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Green Reduction of Graphene Oxide (GO) from Coconut Shell Using Rose Water in Various Temperature

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Abstract: Graphene and its related materials have attracted much interest in various applications regarding its exceptional physical, chemical, and mechanical properties. Reduction of graphene oxide (GO) from natural resources is recognized as one of the promising methods for low-cost and large-scale production of graphene-based materials. However, the reduction of GO is generally involves the application of toxic and poisonous substances. To counter this challenge, the green reduction which employ non-hazardous substances was introduced by numerous researchers. In this research, the green reduction of graphene oxide from coconut shell was investigated using rose water at room temperature, 70, 80, 90, and 100 °C. The prepared GO and green reduced GO (rGO) were characterized by X-Ray diffraction (XRD), Scanning Electron Microscope - Energy Dispersive X-Ray (SEM-EDX), Fourier transform infrared (FTIR), and I-V measurement. The low-cost and easy-handle green reduction of GO was obtained by immersing in rose water at room temperature which exhibit carbon to oxygen ratio, C/O of 2.97. Moreover, the effect of oxygenated-functional group to the electrical properties was also strongly discussed.

Keywords: Reduced graphene oxide; Coconut shell; Green reduction; Rose water.

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I. INTRODUCTION

Graphene is the promising and rising star among the materials science. Discovered in 2004, graphene is the only zero-gap material [1]. Graphene which is two dimensional (2D) honeycomb carbon structured in flat monolayer has attracted much interest among researchers since it was widely known as the first two dimensional atomic crystal [2]. The uses of graphene are very interesting as a new material with unique properties. Those sophisticated properties lead the expanded utilization of graphene in numerous applications such as solar cell [3], battery [4], sensors [5], and other electrochemical-devices [6]. Moreover, the reports of producing low cost solution based graphene precursor such as graphene oxide has recently attracted much interest among the researchers. Graphene oxide has originally similar structure to graphite with highly-oxygenated carbon rather than that of graphite structure [1]. Graphene oxide is derived from graphene by introducing covalent C-O bonds. Graphene oxide typically has been synthesized by chemically exfoliation of graphite oxide. Graphite oxide was first synthesized by Brodie in 1855 [7] followed by Staudenmaier [8] and Hummers [9] method, or some variation of these methods [10].

Graphene can be synthesized through CVD grown-graphene with CH_4 gas source or mechanically-exfoliated graphene from graphite material [1]. Those synthesis method produced high quality graphene but difficult to achieve mass-production of graphene. Another method to synthesize graphene is from reduction of graphene oxide. The main base material utilized in producing graphene oxide using Hummers method is graphite. Graphite is generally produced by so called Acheson process with extensive energy process around 3000 °C leading to graphite's high cost [11]. So far, this graphitization process is highly dependent on the non-renewable carbon precursors such as petroleum coke and coal tar pitch [12]. To counter this challange, biomass-derived carbon is widely explored as an alternatively renewable material due to its low cost and environmentally abundance. These advantages encourage researchers to explore the possiblity of graphite production from biomass-derived carbon of natural resources such as olive stone [13], camellia oleifera shell [14], oil palm fruit bunch [15, 16], coconut shell [17], rice husk [18], and other wooden materials. Moreover, previous works have been reported the establishment of biomass-derived graphite from mangosteen pericarp [19], coconut waste [20, 21] in advance of low cost and easy handled-way.

Bonded with various type of functional groups, such as hydroxyl, epoxy, carboxyl, and carbonyl groups at the sheet edges makes graphene oxide was highly hydrophilic which was easily dispersed in any solvents even water. Having large amount of intercalated water and oxygen containing functional groups, graphene oxide tend to have high resistivity due to the bad electronic transport through graphene caused by distortion of conjugated sp^2 carbon by the existence of those oxygen functional groups. Therefore, either thermal or chemical reduction must be performed to remove the intercalated water and oxygen functional groups in order to restore its properties nearly back to graphene-like material [22]. Thermal reduction at high temperature up to 8000 °C will decompose and introduce the formation of structural defect on graphene sheets [23]. Chemical reduction was also carried out using hydrazine/hydrazine derivatives which are unstable and toxic reducing agents [24]. Therefore, expoloration of various enviromentally friendly reducing agents such as ascorbic acid [25], bacterial respiration [26], anticoagulant [27] including the use of natural resources such as carrot root [28], and grape extract [29]. Rosa species [30, 31] as a mild reducing agent have attracted much interest now days. Antioxidants often act as reducing agents and it is necessary to investigate the potential of natural antioxidants in rose water as green reducing agent. So, herein a simple method is presented for the synthesis of reduced graphene oxide by green reduction using rose water.

