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Research Article

Optimization of oxidation time of Kahatagaha vein graphite and reduction time of microwave assisted hydrothermal reduction of Kahatagaha graphene oxide

L. D. C. Nayanajith[*1], R. C. L. De Silva[1], S. R. D. Rosa[2] and I. R. M. Kottegoda[1]

[1]*Material Technology Section, Industrial technology Institute, Colombo 07, Sri Lanka*

[2] *Department of Physics, University of Colombo, Sri Lanka.*

ABSTRACT

The present study was aimed to obtain the optimum yield of graphene oxide (GO) from Kahatagaha graphite by optimizing oxidation time, and to effectively utilize hydrothermal microwave irradiation technique to produce high quality reduced graphene oxide (rGO) with the optimum level of reduction from Kahatagaha graphene oxide. Kahatagaha vein graphite was specifically selected for the study due to its remarkable morphological, structural, compositional and carbon isotropic variations from the other types of graphite. Oxidation time of Kahatagaha graphite was optimized and subsequently, microwave irradiation time was optimized to obtain maximumly reduced graphene oxide from the synthesized GO. XRD, SEM, FTIR and gravimetric analyses were employed to characterize the synthesized GO and rGO. The optimized oxidation time for the complete conversion of Kahatagaha graphite to GO was 5 hours that resulted in a yield of 170 % (w/w) with respect to the amount of graphite used. This level of yield would be highly beneficial for commercial productions of GO. The maximum level reduction of GO (production of rGO) was achieved in 20 minutes

* Corresponding author: cnayanajith@yahoo.com

https://orcid.org/0000-0002-6123-0331

of microwave irradiation at 160 ºC with the microwave power of 500 W. Microwave-assisted hydrothermal reduction of graphene oxide is highly beneficial in term of energy consumption (low temperature and short processing time) and eco-friendliness (no solvents involved).

Keywords: Vein graphite, Graphene, Oxidation, Reduction, rGO, GO, microwave irradiation.

1. INTRODUCTION

Flake graphite, vein graphite and microcrystalline graphite occur naturally, out of which the vein graphite reported to be the purest and highly crystalline. It occurs as a filling fissure in veins of metamorphic or igneous rocks. Vein graphite deposits in Sri Lanka are the largest in the world and Sri Lanka is the only commercial miner of vein graphite. The main commercial mines are located in Kahatagaha and Bogala areas, of which the graphite claims to have purity of nearly 99 % which is exceptionally high compared to that of the other types of natural graphite [1]. High-quality Sri Lankan graphite stands out as a key raw material in manufacturing high-end technical products such as micro-processors, integrated circuits, electronic and optoelectronic devices. Several studies have also been done to identify its potential as anode material for Li-ion batteries [2, 3]. However, Sri Lanka has been exporting bulk quantities of high purity raw graphite without any value addition since 19th century resulting in heavy revenue losses and faster depletion rate of graphite deposits. Even in the year 2020, the raw graphite had been exported for US$ 2300 per Mt while the value-added products are priced up to 100,000 US$/kg [4]. Sri Lanka had been producing 30,000 tons of raw graphite by 1899 [5], since then it has gradually been declined to around 3800 Mt in recent years, which implies the magnitude of depletion of graphite deposits. Production of highly value-added products such as graphene oxide (GO), reduced graphene oxide (rGO) and graphene (Gn) has been identified as one of the cost-effective ways of value-addition because graphite can easily be oxidized to GO by a simple chemical oxidation process followed by a reduction process. GO and rGO are two intermediate products of graphene synthesis through chemical oxidation of graphite which are also raw materials for high-end products such as lithium-ion batteries, solar cells, field effect transistors and so on.

Graphite extracted from Kahatagaha mine was specifically selected for this study since its characteristics differ from other kinds of graphite occurring in the nature [5, 6]. Kahatagaha

graphite is found in the form of needle (acicular graphite) containing more than 99 % of graphitic carbon, whereas other types such as flake graphite which exists as jumbo flake, large flake, medium flake and fine flake with a purity of 90-95% of graphitic carbon [7]. On the other hand, vein graphite in other mines (such as Bogala) is found in large size crystals with purity less than 95 %. The ashes of Kahatagaha graphite contain silica predominantly (> 90%) but those of Bogala graphite contain silica and iron oxide equally [5]. Meanwhile XRD diffraction information shows that the interlayer spacing (d002) of Bogala graphite (c = 6.72 Å) is slightly different from that of Kahatagaha graphite (c= 6.70 Å) [8]. The carbon isotopic data for Bogala graphite, expressed as $\delta^{13}C$, are in the range of –8.3 and –10.4 %, whereas for Kahatagaha graphite, they are in the range of –7.9 and –9.3 % [9].

