



Effects of electron beam irradiation on characteristic properties of expanded graphite

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Abstract: Vietnamese graphite powder was irradiated by electron beam radiation (EB) at a range of dose from 0 to 120 kGy, then the graphite samples were expanded with a mixture of H₂O₂:H₂SO₄ (1,4:20, v/v) incorporating microwave treatment at 700 W for 30 seconds. The characteristic properties of graphite before and after expansion were evaluated by methods of FTIR, Raman, SEM and XRD. Besides the self-assembled of the graphite's structure after irradiation, the electron beam radiation also facilitated intercalation processing to make expanded graphite, with coefficient of expansion (K_v) 35% higher than that of pristine graphite.

Keywords: Graphite, Irradiation, electron beam, expanded graphite.

I. INTRODUCTION

Graphite (G) is one of three allotropes of carbon (graphite, diamond and amorphous coal) that exist in nature and was a crystalline substance with a hexagonal, lamellar crystal structure [1]. Graphite had adsorption capacity, large surface area, porous structure, chemical and heat resistance, so it was widely used in the fields of: adsorbent materials, water treatment, lithium batteries, fuel cells or fabricate graphene... [2, 3]. In addition, graphite was also modified to make expanded graphite (EG) to increase surface area, increase porosity, leading to increased efficiency of dyeing adsorption [4, 5], heavy oil [6], metal ions [7, 8] and can be desorption of oil compared with straw, rice husks, bagasse or porous polymers (propylene and ethylene terephthalate)..., or make antibacterial composites [9] or using EG instead of G to

increase efficiency in making graphene oxide and graphene.

Expansion graphite has been studied and fabricated by many different methods such as using chemical agents inserting graphite structure and then thermal shock at high temperature [6, 11-13] or by microwave [4, 14]. In addition, direct treatment of graphite by ionizing radiation (gamma rays, electron beams...) to change the structure was also studied [15-18].

Graphite (G), as a crystalline substance with a hexagonal, lamellar crystal structure, is one of three allotropes of carbon (graphite, diamond and amorphous carbon) that exist in nature. Thanks to its adsorption capacity, large surface area, porous structure, chemical and heat resistance, graphite has widely been used in fields of adsorbent materials, water treatment, lithium-ion batteries, fuel cells, and

graphene synthesis. In addition, graphite can be modified to fabricate expanded graphite (EG) to increase surface area and porosity, leading to an increasing efficiency of dyeing adsorption, heavy oil, and metal ions. Expanded graphite can also be utilized in desorption of oiled compared with straw, rice husks, bagasse or porous polymers (propylene and ethylene terephthalate), in antibacterial composites synthesis, or as an alternative of G to increase efficiency in graphene and graphene oxide preparation.

In Vietnam, graphite mines with large reserves were concentrated in the provinces of Lao Cai, Yen Bai, Quang Ngai and were used in different products: batteries, alkaline batteries, electrodes, coal for welding electricity, molds, electrolysis tanks, pencils, paints, abrasives, anti-rust materials... [3]. Currently, in Vietnam there were not many researches on applying radiation technology to transform graphite, especially Vietnamese graphite into advanced materials such as graphene oxide or graphene, possibly because there was cannot be produced graphite with high purity for applications in high-tech engineering industries, so promoting Vietnamese graphite modification studies [3,4] by radiation technology will also contribute to promoting the development of our country's graphite industry.

