RESEARCH ARTICLE

Synthesis and characterization of graphene derived from rice husks

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Abstract

Graphene was successfully synthesized by activating rice husk ash (RHA) using potassium hydroxide (KOH) at 800 ºC with 1:2 impregnation ratio. Raman spectroscopy analysis confirmed the presence of graphitic structure. The demonstrated methodology utilizes RHA as carbon source and used as sacrifice to prevent oxidation during synthesis process on the mixture of KOH and RHA against air at high temperature. The novelty of this synthesis methodology use environmentally-friendly biomass resource as a starting material, does not utilize catalysts, and prove that graphene can be synthesized at a relatively low synthesis temperature.

Keywords: Graphene, rice husk, potassium hydroxide, Raman spectroscopy

INTRODUCTION

The discovery of a new class of two-dimensional carbon-based materials, graphene has brought together chemists, physicists, and engineers working towards wondrous potential modern applications which would revolutionize every part of our life. These carbon-based nanostructured materials possess remarkable features which offer wide-ranging opportunities for the advancement of research and development in this century. There are four major methods for synthesis of graphene, namely chemical vapor deposition (CVD), epitaxial growth on silicon carbide, exfoliation of graphite, and chemical reduction of graphene oxide.

Recently, researchers have developed green production methods for synthesizing graphene using environmentally-friendly biomass resource (e.g., sugar, chitosan, alfalfa plants, foodstuffs) (Zhu et al., 2010; Ruiz-Hitzky et al., 2011; Muramatsu et al., 2014; Singh et al., 2017). The main objective of green production method is to utilize less toxic chemicals and natural precursor (Singh et al., 2017).

Muramatsu et al. (2014) have first reported the synthesis of graphene from rice husk using potassium hydroxide (KOH) and carbon black as protective barrier against oxidation during synthesis process (Muramatsu et al., 2014). Then, Singh et al. (2017) have updated the synthesis method by replacing carbon black with rice husk itself (Singh et al., 2017). Rice husk is the highest worldwide production of agriculture material which is approximately 120 million tons per year in the world (Tuck et al., 2012) and its effective utilization is required.

In this research work, graphene was successfully synthesized by activating rice husk ash (RHA) using KOH at 800 ºC with 1:2 impregnation ratio. Raman spectroscopy analysis confirmed the presence of graphitic structure. In this research's synthesis process, low activating temperature and low impregnation ratio of RHA:KOH has been used and replacing carbon black with sacrificial RHA.

Brief history of graphene

Graphene was first explored as theoretical research by Wallace (1947) in his text book example as the starting point to understanding the electronic properties in three-dimensional graphite. He had predicted the graphite's electronic structure and distinguished the linear dispersion relation. Then, McClure (1956) had written the wave equation for excitations. Afterwards, in 1984, Semenoff, DiVincenzo and Mele (1984) had pointed out the emergent massless Dirac equation. However, almost 80 years ago, the physicists which name Landau and Peierls had predicted theoretically that their two-dimensional crystals are incapable of existing in the free state because of the thermal fluctuation would destroy the long-range order of two- dimensional lattices at finite temperature. Nonetheless, the experimental research of producing two-dimensional materials still uninterrupted.

Early efforts to isolate graphene were focused on chemical exfoliation method. As early as 1859, English chemist, Brodie recognized the highly layered nature of thermally reduced graphite oxide and reported the atomic weight of graphite in the Philosophical Transactions of the Royal Society of London. In 1946, German chemists had published the earliest transmission electron microscope (TEM) images of few-layer graphite (Ruess and Vogt, 1946). Then, in 1962, Boehm and colleagues had reported a detailed study on producing monolayer flakes of reduced graphene oxide by using TEM and X-ray diffraction (XRD).