Hummers' method [10] is widely used to synthesize GO, where graphite is oxidized using proportional amounts of potassium permanganate, sodium nitrate and concentrated sulfuric acid. GO production via Hummers' method involves several distinct steps; they are intercalation of oxidants into the graphene layers of graphite, oxidation of graphitic carbon, hydrolysis and exfoliation of the functionalized graphene sheets by ultrasonication. The Hummers' method stresses that the intercalation shall be carried out in low-temperatures (0 ~ 5 ºC), the oxidation at ~35 ºC and hydrolysis at 98 ºC [11].

However, depending on the nature of graphite used, certain modifications for these steps are often needed so as to obtain the optimum level of product quality, yield and process efficiency with low cost. In previous studies, the hydrolysis time has been varied up to 96 hours while the temperature is maintained at 98 °C as per the original Hummers' method. Also, the oxidation time has been varied from 30 minutes to one hour keeping the oxidation temperature often fixed at 35 °C [12-28]. Since Kahatagaha graphite is specific in some characteristics as aforesaid, in order to acquire the optimum level of yield and quality of GO, the oxidation time was studied by varying from one hour to six hours while maintaining the other process parameters as in the original Hummers' method [3].

Similar to GO, rGO is also a value-added product. In addition, rGO has become a more valued product than GO since rGO possesses rather enhanced characteristics which are closely comparable with those of graphene [29]. rGO consists of greater number of sp^2 carbon atoms and a smaller number of carbon atoms bearing oxygen functional groups (low C/O ratio smaller than 0.4 wt.%), resulting in more thermal and electrical conductivity than GO [30]**.** GO could be chemically reduced to form rGO, for which solvent based chemical

reduction, thermal annealing and microwave assisted reduction techniques have been reported. However, use of microwave irradiation in this regard is less common and yet to investigate its performance on GO prepared from vein graphite such as Kahatagaha. Moreover, it is worthwhile in studying the performance of the microwave methods on the production of rGO since the chemical reduction process of GO is considered to be hazardous, expensive, non-ecofriendly and time consuming. Meanwhile the thermal reduction process, on the other hand, is energy intense and requiring inert atmospheres. Microwave technique is particularly useful for a large-scale fast and ecofriendly synthesis which requires no complicated preparation conditions [31].

2. EXPERIMENTAL

2.1 Materials

Pulverized vein graphite (40-100 µm, purity ~ 99%) was obtained from Kahatagaha Graphite Ltd, Sri Lanka and analytical grade 98% sulfuric acid (H_2SO_4), potassium permanganate (K_2MnO_4), sodium nitrate ($NaNO_3$), 30 % hydrogen peroxide (H_2O_2), silver nitrate ($AgNO_3$), barium chloride ($BaCl_2$), hydrochloric acid (HCl) were purchased from Sigma-Aldrich.

2.2 Pre-treatment of graphite powder

A mixture containing 25 g of pulverized Kahatagaha graphite and 75 mL of 98% H_2SO_4 in a 250 mL round bottom flask was kept on stirring for 4 h at 90 $^{\circ}$C. Then, it was ultrasonicated for 2 h at room temperature. H_2SO_4 was filtered off and the residue was washed thoroughly with distilled water until the filtrate became neutral. The washed residue was dried at 105 °C in an oven overnight and labeled as pGr.

2.3 Synthesis of GO and Optimization of oxidation time (t)

One gram of pGr and 0.5 g of $NaNO_3$ were thoroughly mixed with a mortar and pestle. The mixture was slowly transferred to a flask containing 23 mL of 98 % H_2SO_4 and stirred for 1h at 0 ºC. 3g of $KMnO_4$ was slowly added to it while stirring the mixture. Then. its temperature was raised to 35 °C and kept the mixture at this temperature for one hour (**T**, oxidation time). 50 mL of distilled water was added to it slowly. The temperature was raised to 98 °C and continued for one hour while stirring. After that, 150 mL of distilled water was added to it, followed by the addition of 10 mL of H_2O_2 (30%). The mixture turned bright yellow. The solid part of the mixture was separated out by centrifuging and washing with

HCl (5%) repeatedly until no sulfate could be detected to $BaCl_2$. Then the residual chloride ions were removed also by centrifuging and washing with distilled water until the chloride ions were not detected to $AgNO_3$.The purified product (graphite oxide) was dried in an oven at 60 ºC overnight. The dried graphite oxide was dispersed in water and ultrasonicated at 40 kHz for two hours. The ultrasonicated dispersion was centrifuged to extract its solid component (GO) which was then dried in an oven at 60 ºC. The unreacted graphite content retained in the final product was determined by heating at 600 ºC until a constant weight was obtained. This procedure was repeated for another five oxidation time periods, **T** = 2 h, 3 h, 4 h, 5 h and 6 h.

