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SYNTHESIS OF GRAPHENE OXIDE FROM AGRICULTURAL WASTE

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ABSTRACT

Agricultural waste products are very rich in carbon and can be used to produce materials which have significant importance both scientifically and commercially. This study is aimed at producing graphene oxide from agricultural waste using groundnut and almond shells as starting materials. Hummer's method was adopted with some modifications which involved carbonizing, conversion of carbonized products to graphite and conversion of graphite to graphene oxide. The produced graphene oxide powder was characterized using FTIR and XRD. The FTIR results for the determination of functional group showed peaks at 3407 cm^{-1} and 1712 cm^{-1} (from groundnut shell) and peaks at 3457 cm^{-1} and 1712 cm^{-1} (almond shell) corresponding to hydroxyl and carbonyl groups respectively which indicates proper oxidation. The XRD result showed two peaks for both samples at 2θ. The percentage yield of graphene oxide from groundnut shell (11.5%) is less than the percentage yield of graphene oxide from almond shell (42.5%). The high yield production of graphene oxide, from almond shell is a better raw material than that from groundnut shell. Graphene oxide from almond shell is more crystalline and gives sharper peaks compared to that from groundnut shell. The method used in this work for the production of graphene oxide supported the use of almond shell better than groundnut shell. Large scale production of more purified form of this useful material should be looked into using agricultural waste.

Key words: Graphene; groundnut shell; carbonization; almond shell; characterization

INTRODUCTION

Over the years, waste management has posed a very serious issue of major concern due to the detrimental effect of poorly treated waste. Waste from the agricultural sector is not left out of this major concern. In response to solving the problem of waste management and treatment, agricultural waste has been used in the production and modification of other materials which are of great importance and use. Agricultural waste has been used to produce carbonaceous materials which can be utilized in different areas of science, and as a source of income and economic sustainability (Taniya et al., 2017).

Graphene, an atomically thin layer of carbon is one of the materials that can be produced from agricultural waste products (Geim and Novoselov, 2007). Although recent research shows that graphene can be produced from materials like "graphite" depending on what the product will be used for (Park and Ruoff, 2009). This work was centered on the production of graphene from agricultural waste, as a mean of reducing excess waste in the environment. It is an extremely promising two dimensional (2D) material (Geim and Novoselov, 2007), consisting of a network of sp^2-bonded carbon atoms and represents the “thinnest material” which is stable in its free form (Novoselov et al., 2004). Its excellent electronic properties (Schwierz, 2010), thermal conductivity (Balandin et al., 2008), optical transparency, enormous theoretical surface area (2630 m^2g^{-1}) ((Liu et al., 2012), combined with its unusual mechanical properties and good dispersion performance, make graphene a promising candidate for structural modification of composite materials and several other applications (Song et al., 2011; lee et al., 2008; Lu et al., 2011). Based on these properties, it can be used in adsorbing organic metabolites in pharmaceutical waste water and in the removal of heavy metals in water. It can also be applied in graphene-based material for gas sensors, energy storage and other functional devices (Lee et al., 2008; Novoselov et al., 2012).

Several methods have been employed over the years in its production and they are; chemical vapor deposition (CVD) from decomposition of methane/acetylene/ethylene on metal surface, micromechanical exfoliation or scotch tape method from graphite (Novoselov et al., 2012), epitaxial growth on electrically insulating surface (Berger, 2006), chemical method for the production of graphene or reduced graphene oxide (rGO) (Chua and Pumera, 2014) and carbonization of biomass and agricultural wastes. Recently, researchers are involved in developing a profitable and suitable technique for the large-scale production of carbon nanomaterial including graphene from natural sources (like plant leaves, bio char, waste corn shell, fungus, eggshell, and even human hair) (Zhu .et al., 2011; Wang et al., 2014; Qian et al., 2015).

Agricultural wastes have been classified as a form of bio-waste materials and are currently the center of attraction because of their abundance, need for recycling and being a major and sufficient source of carbon. Lignin, cellulose, hemicelluloses and small amount of other materials like protein, starches and lipidsare the main components of many agricultural wastes (Anwar et al., 2014). The management of agricultural waste has always been a big challenge in developed and developing cities. Hence, agricultural waste can be converted to carbonaceous materials to produce economically-worthwhile products for its emergent applications (Biswal et al., 2013). Agricultural waste materials such as food, shells, wood waste and other materials have been utilized for the eco-friendly sources for graphene synthesis (Chen et al., 2016; Jacob 2015).

