

Preparation and Characterization of Graphene Oxide and Graphene Synthesized from Rice Straw

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Abstract

Rice straws (RS) are good sources of low-cost adsorbents. Graphene Oxide (GO) and Graphene (G) have a huge absorption capacity for methylene blue (MB), which is competitive with other high-performance adsorbents. The main aim of this research is to prepare GO that synthesized from carbon powder of rice straw (CRS) by using modified Hummer's Method. After that Graphene (G) was prepared by using chemical reducing method. (RS) was collected from Einkyitaw Village, Mahlaing Township, Mandalay, Myanmar. The physicochemical properties of rice straw, GO and G were characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT IR), X-Ray Diffraction Spectrometer (XRD), and UV-Vis spectrophotometer (UV). Surface areas and crystallite size of CRS, GO and G were calculated by using Sear's method and Debye Scherrer equation. Characteristic results revealed the facts that GO and G which were successfully synthesized from carbon powder of rice straw for potential application wastewater treatments

Key words: Carbon Powder, Graphene, Graphene Oxide, Modified Hummer's Method, Rice Straw.

Introduction

Myanmar has a large agricultural potential such as rice straw (RS) that can support economic activity. The carbon content in rice straw is relatively high silicon dioxide (over 65 %) of the total mass of rice straw ash (RSA), other metallic oxides present are CaO (about 2.4 %), Al₂O₃ (1.78 %), MgO (3.11 %) in addition to traces of ferric oxide. For example, rice straw has been used to produce silica as a raw material for biosorbents (Ugheoke, and Mamat 2012), Several methods have been applied to improve the economic value of these biosorbent wastes. Recent advances in nanotechnology have made the nanoscience field a hot area of research and one of the most researched areas of science in the past two decades. Moreover, Graphene (G) and graphene oxide (GO) synthesized from agricultural biomass have started to attract attention from researchers as adsorbent in removing heavy metal ions and dyes from aqueous solutions (Dong *et al.*, 2018). Graphite can be converted to graphene oxide using the modified Hummer's method (Hummers and Offeman, 1958). The preparation of GO using rice straw biomass (RSB) has been developed for adsorption some dyes and wastewater treatment (Papita *et al.*, 2016). However, it is a big challenge to use new materials, especially graphite from Myanmar biomass for preparation of GO. G is newly emerging member of carbon materials. Graphene was produced carbon powder such as graphite, from rice straw using chemical reduction method of graphene oxide aqueous solution with a reducing agent (Liu *et al.*, 2012). The production of GO using graphite from rice straw was performed and developed in this research. This simple and low-cost process could lead to new opportunities for cost-effective production of GO and G (Zhao *et al.*, 2011).

Materials and Methods

Carbon powder synthesized from rice straw (CRS) and graphene oxide (GO) and graphene (G) synthesized from this carbon powder of rice straw (CRS) by using Modified Hummer's method whereas the produced GO was subjected to chemical reduction method with the use of hydrazine hydrate. Characterizations of CRS, GO and G were analyzed by using SEM, FT IR, XRD and UV-Vis spectrophotometer. Surface areas and crystallite size of CRS, GO and G were calculated by using sear's method in equations (1) and Debye Scherrer equation (2) (Sears, 1956), (Scherrer, 1918), (Langford, and Wilson, 1978),

Preparation of Carbon Powder from Rice Straw

Rice straw was chopped into 3 cm pieces by using scissors and was washed several times with distilled water to remove any adhering dirt and particulate material from their surface. After that, the samples were dried in the air. And then, the sample was burned at 500 °C for 3 h to produce carbon powder like graphite powder. The resulted samples were taken out and then stored in airtight desiccators before use.

Preparation of Graphene oxide

GO was prepared by using the modified Hummer's method. 2 g of CRS was added in 250 mL of beaker. Then, 20 mL of concentrated H₂SO₄ was added with continuous stirring at hotplate magnetic stirrer and placed in an ice-water bath for 1h and then 0.6 g of KMnO₄ was slowly added into this mixture. After that, this mixture was continuously stirred for 30 min in the ice-water bath. Then 15 mL distilled water was

added to this mixture and was placed in an orbital shaker bath at 45 °C for 3 h. The mixture was ended by adding 20 mL distilled water and 15 mL H₂O₂ aqueous solution. The yellow slurry was obtained. The slurry was placed in a digital ultrasonic cleaner for 15 min to get uniform particle size. Finally, the mixture was filtered with filter paper and washed with 5 % HCL and distilled water using a centrifuge to remove acid and metal ions. Then GO and the strong acid filtrate were obtained. The GO was dried in hot air oven at 60 °C for 10 h.