2.4 Microwave assisted hydrothermal synthesis of rGO

2.5 g of the synthesized GO (Graphite oxidation time = 5 h) was dispersed in 50 mL of distilled water by means of ultrasonication. The prepared dispersion was irradiated hydrothermally with microwave at 160 ºC using "MileStone-MicroSynth" microwave lab-station at the microwave power of 500 W. Eight samples of GO were irradiated by varying only the irradiation time as 5, 10,15,20, 25, 30, 35 and 40 min. The solid component (rGO) of resulting samples were collected by filtering off their liquid part and drying the residue at 105 ºC in an air circulating oven. (Note: the rGO samples were labeled as rGO_5, rGO_{10}, rGO_{15}, rGO_{20}, rGO_{25}, rGO_{30}, rGO_{35} and rGO_{40} representing the irradiation time of 5, 10, 15, 20, 25, 30, 35 and 40 min. respectively.)

2.5 Characterization

The pre-treated graphite, graphene oxide and reduced graphene oxide were characterized using RIGAKU Ultima-IV X-ray Diffractometer operated at 40 kV voltage, 30 mA current with a scan speed of 4.00 deg/min at a step of 0.02° using Cu $K\alpha_1$ - 1.4506 Å (XRD) and BRUKER Tensor 27 Fourier Transform Infrared spectrophotometer (FTIR).

The unreacted graphite retaining in GO at each oxidation time period 1, 2, 3, 4, 5 and 6 h was determined by heating a known amount (W_i) of dried GO sample in a furnace at 600 ºC until the final weight (W_f) of the sample became constant. After the heat treatment, the residue was analyzed using XRD and FTIR. Equation (1) and (2) were used to determine the unreacted graphite content and the percentage of the GO produced respectively.

$$Unreacted\ graphite\ content, \% = \frac{W_f}{W_i} \times 100 \text{ --------- (1)}$$

$$GO, \% = \frac{W_i - W_f}{W_G} \times 100 \text{ ---------- (2)}$$

Where W_G is amount of graphite used.

3. RESULTS AND DISCUSSION

3.1 Pre-treatment of graphite

Although Kahatagaha vein graphite is said to be very pure (98-99%), it might potentially contain various impurities in minute quantities. Acid treatment (conc. sulfuric acid) of graphite can remove acid soluble materials, such as derivatives of N, P, Si, Ca, Na, K, Al, Zn and Fe [32]. According to gravimetric analysis performed on the samples before and after the acid treatment, the acid soluble content was found to be approximately 1.7 % (w/w). In addition to the removal acid soluble impurities, it can cause hydrophilization of structural carbon, which provides graphite with reactive sites "activation" [33].

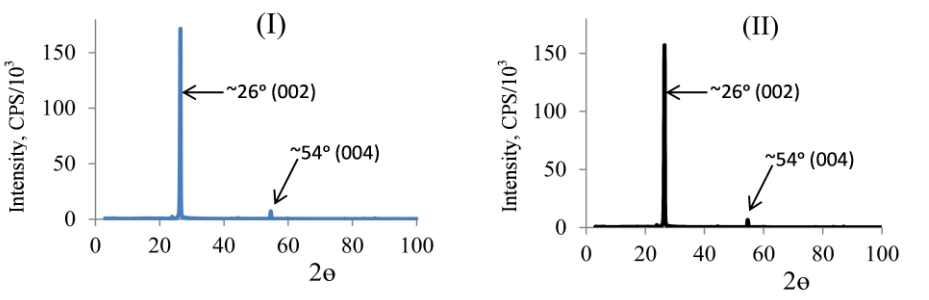

Figure 1. : XRD spectra of Kahatagaha vein graphite (I) before (II) after acid treatment

Powdered Kahatagaha graphite samples before and after the acid treatment were analyzed using XRD spectroscopy. XRD spectra of Kahatagaha graphite before and after the acid treatment (I and II in Figure **1,**) indicate identical spectral signatures where the characteristic peaks of graphite due to (002) and (004) planes were positioned at 2θ~26º and 2θ~54º respectively [34]. This spectral identicalness infers that the pre-treatment process employed has caused no adverse effects to the structural properties of the graphite used. FTIR spectra of the acid-treated and neat graphite show no significant IR absorption in their spectra, which is very typical of pristine graphite [35] (refer to Figure **2: A.** before treatment and **B.** after treatment). This spectral indistinguishability implies that the acid treatment process has not brought about any significant change in chemical properties of graphite.

