

Effects of Different Activating Agent on the Physicochemical Properties of Rice Husk Derived Graphene (GRHA)

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Abstract. This paper proposes the preparation of rice husk derived graphene (GRHA) via chemical activation method using two different chemical activating agents namely phosphoric acid (H_3PO_4) and potassium hydroxide (KOH). The purpose of this study is to study the impact of different activating agent on the physicochemical properties of GRHA. The rice husk was carbonized at 350 °C for 2 h and activated at 900 °C and 700 °C for GRHA-KOH and GRHA- H_3PO_4 respectively. The prepared GRHA was characterized using X-ray Diffraction (XRD) analysis, Raman Spectroscopy and BET analysis. The crystallinity of each sample shows that the prepared GRHA is in amorphous state. On the other hand, the I_D/I_G ratio of GRHA-KOH is 0.45 while GRHA- H_3PO_4 is 0.68 which suggest that both samples have high degree of graphitization. Interestingly, it was discovered that activation using KOH possesses a higher BET specific surface area (BET_{SSA}), 518.11 m^2/g as compared to H_3PO_4 which is only 315.07 m^2/g . Thus, it shows that KOH was able to form GRHA with higher surface area and porosity.

1. Introduction

Graphene has been synthesized in 2004 by Novoselov and co-workers [1]. Graphene is a well-known material that is made up of single layer of carbon atoms structure with honeycomb crystal lattice. Graphene plays a vital role in various fields of applications such as supercapacitors [2], fuel cell [3], adsorption [4] and biological application [5]. The reasons that have made the carbon materials like graphene a basic source for such applications is due to its' high conductivity, excellent mechanical flexibility and high surface area [5]. The preparation of graphene can be divided into two which are top-down and bottom-up approach. The top-down approach requires the structural breakdown of precursor such as graphite followed by the interlayer separation to produce graphene sheets. Mechanical exfoliation, oxidation-reduction of graphene oxide (GO), liquid phase exfoliation and arc discharge are some examples of top-down approach. On the other hand, the bottom-up technique includes chemical vapor deposition (CVD), epitaxial growth and total organic synthesis utilize carbon source gas to synthesize graphene on a substrate [6].



Recently, bio-waste materials can be a considerable source for production of carbon. Plus, bio-waste materials are ample and need a proper disposal. On top of that, the management of waste biomass is challenging especially in developing countries. Therefore, it is suggested to convert the material into carbonaceous materials which can be used in enormous applications [7]. This has been a turning point to the researchers to synthesize graphene using biomass precursors such as waste corn shell [8], rice husk [9], [10] and gelatin [11]. About 120 millions of rice husk are produced in the world each year [12]. In Malaysia, 3 millions of rice husk is generated from approximately 680,000 acres of paddy field annually [13]. Due to the large production of rice husk, it received a significant of attention as a precursors to prepare graphene [12]. Theoretically, rice husk is insoluble in water, high chemical and mechanical stability and exhibits granular structure [14]. It is made up of ~22 % lignin, ~38 % cellulose, ~20 % hemicellulose and 20 % of silicon dioxide (SiO₂). Therefore, rice husk can be a great starting material to produce carbon based materials which include activated carbon (AC) and graphene [15].

The rice husk derived graphene (GRHA) can be prepared using chemical activation as reported by [12], [13], [16], [17]. There are various types of chemical activating agent that able to prepare high surface area of graphene namely, potassium hydroxide (KOH) [11], phosphoric acid (H₃PO₄) [18], hydrochloric acid (HCl) and zinc chloride (ZnCl₂) [19]. In this study, rice husk was carbonized at 350 °C to form rice husk ash (RHA) to maximize the carbon content in the material [16]. During the activation process, RHA will be activated using two different activating agents, KOH and H₃PO₄ at different temperature, 900 °C and 700 °C to study the effect of each of the activating agent on the physicochemical properties of GRHA.

2. Materials and Methodology

2.1. Materials

Rice husk was collected from Johor (Kilang Beras Jelapang Selatan Sdn. Bhd.). Potassium hydroxide (KOH) was purchased from Quality Reagent Chemical (QReC). Phosphoric acid (H₃PO₄) (98 %) was purchased from Acros Organics.

2.2. Synthesis of GRHA-KOH

Rice husk was carbonized at 350 °C for 2 h to form rice husk ash (RHA). RHA (3 g) was mixed with KOH powder (15 g) and the mixture was annealed in a muffle furnace at 900 °C for 2 h. The GRHA was sonicated for 30 mins and washed with distilled water. Later, it was centrifuged at 3200 rpm for 10 mins for several times until neutral pH was obtained. Lastly, GRHA was dried in an oven at 80 °C overnight [9].