In the early 1970s, the scientific community had concentrated on surface science on how to grow thin carbon film epitaxially using carbonaceous precursors on metal substrates by chemical vapor deposition and thermal decomposition of silicon carbide (SiC). Eizenberg and Blakely (1978) had reported a condensed monolayer of carbon on the nickel substrates using graphite. Such monolayer of carbon was studied by surface science technique but the quality and continuity remained unidentified. After few decades, a few-layered graphene obtained using thermal decomposition of SiC was characterized by focusing on electronic properties, high crystallinity, and high mobility charge carriers (Berger et al., 2004; Berger et al., 2006).

In 2010, Andre Geim and Konstantin Novoselov had received the Nobel award in recognition for their groundbreaking experiments toward graphene. In October 2004, they have presented their results on

graphene structures in describing the fabrication, identification, and Atomic Force Microscopy (AFM) characterization of graphene. They utilized a simple mechanical exfoliation method for extracting single-atom-thick layers of graphite from bulk graphite crystal with scotch tape and then transferred these layers to a silicon substrate (Novoselov et al., 2004).

Graphene: The two-dimensional material

Graphene is the first discovered two-dimensional lattice with organized in honeycomb hexagonal carbon network that are connected to each carbon atoms with sp2 bonding. The term "Graphene" combines the information of "graph" because of the graphite and "ene" for organic compounds with carbon-carbon double bonds. Graphene has been normally defined as "a single-atom-thick sheet of hexagonally arranged, sp2-bonded carbon atoms that is not an integral part of a carbon material, but is freely suspended or adhered on a foreign substrate" (Bhuyan et al., 2016).
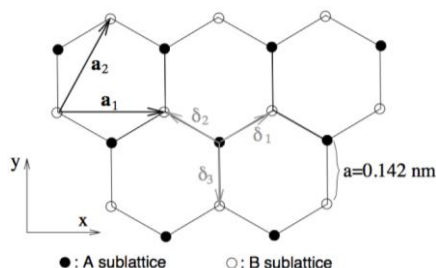

Figure 1 The graphene's honeycomb lattice.

Figure 1 shows the structure of graphene which is usually called as honeycomb lattice. The honeycomb lattice is not a Bravais lattice because of the two neighboring sites are not equivalent. The figure illustrates that a site on the A sublattice has nearest neighbors in the directions of north-east, north-west, and south, while a site on the B sublattices has nearest neighbors in the directions north, south-west, and south-east. Both A and B sublattices are triangular Bravais lattices and one may view the honeycomb lattice as a triangular Bravais lattice with a two-atom basis (A and B). The vectors $\delta 1$, $\delta 2$, and $\delta 3$ connect nearest neighbors' carbon atoms, separated by a distance a = 0.142 nm, which is the average of the single (C-C) and double (C=C) covalent σ bonds. The vectors a1 and a2 are basis vectors of the triangular Bravais lattice (Pauling,1960).

The sp2 hybridized where one carbon atom is covalently bonded, forming σ-bond with three other adjacent carbons with interatomic spacing of 1.421Å and a uniform bond angle of 120°. This sp2 bond is the strongest in nature, even stronger than that of tetrahedral sp3 bonds in diamond. For a carbon atom in graphene, two electrons are filled in the 1s orbital while three electrons in the sp2 orbitals are involved in the strong σ-bond, leaving one free electron in the 2pz orbital. This free electron is delocalized, forming π-bonds (pi orbitals) which responsible for the electrical conductivity of graphene. These pi orbitals overlap and help to enhance the carbon to carbon bonds in graphene.

Fundamentally, the electronic properties of graphene are dictated by the bonding and anti-bonding (the valance and conduction bands) of these pi orbitals. These intrinsic properties of graphene indicate that graphene has high intrinsic mobility and ballistic transport of 200,000 cm ^{2}v^{-1}s^{-1} (Bolotin et al., 2008; Morozov et al., 2008), high Young's modulus which around 1.0 TPa (Lee et al., 2008), thermal conductivity about 5000 Wm^{-1}K^{-1} (Balandin et al., 2008), its optical transmittance of 97.7 %, excellent room temperature electrical conductivity of 7200 S/m at room temperature (Li et al., 2008), and displaying tensile modulus up to 35 GPa (Goh and Ismail, 2015) and able to with stand current density of 108 A/cm^2 (Moser et al., 2007) due to the strength of its 0.142 Nm carbon bonds. Graphene has large theoretical specific surface area of 2630 m^2/g with hydrophobic nature (Goh and Ismail, 2015), which is double that finely divided activated carbon (Singh et al., 2011; Stoller et al., 2008).