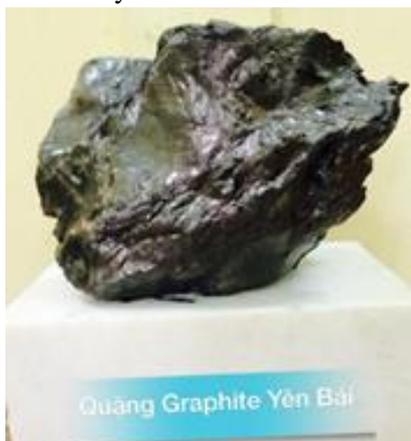


Fig.1. Photograph of Yen Bai graphite ores

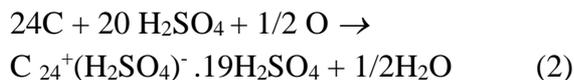
Normally, EG was fabricated by using chemical agents inserted between the structural layers of G and then thermally shocking the mixture at high temperature [2] or by microwave at high power [3]. In this study, VN graphite was irradiated by electron beam first, and then used a mixture of H_2O_2 : H_2SO_4 inserted the G structural layers to fabricate EG. The results showed that the combination of EB irradiation and thermal shock, inserting G was effective in the fabrication of EG. The pre-irradiation of graphite aims to simplify the process, reduce the amount of chemicals used compared to the conventional way of synthesizing EG and using EG instead of G to increase efficiency in graphene and graphene oxide preparation in the next study.

II. EXPERIMENTAL

Preparation of expanded graphite

Vietnamese graphite powder (G) (94% carbon, VPG Vietnam) was irradiated at a room temperature by electron beams (Linear electron accelerator UERL-10-15S2, 10 MeV; manufactured by Corad Services Ltd, Russia) in the range of absorbed doses from 0; 10; 20; 40; 80 and 120 kGy with the dose rate of 3.0 kGy/s and the obtained samples were labeled as G0, G10, G20, G40, G80 and G120 respectively. Expanded graphite (EG) was prepared by adding irradiated graphite powders (1 g) into a glass beaker containing the mixture of H_2O_2 : H_2SO_4 with ratio 1.4: 20 (v/v) and stir slowly for 100 minutes at room temperature. The samples were filtered and washed with distilled water to $\text{pH} = 3$ and then dried at 60°C for 24 hours. After that, the samples were heat-shocked by the microwave at a power of 700 W for 30 seconds. The expanded graphite was labeled as EG0, EG10, EG20, EG40, EG80 and EG120, respectively. The principle of this

process is to use H₂SO₄ acid as an inserting agent in the presence of the oxidizing agent H₂O₂, leading to the decomposition of H₂O₂ to oxidize the structure layers of graphite. It was then combined with HSO⁴⁻ to form an inserted compound of C₂₄ + HSO⁴⁻.19H₂SO₄ according to the reaction mechanism as (1) and (2):



Characterization

- FT-IR absorption spectra were collected by using KBr pellets on the transmission module of a FTIR spectrophotometer (8400S, Shimadzu, Japan) in the range between 4000 cm⁻¹ and 400 cm⁻¹.

- X-ray diffraction patterns of the samples were taken using a XRD D8 Advance diffractometer, Bruker, Germany with monochromatized Cu-K α radiation ($\lambda=1.5406\text{\AA}$) at a scanning rate of 0.13 °/minute in a wide angle range ($2\theta = 5 - 120^\circ$) at ambient temperature.

- The SEM measurements of all samples were performed using a FE-SEM 4800, Hitachi, Japan.

- Raman spectra: Fine powder samples were measured on the Ramma-LABRAM300, Horiba JOBIN YVON, at 532 nm.

- Determination of expansion coefficient: Weigh 1 g of the graphite sample into a 10 ml glass cylinder and record the volume of the sample. The recorded results were the average of the four replicated measurements, expansion coefficient (K_v) of samples were calculated by the following formula [3]:

$$K_v = \frac{V_t}{V_0}$$

Where V_t is the specific volume of the sample after heat-shocking (ml/g) and V_0 is the initial specific volume of the graphite sample (1.8 ml/g).

