

Morphological, Structural and Electrical Properties of Coconut Shell-based Reduced Graphene Oxide

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Abstract

In this work, reduced graphene oxide (rGO) was produced by green reduction process utilizing rose water as reducing agent. Various reduction temperature were also carried out to investigate its effect to the produced rGO. Prior to the reduction process, GO was initially synthesized by Hummers' method utilizing coconut shell (CS) as initial carbon source material. The fabricated CS-based GO and rGO were then characterized to investigate their morphological, structural and electrical properties. Based on the measurement, rGO produced by reduction process at room temperature (RT) possessed the best sample among others. rGO_RT showed the highest electrical conductivity ($0,08793 \pm 0,00174$ mS) compared to CS-based GO or other rGO samples.

Keywords: Coconut shell; Graphene oxide; reduced graphene oxide; Green reduction; Rose water

INTRODUCTION

The progress on science and technology in the 21st century has been widely developed, especially in term of material, such as graphene. Geim and Novoselov have successfully discovered graphene at 2004 which possessed excellent electrical, optical and mechanical properties. Graphene has high electrical conductivity, thin sheet's layer with high transparency [1] and higher mechanical properties compared with steel [2]. These excellent properties have motivated researchers to apply this material for various applications, such as medical, energy and electronic devices. In medical field, graphene was used as a base material for biosensor fabrication [3]; [4] and cancer therapy [5]. Graphene was also used for batteries [6] and solar cell fabrication [7]. Meanwhile, in electronic devices, graphene was applied for supercapacitor [8] and transistor [9]; [10]. These confirm that graphene is very useful for our life thus need to be produced in large scale.

The effort on producing graphene should consider the following aspects; availability of initial material, cost effectiveness, simpler procedure, shorter synthesis time and environmentally friendly. Graphene can be synthesized by mechanical exfoliation (ME) and chemical vapor deposition method (CVD) [11]. Even though ME is a simple method, the low product yield limit this method to be applied for large scale. Meanwhile, CVD can produce high product yield. However, CVD require expensive equipment thus inefficient to be applied. Therefore, other graphene synthesis method need to be developed to replace these methods. Pei et al. (2010) have successfully synthesize graphene by reducing graphene oxide (GO) into reduced GO (rGO).

GO can be synthesized by oxidizing and exfoliating graphite [1]. Oxidizing process can be done by various methods, such as Hummers' method [12]. Meanwhile, reduction process can be carried out by

chemical, electrochemical and thermal reduction [13]. Chemical reduction was usually done by using hazardous chemical reducing agents [14]. Electrochemical reduction was done by coating GO onto the substrate thus require high cost [13]. Meanwhile, thermal reduction was done by heating the GO at very high temperature [13] and need very sophisticated equipment [14]. These mentioned reduction method inefficient to be performed thus need to be replaced by the simpler and environmentally friendly green reduction method. Green reduction was done by utilizing reducing agent-based natural material, such as carrot [15], grape [16], spinach [17] and rose water [18].

On the other hand, initial material for graphene can also be found from natural material, such as rice husk [19], corn stem [20], snake fruit's skin [21] and coconut shell (CS) which have high carbon element. Moreover, Indonesia is one of the biggest country that produced coconut [22]. All parts of coconut can be utilized, including its shell which can be used as craft or charcoal. Charcoal can also be used as graphite as initial material to synthesize graphene. [22] have successfully synthesized graphite from CS by heating process from 400 to 1000°C. Therefore, this work will utilize the waste CS as graphite initial material to produce rGO by using Hummers' method followed by green reduction method utilizing rose water as reducing agent.

MATERIALS AND METHODS

Materials

CS powder, sulphuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), kalium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2) and hydrochloric acid (HCl) were used to synthesize GO. Meanwhile, rose water was used as reducing agent to produce rGO.