II. METHOD

A. Preparation of graphene oxide

The coconut shell was previously cleaned from impurities and dried at 110 °C. The sample was further carbonized at 400 °C for 5 hours in vacuum. 5 grams of coconut shell powder was added in 115 mL sulfuric acid and then stirred for an hour. 2.5 grams of $NaNO_3$ was added in the solution an stirred for 1 hour in an ice bath to maintain the temperature below 20 °C. Potassium permanganate ($KMnO_4$) was gradually added to the solution until it reach the color change to greenish black. The solution was then stirred for 2 hours at 35 °C until it reach the dark brown color. The solution was then dissolved in deionozied water and repeatedly washed by acid solution, 30% H_2O_2 and 10% HCl to attain neutral pH. The GO solution was then dried at room temperature overnight to produce the GO powder.

B. Green reduction of GO

3 mM of GO solution was immersed in 12% commercial rose water with ratio of (1:1). The solution was then heated at room temperature, 70, 80, 90, and 100 °C.

The green-reduced graphene oxide (rGO) was further characterized by X-Ray Diffraction (XRD), Scanning electron microscope - Energy Dispersive X-Ray (SEM-EDX), Fourier-Transform Infrared (FTIR), and electrical measurement by analyzing of I-V characteristic curve.

III. RESULTS AND DISCUSSION

FTIR measurement was performed to detect various types of oxygen-containing functional group on the resulted rGO. FTIR result of rGO prepared by heat treatment at various temperature is exhibited on Fig. 1.

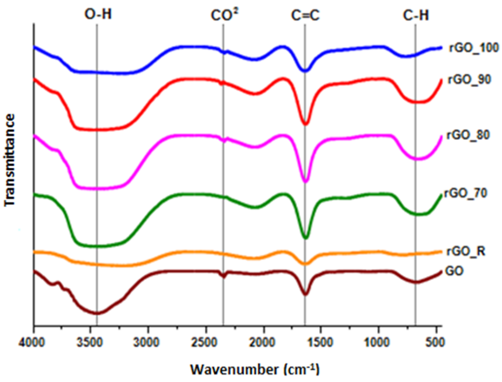


FIG. 1: FTIR result of GO and rGO prepared at room temperature (rGO-R), 70 °C (rGO-70), 80 °C (rGO-80), 90 °C (rGO-90), and 100 °C (rGO-100).

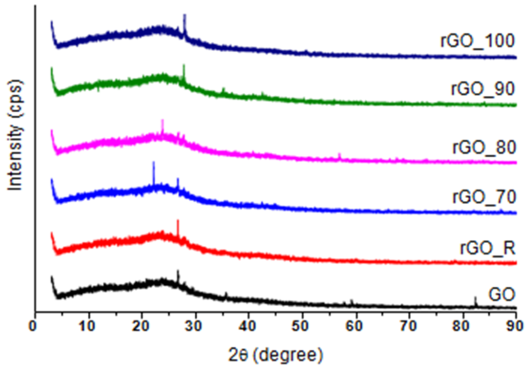
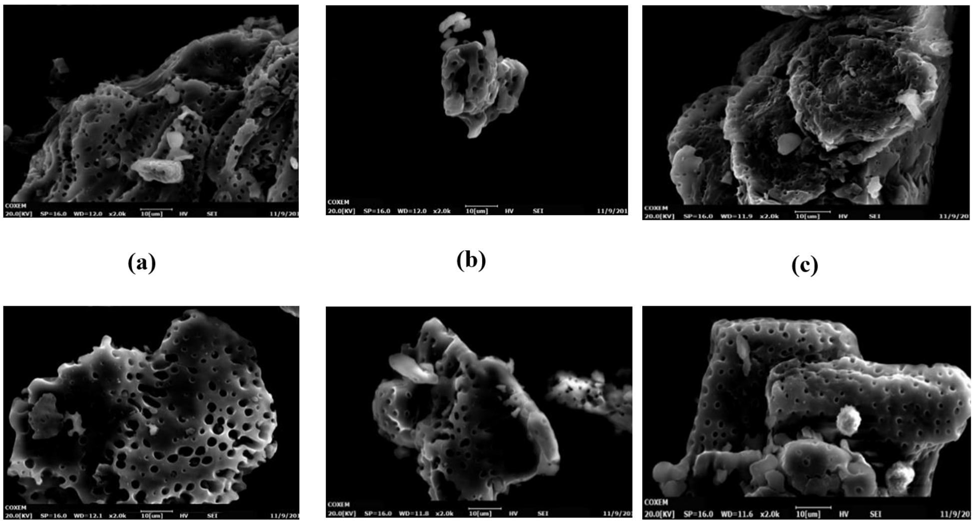


