A RAPID METHOD TO PREPARE EXFOLIATED GRAPHITE USING SRI LANKAN VEIN GRAPHITE

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ABSTRACT: Expansion of graphite using Microwave Irradiation Technique is very promising because it can be performed at room temperature in a short time and less energy consuming with a simple laboratory facility. The aim of this study was to prepare exfoliated graphite from Sri Lankan vein graphite using microwave heating. In the present study, two precursors were prepared by mixing needle platy graphite (NPG) with $KMnO_4$ and HNO_3 at 1:1:2 ratio. After that, the first sample was irradiated with microwave just after mixing and while the second one was irradiated after keeping for 12 hrs. As visual observations, the first sample underwent the maximum exfoliation to graphite. Fourier transmission infrared (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD) and d.c. four probe conductivity characterizations were carried out on the raw and treated samples. Worm-like structure of expanded graphite could be clearly observed from SEM study and the new IR peaks formed during the microwave treatment at 1269cm^{-1} and 1384cm^{-1} could be evidently confirmed intercalation of functional groups. The findings of this study should lead to better understanding of the exfoliation of Sri Lankan vein graphite using microwave irradiation technique within a short period of time.

Keywords: Needle Platy Graphite, Exfoliated Graphite, Microwave Irradiation, Intercalation

16. INTRODUCTION

Exfoliated graphite (EG) can be a potential candidate as a fire suppressant intumescent additive, to manufacture graphite gasket, electrically conductive filler, foundry additive, and in a wide variety of other industrial applications. A sudden, rapid expansion of intercalation agent exerts a force on the adjacent layers of graphite during exfoliation, thus creating a worm-shaped, accordion-like material with low density, high temperature resistance, high lubricity and high flexibility. Typically, EG is prepared by volumetric expansion of graphite layers through intercalation of different atoms in between graphene layers by separating them by rapid heating. Graphite Intercalation compound (GIC) is the intermediate product of the graphite exfoliation process and it can be made using different guest species. The GIC is also known as expandable graphite, since it can be exfoliated upon heating. EG has a higher surface area and that is valuable for applications related to adsorption, electrochemical electrodes, and electromagnetic shielding. Microwave irradiation or thermal shock is the common way to produce EG from GIC [1, 2] (figure 01).

Microwave heating is identified as an efficient method in many industries such as food, ceramic and chemical processes. It is caused by the conversion of electromagnetic energy to thermal energy and the efficiency of the conversion depends upon the dielectric nature of materials [3]. Graphite is a strong microwave absorbing material, which can sustain high temperature and provide high heating rates. During the microwave heating process, graphite materials are reported to generate microplasma when they are heated in the presence of microwaves. During this process, some of the electrons jump out with the increment of their kinetic energy, resulting in ionizing the surrounding atmosphere, which is visualized as sparks of electric arc formation [4, 5]

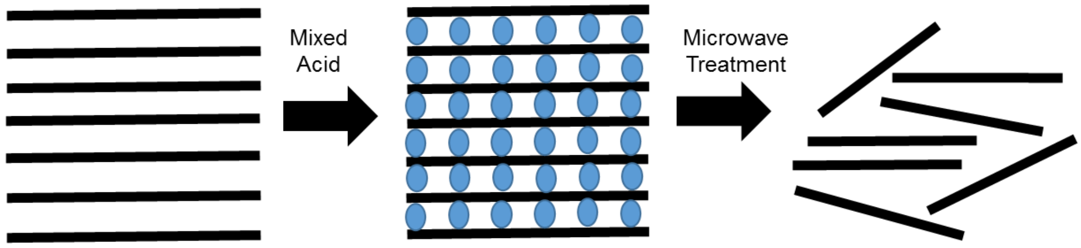

Figure 01: Exfolia tion process of graphite

Graphite

Sri Lanka is well known for high purity and high crystallinity vein graphite and they have been categorized into four morphological verities based on physical and structural characteristics. They are needle platy graphite (NPG), shiny slippery fibrous (SSF), coarse flakes of radial (CFR) and coarse striated flaky (CSF) graphite [6]. All most all these verities possess high initial purity over 98% of carbon content. Among them, NPG has the highest purity and geologically it always present in the middle of the vein [7]. Since from last decade, the attention for application based investigations on Sri Lankan vein graphite has increased and most of them are on electrode applications and EG [8]. Though EG is a promising candidate for many applications including graphene preparation, very few studies have been reported. Therefore, this study is for the preparation of EG from NPG variety of Sri Lankan vein graphite by microwave irradiation method.