Methods

Prior to oxidation process, CS powder as initial graphite material was oven-dried at 110°C for 1 hour followed by heating process in the furnace at 400°C for 5 hours. GO was then initially synthesized by Hummers' method. An amount of CS charcoal powder was stirred in H_2SO_4 solution for 1 hour. Next, $NaNO_3$ was added to the mixture and constantly stirred for another 1 hour in the ice bath. Next, $KMnO_4$ was added into the solution mixture for 1 hour and constantly stirred for another 1 hour at temperature of 0 to 20°C. Stirring process was further continued for about 2 hours at 35°C. Aquades was then added to the mixture and stirred for 15 minutes. In order to eliminate the $KMnO_4$ residue, H_2O_2 was added. The precipitation of this solution was then washed by HCl followed by aquades for several times until neutral pH was obtained. The neutral pH of precipitation (graphite oxide) was dried at room temperature for 1 day. GO was then prepared by dispersing the obtained graphite oxide powder into aquades with the ratio of 7 mg/1 mL. The mixture was constantly stirred at 500 rpm for 6 hours at 70°C temperature. rGO was then produced by adding 12% of rose water into GO solution (1:1 V/V) and heated with various temperature (room temperature (RT), 70, 80, 90 and 100°C) for 5 hours. The solution was further washed with aquades until neutral pH was obtained. The precipitation was then dried at RT for a day.

The produced rGO was then characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD), Fourier transform infrared (FTIR) and current-voltage (I-V) measurement to investigate its morphological, structural and electrical properties.

RESULTS AND DISCUSSION

SEM and EDX analysis

Morphological properties of the fabricated CS-based GO and rGO was investigated by SEM and the results are shown in Figure 1. Based on Figure 1 (a), the synthesized CS-based GO showed an agglomeration of graphene's layer with many pores observed in the entire surface. After reduction process at RT was performed, an agglomeration was still observed with some pores in the CS-based rGO surface. However, the rGO size was observed to be smaller with empty space inside it compared to GO sample (Figure 1 (b)). As the reduction temperature was increases from 70 to 100°C, the agglomeration and pores were still observed in the entire rGO surface (Figure 1 (c)-(f)). Based on these results, the expected 2-D graphene morphology was not observed for all samples, confirmed by an agglomeration and pores. The observed pores in this study was resulted from the structural defect due to the cracking of carbon bond on the CS-based GO and rGO. In addition, carbonization process at 400°C was believed to cause the pores formation. The obtained CS-based GO and rGO morphology was in a good agreement with previous reports which utilize CS as the carbon source [23] & [24].

