Tea waste extracts for carbonaceous material, possible graphite candidacy? Let's explore

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Abstract. The synthesis and application of biomass-based materials has drawn more attention from researchers due to the host of biomass feedstocks available for conversion into useful materials, sustainability, and cost-effectiveness. Graphite, a non-renewable resource, is the most popular material used in lithium-ion batteries (LIB) as an anode material. Current LIB requires critical raw materials, efficient manufacturing, recycling processes and end of life management. To address the later factors, use of biodegradable materials such as biomass to produce useful products is of interest. Biomass conversion into useful materials is one of the contributing factors towards green energy techniques and achieving the set out sustainable development goals. The current work focuses on converting biomass waste as tea extracts into synthetic graphite and analyse it for graphite-like material and potential application in LIB's. Heat is used to process tea waste into desired carbonaceous products. The colour and textural properties of the synthesized tea based carbonaceous material as compared to the synthetic graphite suggests a notably significant degree of graphitization and a high carbon content, which is ideal for candidacy in sustainable energy storage enhancements. Liquid suspension indicates insoluble behaviour normally expected for graphite. XRD spectra indicates peak at $2\theta = 26.5°$ corresponding to the phase (002) dominant for graphite. SEM analysis indicates a layered structure like graphite.

1 Introduction

Carbonaceous materials are used in many applications such as energy storage and conversion, filtration systems, fuel cells, supercapacitors, bioimaging, tissue engineering etc. With the many applications, conventional and sustainable ways of obtaining carbon-based materials is required since they have host of exceptional features such as high electrical conductivity, thermal stability, mechanical strength, high surface area and more, making them versatile for applications in many fields. Nature provides a huge list of environmentally friendly, easy disposable and diverse materials that can be transformed into excellent carbonaceous materials with relevant properties for selected applications. Carbonaceous materials are produced from plant and animal residues and prepared under low oxygen environment at high temperatures, producing black powdered materials having physical and chemical properties with high carbon content, high surface area and low nutrient content resulting in carbon materials [1]. They are considered an attractive choice for at least two reasons: the biomass-derived carbons provide an alternative for by-product and waste management, and the naturally available raw materials are economical for materials engineering. Biomass-based carbon is explored in various applications as a candidate for enhancing the feasibility of smart materials, supercapacitor electrode material and widened application in electrochemical energy storage, solar-light photocatalytic hydrogen generation and as high-quality anode material in LIBs, among others [2]. Numerous biomass feedstocks such as sawdust, cornstalk, coconut shell, wood and bamboo were used to produce high quality graphitic carbon for a broader range of applications [3]. Green tea waste was tried for a supercapacitor electrode by Sanker *et al.* and they obtained nanoflakes with large pore volume and higher surface area leading to potentially higher performance electrode material [4].

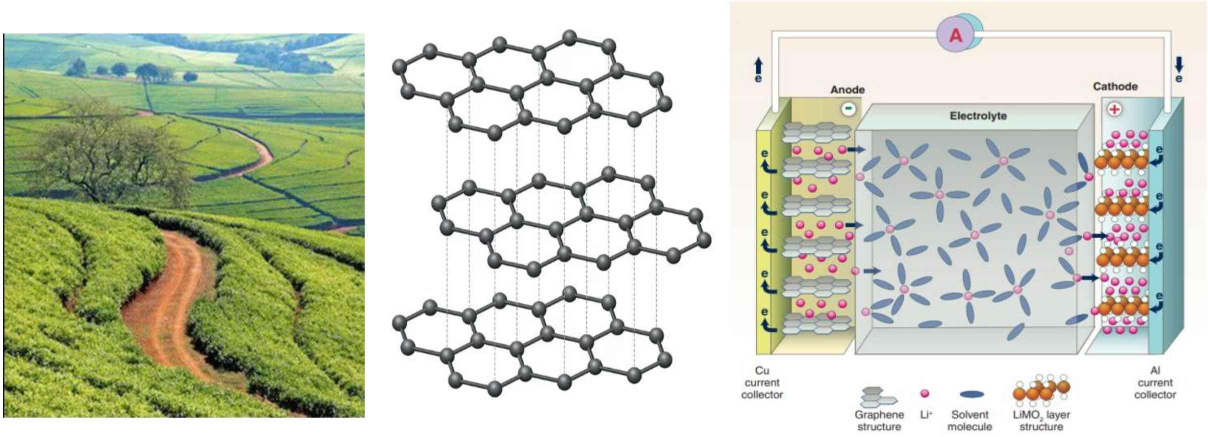

Figure 1: *(a)* Tea plantation, *(b)* graphite structure and *(c)* its application is storage device [5].