2.3. Preparation of GRHA-H₃PO₄

The acid activation was carried out by mixing 3 g of RHA with 50 mL of 3 M H₃PO₄ solution at 80 °C for 2 h. The product was dried in an oven overnight and it was then followed by second activation where the sample will be calcined in a muffle furnace at 700 °C for 2 h. The sample was then washed with warm distilled water was obtained and sonicated for 30 min. After finishing time, it is centrifuged at 3200 rpm for several times until neutral pH was obtained. The sample was collected by vacuum pump and allowed to dry in an oven overnight.

2.4. Characterization

To determine the crystallinity of the samples, X-Ray Diffraction (XRD, Smart Lab, Rigaku) was used. Data was collected using Cu-K α radiation (1.54 nm) in the range of 2 θ from 5° to 50°. Brunauer-Emmett-Teller (BET) was used to analyze the surface area of GRHA-KOH and GRHA-H₃PO₄. On the other hand, Raman spectroscopy (Horiba, Raman Xplora Plus) was used to analyze the degree of graphitization of both GRHA-KOH and GRHA-H₃PO₄.

3. Results and Discussions

3.1. Degree of Graphitization

Figure 1 and Figure 2 depicts the Raman spectrum for GRHA-H₃PO₄ and GRHA-KOH respectively. The pattern of the spectrum is almost the same as reported by Jagiello and colleague (2014) where all peaks at in-plane vibrational D-band (1340 cm⁻¹), disorder-induced G-band (1576 cm⁻¹) and 2D-band (2680 cm⁻¹) can be found which confirms the presence of few layers of graphene [8]. Nevertheless, all the peaks mentioned in GRHA-KOH are low in intensity and not sharp as compared to GRHA-H₃PO₄. This is because, there are some remaining chemical groups such as potassium (K) as metallic K is form during the activation process [21]. Besides that, the presence of multilayer structural defects also lead to this factor [22]. In addition, the presence of defect is further supported by the G and D band which are having almost the same intensity [23].

The intensity (I) ratio of each band will give some information regarding the characteristics of the GRHA obtained [8]. I_D/I_G ratio will provide the quality (degree of graphitization) while I_{2D}/I_G indicates the number of layers [24]. The I_D/I_G of GRHA-H₃PO₄ and GRHA-KOH are 0.68 and 0.45 respectively. This shows a low graphitized disordered carbon structure [25] and the presence of large amount of amorphous carbon [26]. However, since the I_D/I_G of both GRHA-H₃PO₄ and GRHA-KOH is much lower compared to RHA (which is 1.34) it can be deduced that the chemical activation step able to remove some of the amorphous carbons on the GRHA structure [12]. On the other hand, the I_{2D}/I_G of GRHA-H₃PO₄ and GRHA-KOH 1.17 and 0.88. The I_{2D}/I_G of GRHA-KOH is approximately the same as reported by Muramatsu and team [12].

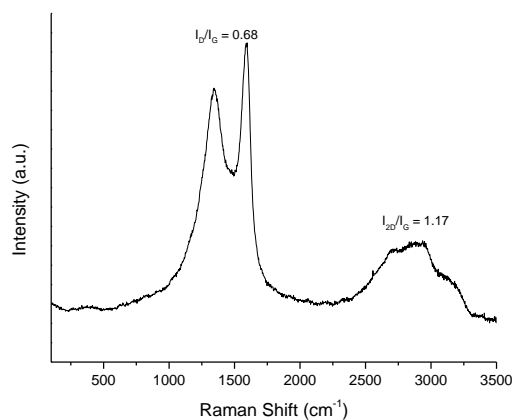


Figure 1. Raman shift of GRHA-H₃PO₄

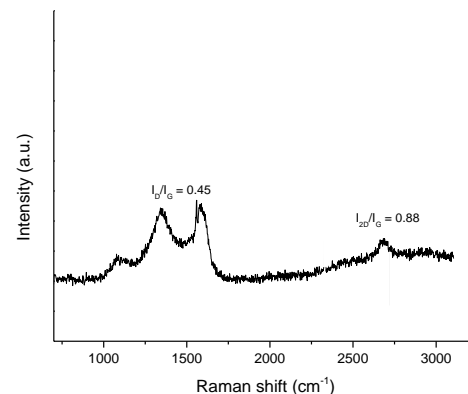


Figure 2. Raman shift of GRHA-KOH

3.2. Crystallinity Study

XRD diffractogram of both GRHA-H₃PO₄ (Figure 3 (a)) shows broad peak around $2\theta = 22^\circ$ corresponding to (002) plane of carbon network while $2\theta = 43^\circ$ correspond to (100) plane [27]. It shows that GRHA-H₃PO₄ has a graphitic like microcrystalline that contain disordered structure based from the diffraction of (100) while the diffraction of (002) comes from the interlayer spacing (0.4 nm) of the graphitic layer. Broad diffraction peaks of (002) and (100) indicates that the GRHA-H₃PO₄ has amorphous feature with small crystalline domains [28]. Besides that, high intensity around $2\theta = 22^\circ$ is due to the high ratio of micropores [29].