Methods for synthesis of graphene

Synthesis of graphene refers to any method for fabricating or isolating graphene from carbonaceous precursor. Numerous methods have been established to synthesis graphene with different desired sizes, purity, and efflorescence of the specific product (Bhuyan et al., 2016). The synthesis of graphene can be divided into two main categories as listed in Table 1: the top-down approach and the bottom-up approach. For the top-down approach, there are two commonly used methods which are the mechanical exfoliation of graphite and the chemical exfoliation of graphene oxide (chemical method). Whereas, for bottom-up approach, the most commonly used methods are chemical vapor deposition (CVD) and epitaxial thermal growth of graphene on substrate.

Table 1 Synthesis of graphene

Type	Method	Figure/Illustration	Advantages	Disadvantages
Top-down approach (From Graphite)	Mechanical exfoliation		Less defects	Neither scalable nor capable for mass production
	Chemical method		Cost-effective and suitable for mass production	Utilize many toxic chemical throughout the synthesis process
Bottom-up approach (From Carbon)	Chemical Vapor Deposition (CVD)		Compatible with the current complementary metal–oxide–semiconductor (CMOS) technology due to large area and high quality graphene produced	Expensive and involves complex transfer process
	Epitaxial growth		No defects for every single graphene island	Discontinuous

The top-down approach focuses on breaking graphene precursor (graphite) into atomic layers. Graphite is a stack of mono-atomic graphene layers that are stacked together by weak van der Waals forces. To separate these graphite layers, the weak van der Waals forces need to be overcome (Edwards and Coleman, 2013). For the chemical method, the interlayer van der Waals forces can be reduced through oxidation of graphite using strong oxidizing agent including concentrated sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), and potassium permanganate ($KMnO_4$) which achieved similar levels of oxidation and was called as graphene or graphite oxide (GO) based on Brodie method (Brodie, 1860), Staudenmaier method (Staudenmaier, 1898), and Hummers method (Hummers and Offeman, 1958). Then, by rapid heating or thermal shock (~1000 ºC), the oxidized graphite will then be exfoliated and become single to few layers of graphene oxide (GO) due to the reduction of the interlayer van der Waals forces. However, the chemical method involves complex processes such as various chemical treatments which are toxic chemicals. Moreover, this method will influence the graphene structure due to oxidation treatment and reduction treatment.

While, for the mechanical exfoliation, the weak van der Waals forces between mono-atomic graphene layers in graphite were overcome by applying external mechanical forces using a variety of technique like scotch tape (Novoselov et al., 2004), ultra-sonication (Ci et al., 2009), electric field (Liang et al, 2008), and transfer printing technique (Liang et al.,2007; Chen et al., 2007). The advancement in the fabrication of graphene mono-layer has been improved at unprecedented pace. Up-scaled roll-to-roll production of graphene sheet reaching up to 40-inch have been demonstrated to be possible (Bae et al., 2010; Vlassiouk et al., 2013). However, this technique is still not suitable for mass production.

The bottom-up approach of graphene synthesis implies that the carbon precursor atoms grown directly on the substrate surface which gives rise to crystal planes of graphene. For the epitaxial thermal growth of graphene on substrate technique, graphene is grown on a single-crystal silicon carbide (SiC) by thermal vacuum graphitization. At approximately 1300 °C under vacuum of SiC results in sublimation of the silicon atoms since the carbon-enriched surface undergoes reorganization and graphitization.

The CVD technique comprise of chemical reaction of carbon precursor molecules in gaseous state which are diffused on a transition metal substrate at high temperature (900-1500ºC). When the substrate is cooled, the solubility of carbon on the substrate will be reduced, and the carbon precipitates to form one to multilayer graphene layers on the substrate. One of the major advantages of the epitaxial and CVD growth techniques is their high compatibility with the current CMOS technology due to large area and high quality graphene can be produced. The important disadvantage of this growth technique is the need of expensive substrate materials, requires high temperature above 900 to 1500 ºC, and the use of expensive flammable high purity gas for graphene growth considerably limiting its applications for large-scale production.