This study chemically synthesized and characterized graphene oxide (GO) produced from agricultural wastes (groundnut shell and almond shell) using modified Hummers’ method.

MATERIALS AND METHODS

Sample collection: Groundnut with shell was purchased from Bodija market, Ibadan, Oyo state. The shell of the groundnut was removed, washed properly with distilled water and sun dried as sample A. Almond fruit was first plucked from Ago-iwoye, Ogun state. The flesh of the fruit was peeled off and the shell was sun dried for one week broken to remove the inner seed and the resulting shell was taken, washed with distilled water and dried as sample B.

Production of graphene oxide: The method involved three step processes which are; carbonization, conversion of the carbonized product to graphite and conversion of graphite to graphene oxide powder.

Carbonization: Both samples were crushed into smaller forms to increase their surface areas after they had been properly air dried. They were then wrapped in an aluminum foil and placed in a furnace at 200 ^{o}C for three days. The resulting product had a black colour, which is its carbonized form. The carbonized product was then crushed into powder in a mortar and used in the graphite production.

Conversion of carbonized powder to graphite: 1.0 g of $FeCl_3.6H_2O$ and 200 ml of distilled water was added to 2.0 g of carbonized powder in a beaker. The pH of the mixture was then adjusted to □ 2 by adding HCl (98 % BDH) acid to the mixture. The mixture was then stirred at 60 ^{o}C for five hours and left for one week for gradual evaporation at room temperature and then finally dried at 100 ^{o}C for 1 hour to obtain a black solid material called graphite. This black graphitized material was then ground in a mortar to obtain powder that was used in graphene oxide production.

Conversion of graphite to graphene oxide (GO): This step involves the conversion of the graphite powder formed in the previous stage to graphene oxide. This was carried out using the modified Hummers method. 2.0 g of each of the produced graphite powder were mixed with 2 g of sodium nitrate in a 1000 ml volumetric flask and 90 ml of H_2SO_4 (98 % BDH) was also added to the mixture and kept in an ice bath at 0-5 ^{o}Cwith continuous stirring for 4 hours. 12 g of $KMnO_4$ was added to the mixture slowly and the rate of addition was carefully controlled to keep the reaction temperature below 15 ^{o}C. The mixture was then diluted with very slow addition of 184 ml of distilled water with continuous stirring for 2 hours. The ice bath was then removed and the mixture stirred at 35 ^{o}C for another 2 hours. The temperature was then reduced to 25 ^{o}C and made to stand for 30 minutes. The reaction was terminated by adding 40 ml of H_2O_2 (30 % BDH) to the mixture and the colour changes to bright yellow. The mixture was then stirred properly and allowed to settle.Itwas then filtered off and the residue was washed with distilled water, 30 % HCl and ethanol consecutively. The residue was then coagulated with diethyl ether. The black residue was dried at 30 ^{o}C in an oven for 15 minutes. The resulting black powder formed is the graphene oxide powder which was then subjected to characterization (Paulchamy et al., 2015).

Characterization: The graphene oxide produced was subjected to characterization using Fourier Transform Infra-red Spectrophotometer (FTIR) for the functional group determination; X-ray Diffractometer (XRD) for the determination of the identity of the crystalline substance and the percentage yield of GO produced. The X-ray diffraction (XRD) pattern was obtained using a RigakuD/Max-IIIC X-ray diffractometer (Tokyo, Japan). This device is equipped with a Ni filter, and generates monochromated Cu-Kα 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° min^{-1} scan rate. FTIR spectra of samples were acquired in the range 380–4000 cm^{-1} at a resolution of 4 cm^{-1} using Spectrum 100 infrared spectrometer equipped with universal diamond crystal attenuated total reflection(ATR) accessory (Perkin Elmer, USA).

RESULTS

Calculation of Percentage Yield

The percentage yield of a substance is necessary to determine the amount of substance obtained at the end of a chemical reaction /analysis. It determines how successful an analysis went and can be used to evaluate the cost of production. Table 1 represents the result of the percentage yield of graphite obtained from the carbonized product (the product obtained after carbonizing groundnut and almond shells) and the result of the percentage yield of graphene oxide obtained from graphite.

Table 1: Results of the percentage yield of graphite and graphene oxide powders obtained from the powdered carbonized agricultural wastes.