III. RESULTS AND DISCUSSION

FTIR spectra

As indicated in Fig. 2, the FTIR spectrum shows that all G samples were appeared characteristic peaks for asymmetric stretching of C-H group at 2.883 cm⁻¹ and for the conjugated C = C coupling of the graphite surface at 1.697 and 1.511 cm⁻¹. In addition to the characteristic peaks such as G, the FTIR spectrum of EGs were appeared peaks at 1.728 and 1.094 cm⁻¹, corresponding to the C = O, C – O – C bonds, respectively. The peaks at 1.191 and 565 cm⁻¹ were belonging to SO₄²⁻[9]. The FTIR analysis results indicated that sulfuric acid was inserted into graphite structure after treatment and the oxygen functional groups on EG were formed by expansion in air. As indicated in Fig. 2, the FTIR spectrum shows characteristic peaks of the asymmetric stretching of C-H group (at 2.883 cm⁻¹) and the conjugated C = C coupling of the graphite surface (at 1.697 and 1.511 cm⁻¹) in all G samples. In addition, peaks at 1.728 and 1.094 cm⁻¹ are observed, which corresponds to C = O and C – O – C bonds, respectively. The peaks at 1.191 and 565 cm⁻¹ were attributed to SO₄²⁻[9]. The FTIR analysis results indicated that sulfuric acid was inserted into graphite structure after treatment and the oxygen functional groups on EG were formed by expansion in air.

Raman spectra

Figure 3 shows the Raman spectroscopy results of samples G and EG. The characteristics of the failure level in the material structure can be seen from peak D (1.343 cm^{-1}) and peak G (1.578 cm^{-1}), corresponding to C-C bonding of Sp^2 hybridization. Peak 2D (2.713 cm^{-1}) is the characteristic for the double bond dispersion of the graphene double layer caused by the interaction of graphene planes in the graphite structure, which was the quadratic phonon effect. In addition, the I_D/I_G intensity ratio shows significant change in the lattice structure of material.

The I_D/I_G intensity ratio of samples G0, G10; G20, G80, G120 are 0.205; 0.181; 0.180; 0.177; 0.156 respectively and of samples EG0, G10; G20, G80, G120 are 0.212; 0.159; 0.099; 0.097; 0.092 respectively. These results indicate that after electron beam irradiation or after thermal shock, the structure of graphite has been self-assembled better than that of the untreated samples; moreover, the combination of EB irradiation and then thermal shock of graphite samples were obtained in the sample

EG10-120 with less defect structure than EG0. In addition, the 2D peak position of the sample is shifted to the position with a lower wave number than G0, indicating a decrease in the number of layers or expansion in the graphite structure after irradiation or heat shock [5, 13,15-17].

Particularly, the Raman results show no D peak on G40. The I_D / I_G intensity ratio of EG40 is close to EG0 (0.211), while the 2D peak shifts strongly to 2.687 cm^{-1} , much lower than that of G40 and G0. It means a significant structural change associated with the graphite after irradiation at 40 kGy. In the graphite irradiating process, electrons created holes and defects (or materials, the direct collision of atoms with gaps) in the graphite's structure. The structural self-assembled and defects depended on the dose rate and absorbed rate. Thus, the graphite structure of G40 rearranged itself and reduced defects, while EG40 experienced a strong gas release of SO_2 from the decomposition of HSO_4^- and H_2SO_4 groups during the thermal shocking. As a result, the layer structures of G40 were expanded and exfoliated, leading to many exposed structural defects.