FIG. 2: XRD pattern of GO (black), rGO-R (red), rGO-70 (blue), rGO-80 (purple), rGO-90 (green), and rGO-100 (navy).

Fig. 1 shows a typical FTIR spectrum recorded for GO (brown colored line) in which a strong and broad absorption band at 3445.04 cm^{-1} due to the O-H stretching mode of intercalated water and weak band at 676.81 cm^{-1} due to the C-H stretching. Also, other characteristic absorption band of GO was discoverd at 1638.12 cm^{-1} due to C=C stretching originated from sp^2 carbon bond. Another weak absorption band was also found at 2346.23 cm^{-1} due to CO_2 strecthing mode originated from infrared background spectrum instead of the samples.

After green reduction using rose water at room temperature (rGO-R), the characteristic absorption bands originated from O-H streching dramatically decreased, indicating the reduction of GO. The absorption band originated from O-H stretching mode is reappeared after heating at 70 °C. The appearance of O-H band is presumably due to the evaporation of antioxidant substances contained in rose water during heating. The reduction of oxygen is further occured on rGO-100 (blue colored line) shown by the decreasing of O-H absorption band which presumably indicates that the mild thermal reduction has controlled the reduction process instead of green-chemical reduction since we assume that the whole antioxidant substances hava been fully evaporated. FTIR results confirm that the oxygenated functional groups decrease after green reduc-



(a) (b) (c)

(d) (e) (f)

FIG. 3: SEM images of GO (a), rGO-R (b), rGO-70 (c), rGO-80 (d), rGO-90 (e), and rGO-100 (f).

TABLE I: Elemental content of GO and rGO

Sample	Element							
	Mass percent (%)				Atomic percent (%)			
	C	O	Al	Si	C	O	Al	Si
GO	35.37	51.41	10.52	2.71	44.32	48.36	5.87	1.45
rGO-R	68.13	30.52	0.58	0.77	74.35	25.00	0.28	0.36
rGO-70	65.44	34.06	0.30	0.20	71.73	28.03	0.14	0.09
rGO-80	58.67	41.02	0.07	0.24	65.48	34.37	0.03	0.12
rGO-90	54.07	41.60	1.20	3.14	62.02	35.82	0.61	1.54
rGO-100	61.08	36.73	0.54	1.66	68.17	30.77	0.27	0.79

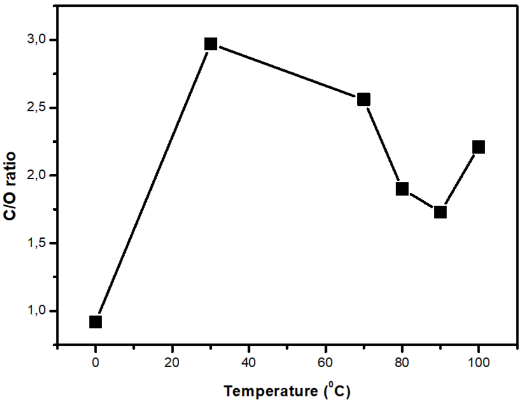


FIG. 4: C/O ratio of GO and rGO prepared at various temperatures.

tion. This statement is further described and supported by elemental analysis result (Table I).

The X-RD patterns (Fig. 2) of the GO and rGO exhibited a diffraction peak I (GO peak) at about $2\theta = 13^o$, corresponding to the C (002) interlayer spacing (d-spacing) of 0.64 nm, which revealed the introduction of oxygenated functional groups. Peak II (rGO peak) is also appeared at about $2\theta = 24^o$, corresponding the d-spacing of 0.36 nm indicating the reduction of GO. The appearance of peak II on GO sample indicates that the as-prepared GO is partially reduced which probably occur due to the uncompleted oxidation process that unable to produce nearly high crystalline graphite oxide with sufficiently broad d-spacing to elaborate the oxidation process.

