this work. However, carbohydrates generally exhibits a "fingerprint" region and are generate the majority of bands in the roast coffee spectrum. Other major compounds includes crude lipids [5]. Lipids are generally exhibit a characteristic band of the carbonyl (C = O) vibrations centred at ~ 1744 cm⁻¹ and ~ 1150 cm⁻¹ (1747 and 1180 cm⁻¹ in this work) two sharp bands that can be viewed in the 3000-2800 cm⁻¹ range at 2924 and 2854 cm⁻¹ can be correlated with stretching vibrations of C-H bond in methyl and methylene groups correspondingly. A band at 1662 cm⁻¹ appears in the spectra obtained by KBr transmission also associated with caffeine absorption [6]. The bands at 1338, 1180, and 1040 cm⁻¹ could be associated to chlorogenic acids [7]. Carbohydrates are shown to exhibit several absorption bands in the wavenumber range of 1400-900 cm⁻¹ [5], so its expected that this class contributes to the several bands in this region.

Carbonisation at 500 °C leads to reduction of bands in the 3000-2800 cm⁻¹ range and a new band appears at 3656 cm⁻¹ which attributed to the presence of oxygenated functional groups (O-H stretching vibrations in carboxyl groups). Significant changes for the oxygen containing functional groups can also be observed in the 1800-1100 cm⁻¹ region C=O structures tend to decrease with carbonisation. The band located at ~ 1600 cm⁻¹ has been often observed for carbonaceous materials and the presence of band located around

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1558 cm^{-1} is result of carbonyls. The C-O-R structures in $\sim 1100 \text{ cm}^{-1}$ range are modified during carbonisation.

Thermal properties of spent coffee were evaluated for sample heated for 200 °C (Fig. 1) Considering the TGA graph (Fig. 1a) it is noticeable that the first thermal degradation step is occurs in range of 70-185 °C (7 wt %) with maximum at 101 °C which may correspond to the moisture content in the sample; in DSC graph (Fig. 1b) moisture evaporation is observed with maximum at 80 °C and the changes in enthalpy 394.9 (given in mJ/mg). Also the experiment shown a fast decomposition between 250 and 400 °C; although the TGA curves of spent coffee evolve monotonically from 210 to 275 °C as if the weight loss were gradual without any sudden transformation, at the same time the DSC spectra (Fig 1b) show an inflexion point at 239 °C (290.4 mJ/mg) that must be associated with a sudden change of state without weight loss.

The final region of the TGA curve allows to determine the percentage of residue; the sample of spent coffee is converted in residue reducing to a value of 2.30 % wt of the original weight at 700 °C. In DTA graph (of sample spent coffee heated for 200 °C a small shoulder is noticeable at 140 °C which corresponds to phase transition of the caffeine [8] and in DSC graph the phase transition of caffeine at 154 °C [9], Moreover it is known that at 141°C the α -polymorph of caffeine transforms into a β -crystal phase and remains in this phase until the melting process at 239 °C [10]. Thereby the caffeine participates in the reactions and transformations that take part in the carbonisation process. During the carbonization of a roasted coffee ground the carbon structures are generated. The slight shrinkage of the carbonizing particles was observed with TEM (Fig. 2).

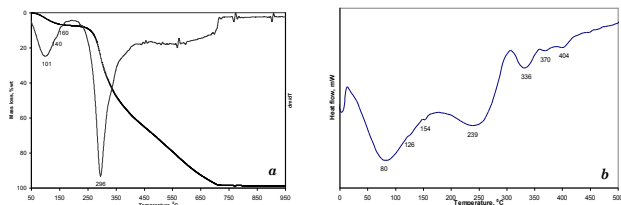


Fig. 1 – TGA-DTA thermogram (a) and DSC graph (b) of coffee cake heated for 200 °C

An untreated coffee ground particles mean diameter was $\sim 450\text{-}500 \text{ nm}$ though particles of $\sim 300 \text{ nm}$ were observed after heating at 300 °C. TEM photographs are shown of the pristine (Fig. 1a) and 400 °C heated coffee

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ground particles (Fig. 1b). TEM revealed the presence of whiskers of tubular structure with a diameter about $\sim 4.5 \text{ nm}$ and their length extending up to 100 nm (Fig. 1b arrows).

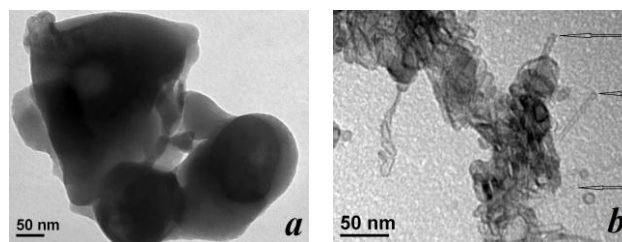


Fig. 2 – TEM images of pristine (a) and 400 C heat-treated coffee ground (b)

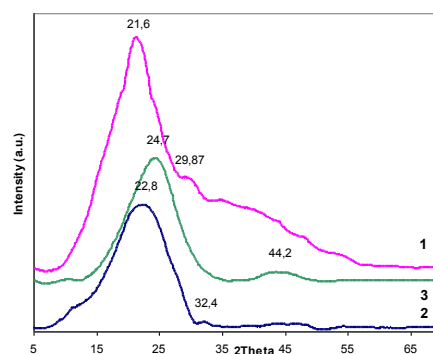


Fig. 3 – XRD patterns of pristine (1), 350 (2) and 500 C (3) heat-treated coffee ground (b)

Peak around $2\theta = 20\text{-}25^\circ$ in XRD corresponds to (002) reflection of carbon due to the stacking structure of aromatic layers [11]. Broadening of the 002 peak can be interpreted in terms of small dimensions of crystallites perpendicular to aromatic layers. The presence of peaks appearing at $2\theta = 26.39^\circ$ and 44.60° in spectra of sample carbonized at 500 °C (Fig. 3, 3) displays the presence of graphitic carbon nanofibres.

4. CONCLUSIONS

Obtained results reveal a potentially useful process for the facile production of carbon nanomaterials from spent coffee ground. Temperature during synthesis reaction was found to strongly influence the particle size and crystalline structure. The type of surface oxides in regards to FTIR analysis are similar to that which can be found for commercial carbons, i.e. carboxylic groups, phenols (and/or ethers) and lactones.

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