Preliminary study of graphene like material fabrication from coconut shell using conventional furnace

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Abstract. Graphene has risen into a very interesting material because of its extraordinary properties. A new breakthrough that challenges the researcher is how to synthesis graphene from biomass as natural waste and plentiful resources. Coconut shell attracts the most attention because it contains the highest carbon atom among others. In this work, we present the experiment using conventional furnace to overcome the expensive one. Unfortunately, the result is not as expected that \(\text{Fe}_2\text{O}_3\) is formed instead of amorphous carbon. We are trying to describe what caused this happen and recommendation to overcome this problem.

1. Introduction

Graphene is one of carbon allotrope with two-dimensional honeycomb lattice that has caught plentiful attention since it was discovered in 2004 by Geim and Novoselov \[1\] Later researches arise to investigate the properties of one single layer of graphite crystal both in theoretical and experimental. Superior properties of graphene that catch much attention such as electrical property in which represented by electron velocity reaching that exceed \(\sim 10^6\) m/s, and electron mobility (up to 200.000 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\)) \[2\], the thermal property of 5000 Wm\(^{-1}\)K\(^{-1}\) for single-layer graphene\[3\], elastic properties and intrinsic strength of 1 TPa and 130 Gpa \[4\], optical property that the transparency is up to \(97.7\%\) \[5\] and calculated specific surface area is 2630 m\(^2\)g\(^{-1}\).

The application of graphene has been found in technology and human life. High conductivity and rapid electron mobility enable graphene used as an energy harvester and storage device such as supercapacitor \[6\], battery, and solar cell\[7\]. A combination of electrical and optical properties make graphene used as the transparent conductive film \[8\] which application can be found in Dye Synthesized Solar Cell (DSSC)\[7\], touch screen and flexible display \[9\]. Graphene also has the semiconductor-like property that enables it used as a Hi-speed transistor \[10\] photodetector \[11\] and LED \[12\]. Many other applications were found in graphene as conductive ink and chemical sensor. \[13\]

Graphene can be synthesized with a variety of methods including the Scotch type method\[1\], CVD\[14\], epitaxial growth\[5\], electrochemical exfoliation, and graphene oxide reduction\[15\]. The scotch tape method produces pristine graphene, but this process has limitations in the amount of product resulted. CVD provides a high quality of graphene, but the procedure of this method was complicated, and the high cost making it limited for laboratory scale. Liquid exfoliation is a method of
exfoliating graphite with the assistance of surfactant or organic solvent with ultrasonication. The epitaxial growth method produces graphene by annealing SiC, but obtained graphene cannot be transferred onto the desired substrate. Graphene can also be synthesized using the electrochemical exfoliation method using pyrolytic graphite, but the fabrication cost is very high because of the high raw material price. Reduction of Graphene Oxide is one of the simple methods by oxidizing graphite, exfoliate oxidized graphite, and reduce oxidized graphene. But pure graphite is needed as a precursor for synthesis.

One obstacle faced in graphene synthesis by mentioned method is the high cost of the raw material of carbon source. Meanwhile, natural resources serve abundant carbon especially biomass products [16]. Burning or heating of biomass reduces oxygen and other organic compound and left behind carbon contain of the substance. Sugar cane trash, coconut shell, rice husk, old corrugated cardboard packages, and chicken feather are biomass wastes that have potentially severed as carbon source material research.[17]

Among the mentioned commodity side product, coconut shell has been identified as the best bioresources for graphene-like material production because it contains relatively high carbon and the fewest ash[18]. Furthermore, coconut shell is widely available all around the world, long-lasting resources, and low cost. Coconut is produced in all continents and has been a wide commodity produced and has become revenue for several countries. The huge production of coconut delivers high coconut shell wastes as side effects making it a long last resource for the research. The abundant amount and spread all over the continent make this good are easy to get with cheap price. [19]

Coconut shell has widely used in carbon active production for capacitor[20], water purification[16], absorbent, air cleaning, etc. Li et al has reported coconut shell conversion into activated carbon prepared by one-step thermal heating followed by steam activation. The product has good performance when applied as a supercapacitor. Porous carbon synthesized from coconut shell reported by jurewitcz and bandosz et al had a good capacitance as serve as a capacitor[21, 22].

The use of coconut shell as a precursor of graphene and used as material for a capacitor had reported by Li et al. The synthesis process includes an annealing process at 900 C using a tubular furnace. We repeated their step and used a conventional furnace because of the availability of equipment especially in our lab. In this work, we describe what we get from the experiment and explain the cause of the phenomenon.

2. Experimental Setup

2.1. Materials
Mature coconut shell was bought from local market. Zinc dichloride and ferric trichloride were purchased from Merck, Indonesia. De-ionized water was obtained from internal refinery of laboratory.

2.2. Pre-treatment of coconut shell
Pretreatment was applied to coconut shell to convert it into charcoal. 20 grams of coconut shell was heated using furnace in temperature of 450 C for 1 hour. Heating process will reduce the mass of coconut shell charcoal produced.