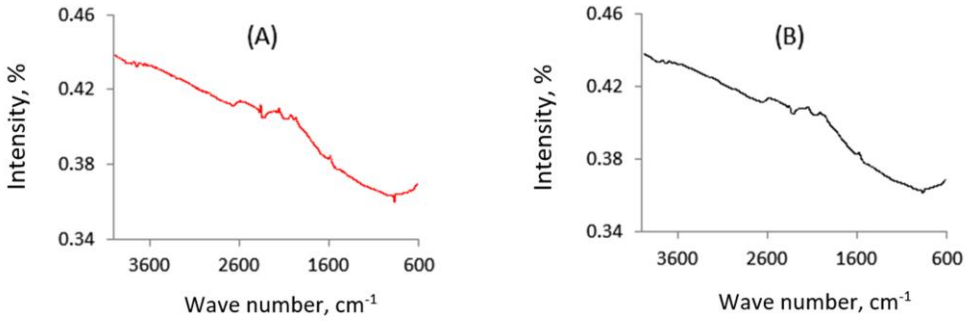

Figure 2: FTIR spectra of Kahatagaha vein graphite (A) before (B) after acid treatment

3.2 Synthesis of GO and Optimization of oxidation time (t)

As Kahatagaha vein graphite is rather different in chemical and structural characteristic from the vein graphite found in other areas in Sri Lanka [5, 6], it was suggested that the oxidation process of the Hummers' method could be modified either by changing oxidation time or temperature. The oxidation temperature is usually kept at 35 °C [10] because control of the extent of oxidation of graphite can be difficult at elevated temperatures. On the other hand, lower temperatures (< 35 °C) can cause slow rates of oxidation, which would consume more time and energy. Unless the extent of oxidation is well controlled, the final products, GO would be full of structural defects which might lead to compromise the quality of the subsequent products of GO such as graphene [36, 37]. In this study, oxidation time, T was varied such that T =1, 2, 3, 4, 5 and 6 hours and the resulted GO samples were labeled as GO_T. At each oxidation time, the content of unreacted graphite retained and GO produced with respect to the amount of graphite used, are shown in the Table 1 and in Figure 3 (a) and (b).

Table 1: Results of retained graphite and yield of GO at each oxidation time

GO_T	GO_1	GO_2	GO_3	GO_4	GO_5	GO_6
Retained graphite, (%)	22	8	6	0.2	0	0
Yield of GO w.r.t. graphite used, (%)	70	90	120	140	170	120

As per Table **1** and Figure **3 (a)** the unreacted graphite does not retain in GO_5 and GO_6, i.e., total amount of graphite used has been oxidized in five hours. This infers that the graphite used requires an oxidation time period of 5 hours at least under the selected process conditions.

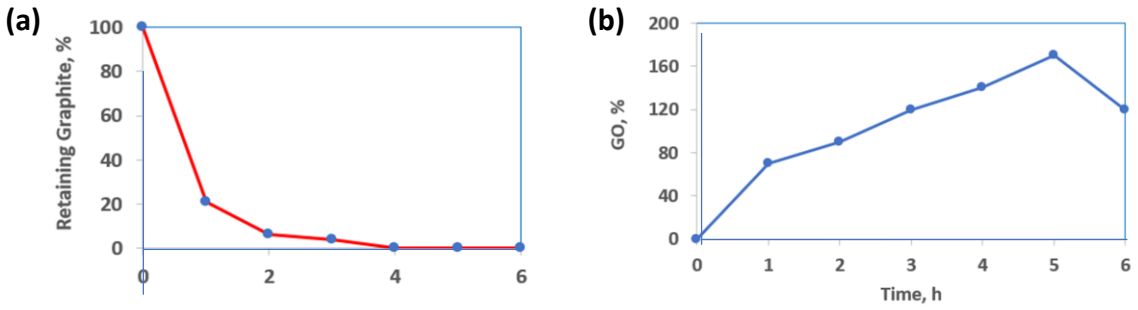

Figure 3: (**a**) Graph of retaining graphite content vs oxidation time, (**b**) Yield of GO vs oxidation time

Also, as in the Figure **3 (b)**, the percentage of yield of GO with respect to the graphite used shows the sequence of $GO_1 < GO_2 < GO_3 < GO_4 < GO_6 < GO_5$. As per the results in Table **1**, the highest percentage of yield (170 %) is shown by GO_5, which can be attributed to the fact that the precursor has been oxidized leaving no unreacted graphite. In contrast, GO_6 shows a much lower percentage of yield (120 %) compared to GO_5 and GO_4, nevertheless, there is no unreacted graphite has left in GO_6. This may be due to over-oxidation of the GO formed. According to the results obtained, it is obvious that the graphite had been reacted completely within five hours at 35 °C. After five hours, GO formed may start to oxidize further provided that the oxidizing agents still remain active, which could result in over-oxidized species and CO_2. The over-oxidized GO is often water soluble, as a result, it can be removed at the purification step of the GO preparation process [37, 38].