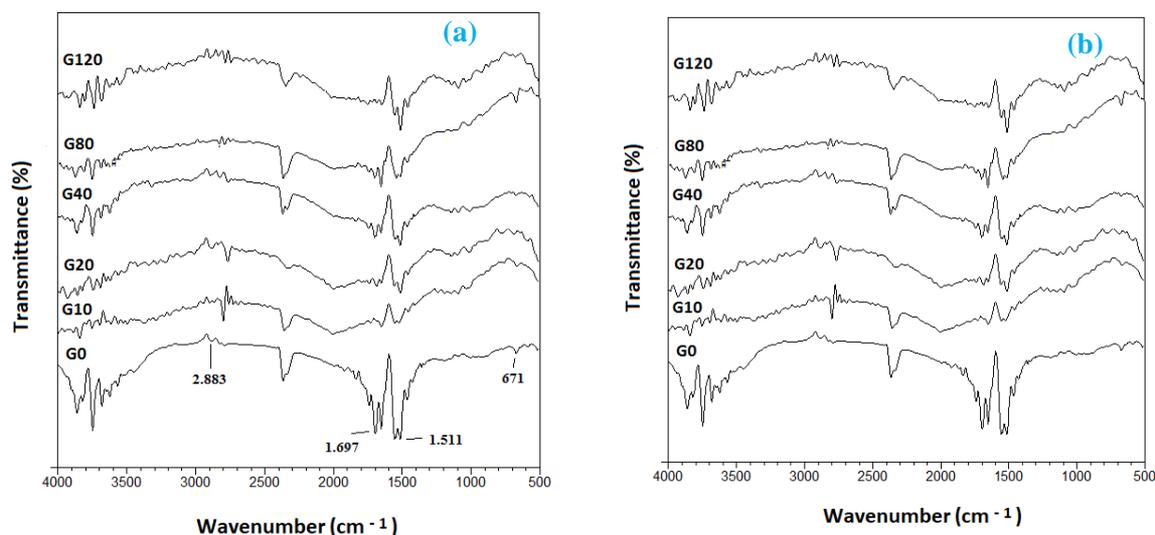


Fig. 2. The FTIR spectra of G0-120 (a) and EG0-120 (b)