Synthesis of graphene using environmentally-friendly biomass resource

Recently, researchers have suggested and develop green production methods for synthesizing graphene using environmentally friendly biomass resources such as sugar, chitosan, and alfalfa plants. The main objective of green production method is to utilize less toxic chemicals and natural precursor (Singh et al., 2017). There are several literature that reported approaches using environmentally-friendly biomass resource as a carbon source and synthesizing graphene without using a catalyst (Zhu et al., 2010; Ruiz-Hitzky et al., 2011; Muramatsu et al., 2014; Singh et al., 2017). For example, it does not use high-purity hydrocarbon gas such as methane used for the conventional carbon source, but uses solid raw materials such as food and sugar as a carbon source or directly synthesizing a carbon-containing solid material as a graphene precursor without using a catalyst, it is possible to reduce the environmental burden during synthesis, reduce the cost of graphene.

Sun et al. (20120) have worked on synthesizing high-quality graphene by CVD method, using copper foil as a catalyst and sucrose as a solid carbon source. They reported on the influence of oxygen contained in sucrose in preparation of relatively high quality graphene. While, the Ruan and colleagues (2011) have succeeded in synthesizing graphene from carbonaceous sources such as foodstuff, insects, and waste by CVD method using copper foil catalyst. Primo et al. (2012) had studied on the utilization of chitosan as carbon source by synthesizing high-quality nitrogen-doped graphene without using metal catalyst foil. Chitosan is a nitrogen-containing biopolymer, which has been successfully prepared for high-quality nitrogen-doped graphene by coating it on a substrate such as glass and thermally decomposing it in Argon gas. Interestingly, in this method, high-quality graphene preparation is confirmed on the substrate without using catalyst metal foil.

The usage of biomass resource and waste materials as carbon sources is a promising method that results in a cost-effective, mass-production of graphene. However, it is difficult to synthesize large amounts of graphene using a catalyst. Additionally, when plants and waste materials are used as a carbon source without using a catalyst, problems such as low quality and high defects might exist.

Synthesis of graphene using rice husk

Rice husk is the highest worldwide production of agriculture material which is approximately 120 million tons per year in the world (Tuck et al., 2012). Due to low commercial value and difficulty to dispose this material, majority of rice producing countries will either burnt or dumped the rice husk (Kumar et al., 2013). This act can cause pollution by contaminating the air which will ultimately affecting human health (Serra et al., 2016). Therefore, utilization of rice husk is crucial to reduce the waste through safe and sustainable approach.

Figure 2 The physical illustration of rice husk (A) and rice husk ash (B).

According to Madhumita et al. (2009), rice husk comprises of 70-85% organic matter (mainly cellulose and lignin) and the inorganic residues (silica and metallic impurities). This composition of rice husk depends paddy type variety, climatic conditions, and geographic location (Della et al., 2002; Madhumita el al., 2009; Geetha et al., 2016). According to Geetha et al. (2016), the properties of rice husk comprise of high resistance to the action of harmful fungi, good anticorrosion properties of steel, aluminium, and copper. The typical analysis of raw rice husk is tabulated in Table 2.

**Table 2** Typical analysis of rice husk (Kumar et al., 2016).

Property	Range
Bulk density (kg/m^3)	96-160
Hardness (Mohr's scale)	5-6
Calorific value (MJ kg^{-1})	12-15
Ash, %	22-29
Carbon, %	~35
Hydrogen, %	4-5
Oxygen, %	31-37
Nitrogen, %	0.23-0.32
Sulphur, %	0.04-0.08
Moisture	8-9

Based on the analysis presented, the rice husk has the potential to be utilized as the starting material to produce high quality graphene from agriculture waste due to its high availability and good composition.

