

Article

## Graphene Oxide Synthesis from Agro Waste

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**Abstract:** A new method of graphene oxide (GO) synthesis via single-step reforming of sugarcane bagasse agricultural waste by oxidation under muffled atmosphere conditions is reported. The strong and sharp X-ray diffraction peak at  $2\theta = 11.6^\circ$  corresponds to an interlayer distance of 0.788 nm ( $d_{002}$ ) for the AB stacked GOs. High-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) confirm the formation of the GO layer structure and the hexagonal framework. This is a promising method for fast and effective synthesis of GO from sugarcane bagasse intended for a variety of energy and environmental applications.

**Keywords:** graphene oxide (GO); natural precursors; value-added reforming

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### 1. Introduction

Graphene and related materials have attracted a great deal of recent interest owing to their unique structure and physical, chemical, thermal, and other properties [1]. Graphene's two-dimensional (2D)

hexagonal lattice consists of a network of  $sp^2$ -bonded carbon atoms and represents the “thinnest material” which is stable in its free form [2]. Excellent electronic properties [3], thermal conductivity [4], and high surface area, combined with unusual mechanical properties and good dispersion performance, make graphene a promising candidate for structural modification of composite materials and several other applications [5–8].

Graphene oxide (GO) has also attracted major interdisciplinary attention because of the broad range of envisaged applications across several scientific and engineering fields including physics, chemistry, biology, and medicine [9–13]. The original method to synthesize GO is based on the addition of potassium chlorate to a slurry of graphite in fuming nitric acid [14]. This synthetic protocol can be improved by using concentrated sulfuric acid as well as fuming nitric acid and adding the chlorate in multiple aliquots over the course of the reaction [15]. In the commonly used Hummers’ method [16], graphite is oxidized throughout treatment of  $KMnO_4$  and  $NaNO_3$  in concentrated  $H_2SO_4$  acid.

All these procedures involve the generation of  $NO_2$ ,  $N_2O_4$ , and  $ClO_2$ , toxic gases which are also explosive. In the past few years, various techniques such as mechanical exfoliation techniques, chemical vapor deposition (CVD) techniques and other chemical techniques have been developed for the synthesis of graphene and graphene oxide materials. However, many of these techniques are highly sophisticated and expensive [17]. Most of the commercially available GO samples were synthesized by Hummers' method or a modified version of it. The cost of the commercially available graphene oxide per gram is approximately \$200. In comparison with the Hummers' method, our method is more environment friendly as it avoids toxic gas emission during synthesis. The synthesis technique reported here is a quite efficient asset demonstrating a new procedure for the production of graphene oxide from agro waste in simple steps. This simple and low-cost process could lead to new opportunities for cost-effective production of GO [18,19].

Here we report on the synthesis of graphene oxide by directly oxidizing sugarcane bagasse under muffled atmosphere. The GO produced by this method is called SOMA-GO (sugarcane oxidized under muffled atmosphere for graphene oxide). Furthermore, the structural characteristics of the obtained product are confirmed by X-ray diffraction, Fourier transmission infrared spectroscopy, field emission scanning electron microscopy, high-resolution transmission electron microscopy, and Raman spectroscopy.

## 2. Experimental Section

### 2.1. Synthesis of GO from Agro Waste

Sugarcane bagasse is a type of agricultural waste (agro waste). After juice was extracted, the remaining fiber was taken. The fiber was crushed and ground well in order to produce powder. This crushing and separating process was repeated several times to obtain fine powder. About 0.5 g of ground sugarcane bagasse powder mixed with 0.1 g of ferrocene was placed in a crucible and put directly into a muffle furnace at 300 °C for 10 min under atmospheric conditions. Next, the as-produced black solid was collected at room temperature. The black solid product was subjected to further analysis (Scheme 1).



