Graphene Oxide from Indonesian Biomass: Synthesis and Characterization

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Graphene oxide (GO) was synthesized from graphite and also produced from waste materials, such as coconut shell, rice husk, and bagasse. The GO obtained from pure graphite was compared with graphite made from Indonesian biomass (coconut shell, rice husk, and bagasse) that had its silica content removed. The characterization of GO was with X-ray diffraction (XRD) analysis, Fourier transform infrared (FTIR) spectroscopy, and Raman spectroscopy. The XRD images showed the formation of the GO and graphite from various angles and revealed that the chemical reaction had an important role in the formation of the GO particles. This was confirmed by the FTIR and Raman spectra, where the presence of various oxygen functional groups was identified. The FTIR spectra showed that the GO had some functionals oxygen groups within its structure.

Keywords: Graphene oxide; Biomass; X-ray diffraction (XRD) analysis; Fourier transform infrared (FTIR) spectroscopy; Raman spectroscopy

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INTRODUCTION

Indonesia has a large agricultural potential that can support economic activity. Sugarcane, coconut, and rice are major agricultural products in Indonesia. Sugarcane (*Saccharum officinarum*) is the largest plantation commodity in Indonesia. Based on the statistical data for Indonesian plantations collected by the Directorate General of Plantation in 2015, the total harvest area for sugarcane in Indonesia was 487,095 ha, and the amount of production reached 2,728,393 t. Therefore, if the bagasse content of sugarcane is approximately 30% to 34%, then the total bagasse waste in Indonesia is approximately 928,000 t. The carbon content in sugarcane is relatively high (47%) (Winaya and Shimizu 2007). The chemical components of bagasse fibers by mass are cellulose (45 to 55%), hemicellulose (20 to 25%), lignin (18 to 24%), pectin (0.6 to 0.8%), ash (1 to 4%), and extractives (1.5 to 9%) (Yadav *et al*. 2015). Another agricultural product of Indonesia is coconut. The coconut production in Indonesia was 3.88 million t in 2005, while the rice production in the Java province of Indonesia was 299 million t from 1961 to 2009 and was produced from 57 million ha of land (Panuju *et al*. 2013). The composition of coconut shell is crude fiber 32%, crude fat 2.14%, crude protein 0.46%, moisture content 10.10%, and ash 2.28% (Ewansiha *et al*. 2012).

The statistical data of the Indonesia plantation by Directorate General of Plantation in 2015 showed that the rice production in Java was 2.31 million t and the production of rice husk as the secondary product from rice was 0.5 million t. The chemical and physical properties of rice husk ash are SiO_2 88.3%, Al_2O_3 0.46%, Fe_2O_3 0.67%, CaO 0.67%, MgO 0.44%, Na_2O_3 0.12%, and K_2O 2.91 % (Habeeb and Mahmud 2010) The waste from these three major agricultural products increases with an increase in annual production.

Several methods have been applied to improve the economic value of these wastes. For example, rice husk has been used to produce silica (Madrid *et al*. 2012; Ugheoke and Mamat 2012), as a raw material for biosorbents (Subki and Rohasliney 2012), an adsorbent for oil purification (Otaru *et al*. 2013), a polyester resin composite (Islam *et al*. 2015), *etc*. Bagasse has been applied as an adsorbent (Gusmão *et al*. 2012), raw material for biosorbents (Said *et al*. 2013), and composite (Patel and Patel 2015), and coconut shells have been used as a raw material for activated carbon (Mozammel *et al*. 2002; Abiko *et al*. 2010).