Muramatsu et al. (2014) have first reported the synthesis of graphene from rice husk using KOH and carbon black as protective barrier against oxidation during synthesis process. Then, Singh et al. (2017) have updated the synthesis method by replacing carbon black by rice husk itself. The graphene derived from rice husk is synthesized by activating rice husk ash using KOH and then washed with distilled water, centrifuged, sonicated, and vacuum-filtered to obtain graphene materials. The detailed synthesis method will be described in the Experimental section.

## Characterization of graphene using Raman Spectroscopy

Raman spectroscopy is a characterization technique that is commonly used for the portrayal of graphene materials (Liao et al., 2013). Raman spectroscopy is useful in determining the number and relative orientation of layers, defects, and functional groups in the graphene. Thus, this tool provides insights regarding all sp^2-bonded carbon allotropes, which is the fundamental building block for graphene (Ferrari and Basko, 2013). In aaddition, Raman spectroscopy can provide key information about chemical composition and material structure. It is based upon the interaction of laser light with the chemical bond within a sample. During the Raman scattering process, it loses parts of its energy to the material, causing some of the atoms to vibrate.
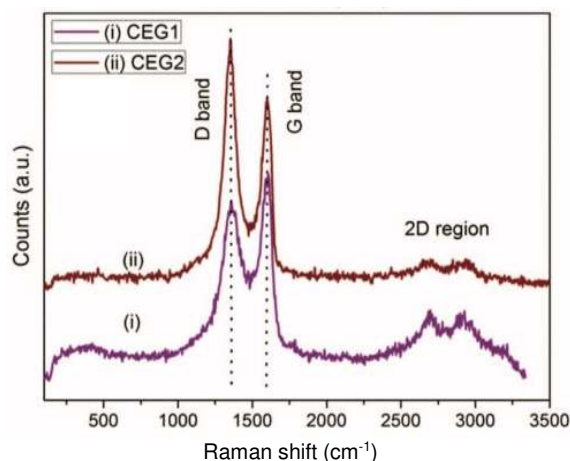

Figure 3 Raman spectrum of chemical exfoliated graphene (Kaniyoor and Ramaprabhu, 2012).

From Figure 3, there are three characteristic features region in Raman spectrum for a chemical exfoliated graphene, called the G band, D band, and 2D region (Park et al., 2009; Malard et al., 2009). The G band is the only peak produced from a normal first order Raman scattering process in graphene.
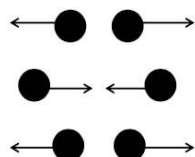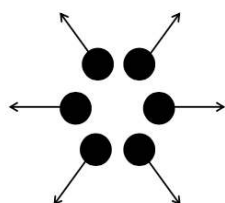
Figure 4 Vibration modes associated with the G and the 2D band of graphene (Wang et al., 2008)

The G band assigned to the E_{2g} phonon of C_{sp2} atoms as shown in Figure 4 (Wang et al., 2008). The G band represents the number of layers (Vasilios, 2014). The D band is for disordered sample or at the edge of a graphene sample (Malard et al., 2009). The G' and D band originate from second order Raman scattering process (Malard et al.,

2009). The G' band is commonly referred to as 2D peak in graphene literature. The height of the D peak depends on the number of the sp^3 carbon atoms of graphene surface and the number of defects of the graphene (Vasillios, 2014).