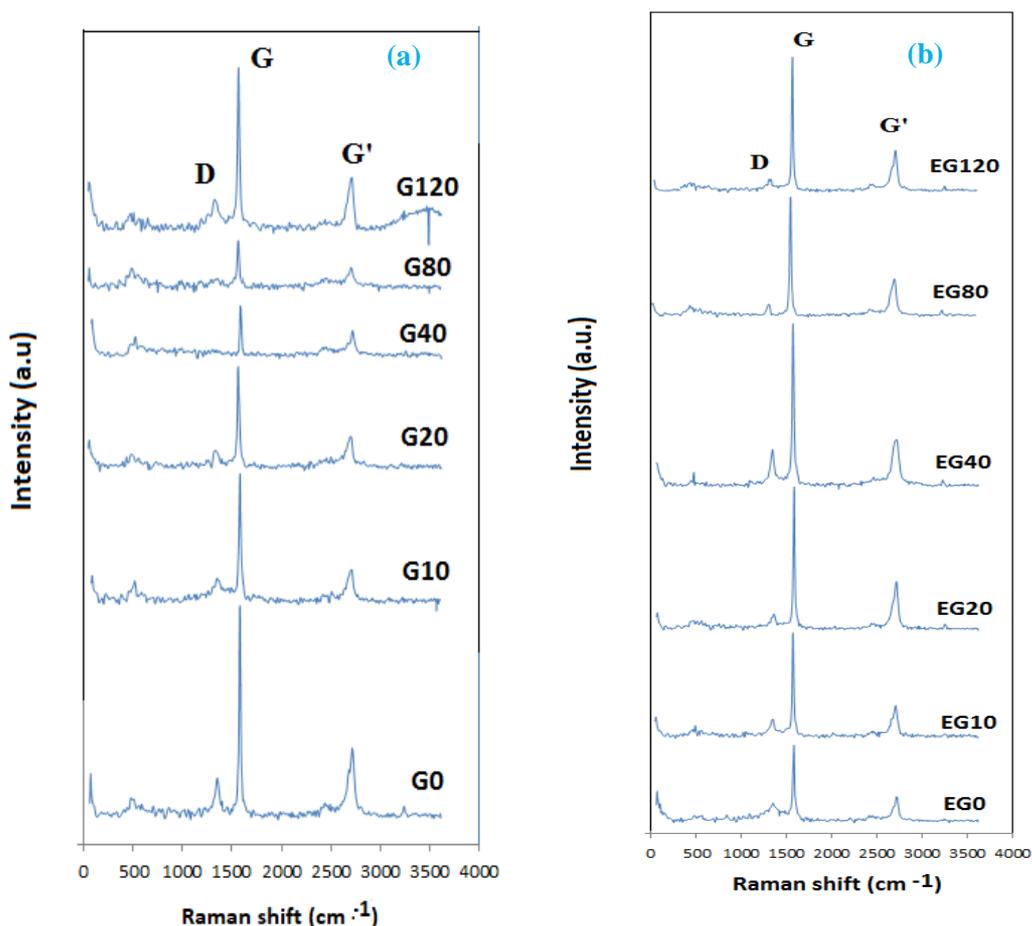


Fig. 3. The Raman of G0-120 (a) and EG0-120 (b)

XRD pattern

XRD patterns of G0-120 and EG0-120 are illustrated in Fig.4, which show sharp and symmetrical peaks at 2θ around 26.39° with high intensity. It indicates that graphite has an orderly crystalline structure. The diffraction peak intensity of G decreases with the increasing absorbed doses, proved reducing of crystalline, on the contrary, when G was expanded to form EG, diffraction peak intensity increases, indicated increasing of crystalline. In the case of G40 and EG40, it can be clearly observed that EG40 was exhibited weaker diffraction peaks at $2\theta = 26.46^\circ$ and 54.56° compared to G40, which was caused by the expansion of lattice of

graphite crystals along the c-axis when the temperature was increased dramatically and drastically, in addition, it was also associated with the self-assembled and stacking of the graphite layers [4,9]. This result was also consistent with the expansion coefficient K_v of EG40 reached of 1.35, highest in the samples as shown in Fig. 5 and Fig. 6. The diffraction peak intensity of G decreases with the increasing absorbed doses, implying a lower level of crystalline. On the contrary, when G was expanded to form EG, diffraction peak intensity increases, which corresponds to a higher crystalline level. In the cases of G40 and EG40, it can be clearly observed that EG40 exhibited weaker

diffraction peaks at $2\theta = 26.46^\circ$ and 54.56° compared to G40, which can be ascribed to the expansion of graphite crystals lattice along the c-axis as the temperature increased. Furthermore, it was also associated with the

self-assembled and stacking of the graphite layers. This result was also consistent with the expansion coefficient K_v of EG40 (1.35), which is the highest value among the samples as shown in Fig. 5 and Fig. 6.