Preparation of Graphene

Reduction method was selected to synthesize graphene by reducing agent that may be able to exterminate the oxide during the reduction process [7]. 1 g of GO was added in 250 mL of beaker. And then, this mixture was added into 100 mL distilled water with constant stirring on hotplate magnetic stirrer. After that 1 mL of hydrazine hydrate was added to this mixture. After stirring for 1 h, the slurry was filtered through a filter paper and was dried in oven at 60 °C for 6 h.

Characterization Techniques

Fourier transform infrared (FT IR) spectra of the samples were recorded by (IR-Tracer 100 Shimadzu, Japan). Ultraviolet-Visible (UV-Vis) spectra of the samples were collected on a UV-Vis spectrophotometer (Thermo Scientific GENESYS 10S UV-VIS, China). X-ray diffraction analysis (XRD) of powders were carried out on X-Ray Diffraction (Rigaku Miniflex 600, Japan), with monochromatic CuK α , radiation ($\lambda=1.5406 \text{ \AA}$). Data were collected from 10° to 80° at a scan rate of 0.1° min⁻¹. The morphologies of the samples were observed under scanning electron microscope (SEM, LEO/Zeiss-SMT, Germany). The surface area according to this method was calculated by the following equation (1): Average crystallite sizes of CRS, GO and G were calculated by using Debye Scherrer equation through the XRD spectrum that described in equation (2).

Calculation of Surface Area of CRS, GO and G According to Sear' Equation,

$$A = 32.V - 25 \quad (1)$$

where, A = Surface area of samples per gram (in m²/g)

V = volume of 0.1N NaOH required to raise the pH from 4 to 9

Calculation of Crystallite Size of CRS, GO and G

According to Debye Scherrer Equation,

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

where, D = average particle size in nm (or) A°

λ = wavelength of X-Ray A° (or) nm

K = Dimensionless shape factor (0.9)

β = FWHM (full width at half maximum of the sharp peaks)

Results and Discussion

Brownish Graphene Oxide and Blackish Graphene that synthesized from rice straw using potassium permanganate (KMnO₄) and sulphuric acid (H₂SO₄) produce brown-colored slurry. The slurry includes residual oxidizing agents (KMnO₄). After repeated dialysis, salts and ions from the oxidation process are removed from the slurry. After reduction of graphene oxide using hydrazine hydrate as a reducing agent, graphene oxide convert to graphene enables by chemical reduction. Thus, graphene oxides are homogenously dispersed in water to turn from brownish to black solution. This is due to the conforming the reduction of graphene oxide to graphene that aggregate and ultimately precipitate. GO is brown in colour and illustrates pale yellow colour. As an impact of this, the color has changed from brownish to dark shown in Figure1 (a) and (b). Graphene oxide is hydrophilic and graphene is hydrophobic (Alam *et al.*, 2017). GO readily forms stable colloidal suspensions in water shown in Figure 1(a) (Titelman *et al.*, 2005), (Szabo' *et al.*, 2006).

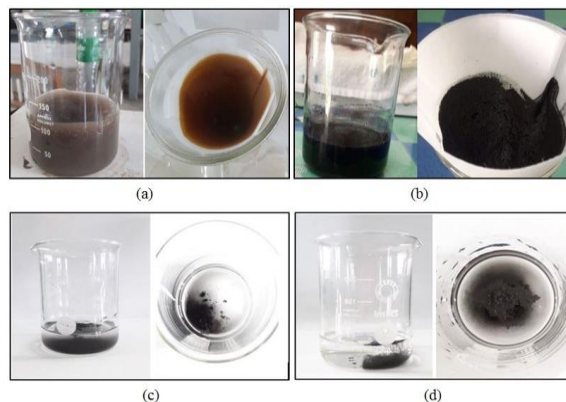


Figure 1. (a) Brownish GO and (b) blackish G (c) GO (Hydrophilic) and (d) G (Hydrophobic)

It is evident that GO is readily miscible in water and gives a light brown solution when dissolved in water. After ultrasonic treatment, its process brings about stable dispersions of graphene oxide is shown in Figure (c) (Stankovich *et al.*, 2006). However, G shows complete immiscibility in water. It is found that hydrophobic in nature indicates in Figure 1 (d). It reveals that GO solution is stable in the water while G can homogenously disperse in water via ultrasonic vibrations but the dispersion can only be stable for few hours due to their hydrophobic nature (Loh, 2010).

Determination of Crystallite Size and Surface Area of CRS, Graphene Oxide and Graphene

The crystallite size and surface area of samples (CRS, GO and G) were presented in Table 1. Crystallinity and verification of available of an oxide in layer structure of samples were determined through by X-ray diffraction (XRD).