Figure 1 (a) shows a large area of tea plantation indicating the large quantity of tea waste that can be produced. Graphite is made up of layers of carbon atoms that are covalently bonded to form hexagonal rings as shown in Figure 1 (b). It is used as an anode material in LIB. Lithium ions flow form the cathode through the semipermeable electrolyte and build up on the anode while electrons flow from the external circuit during charging and vice versa during discharging as depicted in Figure 1 (c). Graphite is dimensionally stable, allowing lithium-ion intercalation without significant damage from swelling, which makes it the dominant anode material in LIBs. In the present work, tea extracts were used as eco-friendly, cost-effective, and commercially viable alternative for the synthesis of activated carbon, due to its carbonaceous similarities to natural graphite. Due to the level of carbonisation, a chemical process involving KOH as an activating agent has been adopted to synthesize the activated carbon. These results are compared with synthetic graphite (SG) as our base material.

2 Methodology

2.1 Materials

Tea extracts from a local plantation were purchased from a local supermarket for convenient. Potassium hydroxide (KOH) was obtained from Sigma-Aldrich. Carbonisation was done through the Muffle Furnace, Model SXC. Magnetic stirrer (FHM instruments, Model SRT1). Aqueous solutions used throughout all the experiments were prepared using deionized water. To characterize the sample, Bruker FTIR spectrometer was used to investigate the presence of the functional groups in the activated tea waste graphitic material (TWGM) sample. Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis were obtained through Zeiss Gemini Sigma 500 VP.

2.2 Synthesis of activated TWGM

Figure 2 shows the experimental setup for the synthesis of TWGM using tea extracts, through electrical furnace-assisted carbonization at very low oxygen levels as described by Sankar *et al.* [4]. KOH activation was used to enhance carbonisation and water treatment. Briefly, A sample of 19 g of tea waste (TW) was transferred into a crucible for thermal treatment. The carbonization temperature ($500^{\circ}\mathrm{C}$) was achieved at a heating rate of $10^{\circ}\mathrm{C}/min$ and maintained for 60 minutes. Thereafter, the carbonized sample was left to cool down to room temperature and then mixed with KOH at a molar ratio of $\mathrm{TW}/\mathrm{KOH} = 1/4$. The activation of TW carbon product proceeded with use of the Muffle Furnace, by thermally treating the mixture at $600^{\circ}\mathrm{C}$, this temperature was also achieved and maintained for 120 minutes through the same heating rate. Thereafter, the KOH-activated TWGM product was ground with a pestle in a mortar. Using a magnetic stirrer at speed of 200 r/min without heating, the fine activated-TWGM powder was mixed with deionized water for 6 hrs. Here, the water treatment process was done with an intention of enhancing the quality and purity of the graphitized activated TW. Schematic illustration with images of the synthesis procedure from TW to TWBGM is summarised in Figure 2.

Figure 2: Schematic illustration of the synthesis method.

3 Results and discussion

3.1 *Physical observations*

Figure 3 (a) shows a pictorial view of commercially available synthetic graphite (SG) while (b) shows current TWGM, (c) and (d) shows TWGM dissolved in deionised water for 0 and 24 hours respectively. SG is in dissolvable in certain fluids such as ethanol and deionised water, our TWGM displays the same characteristics as shown in Figure 3 (d).

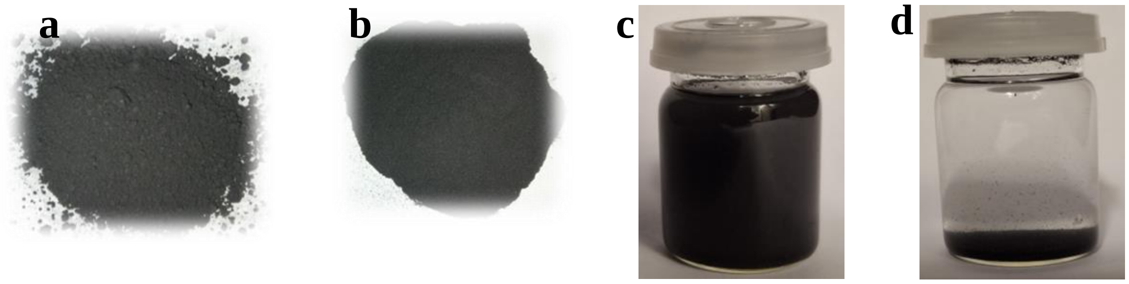

Figure 3: *(a)* SG powder *(b)* produced TWGM *(c)* TWGM mixed with deionised water *(d)* TWGM after 24 hrs in deionized water.