	Carbonized powder (g)	Graphite powder (g)	Percentage yield (%)
Groundnut shell	.00±0.04	.90±0.05	5.0±0.09
Almond shell	.00±0.06	.79±0.04	9.5±0.02
	Graphite powder (g)	Graphene oxide powder (g)	Percentage yield (%)
Groundnut shell	.00±0.02	.23±0.01	1.5±0.04
Almond shell	.00±0.01	.85±0.01	2.5±0.02

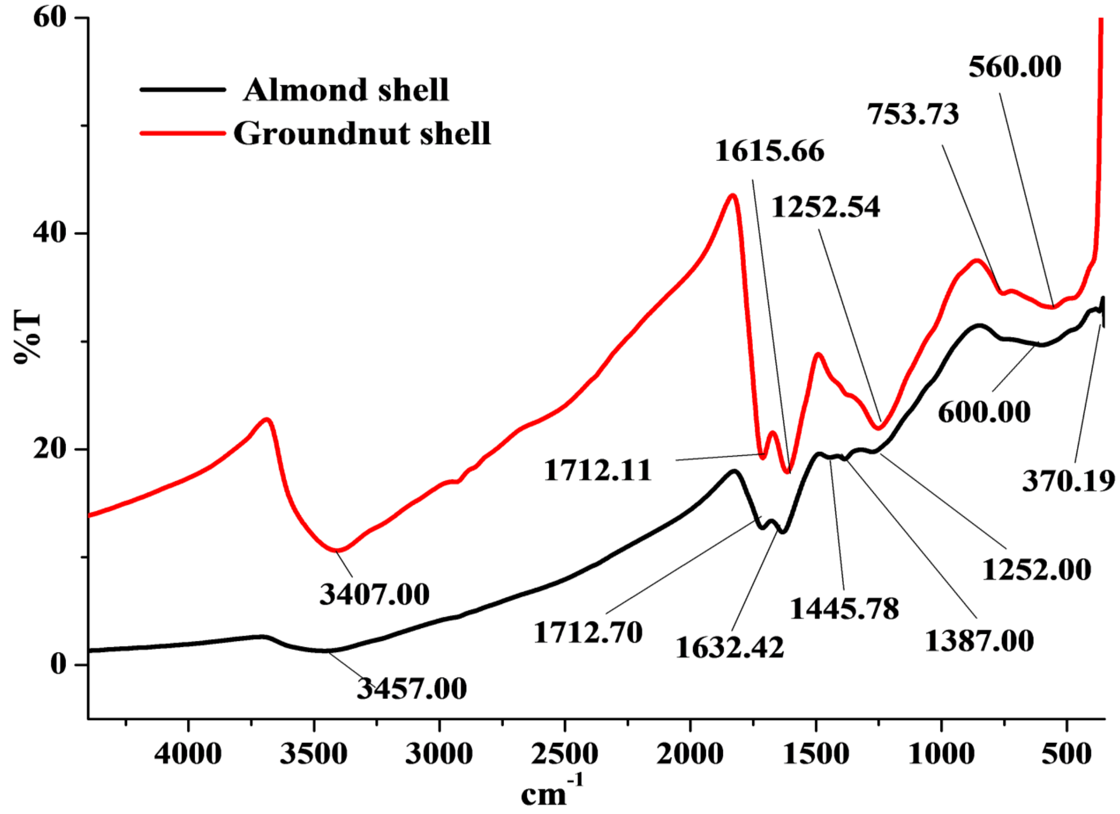

Figure 1: FTIR spectrum of graphene oxide from groundnut and almond shell

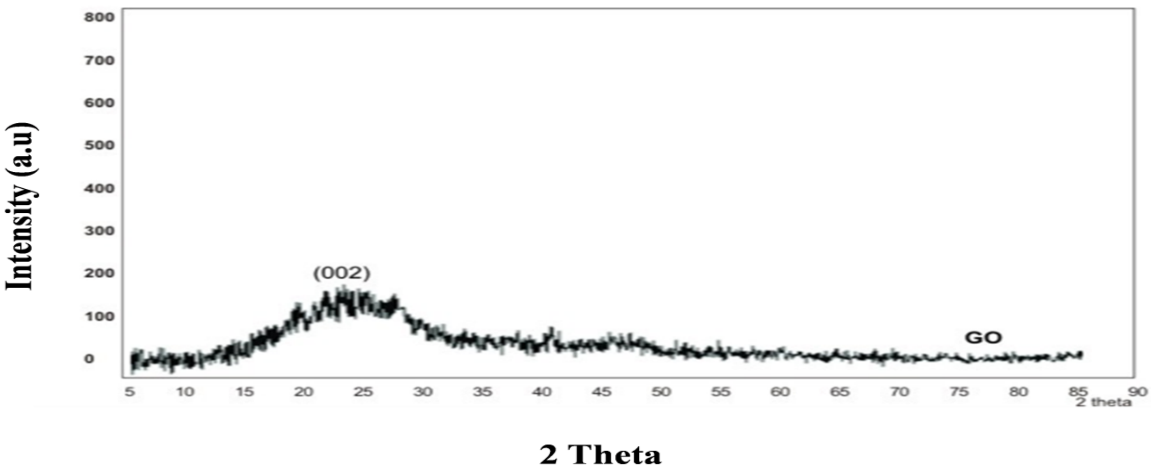

Figure 3: XRD spectrum of graphene oxide from groundnut shell.