3.3 Analysis of prepared graphene oxide, GO_t using XRD

XRD spectral information obtained from the prepared GO samples are given in Figure **4** of which the spectra labeled as **I**, **II**, **III**, **IV**, **V** and **VI** represent the GO with oxidation time 1 to 6 hour respectively. In the spectra, the broad peak appearing at $2\theta \sim 11^{o}$ is characteristic to GO [39] and the sharp peak appears at $2\theta \sim 26^{o}$ is the characteristic peak of (002) plane of graphite [34]. The appearance of this peak indicates presence of unreacted graphite in the prepared GO samples. It does appear in in the spectra **I**, **II**, **III** & **IV**, which indicates presence of unreacted graphite in the GO samples of all GO_1, GO_2, GO_3 and GO_4. Moreover,

the intensity of this peak with respect to the GO peak at 2θ ~ 11º (GO peak) in the spectra from GO_1 to GO_4 is in a decreasing order due to the depletion of unoxidized graphite with time. On the other hand, it does not appear in the spectra **V** and **VI** representing $GO_5$and GO_6respectively, which implies that the amount of graphite used has been completely oxidized to GO by 5 hours.

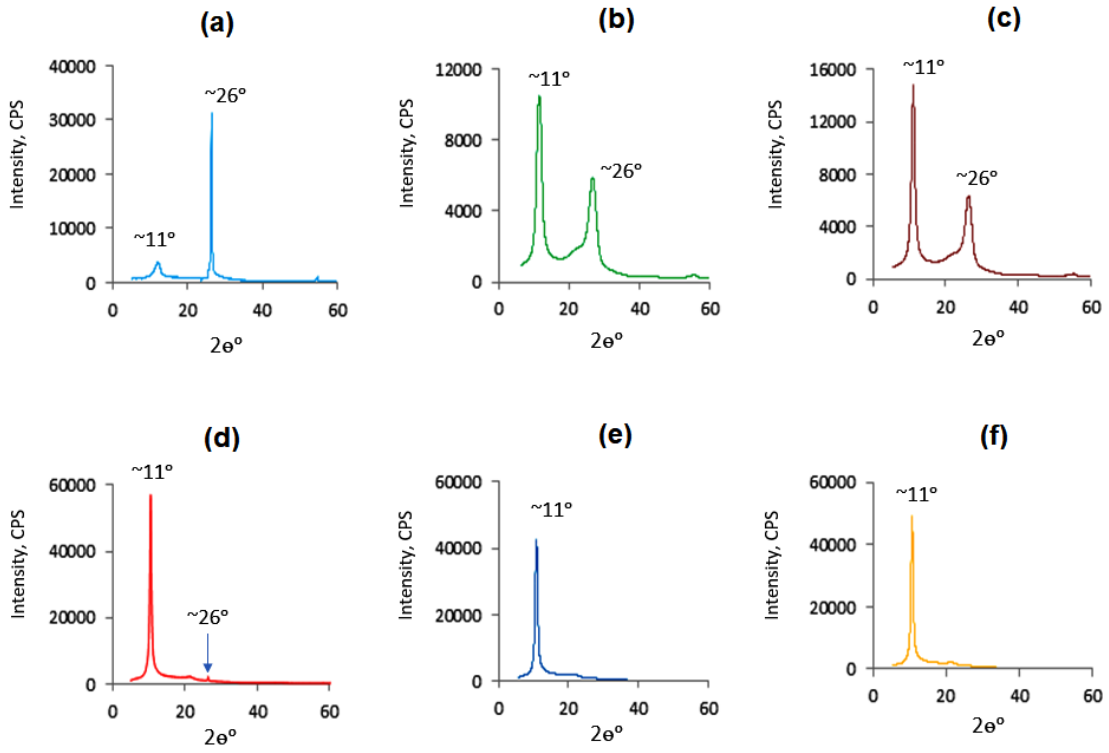

Figure 4: (a), (b), (c). (d), (e) and (f) represent XRD spectra of GO synthesized varying oxidation time 1, 2, 3, 4, 5, and 6 hours respectively. The peaks at 2θ° = 11° and 26° indicate (001) plane of GO and (002) plane of graphite respectively.

3.4 Characterization of GO_t with FTIR spectroscopy

FTIR spectroscopy was used to analyze the functional groups attached to carbon atoms of graphite before and after the oxidation process. As in Figure **2,** graphite does not show FTIR spectral peaks with significant intensities. However, the FTIR spectra taken from the resulting GO_t samples (refer to Figure **5**) include distinct and strong peaks characteristic to O–H, C=O and C–O. The peak appears at approximately 3400 cm^{-1} as a result of stretching vibrations of the hydroxyl groups (O– H), at around 1700 cm^{-1} due to the stretching vibrations of the carbonyl and carboxylic groups(C=O) and at the vicinity of 1200 cm^{-1} related to the stretching vibrations of C–O–C [40, 41]. The intensities of these peaks can be observed to be increasing continually from GO_1 to GO_6, which indicate that as oxidation

time increases the extent of oxidation of graphite increases. (Note: the spectra are in the same scale)

