GREEN SYNTHESIS OF REDUCED GRAPHENE OXIDE USING LIME JUICE REDUCTOR FROM *Citrus aurantifolia*

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Abstract: In this study, the reduced graphene oxide (rGO) synthesized by using lime juice as an environmentally friendly reducing agent and inexpensive cost. The synthesis was carried out by oxidizing graphite with the Hummer method to form graphene oxide (GO) was formed, then the GO was reduced by using lime as the natural reducing agent. X-ray analysis shown a vital diffraction pattern for graphite at $2\theta = 26.4°$, for graphene oxide appears around $2\theta = 10°$ and $43°$, and rGO at $2\theta = 23.8°$. Furthermore, the infrared spectrum of the three samples showed the peak of the hydroxyl group at 3412 cm^{-1}, which appeared on graphene oxide, but was not observed in rGO. The vibrational mode of carbonyl (C=O) at 1723 cm^{-1} was also observed with high intensity on graphene oxide. This information showed that GO has a large number of oxygen-containing groups. Then, in the dissolution test shown that the GO was more soluble in polar solvents such as water than ethanol.

Keywords: lime juice, *Citrus aurantifolia*, green synthesis, reduced graphene oxide (rGO)

Introduction

Reduced Graphene Oxide (rGO) was considered to be one of the excellent adsorbent materials for removing heavy metals containing various reactive oxygen functional groups such as epoxide, hydroxyl, ketones, and carboxyl groups (Agharkar et al., 2014). Also, rGO has a high surface area up to 2620 m^2/g (theoretical value) and can be obtained easily from natural graphite on a large-scale (Lopez et al., 2017). The rGO material was a new type of carbon nanomaterial, which has attracted lots research interest not only in the fields of biology, and electronics but also in wastewater treatment (Silva et al., 2018; Zhang et al., 2013), for example, adsorption of fluoride ions, heavy metals such as As, Cu, Pb, and Cd (Ferrero et al., 2014; Jingjing et al., 2014), and exhibited as a good adsorption dyes material.

Large scale graphene production was very desirable for application certain, meanwhile, the cost was not expensivable. The development of synthesis method for industrial applications mainly depends on the availability of efficient and inexpensive methodologies that enable the preparation and manipulation of this material on a large scale (Tingshun et al., 2015). Synthesis of rGO with chemical reduction method was a promising route towards large-scale rGO production for commercial applications. Chemical reduction was the most versatile method because it could be done in both acid and alkali media, scalable, and economically inexpensive. Various reducing agents such as $NaBH_4$, Zn metal, and $LiAlH_4$ had reported for GO reduction. However, most chemicals used are toxic (Lopez et al., 2017). Therefore, there is a need for an easy, inexpensive, and environmentally friendly method for the synthesis of rGO (Agharkar et al., 2014). Recently, various environmentally friendly green reductions, such as *Psidium guajava*, Thiourea dioxide, Eucalyptus, and Vitamin C have been developed to reduce the GO (Silva et al. 2018).

Lime (*Citrus aurantifolia*) contains components of weak organic acids, especially types of citric acid. This compound is a good and natural preservative, besides being used as a sour flavor enhancer in soft foods and drinks. This substance can also be used as an environmentally friendly cleaning agent and as an antioxidant. Citric acid is found in various types of fruits and vegetables but is found at high concentrations, which can reach 8% dry weight, in lemons and limes (e.g., lime and kaffir lime) (Penniston et al., 2008).

Therefore, to overcome the cost of expensive rGO synthesis that does not endanger the environment, the use of lime as a GO reducing agent is considered in this study.

Material And Methods

Equipment and Material Preparation

Graphite powder (8000 mesh, 99.95% purity) was obtained from Aladdin Reagent Co. Ltd., Shanghai, China, 97% H_2SO_4 (Pudak), 37% HCl (Merck), Sodium nitrate (Merck), Potassium Permanganate (Merck), 35% H_2O_2 (p.a), Lime, and Aquadest.

Graphene Oxide Synthesis

GO was prepared with a modified Hummer method (Agharkar et al., 2014). In detail, 1 g of natural graphite powder was added to 23 mL of H_2SO_4 in a 500 mL glass under stirring in an ice bath. Next, 0.5 g of $NaNO_3$ was added and stirred continuously in an ice bath for 10 minutes. 3 g of $KMnO_4$ slowly added to the above solution and stirred for 2 hours in an ice bath. Then, 3 mL of 30% H_2O_2 was added after 10 minutes (Figure 1).