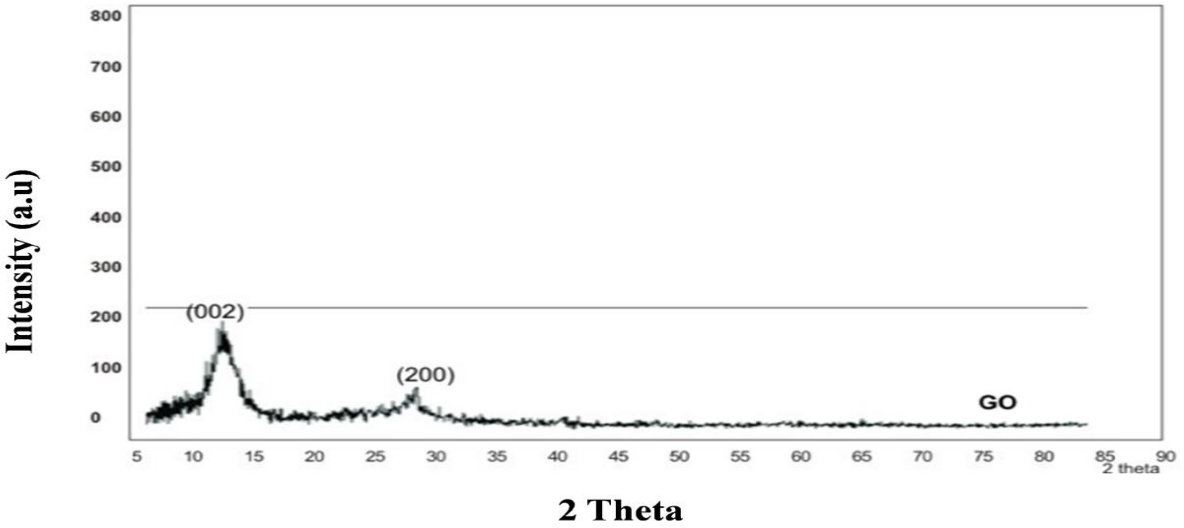

Figure 4: XRD spectrum of graphene oxide from almond shell.

DISCUSSION

Table 1 shows the percentage yield of graphite powder produced from the carbonized agricultural waste (groundnut and almond shell). For groundnut shell, starting with 2 g of the carbonized powder, 1.90 g of graphite which corresponded to 95.0 % yield which is a very positive result, was obtained. For almond shell, starting with 2 g of the carbonized powder, 1.79 g of the graphite powder which corresponds to 89.5 % yield was obtained. From this result, it was observed that the percentage yield of graphite powder from groundnut shell was higher than that of almond shell using the same method and the same amount of reagents. Table 2 which shows the percentage yield of graphene oxide powder obtained from graphite powder. For groundnut shell, using 2 g of graphite as starting material we obtained 0.23 g of graphene oxide powder which corresponds to 11.5 % yield. For almond shell, using 2 g of graphite as starting material we obtained 0.85 g of graphene oxide powder which corresponds to 42.5 % yield. From these observations and values obtained it can be deduced that the percentage yield of the graphene oxide from groundnut shell is less than that from almond shell using the same method and same quantity of reagents.This is however a direct contrast to the results seen in Table 1. It can be inferred from this that, irrespective of the percentage yield of the produced graphite powder, it is independent of the percentage yield of the graphene oxide formed. Also it is observed that for high yield production of graphene oxide powder almond shell is a better starting material than groundnut shell.

Chemical Characterizationof **Functional Groupsusing FTIR**: FTIR is a technique used in the identification and measurement of absorption bands. The knowledge of these absorption bands are essential because they determine the functional groups on the product and the type of contaminant it can adsorbed. Fig. 1 shows the spectra observed from the FTIR analysis of graphene oxide synthesized from groundnut and almond shells.