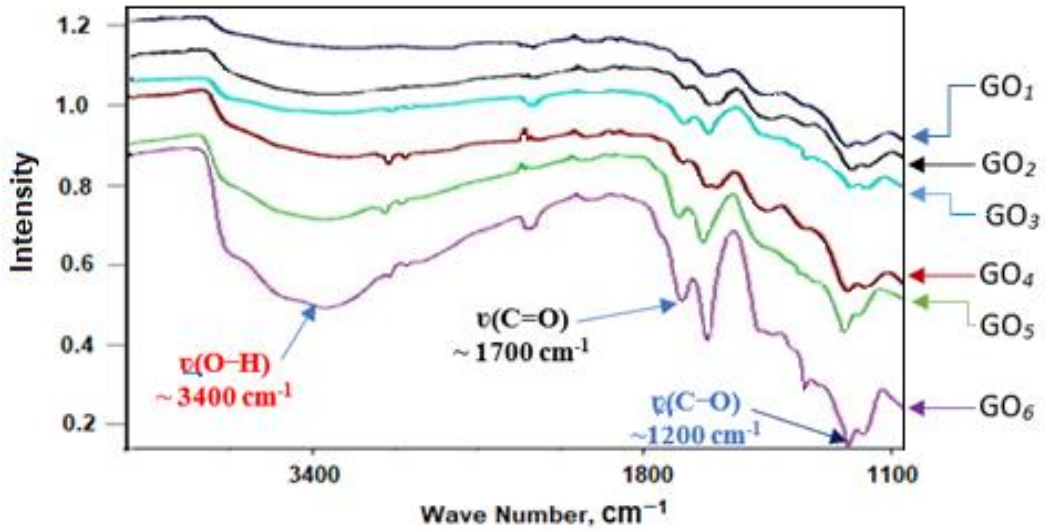

Figure 5: FTIR spectra of GO1, GO2, GO3, GO4, GO5 and GO6. The peaks appearing around 3500, 1700, and 1200 cm-1 indicate presence of O-H, C=O and C-O respectively

3.5 Microwave irradiation on GO

It was observed that the GO samples subjected to the microwave irradiation were transformed into reduced graphene oxide (rGO). The formation of rGO was witnessed by the change of GO nature from dark brown dispersion to black residue [42, 43] as shown in Figure **6** Evaluation of the effect of microwave irradiation time on the degree of reduction of graphene oxide, was studied in detail using XRD, FTIR and SEM.

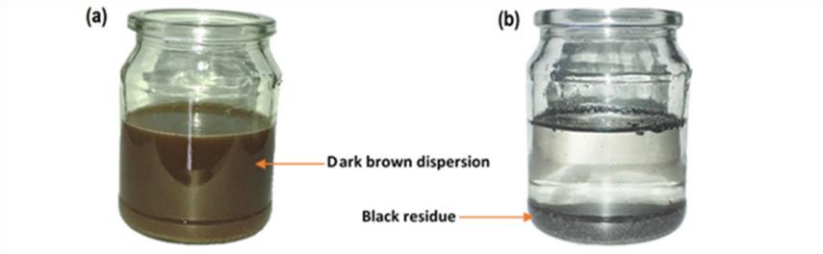

Figure 6: (a) A sample of aqueous dispersion of GO before microwave irradiation (b) GO after irradiation

3.6 Characterization with XRD

XRD spectra of the hydrothermally reduced GO samples after irradiating for 05, 10, 15, 20, 25, 30, 35 and 40 min. are shown in Figure **7**, It can be observed that the characteristic peak

of GO appearing at 2θ ~ 11ºundergoes decrease in intensity with simultaneous peak broadening as the irradiation time increases. Diminishing intensity and widening peak width is caused by the removal of oxygen functionalities and loss of crystallinity-which occurs due to exfoliation of stacked GO layers [44]. In addition, if the peak intensities are closely investigated, it can be seen that a logarithmic decrease occurs up to 20 min., after which the decrease becomes insignificant (refer to Table **2** and Figure **8**). The peak intensity from 20 min. up to 40 min. remains almost as the same level as the peak of 20 min. Hence, it implies that the maximum level of reduction of GO at 160 ºC has reached within 20 minutes. The effect of the microwave irradiation time on the functional groups of GO is evaluated by FTIR spectroscopy.