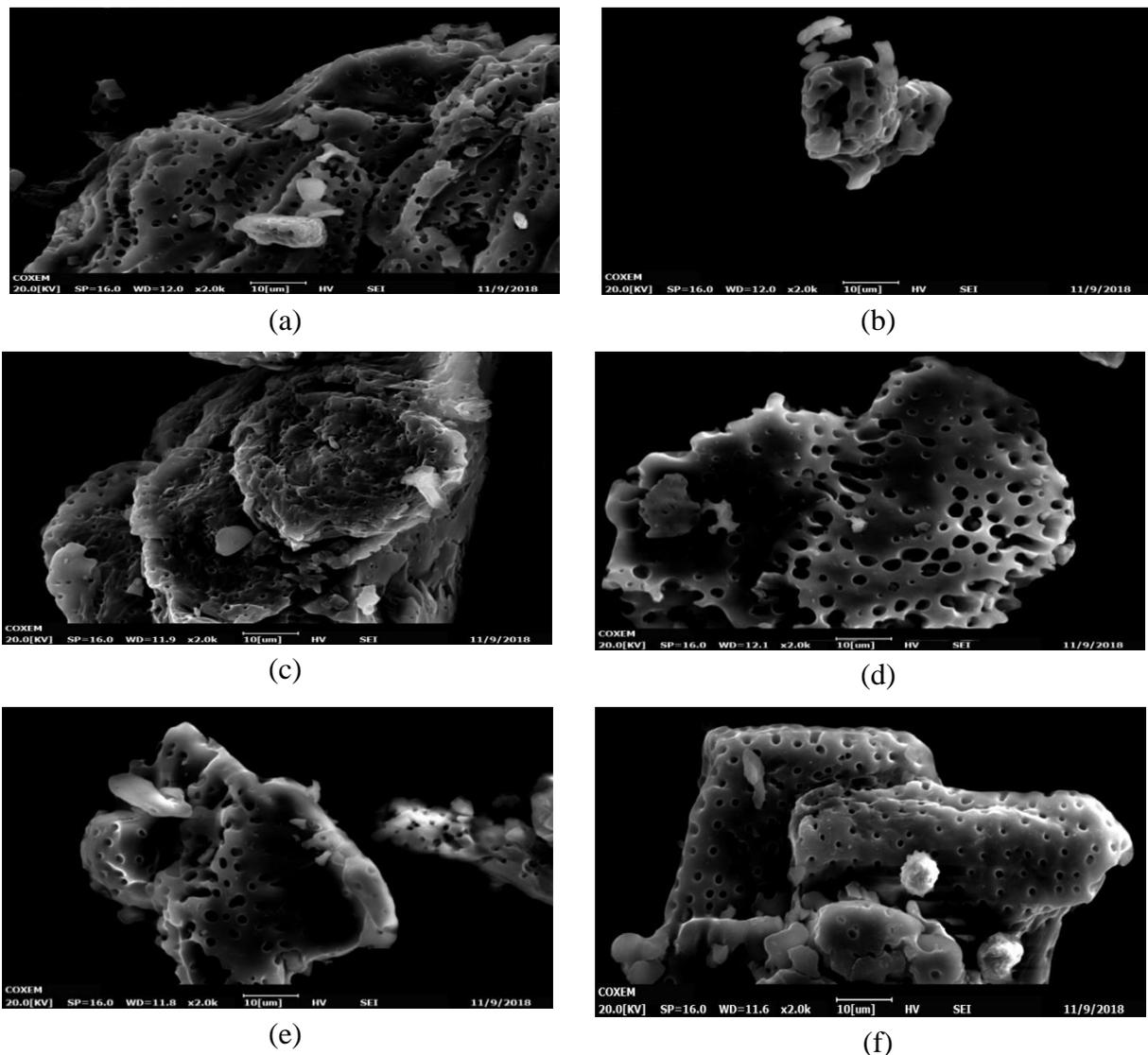


Figure 1. SEM images of the fabricated (a) GO and rGO with different reduction temperature: (b) RT, (c) 70, (d) 80, (e) 90 and (f) 100°C

Further EDX analysis was carried out to investigate the elemental compound of the fabricated CS-based GO and rGO and the results are summarize in Table 1. Based on Table 1, all samples possessed these elemental compound; carbon (C), oxygen (O), aluminum (Al) and silicon (Si). As the main elemental compound of GO and rGO, C and O were dominantly observed compared to Al and Si. Al and Si can be considered as impurities to the produced CS-based GO and rGO since it comes from the used aluminum foil and beker glass during reduction process. The effectiveness of the carried out reduction process was further confirmed by lower O content of CS-based rGO compared to GO samples and the ratio between C and O (C/O). Based on the calculation, rGO produced by RT reduction process resulted the highest C/O ratio (2.97) compared to others, especially GO sample. This result was also in a good agreement with Perkasa et al. (2016). As the reduction temperature increases from 70 to 100°C, lower C/O ratio was observed, except for rGO_100 sample. This lower C/O ratio was caused by higher O content which might be resulted from heating process during reduction process.

Table 1. EDX analysis of the produced CS-based GO and rGO

Sample	Elemental compound weight percentage (%)				Elemental compound atomic percentage (%)				C/O
	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	0.92
rGO_R	68.13	30.52	0.58	0.77	74.35	25.00	0.28	0.36	2.97
rGO_70	65.44	34.06	0.30	0.20	71.73	28.03	0.14	0.09	2.56
rGO_80	58.67	41.02	0.07	0.24	65.48	34.37	0.03	0.12	1.90
rGO_90	54.07	41.60	1.20	3.14	62.02	35.82	0.61	1.54	1.73
rGO_100	61.08	36.73	0.54	1.66	68.17	30.77	0.27	0.79	2.21