Ratio of the intensity of D band and G band is frequently used for characterization of graphitic structure present in the material to estimate number and size of the sp^2 cluster (Ferrari et al., 2006).
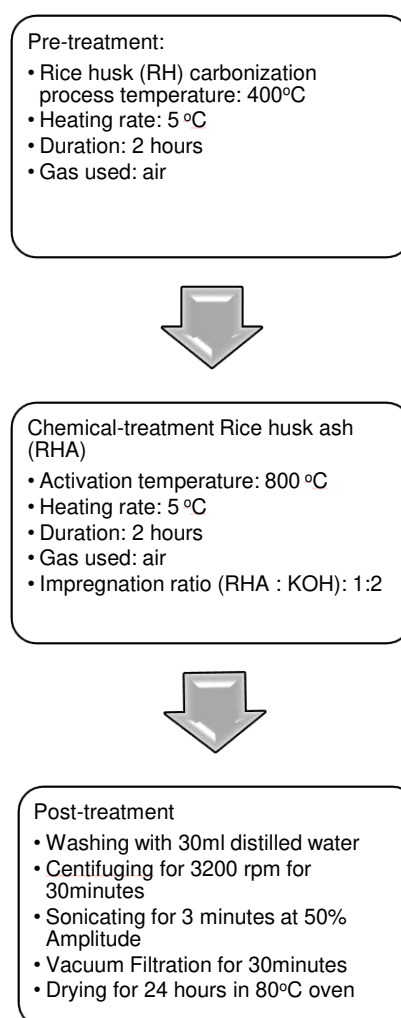
EXPERIMENTAL

Materials

The starting materials, rice husk was purchased from Kilang Beras Jelapang Selatan Sdn. Bhd, local paddy mill in the state of Johor, Malaysia. Potassium hydroxide pellets (KOH, Sigma-Aldrich) was used as the activating agent.

Synthesis of rice husk derived graphene

The synthesis process of rice husk-derived graphene was performed in accordance with the process described by Muramatsu et al. (2014) as illustrated in Figure 5. As shown in Figure 4, 5 g of raw rice husk was grounded and treatment inside Carbolite furnace for 2 hours at 400 °C. The solid residue obtained were called as rice husk ash (RHA).

**Figure 5** Experimental flowchart of synthesis graphene derived from rice husk.

Then, the RHA was chemically activated using KOH with impregnation ratio of 1:2 of KOH powder. The mixture was then compacted in a ceramic crucible. Next, the crucible was placed in the midpoint of a larger ceramic crucible. As shown in Figure 6, the empty space around ceramic crucible was fully covered by sufficiently

pressing and packing the sacrificial RHA. The sacrificial RHA used to prevent oxidation on the mixture against air at high temperature. The crucibles were heated at 800 °C for 2 hours.

Figure 6 Schematic diagram for the preparation of KOH chemical activation process.

After the chemical activation process was performed, the post-treatment was carried out as shown in Figure 7 where the chemically activated RHA was poured in 50 ml deionized water (DI water) and stirred for 30 minutes to remove potassium ions residue. The sample was centrifuged at 3200 round per minutes (RPM) for 30 minutes. Then, the sample was sonicated in 100 ml of DI water for 3 minutes with amplitude of 50%. After that, the sample was rinsed in 50 ml DI water using vacuum filtration over a PTFE membrane with 0.22 mm pore size. Next, the sample was dried in vacuum oven for 24 hours at 80 °C to remove moisture.
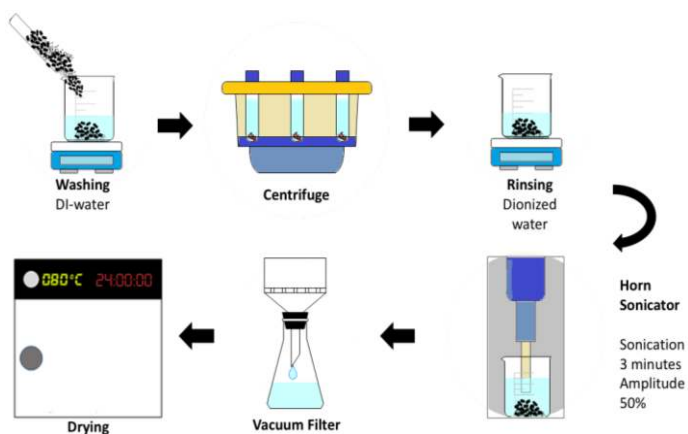
Figure 7 Schematic preparation of post-treatment.

Characterization of rice husk-derived graphene

The powdered sample was spread on a 3 mm thick square glass plate. Then, the sample was characterized using Raman spectroscopy (Horiba, LabRam HR) using 532 nm laser wavelengths using streamline scan mode. Measurements were carried out at 514 nm ar-ion laser excitation and 10 s exposure with working power of 20 mW. The Raman spectrum peaks were in the range of 200 nm until 4000 nm laser excitation wavelength.