These materials have also been used to produce graphite. Graphite can be converted to graphene oxide (GO) using the modified Hummers method (Hummers, Jr. and Offeman 1958). Graphene oxide and its derivatives are used as a nanomaterial-based material. The GO nanomaterial has interesting characteristics because of its particularly large surface area and superior chemical strength (Kong *et al*. 2016). The applications of GO include sensors (Park and Rodney 2009) and transparent conductive films (Guo *et al*. 2013). Few-layer graphene has shown great potential as next-generation electrode materials for a green energy storage system due its higher electrochemical performance, with the specific capasitance 180 Fg^{-1} in a 1 M Na_2SO_4 (Li *et al.* 2012). The preparation of GO using rice straw biomass (RSB) has been developed for adsorption some dyes such as crystal violet (CV) and basic azine dye (Goswami *et al*. 2017). The preparation of GO using Indonesian biomass from plantation and agricultural wastes for degradation of antibiotic has not been well-developed so far. However, it is a big challenge to use new materials, especially graphite from Indonesian biomass for preparation of GO. In addition, these natural materials have eco-friendly, cheap, and renewable. Graphene oxide also contains carbon (C)-based hexagonal rings with the hybridization of C sp^2 and sp^3 atoms in two-dimensional structures containing oxygen atom surface functional groups, such as epoxys, carbonyls, hydroxyls, and carboxyls. The production of GO using graphite from bagasse, coconut shell, and rice husk was performed and developed in this study.

EXPERIMENTAL

Materials

Chemicals

The graphite used in this experiment was prepared using rice husk obtained from Pasuruan, Indonesia, bagasse obtained from Sidoarjo, Indonesia, coconut shell obtained from Surabaya, Indonesia, and a commercial graphite. Preparation of the GO used graphite from the three waste materials, a commercial graphite, and the following materials from Merck & Co. (Surabaya, Indonesian): sulfuric acid (98% H_2SO_4), peroxide acid (30% H_2O_2), hydrochloric acid (5% HCl), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), and hydrogen fluoride (HF); as well as deionized (DI) water.

Instruments

To perform the X-ray diffraction (XRD) analysis, a multipurpose diffractometer (X'Pert MPD, Philips, Idaho, USA) with Cu-Kα radiation was used. The Fourier transform infrared (FTIR) spectroscopic analysis of the solid samples was conducted in the ATR mode on a JASCO FTIR 6300 IR spectrophotometer (Jasco Ltd, Tokyo, Japan). The Raman spectra of the samples were recorded with a Horiba JobinYvon, France at a λ of 532 nm, laser power of 1.7 mW, 100× objective lens, and 0.9 NA. The XRD analysis measured the crystalline phases of the graphite and GO, and the FTIR and Raman spectra determined the functional groups of the graphite and GO.

Methods

Preparation of the graphite

Graphite was produced from bagasse, coconut shell, and rice husk. First, these wastes were washed with water to remove the water-soluble contaminants and oven-dried for 24 h. The material was then ground and screened. The screened wastes were placed and burnt in a furnace at 550 °C for 3 h, under atmospheric pressure. The three materials contain high amounts of silica. As such, the silica was removed using HF. A total of 10 g of graphite were dissolved using 30 mL of 40% HF, which was then heated and stirred for 3 h. Then, the suspension was washed using distilled water and dried. The graphite was then analyzed using the XRD and spectroscopic instruments.

Preparation of the graphene oxide

The GO was prepared according to the modified Hummers method. A total of 5 g of graphite were added to 2.5 g of $NaNO_3$ and 115 mL of H_2SO_4 (98%), and the rate of addition was carefully controlled. A sudden increase in the temperature reaction was avoided using an ice bath. Stirring was continued for 2 h. Then, 15 g of $KMnO_4$ were slowly added to the reaction, and it was stirred for 2 h. The ice bath was removed, and then the reaction mixture was covered with aluminum foil and stirred for 30 min to form a brown paste. Next, the reaction mixture was diluted with 230 mL of DI water, and the temperature was kept below 100 °C. The mixture was stirred for 1 h and further diluted with approximately 700 mL of DI water. Afterwards, 10 mL of 30% H_2O_2 were added to the mixture, which changed its color to a brilliant yellow. The resultant mixture was centrifuged and washed several times with 5% HCl aqueous solution and DI water. Finally, the resulting solid was dried at 60 °C for 24 h, and a loose brown powder was obtained. The GO was analyzed using the XRD and spectroscopic instruments.