17. METHODOLOGY

Graphite samples were collected from Kahatagaha-Kolongaha mine and NPG variety was selected from visual observations. The selected samples were subjected to crush and separate using a laboratory disk mill and sieve set, respectively. Powdered NPG (<53 micron), nitric acid (69%), and potassium permanganate were mixed in weight ratio of 1: 2: 1 [6] and agitated by a glass bar in a porcelain crucible for 3 minutes at room temperature. After that, the porcelain crucible was directly placed in a domestic microwave oven at 900 W for one minute. Likewise, another sample was prepared by following the same procedure and it was irradiated with microwave after 12 hours. They were named as NPG-MI-01 and NPG-MI-02 respectively.

2.1. Characterizations

The morphology and microstructure of graphite powders were observed with Scanning Electron Microscopy (SEM) (JSM 6400 and Gemini zeiss ultra-scanning electron microscope) and X-Ray Diffraction (XRD) (Rigaku-ultimate IV X-ray Deffractometer Cu K_{α} radiation, 1.54 A^{o}). The functional groups on the surface of graphite were analyzed by Fourier Transform Infrared (FTIR) spectroscopy (Nicolet 6700). The conductivity measurements were carried out using the d.c. four probe technique.

18. RESULTS AND DISCUSSION

The conversion of graphite to EG was completed using microwave irradiation method with short time period. The process of mixing with HNO_3 has led to the formation of graphite intercalation compound. Then it was treated with microwave and directed to the EG preparation. After the exfoliation, completeness of the process was verified by the disappearance of fuming, lightening and formation of gases. EG could be successfully obtained with in a hundreds of times larger volume than of the original graphite volume (figure 02)

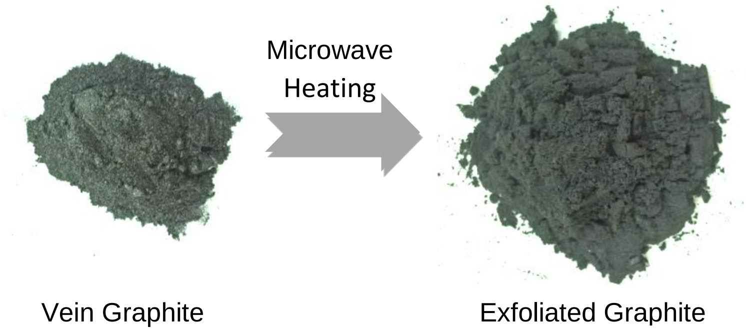

Figure 02: Vein graphite and exfoliated graphite

Figure 03 shows the XRD patterns of natural graphite and exfoliated graphite. The strong and sharp diffraction peak, in raw NPG, visible at 2θ = 26.45˚ corresponds to a d-spacing of 3.37 Å, by confirming the high crystallinity of this vein graphite (JCPDS card no. 41-1487). Also the absence of impurity peaks explains the very high purity of this NPG variety. After the irradiation with microwaves, the XRD pattern shows a change in crystalline structure of NPG-MI-01 resulting in a slightly different expected pattern of exfoliated graphite, as shown in figure 3(b)