XRD analysis

The structural properties of the fabricated CS-based GO and rGO were further analyzed by XRD and the results are shown in Figure 2 and summarized in Table 2. Based on Figure 2. There are two peaks observed for all samples. First peak of GO observed at $13.2 \pm 0.12^\circ$ correspond to (001) plane and confirmed the oxidation process of CS into GO. Second peak observed at $23.65 \pm 0.07^\circ$ correspond to (002) plane and showed the unsuccessful oxidation process of CS. Based on the calculation, GO's crystallite size based on these peaks were $820 \pm 19 \times 10^{-3}$ and $894 \pm 14 \times 10^{-3}$ nm, respectively. After reduction process, these peaks were shifted as summarized in Table 2. Based on the calculation, higher d-spacing were observed in GO compared to rGO samples. This indicated that GO has wider planar distance compared to rGO. In addition, it also confirmed the oxygen functional group reduction on rGO samples. The lowest d-spacing value was then observed for rGO_RT sample. Based on these results, it also can be concluded that the utilization of rose water as reducing agent during reduction process only partially remove the oxygen functional group of GO.

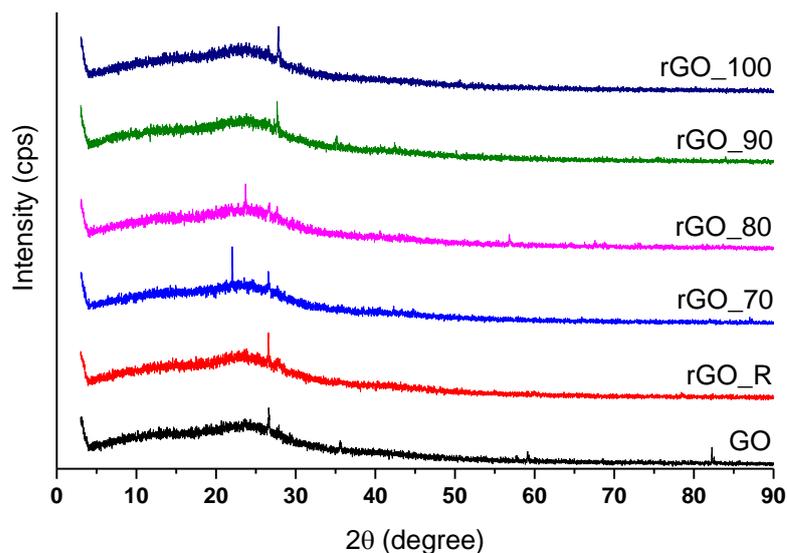


Figure 2. XRD analysis of the fabricated CS-based GO and rGO

Table 2. XRD analysis of the fabricated CS-based GO and rGO

Sample	1 st peak			2 nd peak		
	Position (°)	d-spacing (Å)	Crystallite size (nm)	Position (°)	d-spacing (Å)	Crystallite size (nm)
GO	13.2 ± 0.12°	(670192 ± 1.1) × 10 ⁻⁵	(820 ± 19) × 10 ⁻³	23.65 ± 0.07°	(375897 ± 1.9) × 10 ⁻⁵	(894 ± 14) × 10 ⁻³
rGO_RT	13.88 ± 0.21°	(637508 ± 2.0) × 10 ⁻⁵	(650 ± 20) × 10 ⁻³	24.34 ± 0.09°	(365395 ± 2.6) × 10 ⁻⁵	(858 ± 15) × 10 ⁻³
rGO_70	13.75 ± 0.24°	(643506 ± 2.3) × 10 ⁻⁵	(645 ± 24) × 10 ⁻³	24.05 ± 0.10°	(369735 ± 2.8) × 10 ⁻⁵	(906 ± 20) × 10 ⁻³
rGO_80	13.37 ± 0.21°	(661709 ± 1.9) × 10 ⁻⁵	(675 ± 22) × 10 ⁻³	24.04 ± 0.10°	(369886 ± 2.8) × 10 ⁻⁵	(856 ± 18) × 10 ⁻³
rGO_90	13.26 ± 0.11°	(667173 ± 1.0) × 10 ⁻⁵	(797 ± 19) × 10 ⁻³	23.88 ± 0.06°	(372328 ± 1.7) × 10 ⁻⁵	(927 ± 14) × 10 ⁻³
rGO_100	13.61 ± 0.27°	(650094 ± 2.5) × 10 ⁻⁵	(673 ± 33) × 10 ⁻³	24.03 ± 0.13°	(370038 ± 3.7) × 10 ⁻⁵	(844 ± 20) × 10 ⁻³