**Scheme 1.** Schematic representation of graphene oxide synthesis from agro waste.

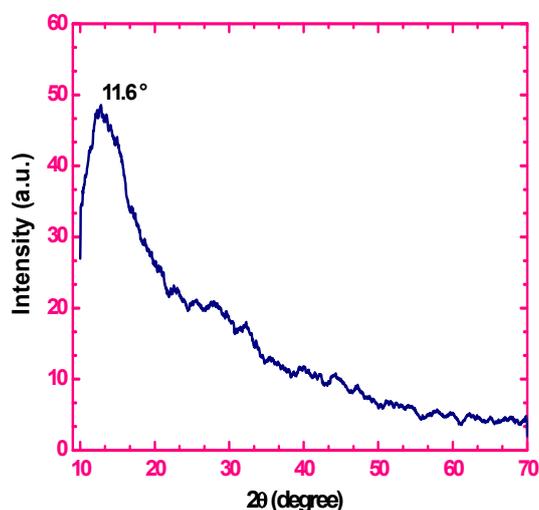
## 2.2. Characterization of GO

The X-ray diffraction (XRD) pattern was obtained using a Bruker D8 Advance X-ray diffractometer (Berlin, Germany). This device is equipped with a Ni filter, and generates monochromated Cu-K $\alpha$  radiation ( $\lambda = 0.154$  nm) operated at 40 kV accelerating voltage and 30 mA current. The samples were scanned in step mode with a  $2^\circ \text{ min}^{-1}$  scan rate. Fourier transform infrared spectroscopy (FT-IR), Avatar 370, Thermo Nicolet (Berlin, Germany) was carried out to study the bonding configuration in the synthesized graphene oxide. High resolution transmission electron microscopy (HRTEM) was performed using a JEOL JEM-3000F microscope (Tokyo, Japan) operating at 300 kV to study the microstructure of the GO structures. Field emission scanning electron microscopy was carried out using a JEOL JSM 7800F revealed the morphological features of the GO structure.

## 3. Results and Discussion

### 3.1. X-Ray Diffraction Measurements

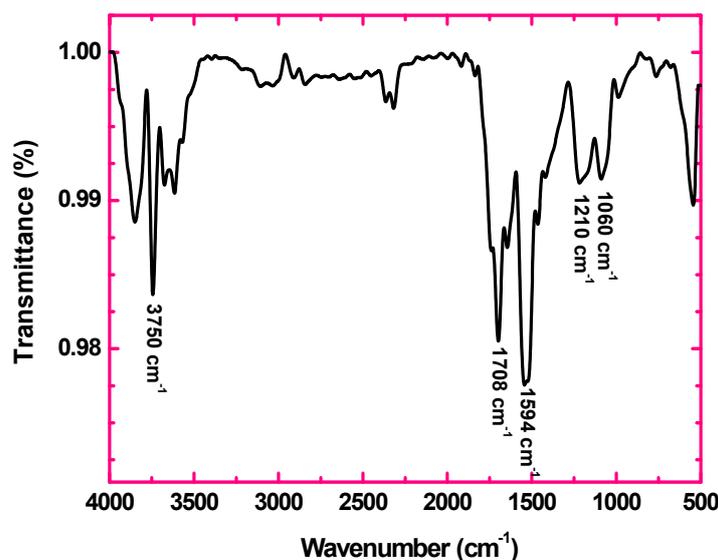
The structural and chemical analysis of sugarcane bagasse is clearly described by previous investigators [20–22]. In this study, we have presented the XRD pattern of the GO which is shown in Figure 1. The peak at  $2\theta = 11.6^\circ$  indicates that the agricultural sugarcane bagasse is fully oxidized into graphene oxide with the interlayer distance of 0.79 nm. The  $2\theta$  peaks of the GO obtained by the single-step oxidation of sugarcane bagasse are consistent with the results of previous studies [23,24]. This XRD pattern can be attributed to well graphitized two-dimensional structures made of GO sheets.



**Figure 1.** X-ray diffraction (XRD) pattern of graphene oxide.

### 3.2. FT-IR Spectroscopy

The FT-IR spectrum of GO shown in Figure 2 confirms the introduction of oxygen containing groups such as functional hydroxyl, epoxy and carboxylic groups upon oxidation of sugarcane bagasse. The strong band at  $1708\text{ cm}^{-1}$  is attributed to stretching vibration modes of C=O in carboxylic acid and carbonyl groups. The peak at  $1594\text{ cm}^{-1}$  is assigned to the skeletal vibrations of un-oxidized graphitic domains. The band at  $1060\text{ cm}^{-1}$  is assigned to C–O (epoxy) groups while the band at  $1210\text{ cm}^{-1}$  is usually attributed to C–OH stretching vibrations [25–27]. The strong peak around  $3500\text{--}4000\text{ cm}^{-1}$  can be attributed to the O–H stretching vibrations of the C–OH groups and water [27].