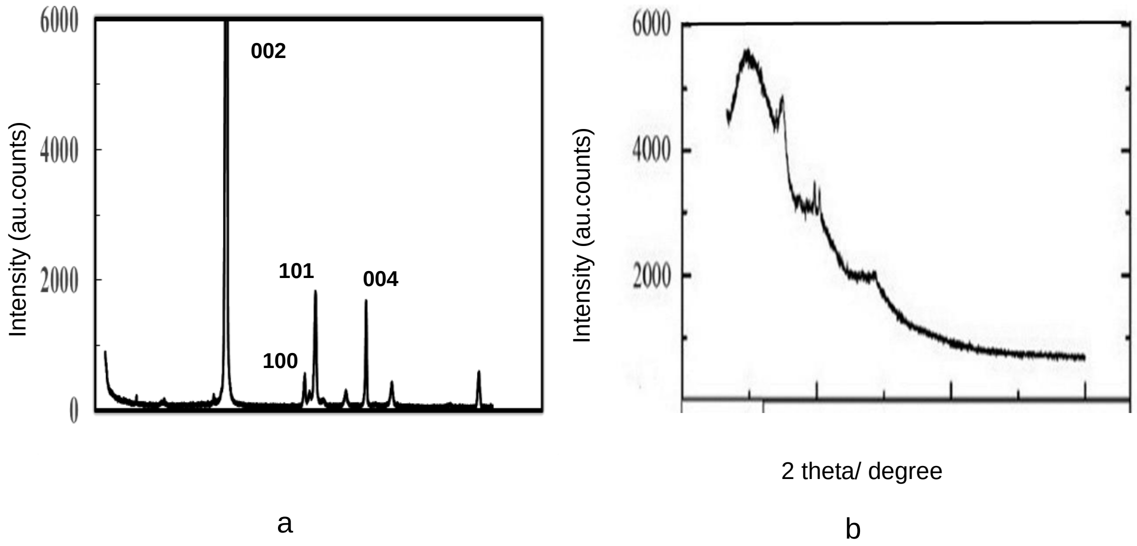

Figure 03: XRD patterns of (a) natural vein graphite and (b) exfoliated graphite [10]

FTIR measurements were carried out with the KBr pellet technique, prepared with a sample: KBr ratio of 1:150 by weight. The prepared EG shows a specific band maximum in the 3600~3200 cm^{-1} region may be due to the O-H stretching vibration of intercalated water. The newly formed peaks in microwave treated samples at 1269cm^{-1} and 1384cm^{-1} can be assigned to C-O and O-H groups, respectively. The intensity of all the peaks has increased in NPG-MI-01 than the NPG-MI-02, which meant that the optimum time of sample mixing is 3