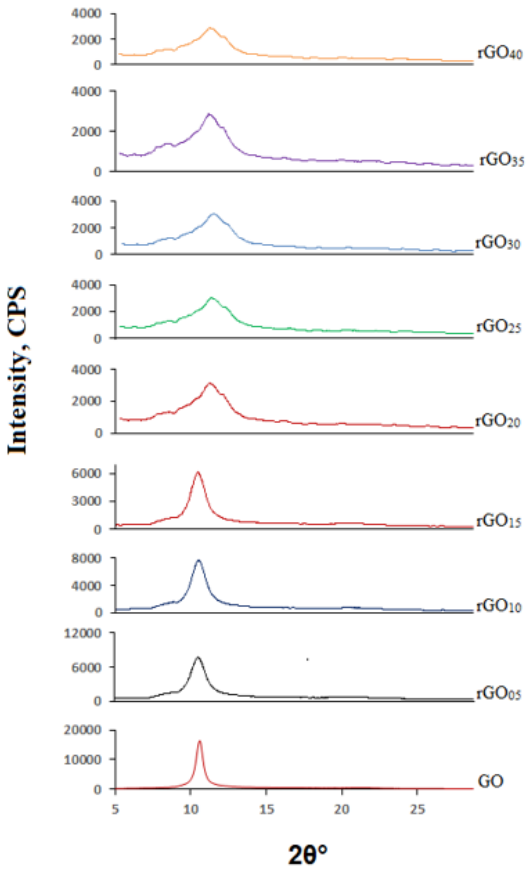

Figure 7: XRD spectra of GO samples irradiated with microwave for 5, 10, 15, 20, 25, 30, 35 and 40 min. at 500 W microwave power.

Table 2: Intensity of the peaks appearing at 2θ=11° in XRD spectra of the samples.

Irradiation Time, min.	Intensity, CPS
00	15064
05	8813
10	7972
15	6005
20	3017
25	3102
30	3061
35	2874
40	2909

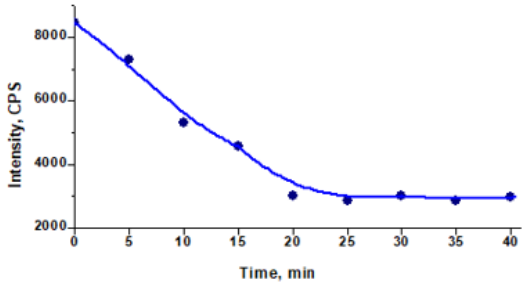

Figure 8: Intensity (CPS) of the peak at 2θ=11° with microwave irradiation time (minutes).

3.7 Characterization with FTIR

FITR spectroscopy is used to characterize the functional groups attached to the structure of GO especially hydroxyl (O-H), carbonyl (C=O) and epoxy (C-O-C) groups of which the presence is indicated by the peak in the spectrum appearing around 3400 cm^{-1}, 1700 cm^{-1}

and 1100 cm^{-1} respectively [40, 41]. The intensity of the peaks implies the number of each functional group possessed by GO. Figure **9** shows the FTIR spectra of the neat GO (GO_5) and some selected samples of GO after being irradiated for 10, 20 and 40 minutes. Similar to the XRD spectral pattern, as the irradiation time increases up to 20 min. FTIR spectra also show declining intensities of the peaks related to the main functional said above, after which the reduction of peak intensities become insignificant.