Synthesis of Reduced Graphene Oxide

Commercially available lime juice was squeezed into a container, then diluted with 100 mL distilled water according to the desired concentration. 100 mg GO was added to this solution and sonicated for 30 minutes until it formed a well-dispersed brown solution. The solution was centrifuged at 4000 rpm for 30 minutes, and then both solution was placed in a microwave oven at 800 W for 1 minute.

Characterization of Product

The diffraction pattern were collected with Rigaku-Denki diffractometer in a Bragg–Brentano configuration using Cu-sealed tube (Kα : 0,154 nm). This measurement was operated at 40 kV and 20 mA with stability of 0.01%/8 h, and the refraction data were recorded at 2θ angel between 5º to 80º with a step of 0.04º and counting rate of 5 s/step. The FT-IR spectroscopy study was done, which the sample in press together with KBr to form pellet in KBr matrix, then analyzed by Bruker Alpha FTIR, with range of wave number 550 - 4000 cm^{-1} and scanning counted 16 times. Lastly, the solubility test was conducted with water and ethanol solvent.

Discussion

Reduced Graphene Oxide Synthesis Process

The oxidation reaction was the first process to produce GO. After obtaining GO, the GO is then reduced to rGO using natural reducing agents of the lime juice. Graphite Intercalation Compound (GIC) was formed from graphite that was easier to oxidize. During this process, several functional groups such as phenol, epoxy, ketone, carboxyl, and carbonyl were formed on carbon (Figure 2). This functional group generated the material to be highly hydrophilic and easily peeled off to GO. Reducing process of GO with lime juice served to restore structural defects in the carbon lattice by returning the conjugation π and to remove the functional group of Figure 2.
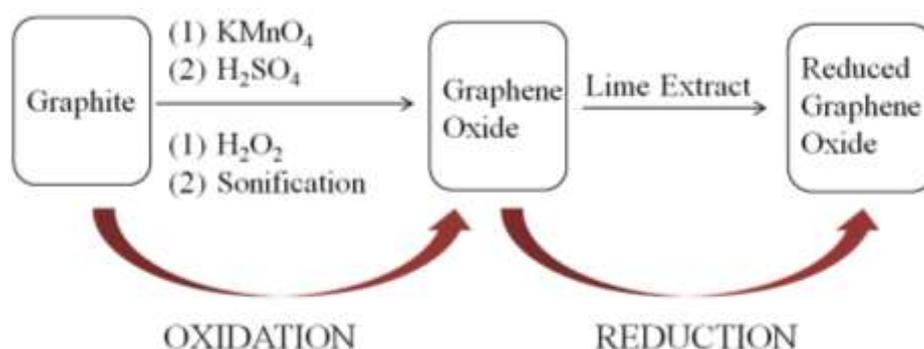

Figure 1. Schema of Reduced graphene oxide synthesis process

The process of graphene synthesis was conducted using a modification of the Hummer method. 2 grams of graphite powder was dissolved into 98 mL of 98% H_2SO_4, then 4 gram of $NaNO_3$ were added when the stirring process lasts for 1 hour. Addition of 8 gram of $KMnO_4$ was carried out gradually into the mixture after stirring lasted 2 hours. The temperature was maintained for 4 hours at 20-30 °C. The mixture was stirred slowly until it turned into a greenish-black. The stirring process was continued for 20 hours at 35 °C. After 24 hours of stirring, the mixture was turned into a light brown. The formation of this light brown provedthat the oxidation process of graphite has taken place. Then, the ultrasonication of ultrasonic waves 50/60 Hz for 90 minutes was carried out, and the mixture was dried again at 160 ºC until dark black, red deposits were called graphene oxide (GO) (Agharkar et al., 2014).
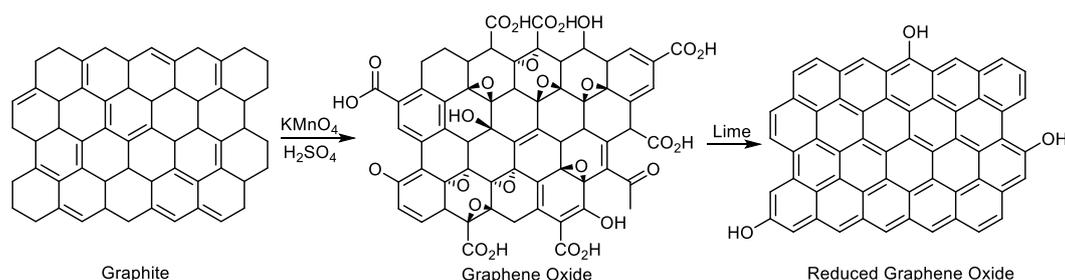

Figure 2. The reactions that occur during the synthesis process of rGO

The GO was reduced by adding 20 mL of lime juice, then stirring for 5 hours. After 5 hours of stirring, 20 mL of 35% HCl was added and followed by a stirring process for 5-30 minutes, then washed with distilled water and lime juice. The washing process was repeated using distilled water until the mixed pH becomes neutral. The results of the black precipitate in the washing process were put into small Teflon in a stainless steel tube and heated in a kiln at 160 °C for 18 hours. The product obtained was referred to as reduced graphene oxide (rGO).