FTIR analysis

FTIR analysis result of the fabricated CS-based GO and rGO are shown in Figure 3. FTIR graph of CS-based GO showed several peaks at 676.81, 1638.12, 2346.23 and 3445.04 cm⁻¹. These peaks were correlated to the bending of C-H, the straining of C=C, the bonding of CO₂ and the straining of O-H, respectively. After reduction process, these peaks were slightly shifted as summarized in Table 3. The observed O-H peak confirmed the successful oxidation process, while C=C peak were the base structure of GO and rGO (sp² carbon). Based on Figure 3, lower O-H peak intensity of rGO_RT and rGO_100 were observed compared to other samples. This lower intensity confirmed the successful reduction process of these samples.

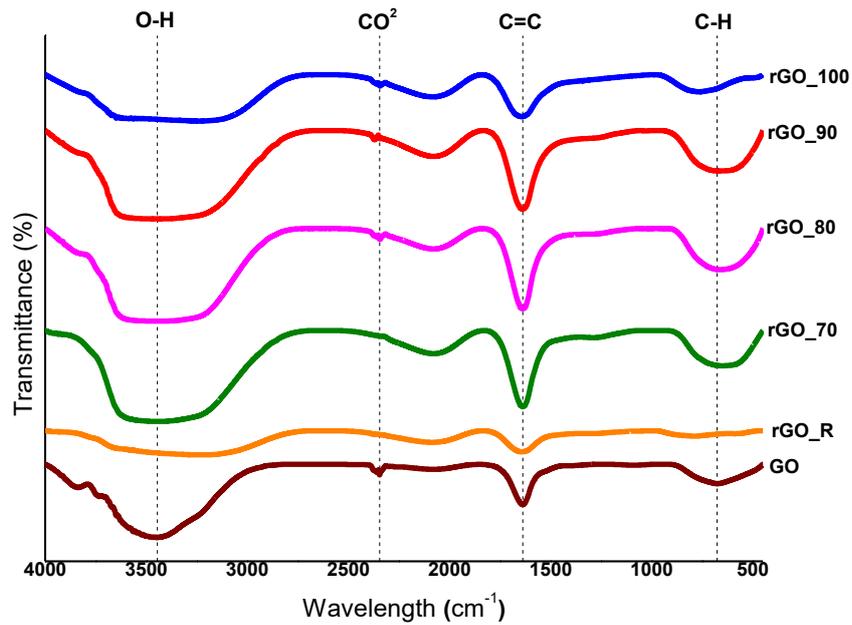


Figure 3. FTIR analysis of the fabricated CS-based GO and rGO

Table 3. FTIR analysis of the fabricated CS-based GO and rGO

Sample	The observed peak (cm ⁻¹)			
	C-H	C=C	CO ₂	O-H
GO	676.81	1638.12	2346.23	3445.04
rGO_RT	784.26	1642.65	-	3200-3600
rGO_70	655.91	1634.12	-	3200-3600
rGO_80	658.71	1638.3	2344.47	3200-3600
rGO_90	668.5	1634.36	2369.59	3200-3600
rGO_100	764.01	1644.72	2343.18	3200-3600

I-V analysis

The electrical conductivity of the fabricated CS-based GO and rGO are summarized in Table 4. Overall, rGO samples possessed higher electrical conductivity compared to GO sample. This indicated that rGO has higher ability to transfer electron. Based on the analysis, it also found that the highest electrical conductivity was achieved by rGO_RT sample. This result is in line with d-spacing measurement and C/O ratio based on XRD and EDX analysis, respectively. This result further confirmed that the decrement of oxygen functional group resulted in the electrical conductivity increment.

Table 4. Electrical conductivity of the fabricated CS-based GO and rGO

Sample	Electrical conductivity (mS)
GO	0,06742 ± 0,00231
rGO_RT	0,08793 ± 0,00174
rGO_70	0,08466 ± 0,00294
rGO_80	0,07403 ± 0,00322
rGO_90	0,07224 ± 0,00280
rGO_100	0,07823 ± 0,00241

CONCLUSION

CS-based GO and rGO have been successfully fabricated via Hummers' followed by green reduction process utilizing rose water as reducing agent. Based on several characterizations, the best sample was rGO_RT which possessed the highest C/O ratio and electrical conductivity.

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