RESULTS AND DISCUSSION

The XRD analysis was performed to confirm the formation of various phases. A comparison of the results between the XRD patterns before and after the desilication process is shown in Figs. 1 and 2. None of the graphite patterns nor GO patterns had broad patterns in Fig. 1 before the graphite desilication, which meant that there was silica present. After the silica in the graphite base material was removed by the HF solution, the diffractogram patterns became slightly thinner and the patterns were not as wide as before the silica removal. The widening of the diffractogram patterns is likely to be debated because the crystals of graphite and GO were still covered by silica, which has the same peak as graphite and GO.

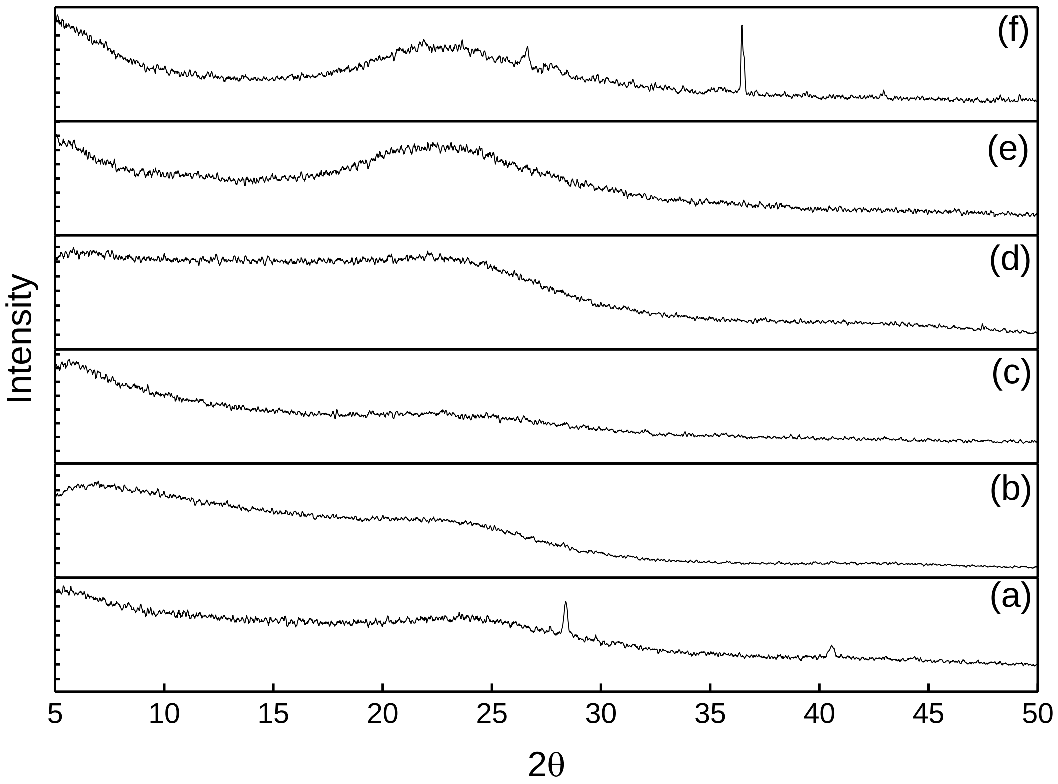

Fig. 1. XRD patterns of the graphite from (A) coconut shell, (B) rice husk, and (C) bagasse before desilication; and the XRD patterns of the GO from (D) coconut shell, (E) rice husk, and (F) bagasse before desilication

The GO was made from graphite derived from bagasse, coconut shell, and rice husk, and a commercial graphite. The GO was synthesized using the modified Hummers method (Hummers and Offeman 1985). Concentrated H_2SO_4 was used to exfoliate a number of layers from the graphite flakes, and $KMnO_4$ was used as an oxidizing agent. The $KMnO_4$ was added slowly to avoid an exothermic reaction and bumping. The temperature needed to be maintained under 20 °C. The results were a suspension. After adding water, the temperature of the suspension increased and the color changed from brown to a brilliant yellow. After adding H_2O_2, GO formed.