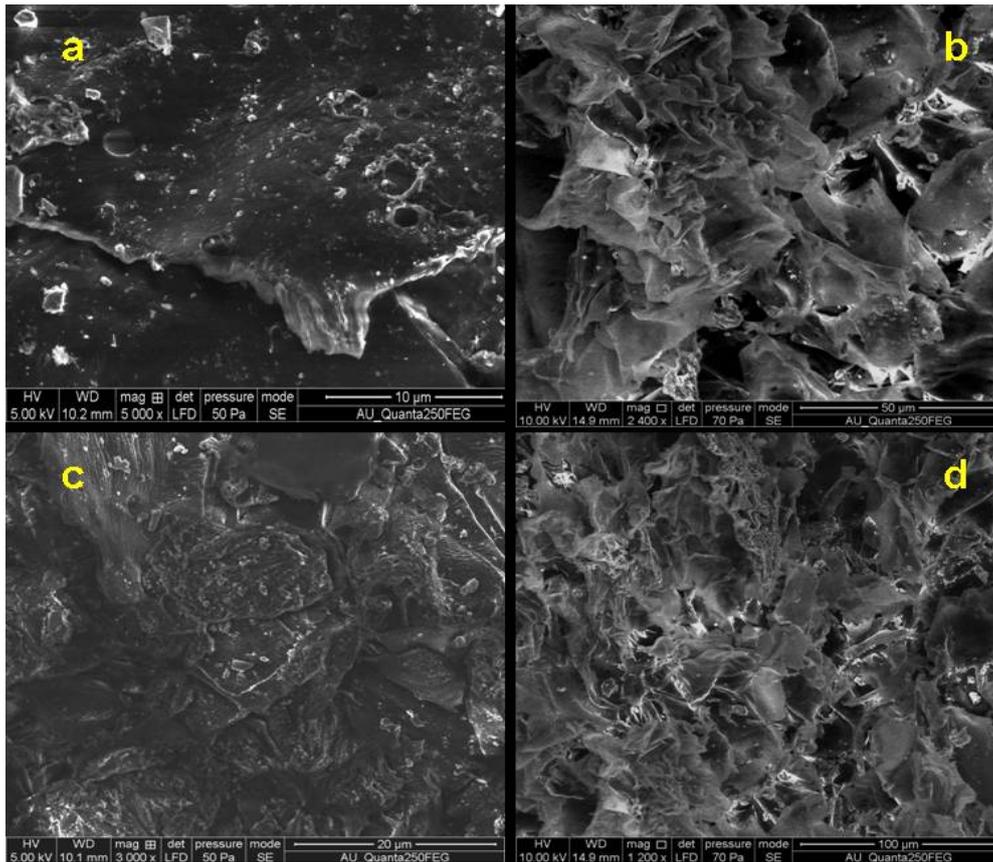


**Figure 2.** Fourier transform infrared spectroscopy (FT-IR) spectrum of graphene oxide.

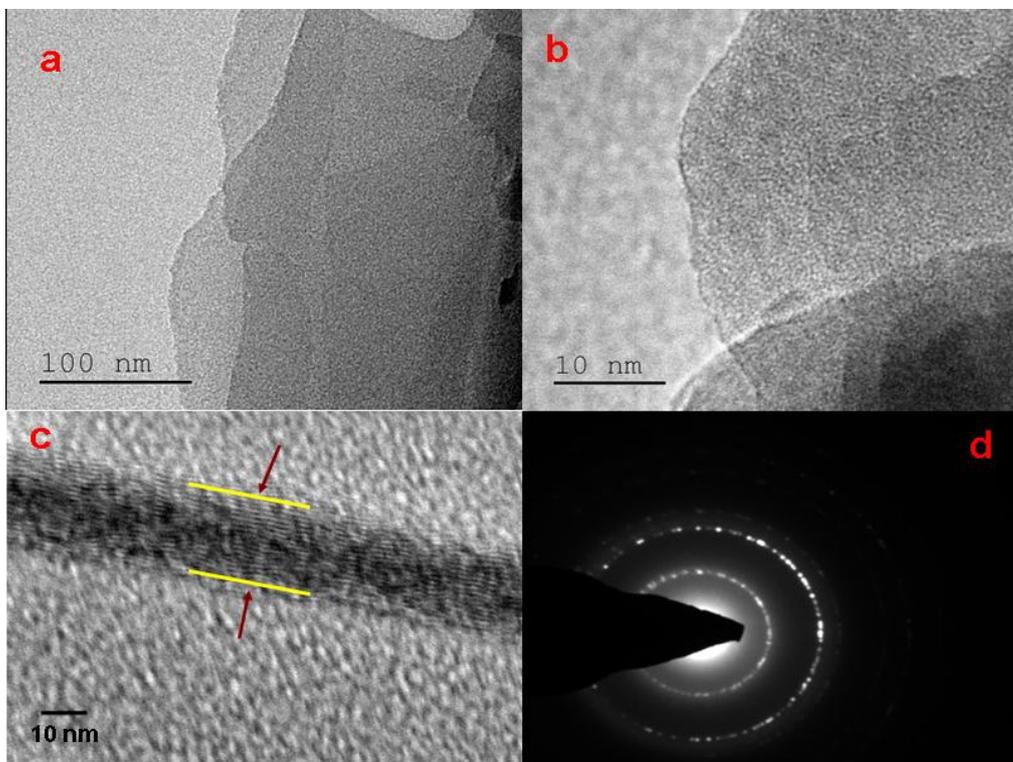
### 3.3. SEM and HRTEM Analysis

The surface morphology of the graphene oxide (GO) produced by sugarcane bagasse oxidation is identified by FESEM. The SEM image of the GO shown in Figure 3a,c clearly reveals its sheet-like structure. The morphology of the synthesised GO resembles flake-like structures as shown in Figure 3b,d. Quite similar textures have been reported by other authors [28].