Characterization of Graphene Oxide and Reduced Graphene Oxide

X-ray Diffraction (XRD)

The X-ray diffraction pattern for graphite, graphene oxide, and reduced graphene oxide was shown in Figure 3. The diffraction peak for graphite was appeared at $2\theta = 26.4°$ with the layer distance (d-spacing) 0.34 nm. After graphite oxidation, the diffraction peak for graphene oxide was appeared around $2\theta = 10°$ with a layer distance of 0.88 nm. The diffraction pattern on graphene oxide shown a greater distance between layers compared to layers in graphite. This was caused by the insertion of an oxygen-containing functional group between the layers on graphene oxide. Besides, the diffraction peak appeared around $2\theta = 43°$ in the XRD pattern of graphene oxide, and this indicates that graphene oxide showed turbostratic interference (Kyzas et al., 2018). XRD analysis for reduced graphene

oxide showed a diffraction peak of $2\theta = 10°$ which shifted to $2\theta = 23.8°$ (diffraction peak from graphene oxide to reduced graphene oxide), with d-spacing which was 0.37 nm. The decrease in d-spacing shows that when graphene oxide is reduced to reduced graphene oxide, the distance between layers was reduced because the functional group loses back. Therefore the rGO has a layer that looks like graphite before.
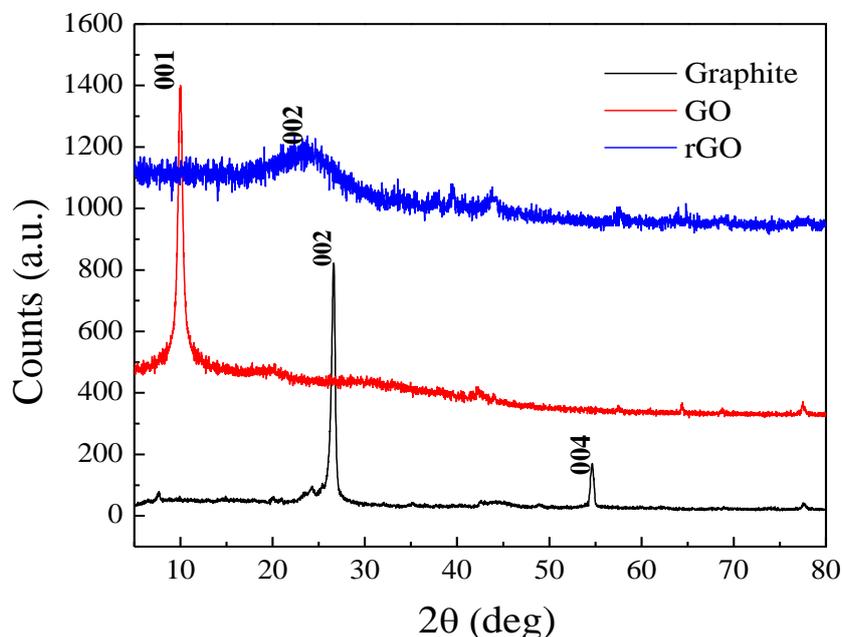

Figure 3. Diffraction patterns from X-rays to samples of graphite, graphene oxide, and reduced graphene oxide

The morphology of rGO was more amorphous compared to GO and graphite. Graphite in the form of silver powder, GO in the form of blackish brown powder. But the rGO was a wonderful black powder. This morphology corresponds to the XRD chart in figure 3, where the rGO does not showed sharp peaks such as GO and graphite. Therefore, rGO has a low level of crystallinity (Liu et al., 2016).