Figure 2 shows the common characteristic peaks of the graphite patterns after treatment with the HF solution, which is defined by peaks at 26.1° (Rajesh *et al*. 2016) and 26.4° (Goswami *et al*. 2017). The commercial graphite pattern had a characteristic peak at 26.73°. The graphite from the coconut shell had characteristic peaks at 24.00°, 28.42°, and 40.58°. The rice husk pattern had characteristic peaks at 22.36° and 28.28°, and the bagasse pattern had peaks at 22.86° and 24.72°. After oxidation, the characteristic peaks of the graphite patterns were small, and the characteristic peaks for the coconut shell, rice husk, and bagasse patterns were found at 23.11°, 26.65°, and 24.56°, respectively. The pattern of the GO from the commercial graphite was defined by a peak from 10° to 11°, but it was different for the GO made using graphite from a waste. According to Aarthi and Lalithambika (2014), the XRD spectrum of GO nanoplatelets from carbonized agro waste was characterized by a peak at 26.60°.

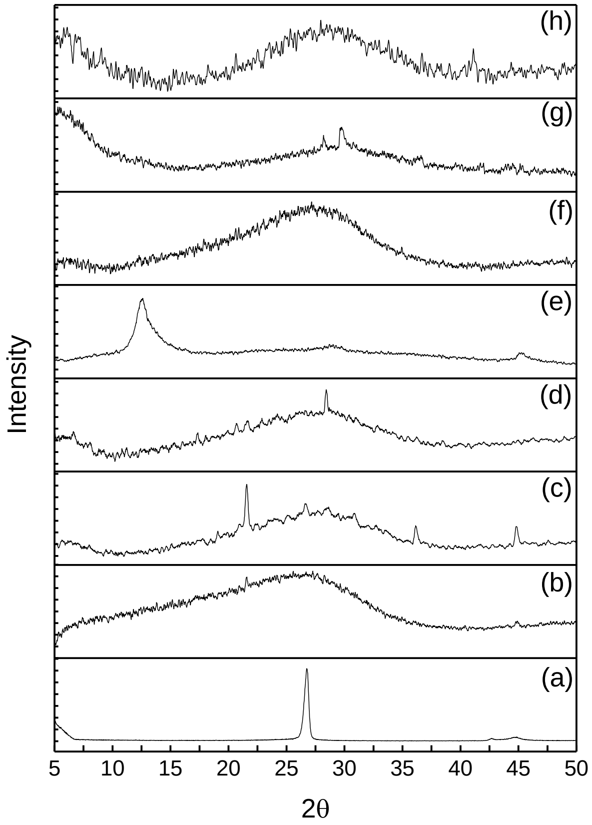

Fig. 2. XRD patterns of the graphite from (A) coconut shell, (B) rice husk, (C) bagasse, and (D) commercial graphite after desilication; and the XRD patterns of the GO from (E) coconut shell, (F) rice husk, (G) bagasse, and (H) commercial graphite after desilication