SEM images of the prepared GO and rGO are shown in Fig. 3. The typical agglomerated and wrinkled porous crumples made up of many stacked layers graphene with numerous edges are observed in Fig. 3. Those images shows that the samples are graphenic carbon structure rather than rGO. Furthermore, the modest elemental analysis was exhibited by Energy Dispersive X-Ray (EDX) shown in Table I and Fig. 4.

Elements contained in GO and rGO is shown in Table I. The elements are dominated by carbon and oxygen with the present of low impurities of Si. The modest calculation result of carbon to oxygen ratio (C/O) was performed in Fig. 4. The C/O increases from 0,92 to 2,97 after green reduction at room temperature indicating the removal of oxygen containing functional groups. The C/O ratio gradually decreases to 1.73 after heating up to 90 °C which presumably due to evaporation of reducing agent. The C/O reascend to 2.21 after heating at 100 °C due to the evaporation of intercalated water and thermal reduction dominate at this applied temperature.

In summary, FTIR and elemental analysis results confirm that the green reduction using rose water at room temperature produces the highest degree of reduction among other samples, indicated by decreasing the amount of oxygen in the sample. The increasing of applied temperature up to 90 °C lower the degree of reduction, indicated by increasing the amount of oxygen in the samples. Yet, the oxygen decreeing is peculiarly observed after heating at 100 °C. The amount of oxygen highly affects the electrical properties of rGO (Fig. 5).

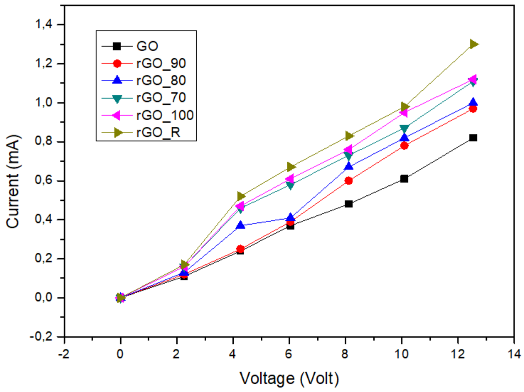


FIG. 5: I-V measurement of GO and rGO prepared at various tempeatures.

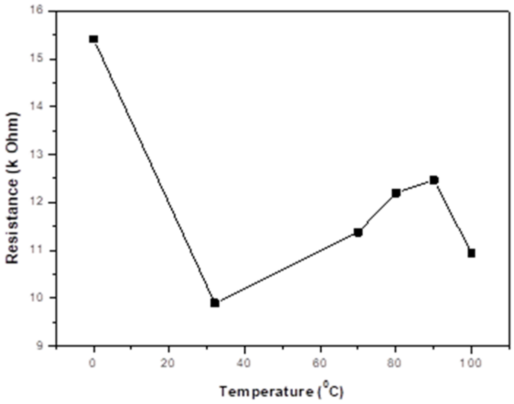


FIG. 6: The resistance of GO and rGO prepared at various temperatures.

Fig. 5 shows the I-V characteristic of GO and rGO at various temperatures. The metal-semiconductor interface is assumed to be Ohmic contact. Linear regression was performed to define the slope and calculate the resistance (Fig. 6).

Fig. 6 shows that the green reduction at room temperature restore its conductivity indicated by the diminishing of resistance from 15.4 to 9.8 kΩ. This indicates the green reduction at room temperature is successfully restored the electrical properties from GO to rGO along with the removal of oxygen containing functional groups. The resistance gradually increase from 9.8 to 12.5 kΩ after heating from room temperature up to 90 °C and decrease to 10.9 kΩ. This phenomena is strongly depended on the amount of oxygen contained in samples (see the C/O ratio result in Fig. 4). The higher amount of oxygen attains the lower electrical conductance.

IV. CONCLUSION

Biomass-derived graphene oxide from coconut shell was produced by Hummers methods and reduced by rose water at various temperature to restore its electrical properties. The highest conductance was achieved after green reduction at room temperature due to the removal of oxygen containing functional groups described by the rise of the carbon to oxygen ratio. The increase of temperature up to 90 °C will gradually reduce the conductance accounted by the restoration of oxygen contained on the samples expressed by the decreasing of C/O ratio. The C/O ratio reascend after heating at 100 °C giving the rise of electrical conductance. Those conclude that the oxygen containing functional groups attain to reduce the electrical conductance and vice versa.

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