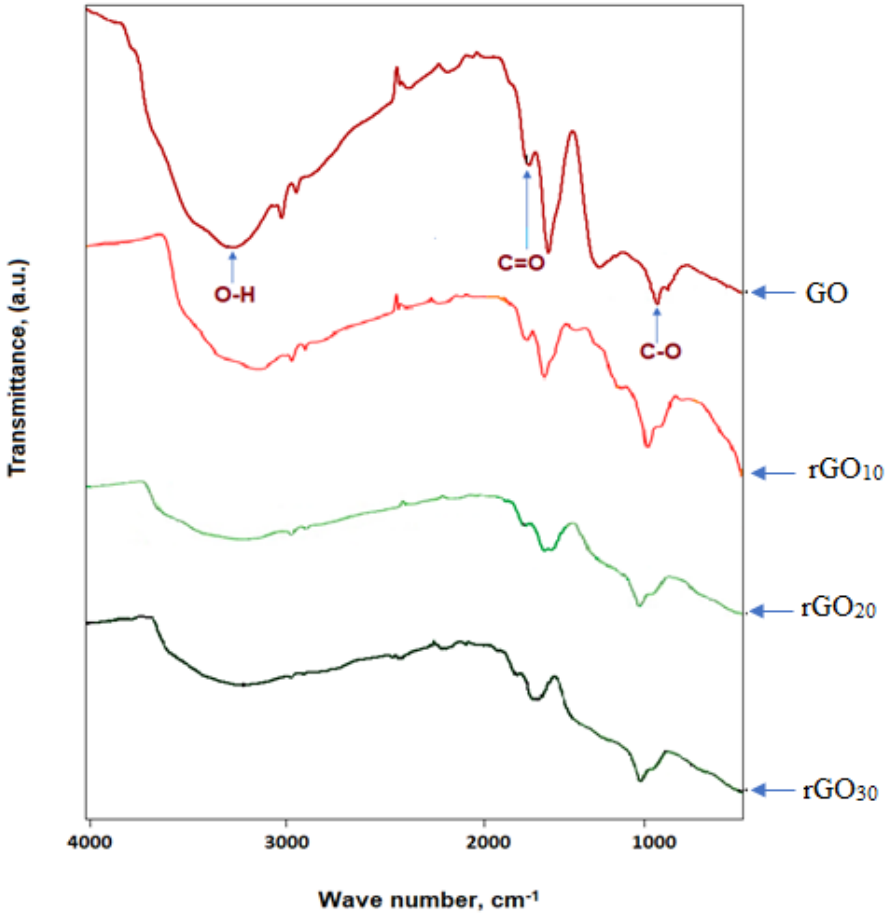

Figure 9: FTIR spectra of the neat GO and rGO_{10}, rGO_{20}, rGO_{30} after being irradiated for 10, 20, 40 minutes respectively, of which the characteristic IR absorptions due to (O-H), (C=O) and (C-O-C) groups take place around 3400 cm^{-1}, 1700 cm^{-1} and 1100 cm^{-1} respectively.

3.8 SEM Analysis

Figure 10 (a) and (b) are the FE-SEM images of GO and rGO_{20} taken at the magnification of 50,000X with the working distance of 7.90 mm, where the morphology of GO appears to have firmly intact layers, but rGO demonstrates an ultrathin flexible sheet-like structures which are partially exfoliated. The intact GO layer morphology can be attributed to the existence of great number of functional groups in the GO structure, which creates Wader Vaal forces between them making the layers firmly intact. On the other hand, rGO's partially

detached layer morphology can be ascribed to the tendency of layers detaching themselves on reduction.

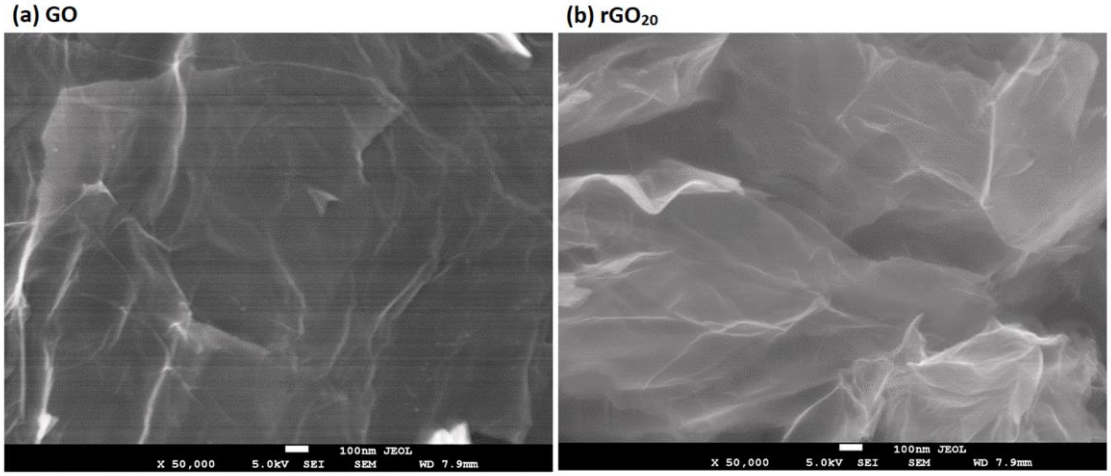

Figure 10: FE-SEM images of and taken at the magnification of 50,000X with the working distance of 7.90 mm. **(a)** GO and **(b)** rGO_{20}

4. COCLUTION

In order to obtain an optimum yield of GO, oxidation of Kahatagaha graphite can be optimized by adjusting the oxidation time of graphite in the Hummer's method which stipulates the oxidation time to be 30 minutes at 35 °C for powdered flake graphite. In fact, Kahatagaha graphite is not flake graphite, but is acicular vein graphite of which the structural and chemical characteristics are rather different from the other types. According to the present study, the oxidation time could be adjusted to 5 hours in order to obtain the maximum yield of GO from Kahatagaha mine's graphite (170 % with respect to graphite used) at the same temperature. Subsequently, the produced GO thereby can be reduced successfully from the microwave-assisted hydrothermal method used in the present study. According to the XRD, FTIR and SEM analysis, the optimal level reduction of GO can be achieved in 20 minutes of microwave irradiation at 160 ºC with microwave power of 500 W.

Microwave-assisted hydrothermal reduction of graphene oxide is highly beneficial in term of energy consumption (low temperature and short processing time) and eco-friendliness (as no solvents are involved). This reduction process could be further potentially investigated for graphene synthesis, for which it could be experimented with various reaction

temperatures, changes of microwave power and various reducing agents. The Sri Lankan vein graphite has a potential in commercial production of GO and rGO.

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