Figure 3 shows the FTIR spectra of the GO made with graphite from coconut shell, rice husk, and bagasse. The coconut shell had broad bands OH vibrations at 3591.8 cm^{-1} and 3202.0 cm^{-1}, C=C=O stretching vibrations at 2549.0 cm^{-1}, carboxylates or ketones C=O stretching at 1719.7 cm^{-1}, C-O stretching vibrations at 1283.3 cm^{-1}, and C-H stretching vibrations at 820.46 cm^{-1}. The rice husk had broad bands OH vibrations at 3342.0 cm^{-1}, C=C=O stretching vibrations at 2456.3 cm^{-1}, aromatic C=C stretching vibrations at 1656.5 cm^{-1}, epoxy C-O stretching vibrations at 1213.3 cm^{-1}, and C-H stretching vibrations at 847.5 cm^{-1} and 587.2 cm^{-1}. The bagasse had broad bands OH vibrations at 3425.5 cm^{-1}, C=C=O stretching vibrations at 2549.0 cm^{-1}, aromatic C=C stretching vibrations at 1966.4 cm^{-1} and 1686.6 cm^{-1}, C-O stretching vibrations at 1250.1 cm^{-1}, and C-H stretching vibrations at 680.5 cm^{-1}. The FTIR spectrum of the commercial graphite was defined by broad bands OH vibrations at 3055.3 cm^{-1}, C=C=O stretching vibrations at 2262.9 cm^{-1}, C=C stretching vibrations at 1749.8 cm^{-1}, C-O stretching vibrations at 1210.2 cm^{-1}, and C-H stretching vibrations at 636.9 cm^{-1}. The FTIR spectra of the waste materials were similar to the FTIR spectrum of the commercial graphite. The FTIR spectra of the GOs were similar to the FTIR spectra of the corresponding graphite. In the study by Aarthi and Lalithambika (2014), the FTIR spectrum of GO was defined by bands at 671 cm^{-1} from C–H bonds, and 2360 cm^{-1} from C=C=O bonds, and 3413 cm^{-1} from O–H bonds. Spectral results reported by Guo *et al.* (2013) exhibited the characteristic peaks for C=O at 1719 cm^{-1}, aromatic C=C at 1621 cm^{-1}, epoxy C-O at 1223 cm^{-1}, C=C bonds at 1646 cm^{-1}, C=C=O bonds at 2074 cm^{-1}, 2338 cm^{-1}, and 2360 cm^{-1}, and O–H bonds at 3413 cm^{-1}.

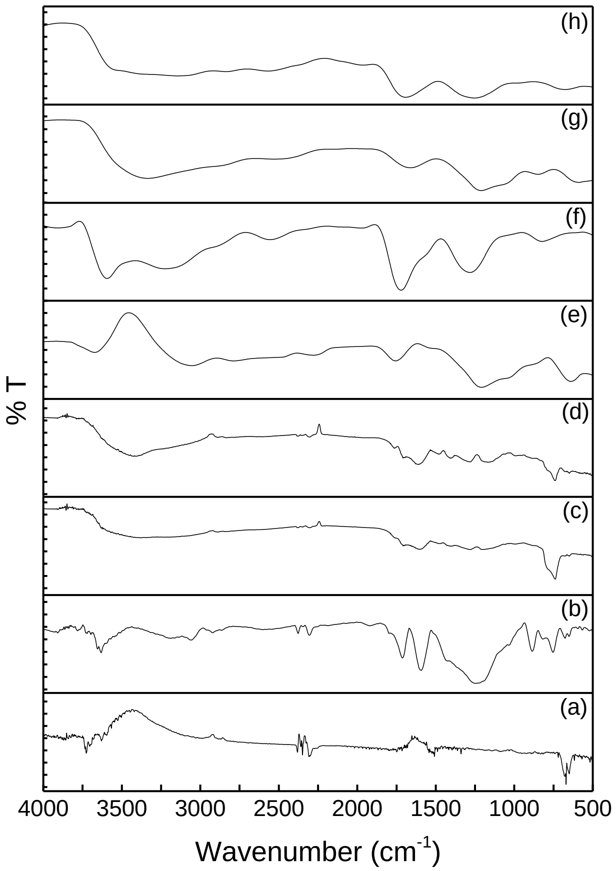

Fig. 3. FTIR spectra of the graphite from (A) coconut shell, (B) rice husk, (C) bagasse, and (d) commercial graphite; and the FTIR spectra of the GO from (E) coconut shell, (F) rice husk, (G) bagasse, and (H) commercial graphite