From Figure 1 showing the FTIR spectrum of graphene oxide from groundnut and almond shells several similar peaks were observed. The peak on 3407 cm^{-1} corresponds to the presence of O-H stretching vibrations which can be from hydroxyl, carboxyl or water molecule. The peak corresponding to 1712.11 cm^{-1} indicates the presence of a C=O stretching vibration from a carbonyl and carboxylic groups. The peak seen on 1615.66 cm^{-1} corresponding to a C=C stretching vibration for alkenes which can be assigned to the skeletal vibrations of graphitic domains (Yang et al., 2014; Eluyemi et al., 2016). A peak is also observed on 1252.54 cm^{-1} corresponding to a C-O-C group for an ether or carbonyl group (Krishnamoorthy et al., 2012).
The peaks at 1387 cm−1 corresponded to the stretching vibrations of C-OH found in almond shell (Bhattacharyya et al., 2017).

The FTIR results from this study compared favourably with the results of Thirunavukarasu et al., (2015), Tanya et al., (2017) and Paulchamy et al., (2015)on synthesis of graphene oxide from wastes using Hummer's method. The presence of oxygen-containing groups on the synthesized graphene oxides from both groundnut and almond shells reveals that the graphite has been oxidized. The indication of polar groups (surface hydroxyl groups), enhances formation of hydrogen bonds between graphite and water molecules, making the produced GO to be hydrophilic in nature (Alam et al., 2017). This also supports the fact that GO is a highly absorptive material (Paulchamy et al., 2015). The presence of these functional groups enhances the ability of the produced GO as ion exchangers, catalysts, catalyst supports and adsorbents for both polar and organic contaminants especially in water treatment (Luo et al., 2013).

Characterization using XRD: The structural analyses of the samples were characterized using X-ray diffraction. The X-ray diffraction is a method of analysis used in identifying crystalline substances. This analysis was used in characterizing and the results can be seen in Fig. 3 which shows the XRD result for graphene oxide from groundnut shell and Fig. 4 which shows the result for the graphene oxide from almond shell.

The xrd spectrum for GO from groundnut shell showed that the peaks were not very sharp indicating amorphous nature but, that of almond shell showed slightly sharp peaks which indicated crystalline nature (Figures 3 and 4). The XRD spectrum of graphene oxide from groundnut shell showed two notable peaks. For the first peak, a slightly broad (002) peak at $2\theta = 24.3^\circ$ having a d-spacing of 3.33 nm and relative intensity of 11°. Its second peak showed the value at 2θ to be 41.6 °, with d-value of 3.21 nm and relative intensity of 14°. Fig 4 showed the XRD spectrum of graphene oxide from almond shell at 2θ and it also had two peaks. The first peak has its value at 2θ to be 12.4 ° and d-value at 3.52 nm with relative intensity at 10°. The second peak has its value at 2θ at 27.1 ° with d-value at 3.42 nm and relative intensity at 11°. Xrd pattern with a broad peak at 2θ = 24.3˚may indicate the exfoliation of chemically reduced graphene oxide into a few layers. This may be due to the presence of graphene (Paulchamy et al., 2015). It may also be due to mild oxidation of graphite (Jeong et al., 2009). The small peak indicated at 2θ = 24.3° may also be due to the presence of amorphous halo at 2θ = 23−25 degree. This is amorphous like carbon which comprises many defects, folding structures, impurities, sp1, sp2, and sp3 hybridization structures (Huh 2011).

The (002) reflection peak at 2θ = 12.43 degree have been indicated to be due to complete oxidation of the graphene into graphene oxide (Huh 2011; Shalaby et al., 2015). The peak observed at 2θ = 27.1° corresponding to d spacing of 3.42 nm might be attributed to very thin reduced graphene oxide layers due to high degree of exfoliation (Huh 2011; Thirunavukarasu et al., 2015; Alam et al., 2017). GO from almond shell is more crystalline and gives sharper peaks compared to that from groundnut shell. The GO produced from almond shell compared more favourably with the GO reported in literature (Alam et al., 2017). The method used in this work for the production of graphene oxide supported the use of almond shell better than groundnut shell.

Graphene oxide has been synthesized using agricultural waste (groundnut and almond shell) through a modified Hummers' method. Almond shell gave more yield of the produced graphene oxide that compared favourably with those reported in literature than groundnut shell. Large scale production of more purified form of this useful material should be look into using agricultural waste. This is a way of reducing the problem of waste disposal,leading to cleaner and safer environment as well as generating additional source of income.

Conflict of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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