HRTEM micrographs of GO are shown in Figure 4. Bends wrinkles, and edges on graphene oxide nanosheets are seen in several places in Figure 4a,b. Various defects and functional groups containing  $sp^3$  hybridized carbon atoms may also be introduced during the oxidation process. Figure 4c shows that the flakes contain a few layers of graphene oxide. The selected area of electron diffraction (SAED) pattern shown in Figure 4d indicates the presence of a polycrystalline structure corresponding to graphene oxide [29–33]. Thus, transmission electron microscopy (TEM) analysis confirms the presence of graphene oxide in the oxidized carbon samples.



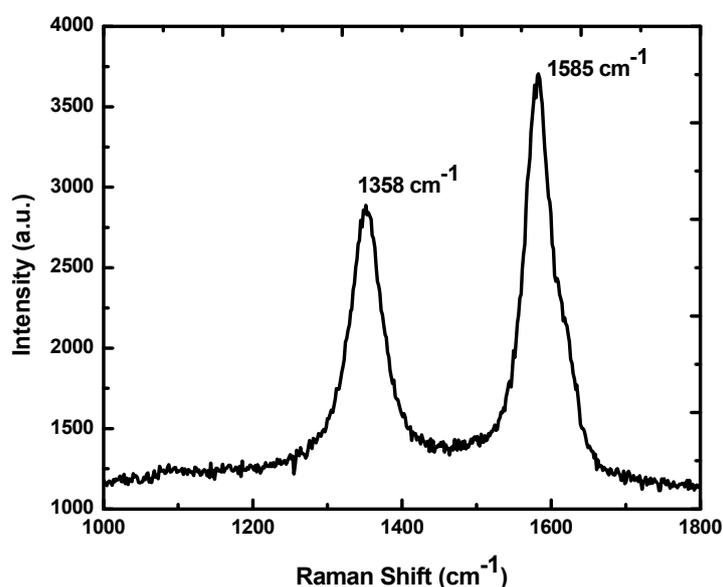
**Figure 3.** FESEM images of GO obtained from sugarcane bagasse.



**Figure 4.** High-resolution transmission electron microscopy (HRTEM) images of GO obtained from sugarcane bagasse.

### 3.4. Raman Spectroscopy

The Raman spectrum of graphene oxide synthesized from sugarcane bagasse is shown in Figure 5. The spectrum of GO displays two prominent peaks at 1358 and 1585  $\text{cm}^{-1}$ , which are attributed to the local defects (found at the edges of graphene sheets) and the  $sp^2$  graphitized structure, respectively. The G peak formation is due to the double degenerated zone center  $E_{2g}$  mode [34,35]. The functionality and reduction in particle size of  $sp^2$  plane domains are possibly due to the extensive oxidation of sugarcane bagasse [24]. The two D and G bands at 1358  $\text{cm}^{-1}$  and 1585  $\text{cm}^{-1}$  [36] indicate the clear  $sp^2$  carbon hybridization in the observed multi-layer stacks [31]. Thus,  $I_D/I_G$  peak intensity ratios are assigned to lower defects/disorders. Raman spectra show an intensity ratio of  $I_D/I_G$  at 0.76 for GO which is in line with previous investigations [24,37,38].



**Figure 5.** Raman spectrum of GO obtained from sugarcane bagasse.

## 4. Conclusions

A simple and rapid method is shown here to effectively convert solid sugarcane bagasse waste into value-added graphene oxide. The produced graphene oxide presents a well-graphitized structure. In comparison with the commonly used methods, our method is more environment friendly as it avoids toxic gas emission during the synthesis. This simple and low-cost synthesis process could lead to new opportunities for cost-effective production of graphene-based materials for gas sensors, energy storage, and other functional devices.

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## Author Contributions

The manuscript was prepared using contributions from all authors. Thirunavukkarasu Somanathan designed the work, conducted the synthesis of graphene oxide from agro waste, analysed the results and led the manuscript preparation. Karthika Prasad prepared agro waste materials and conducted the synthesis and characterization experiments. Kostya (Ken) Ostrikov contributed to the analysis of the results and manuscript writing. Arumugam Saravanan and Vemula Mohana Krishna conducted FE-SEM and HRTEM observation and analyzed the results. All authors have given approval to the final version of the manuscript.

## Conflicts of Interest

The authors declare no conflict of interest.

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