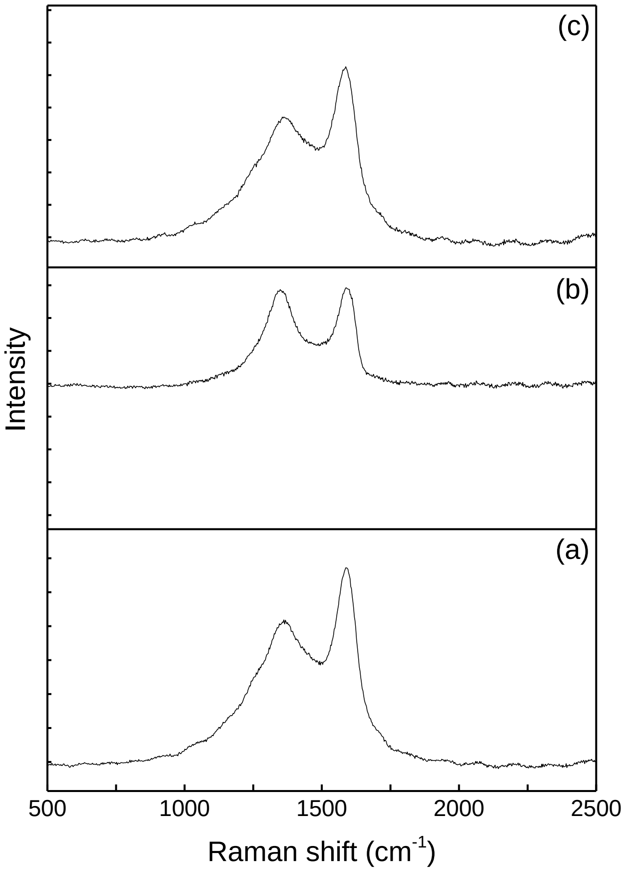

Fig. 4. Raman spectrum of the GO from (A) coconut shell, (B) rice husk, and (C) bagasse

The Raman spectra of the GO synthesized from the coconut shell, rice husk, and bagasse are shown in Fig. 4. The spectra of the GO made from coconut shell, rice husk, and bagasse each displayed two prominent peaks at 1361 cm^{-1} and 1588 cm^{-1}, 1348 cm^{-1} and 1588 cm^{-1}, and 1358 cm^{-1} and 1582 cm^{-1}, respectively, where the first peak in each pair was attributed to local defects found at the edges of the graphene sheets and the second peak in each pair was the sp^2 graphitized structure. The G peak formation was because of the double degenerated zone center E$_2$g mode (Somanathan *et al*. 2015).

The functionality and reduction in the particle size of the sp^2 plane domains were possibly because of the extensive oxidation of the coconut shell, rice husk, and bagasse. The two D (I_D) and G bands (I_G) at 1361 cm^{-1} and 1588 cm^{-1} for coconut shell, 1348 cm^{-1} and 1588 cm^{-1} for rice husk, and 1358 cm^{-1} and 1582 cm^{-1} for bagasse, respectively, indicated clear sp^2 carbon hybridization in the observed multi-layer stacks. Thus, the I_D/I_G peak intensity ratios were assigned to lower defects and disorders (Kaniyoor and Ramprabhu 2012).

CONCLUSIONS

1. The synthesis of graphene oxide (GO) from environmental waste (Indonesian biomass) as sustainable alternative was carried out using the modified Hummers method.
2. The XRD images showed that the formation of GO using pure graphite was defined by a peak from 10° to 11°, and graphite from Indonesian biomass (rice husk) was found at 26.65°. Promising results were obtained for preparation of GO from graphite that had been obtained from rice husk. This was confirmed by the FTIR spectra, where the presence of various oxygen functional groups was identified. This was also confirmed by the Raman spectra, where two D and G bands indicated clear sp^2 carbon hybridization in the observed multi-layer stack.

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