Table 1. Crystallite Size and Surface Area of CRS, GO and G

Sample	X-ray Diffraction		Surface Area (m ² /g)
	Crystallite Size (nm)	Crystal Structure	
CRS	171	-	167
GO	36	Hexagonal	551
G	46	Hexagonal	359

These results present some useful mathematical equations for the quantitative determination of in-plane and across plane crystallite sizes, average number of CRS, GO and G were 171 nm, 36 nm and 46 nm respectively. Therefore, their average crystallite sizes are negatively related to their surface areas shown in Table 1. GO with the large surface area value is (551 m²/g). It may be graphene oxide had the largest pore size, pore diameter and pore volume, it might be ascribed to the sample expansion and cleavage with temperature rise during the procedure of GO. (Wang *et al.*, 2008)

SEM analysis of CRS, graphene oxide and graphene

The morphological structure of samples (CRS, GO and G) are analyzed by using SEM. These results confirm their surface's roughness and smoothness. Figure 2(a) shows that the carbon powder of rice straw contains cracking wafer shape like which consists of the system of adjacent cavities with an organized network of macro-pores (Wang *et al.*, 2017). GO clearly shows that large pores and channel like structures shown in Figure 2(b). G provides rough crushed surface and irregular shape with nonuniform particle size indicated in Figure 2(c) (Madzlan, 2014).

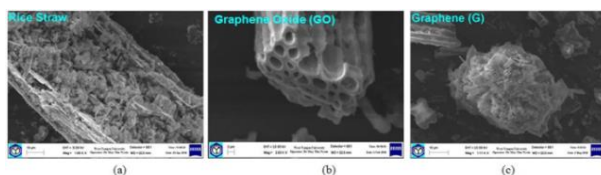


Figure 2. SEM images of (a) CRS (b) GO and (c) G

FT IR Analysis of CRS, Graphene Oxide and Graphene

The FT IR spectra of CRS, GO and G are obtained in the absorption band of 4000 to 500 cm⁻¹ as shown in Figure 3 (a), (b) (c). A broad band is ascribed to the O-H stretching vibrations between range of 3330 and 3440 cm⁻¹. The absorption peak at 1430 cm⁻¹ and 1620 to 1680 cm⁻¹ of CRS depict the presence of C=C stretching of aromatics groups. Besides that, band between 1106 cm⁻¹ and 1005 cm⁻¹ of CRS is corresponded to C-O-C (epoxy) groups shown in Figure (a) (Kannan *et al.*, 2008). The absorption peak of small band at 877 cm⁻¹, 1630 cm⁻¹ and 1730 cm⁻¹ can be assigned to C=O stretching of carboxylic and/or carbonyl functional groups (Kumar and Rajkumar, 2014). The absorption peaks of GO at 799cm⁻¹, 460cm⁻¹ and 468 cm⁻¹ are assigned asymmetric bending vibrations of Si-O-Si and symmetric stretching vibrations of Si-O, which are related to Al-O and Si-O in plane and bending modes (Palomo, and Glasser, 1992). FT-IR spectra of graphene described as hydroxyls, carboxyls, ethers, epoxides, and ketones are obtained at 1000-1180 cm⁻¹ shown in Figure. 3. The peaks at 600 cm⁻¹ and 900 cm⁻¹ are aromatic group of C-H bend respectively. FT IR spectrum of nanosilica contributes that unexpected peaks of any organic and inorganic compounds do not appear. However, the FT IR results indicate that the spectrums which display the characteristic peaks of the functional groups presenting in the SiO₂ (Pham, *et al.*, 2017).

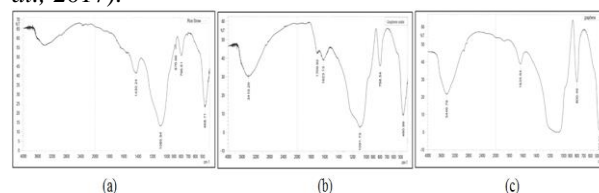


Figure 3. FT IR analysis of (a) CRS (b) GO (c) G

XRD Analysis of CRS, Graphene Oxide and Graphene

X-ray diffraction of rice straw are quartz and silicon oxide appeared at $2\theta = 29.5^\circ$, 43.3° and 48.6° , which correspond to lattice planes of (011), (102) and (200) were shown Figure 4.