Infrared Spectrum (FTIR)

The FTIR spectrum of the three samples was shown in Figure 4. Based on the spectrum obtained, the peak at 3412 cm^{-1} showed stretching of the hydroxyl group. The vibration mode of carbonyl (C=O) occurred by stretching at 1723 cm^{-1}. The C─O group epoxide group occurred stretching in 1178 and 1073 cm^{-1}. The high intensity of the main peak in GO reveals that a large number of oxygen-containing groups exist after the oxidation process. The peak at 1620 cm^{-1} was related to the stretching of the alkene group (C=C) (Lopez et al., 2017). After reduction, the intensity of the rGO peak for the carbonyl and hydroxyl groups decreased significantly, while the intensity of the C=C group stretching at 1630 cm^{-1} increased. All suitable peaks in rGO have a smaller intensity compared to GO.
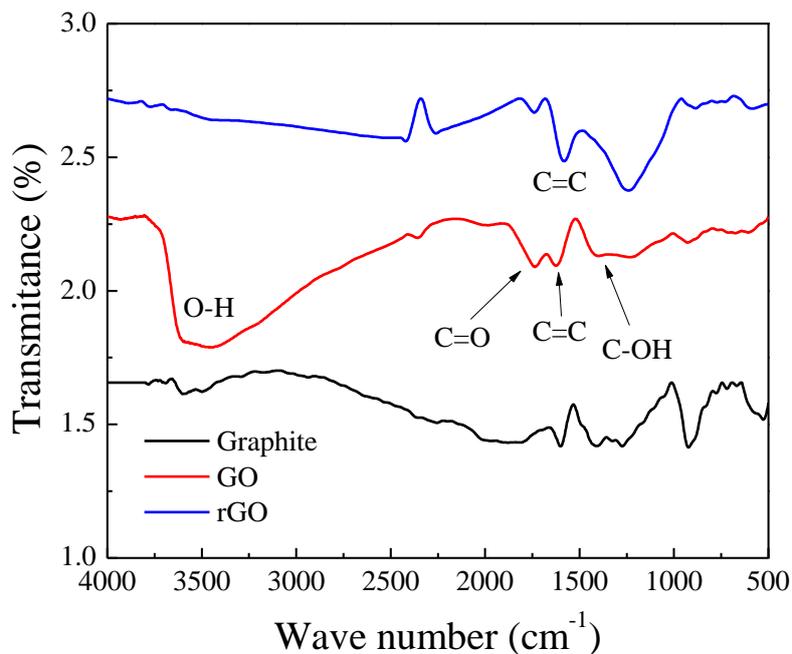
Figure 4. FTIR spectrum of graphite samples, graphene oxide, and
reduced graphene oxide

Dissolution Test

The dissolution test was carried out by dissolving the three samples using 2 different solvents. The solvents used are water and ethanol because to know the different their solubility. The results of this test can be observed in Figure 5. GO was more soluble in water than ethanol which is slightly less polar than water. This can be proven through IR spectrum measurements that in GO material there are many functional groups containing oxygen such as alcohol. In addition, rGO looks slightly soluble in ethanol solvents compared to water solvents. Furthermore, graphite is also slightly dissolvable in ethanol compared to water because a lot of polar fungtional group (Kyzas et al., 2018).
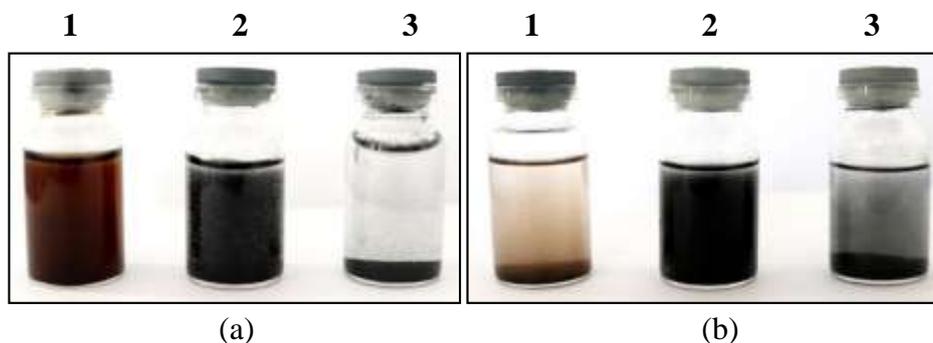
Figure 5. Sequential dissolution of samples, namely (1) GO, (2) rGO and
(3) graphite in a) water and b) ethanol

Conclusions

The synthesis of rGO using lime juice as the reducing agent was successfully carried out. The results of X-ray diffraction patterns indicate peaks that are following the material expected at each step of the synthesis. XRD analysis for reduced graphene oxide showed a diffraction peak of $2\theta = 23.8°$ (d-spacing, ie 0.37 nm) while graphene oxide at $2\theta = 10°$ (d-spacing, ie 0.88 nm). The decrease in d-spacing shows that the distance between the rGO layers is reduced because of the loss of functional groups that have GO. This was proved by FTIR measurements which show high intensity hydroxyl and carbonyl vibrations on GO. Solubility testing also shows that GO is more soluble in water than rGO.

Acknowledgments

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