The black colours of SG and TWGM suggests similar morphologies and microstructural properties which we intend to confirm and compare using material measurements techniques through SEM, FTIR and XRD analysis. The textural properties of both the SG and TWGM had very similar characteristics i.e., soft, and refined feel delicate at hand contact. The SG tended to form clusters as evident in figure 3 with the appearance of solid granule-like formations. The compact appearance of TWGM powder in Figure 3 mainly attributes to the grinding process done posterior to KOH activation and water treatment, resulting in a greater degree of refinement. Against these observations, this work intends to demonstrate that biomass as tea waste could have ideal properties necessary for enhancement of various technological advancements i.e., sustainable energy storage enhancement.

3.2 SEM and EDX analysis

Graphite is a layered structure with interconnected flakes. Our TWGM displays the stacking of layers giving layered structure normally observed for graphite. The corresponding EDX spectra shows a significant presence of carbon which is also desirable for graphite-based materials. Strong presence of potassium is observed from the EDX spectra.

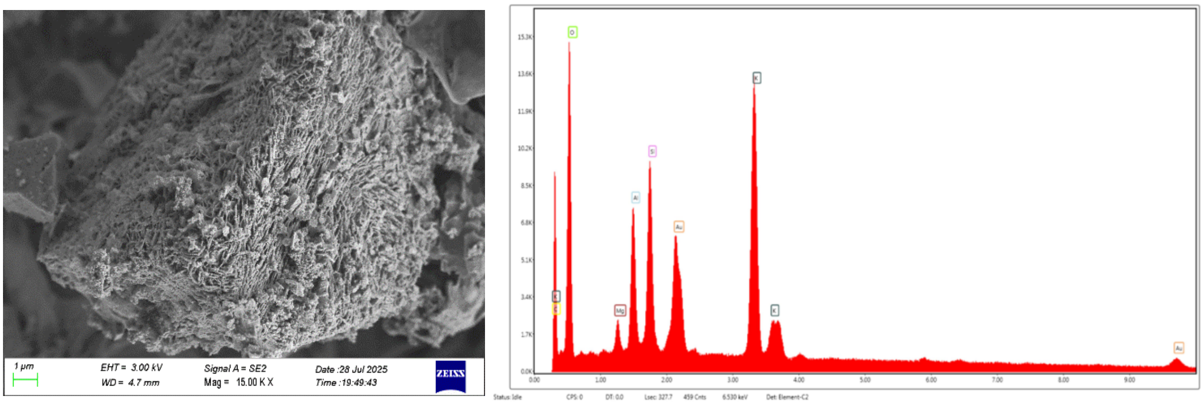

Figure 4: SEM and EDX spectra for TWGM.

3.3 FTIR analyses

The surface chemical properties of TWGM as analysed by FTIR and are shown in Figure 5. The faint appearance of an absorption band at 3 627.15 cm^{-1} owes to the $O-H$ stretching vibration of the hydroxy functional group [3]. The band at 2 658.15 cm^{-1} corresponds to the $O-H$ of the carboxylic acids. The band at 2 352.15 cm^{-1} corresponds to the possible presence of the $C=C$ stretching. The bands at 2 158.35 cm^{-1}, 2 029.82 cm^{-1}, 1 976.78cm^{-1} corresponds to the presence of $X=C=Y$ (Allenes, ketenes, isocynates, isothiocynates); with 2 158.35 cm^{-1} attributed to $C=C$ of the Alkyne. The peak at 1 699.34 cm^{-1} corresponds to $C=O$ amide group, and 1 389.26 cm^{-1} corresponds to the possible presence of the Nitro ($R-NO_2$) group, but according to literature, it is more likely to be the C-N Amine group [8]. The band at 975.13 cm^{-1} corresponds to a $C-H$ Alkene (Out-of-plane bend). The band at 795.61 cm^{-1} corresponds to $C-H$ Aromatic (Out-of-plane bend). The average intensities of the peaks show very small traces of oxygen and nitrogen containing functional groups, which suggests successful elimination of volatile compounds during heat treatment.