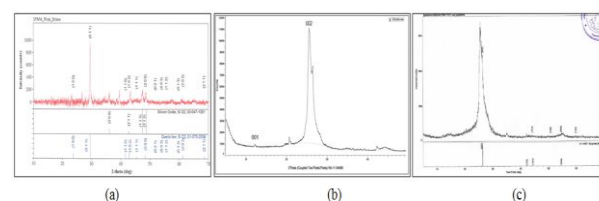


Figure 4. XRD analysis of (a) CRS (b) GO (c) G

Characteristic peaks of crystalline-phase silicon oxide appear at $2\theta = 36.1^\circ$, 47.5° and 48.6° , which correspond to lattice planes of (200), (113) and (212) shown in Figure 4 (a). A low intensity peak at $2\theta =$

12.2° can be assigned to the (001) reflection peak and might depend on the method of preparation and on the number of layers of water in the gallery space of GO as described in Figure 4 (b). However, the sharp diffraction peak of 002 crystalline is presented at $2\theta = 25^\circ$ due to the amount rich of silica from rice straw. Additional reflex at $2\theta = 10.54^\circ$ (GO (002)) is associated with GO structure obtained by electrochemical oxidation of polycrystalline of rice straw like graphite. The similar report of GO synthesized from broad peaks at around 26° , which can be ascribed to the amorphous nature of the nano-silica particles. The X-ray diffraction pattern of graphene obtained from graphene is shown in Figure 4 (c). These peaks could be ascribed to the (002), (101), (102), (004) and (103) crystal planes of graphene (Wu *et al.*, 2010). XRD for graphene has a very sharp peak for (002). All the carbons have a significant indexed (002) plane for different graphene products at $2\theta = 26.4^\circ$ and 004 at $2\theta = 54.2^\circ$ indicate the same peak trend of graphite.

UV-Visible Spectrophotometer Analysis of Graphene Oxide and Graphene

Figure 5 reveals UV-Vis spectra of the GO and G. Sun and coworkers have been reported that GO shows the absorption peak at around 230 nm that attributed to the $\pi \rightarrow \pi^*$ transitions of aromatic C–C bond due to the absorption peak varies on the oxidation of carbon powder from rice straw substitute of graphite (Sun, *et al.*, 2008).

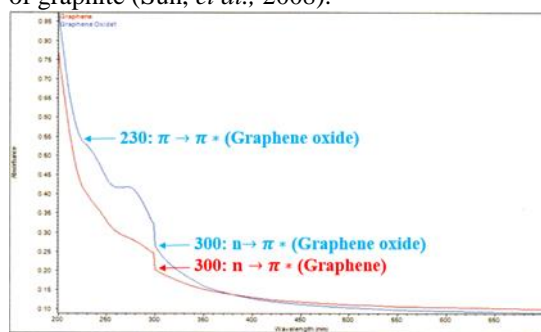


Figure 5. Absorption spectra of GO and G

Wang *et al.*, 2008 also reported that the main absorption peak at about 230 nm and a shoulder at about 300 nm can be assigned to the $n \rightarrow \pi^*$ transitions of C=O bonds. When GO is being reduced, the absorption peak of oxidized graphene shifts to a greater wavelength from 215 nm to 267 nm. While for G, the absorption peak is shifted to 268 nm, suggesting that the covalent attachment to the graphene surface (Mohamed *et al.*, 2015). In this research, red shift peak of the graphene presents at 260 nm because the electronic conjugation in the graphene and due to desorption of the oxygen attached to the graphene layers.

Conclusion

Agricultural residues such as rice straw is applied to synthesize GO and G using modified Hummer's method as basic bio-adsorbents for dye removal from synthesis wastewater. So, it can be substituting other expensive bio-adsorbents. Resulted surface area of graphene oxide has ($551 \text{ m}^2\text{g}^{-1}$) and graphene ($359 \text{ m}^2\text{g}^{-1}$). It is found that average crystallite size of graphene oxide and graphene are 36 nm and 46 nm. Therefore, their average crystallite sizes are negatively related to their surface areas. The FT IR spectra of GO at 1709 cm^{-1} is attributed to stretching vibration modes of C=O in carboxylic acid groups. The peak also found at 1620 cm^{-1} assigns to the C=C stretching and 3410 cm^{-1} for the OH (hydroxyl group) stretching vibrations of adsorbed water molecules. The XRD spectra of GO show a little diffraction peak at $2\theta = 12.2^\circ$. XRD spectrum of G shows a sharp peak at $2\theta = 26.4^\circ$ which can be assigned as 002 indexed peak with hexagonal crystal structure. A characteristic of GO presented by characteristic peak at 230 nm corresponding to $\pi \rightarrow \pi^*$ transitions of aromatic C–C bonds thus showing strong absorption. The main absorption peak of G around 300 nm can be assigned to the $n \rightarrow \pi^*$ transitions of C=O bonds. As a cost-effective, easily prepared, and environmentally-friendly biosorbent, can be applied for polluted water treatment.

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