2.3. Synthesis of graphene like material
Synthesis of graphene from coconut shell was carried out by mixing 3 grams of coconut shell charcoal and 9 g of Zinc Dichloride in 3 M Iron Trichloride solution. The mixture was stirred for 2 hours at 800 C. Evaporation will occur during the stirring process. Furthermore, heating process was carried out at a temperature of 100 C in the oven to release the solvent. The activation and graphitization process were carried out by heating the sample in a conventional furnace that set at 900 C for 1 hour with an increase in temperature of 5 C / minute.
2.4. Instrumental methods
In this study, the constituent of the sample was evaluated by using XRD measurement and organic bonding exist was measure by FTIR.

3. Result and Discussion
The initial step in the synthesis process was the carbonization of the coconut shell to release water and other elements, leaving the dominant content of carbon material. The heating process of coconut shell at 450 °C for 1 h produces reduced mass charcoal that ~18 % left of the initial mass (idrus2013). Carbonized coconut shell charcoal flakes were mashed by grinding the sample to obtain coconut shell carbon powder that represented in Figure 1.

Activation with zinc dichloride activator is in the purposes of making layer structures of carbon to produce graphene structures. In addition, a ferric trichloride catalyst is also provided to form a porous template to produce porous graphene material. The result of activation using zinc dichloride and ferric trichloride catalyst produces the sample with greyish colour that represented in Figure 2.

The crystal structure and constituents in the sample are examined using X-Ray Diffractometer (XRD). The desired result is that the sample is consist of dominantly by carbon structure in which the structure is building block of the graphene material. Graphene is built of sp2 bond that give pathway of electron and produces high electrical conductivity. The sample that has been synthesized gives a pattern of XRD test results as shown in Figure 3.
Unfortunately, the result of XRD measurement is major peaks appearing at position 2θ at 33, 35,6 and 54 in which indicate the crystal of hematite $\text{Fe}_2\text{O}_3$ based on the ICCD database. Meanwhile, the graphene pattern should show the peaks in position of 2θ at 24.5 that indicate distance of graphene layer (stobinski2014.). This result probably in consequence of catalyst FeCl$_3$ that is still left in the sample. Although FeCl$_3$ has volatile property in high temperature[23], there are several reactions in annealing process as shown in reaction (1), (2) and (3) [24].

\begin{equation}
200 - 300 \degree C : \text{FeCl}_3 + H_2O \rightarrow \text{FeOCl}\cdot H_2O + 2HCl \rightarrow \text{FeOOH} + 2HCl
\end{equation}

\begin{equation}
330 - 430 \degree C : 2\text{FeOOH} \rightarrow \text{Fe}_2\text{O}_3 + H_2O
\end{equation}

\begin{equation}
500 - 700 \degree C : 3\text{Fe}_2\text{O}_3 + C \rightarrow 2\text{Fe}_3\text{O}_4 + CO
\end{equation}

The formation of $\text{Fe}_2\text{O}_3$ happens at 330 – 430 °C. This product should experience further reaction with amorphous carbon expectedly formed in the process and results $\text{Fe}_3\text{O}_4$ along with temperature increase into 500-700 C. In our sample, the existence of $\text{Fe}_2\text{O}_3$ caused by an unfinished reaction process because of the limited capability of the conventional furnace. After re-check into actual temperature in the furnace while the experiment is happening, we found the temperature of 650 °C. This means the temperature does not support the formation of amorphous carbon and leaving $\text{Fe}_2\text{O}_3$ that formed in lower temperature. Based on reaction (3) $\text{Fe}_2\text{O}_3$ should has converted into $\text{Fe}_3\text{O}_4$, but in our sample, such a substance is not detected. This phenomenon was caused by amorphous carbon as fuel in the reaction is not formed yet because carbonization process take place at temperature of 700 – 1100 °C. [25]

Meanwhile, a conventional furnace does not guarantee a wild reaction between sample reacting between free air. There is the possibility of an unexpected reaction in high temperature because the matter is very active. Nitrogen or argon-based furnace is recommended to carried out this experiment. Noble gassed has self-defense to avoid them react with the sample.
4. Conclusion
The initial study of graphene like material synthesis using conventional furnace was performed. This experiment was expected to produce a high value of material. Meanwhile the annealing process that carried out in conventional furnace results formation of Fe2O3 instead of amorphous carbon. This phenomenon was caused by un-finished reaction due to lack of furnace ability. The reaction took place at 650 instead of 900°C produces Fe3O2 as pathway to produce amorphous carbon via FeCl3 catalyst. The temperature is not sufficient to ignite the reaction. Meanwhile the expected amorphous carbon is also not formed because carbonization process must be happened at temperature of 700 – 1000°C. To overcome this problem, it is recommended to use precise and advance furnace. Noble gas based furnace is prefer in order to prevent wild reaction between sample and air.

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