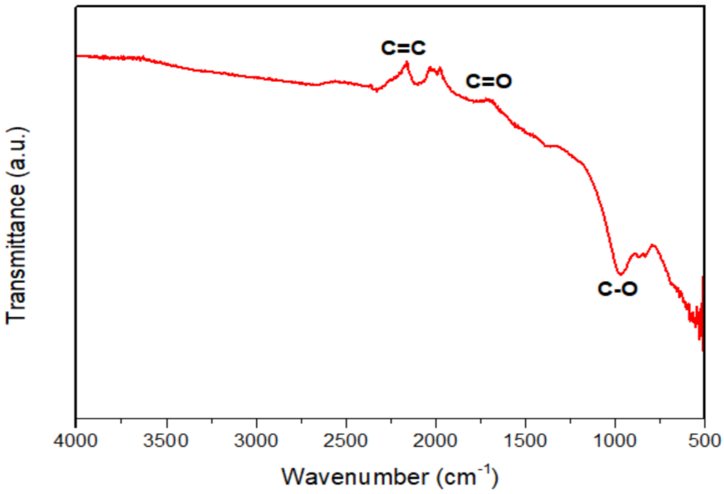

Figure 5: FTIR spectra for TWGM

3.4 XRD analyses

As shown in Figure 6, a peak is observed in the region between $2\theta = 25.00°$ and $27.00°$ respectively corresponding to the desired dominant peak for a graphite material. A strong XRD peak was observed by Ain *et al.* at $2\theta = 26.5°$ and a light peak at $2\theta = 54.5°$ specific to the (002) and (004) planes with d-spacing of 3.5 Å and 1.9 Å respectively [6]. The enlarged peak of Figure 7 shows a potentially smaller peak at the region corresponding to the (002) plane.

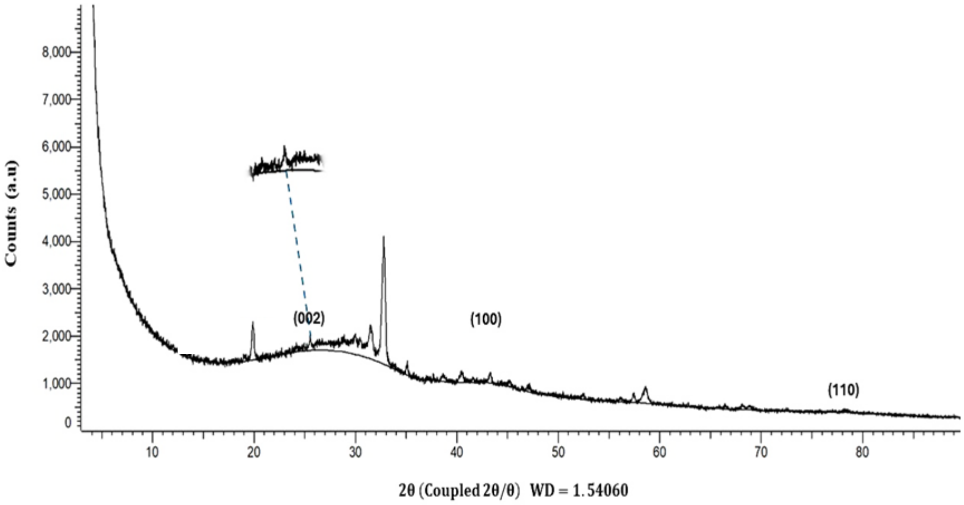

Figure 6: FTIR spectra for TWGM

Table 1 compares the feedstock mass to obtained carbonaceous product; this indicates that more biomass feedstock is required to obtain sufficient product. The mass loos percentage was calculated by equation 1 below.

$$x = \frac{w_0 - w_t}{w_0 - w_f} \times 100\ \% \qquad (1)$$

where w_0 is the initial mass, w_f is the final mass and w_f is the mass over time [7].

Biomass	Pre-carbonisation mass (g)	Mass over time (g)	Post-carbonisation mass (g)	Mass Percentage loss (%)
Tea extract	19.00	8.83	5.10	73.16

Table 1: Biomass feedstock to product mass comparisons

73.16 % of initial mass is lost during the carbonisation process. Calcination at very high temperatures usually removes liquids and other impurities in the samples resulting in reduced mass. The mass measurements and weight comparison of the TWGM throughout the experiment, from pre-carbonization until the final product was obtained, revealed that the TWGM was 26.84 % of the original mass without the use of a catalyst, which implied 73.16 % elimination of volatile traces.

4 Conclusion

The TWGM was successfully synthesized using tea waste as a high carbon content biomass resource. The color and textural properties of TWGM as compared to the SG suggests a notably significant degree of graphitization. The quantitative results showed that tea waste has a high carbon content, which is ideal for candidacy in sustainable energy storage enhancements. XRD reveals a potential peak corresponding to the (002) plane dominant for SG.

5 Acknowledgements

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