For GRHA-KOH (Figure 3 (b)), the existence of graphene sheets can be confirmed by the strong characteristics graphitic peaks which is found at $2\theta = 26^\circ$ (002) and 43° [21]. The broad diffraction peak at (002) indicates the breakage of the interplanar C bonds and the formation of graphene [15]. Furthermore, peak at (002) is observed at $2\theta = 26^\circ$ corresponding to the d-spacing which is around 0.3 nm. This result is aligned based on what has been reported by [30] which is in good arrangement of

interlayer spacing of graphene. It can be seen that both of the sample exhibit a peak at $2\theta = 43^\circ$ which correspond to the formation of pores by the decomposition of carbon along the direction of the graphitic structure. This will give rise to relatively well-organized aromatic carbon that is much stable than amorphous carbon [31].

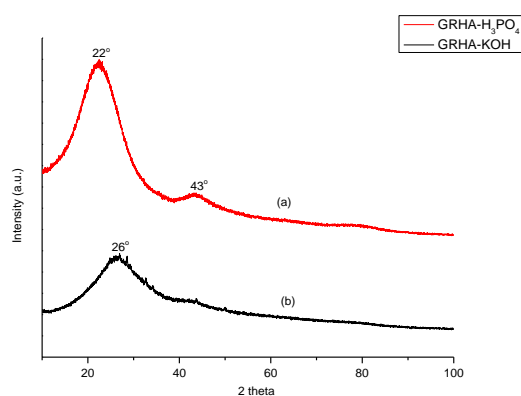


Figure 3. XRD spectrum of (a) GRHA-H₃PO₄ (b) GRHA-KOH

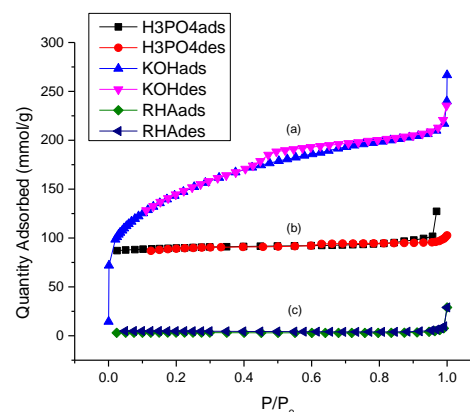


Figure 4. N₂ Adsorption-desorption isotherm of (a) GRHA-KOH (b) GRHA-H₃PO₄ (c) RHA

3.3. Surface Area Analysis

Figure 4 illustrates the typical Type I isotherm which suggest that GRHA-KOH and GRHA-H₃PO₄ are composed of microporous structure [32]. It shows that the activation of RHA by KOH and H₃PO₄ greatly increase the surface area of GRHA. However, GRHA-KOH shows a higher BET_{SSA} which is 518.11 m²/g comparing to GRHA-H₃PO₄, 315.07 m²/g. This shows that KOH able to form GRHA with a better surface area as well as porosity (Table 1).

Theoretically, the phosphoric acid will be introduced in the internal structure of rice husk (lignocellulosic) in order to generate porosity during the chemical activation process. The porosity in the carbon structure is greatly formed when phosphoric acid is removed via washing [33]. On the other hand, KOH will form metallic potassium (K) during the activation process. When the temperature reaches 760 °C, K will create pores in GRHA which increases the porosity and the surface area. KOH also able to react with the reactive centre of the carbonized material like disorganized carbon, carbon with heteroatoms and carbon on graphene edges thus created new pores and widening the existence ones [10,29].

Table 1. Specific surface area and porosity data

Sample	BET _{SSA} (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)
RHA	8.3702	0.0118	0.0032
GRHA-KOH	518.11	0.3346	0.2927
GRHA-H ₃ PO ₄	315.07	0.1577	0.1384

4. Conclusions

GRHA was synthesized through chemical activation using KOH and H₃PO₄. The degree of graphitization of GRHA-KOH (0.45) and GRHA-H₃PO₄ (0.68) are relatively high. Meanwhile, the I_{2D}/I_G ratio indicates that both of samples are consist of few layers of graphene. The prepared GRHA exhibit amorphous with small crystalline domain when analyzed using XRD. Both of the samples show diffraction at plane (002) which correspond to carbon network. The GRHA-KOH exhibit higher BET_{SSA} which is 518.11 m²/g as compared to GRHA-H₃PO₄, 315.07 m²/g. Furthermore, KOH also able to form

GRHA with an enhanced porosity. Thus, it can be deduced that KOH able to form GRHA with higher surface area and porosity.

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