RESULTS AND DISCUSSION

Prior to the pre-treatment process, 5 g of raw rice husk were ground and heated inside Carbolite furnace for 2 hours at 400 °C in air. The solid residue called rice husk ash (RHA) was obtained as shown in Figure 8. The RHA was weighed and the yield was 47 %. Then, the RHA was mixed with KOH for activation process with impregnation ratio of 1:2 of KOH powder at 800 °C for 2 hours in air. After that, activated RHA was washed with DI water, centrifuged, sonicated and filtered The sample was then dried in oven for 24 hours at 80 °C to

remove moisture. Then, the sample was characterized using Raman spectroscopy using 532 nm laser wavelengths using streamline scan mode. The Raman spectrum is shown in Figure 9.

Figure 8 Rice husk ash (RHA) obtained after 400 °C heat treatment.

From the Raman spectrum, the sample displayed three characteristic features region for a chemical exfoliated graphene, called the G band, D band, and 2D region (Park et al., 2009; Malard et al., 2009). From Figure 9, the sample produced the G band as a sharp peak that appears at 1600 cm^{-1}. The band was an in-plane vibrational mode comprising the sp^2 hybridized carbon atoms. While, the D band that appeared significantly at 1375 cm^{-1}. The D band is typically very weak in graphite and high quality graphene. Thus, the sample showed that there are a lot of defects in the material.
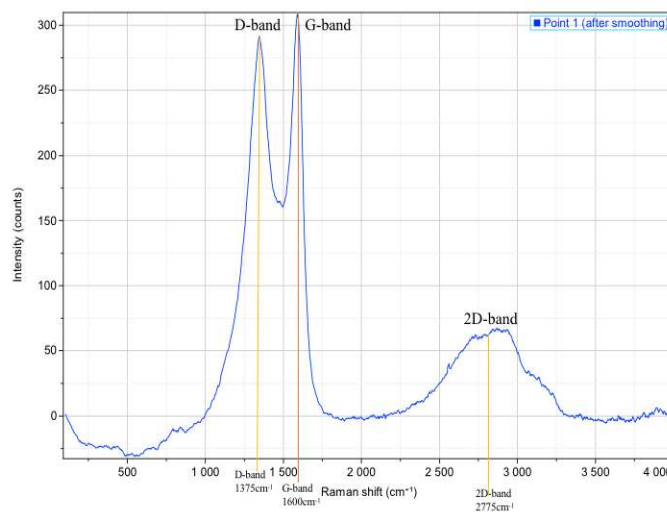
Figure 9 Raman spectrum for graphene derived from rice husk sample.

Finally, the 2D band appeared very weakly at 2775 cm^{-1}. The 2D band appeared wider and suppressed due to the influence of successive multilayers of graphene. However, this indicated that the sample has dominant amorphous carbon structure (Manukyan et al., 2013). Kaniyoor and Ramaprabhu (2012) have mentioned that the suppression of the 2D band is due to surface defects in the form of wrinkles. Furthermore, these band may merge due to broadening, effectively giving a bump similar to the obtained 2D band.(Kaniyoor and Ramaprabhu, 2012).

The I_{2D}/I_G intensity ratio was ~0.2 suggesting that graphene sample was multilayered (Liao et al., 2013). While, the I_D/I_G intensity ratio is ~0.9024, which is smaller compared to typical reduced graphene oxide which is usually more than 1 (Cao et al., 2013). Thus, this indicated that this green method has potential in developing high quality graphene.

CONCLUSION

As demonstrated in this work, we can conclude that it is possible to synthesize graphene using rice husk as a raw material. Additionally, since the synthesis process is cost-effective and involves simple procedure, this approach has a potential to be applied in synthesizing

graphene structures in large quantities. In addition, although this method does not utilize catalysts, graphene can be synthesized at a relatively low synthesis temperature.

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