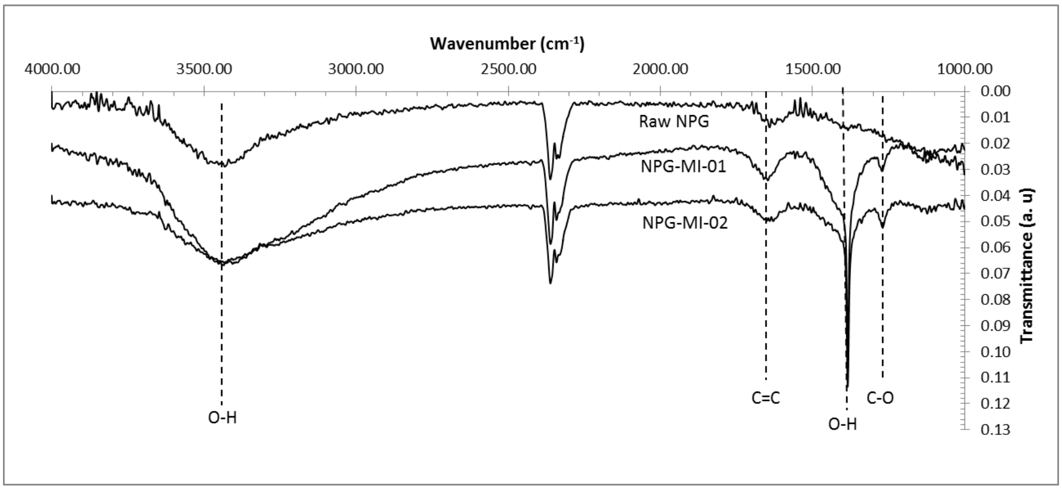

Figure 04: FTIR graphs of raw NPG sample and the microwave treated sample

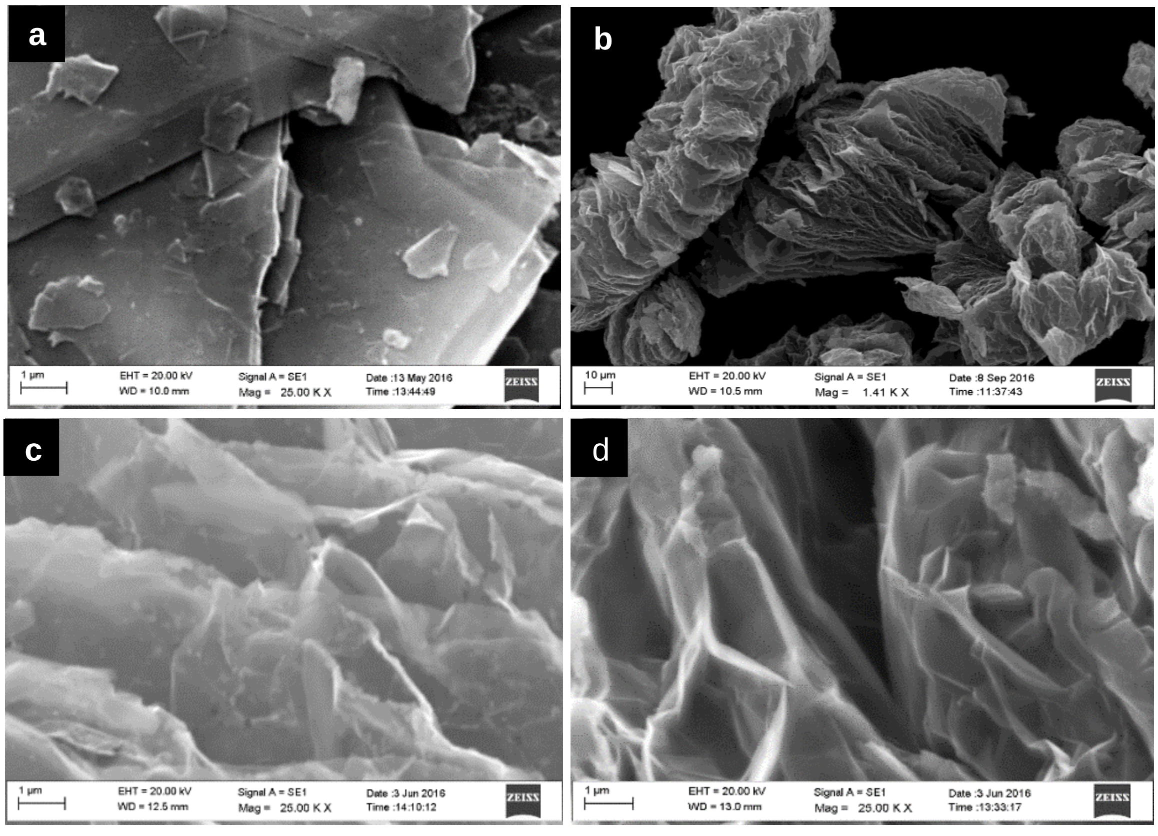

Figure 5: (a) SEM images of raw NPG, (b) EG at 1410X magnification, (c) Irradiated with microwave in 3 min after mixing at 25000X magnification and (d) Irradiated after 12 hrs at 25000X magnification

According to the SEM images (figure 05), the pore structures stretched perfectly with different pore sizes and shapes, like an oval, fracture-like or irregularly shaped on the surface of the exfoliated graphite. Almost every expanded graphite particle show a kind of rough, uneven and honeycomb-like surface morphology and while the EG has an abundant net pore structure. The SEM image of NPG-MI-02 is not showing any significant difference than NPG-MI-01. Hence it indicates that the mixing time is not a significant factor for exfoliation.

Table 01 shows the electrical conductivity obtained for raw [11] and exfoliated graphite. The EG shows a remarkable improvement in electrical conductivity after the microwave irradiation process.

Table 01: Electrical conductivity of the raw and treated graphite

	Conductivity value (S/cm) at 25 ^{0}C
Raw graphite	4.8
Microwave treated graphite (NPG-MI-01)	6.1

19. CONCLUSION

The EG was synthesized, within a very short time, using Sri Lankan needle platy vein graphite variety, by a prompt and efficient method using microwave irradiation technique. Interestingly, the shorter mixing time resulted the maximum yield of EG. The prepared EG shows a larger surface area and higher electrical conductivity than the raw graphite. Therefore this EG can be a potential candidate for novel applications such as for oil absorbing, synthesizing graphene oxide etc., which requires very high specific surface area.

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