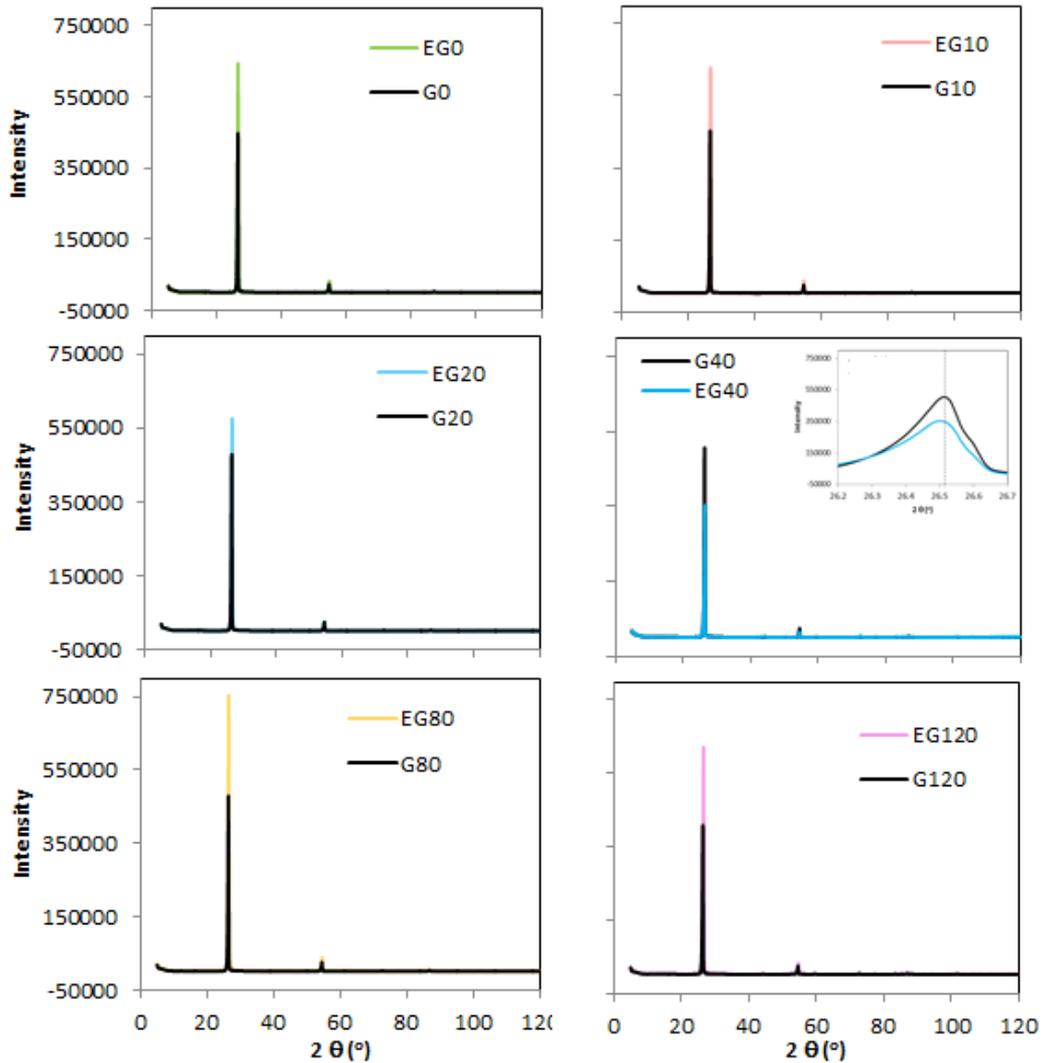


Fig. 4. XRD patterns of G0 to G120 and EG0 to EG120

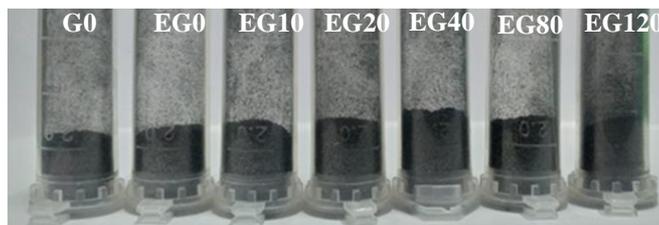


Fig. 5. Photograph of graphite (G0) and expanded graphite (EG0-120)

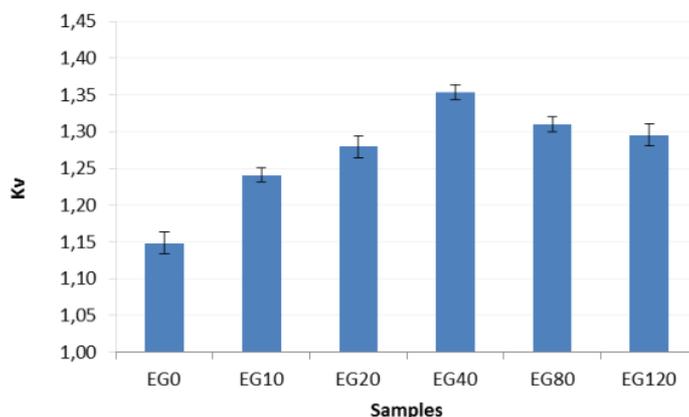


Fig. 6. The results of expansion coefficient (K_v) of EG0 to EG120

SEM images

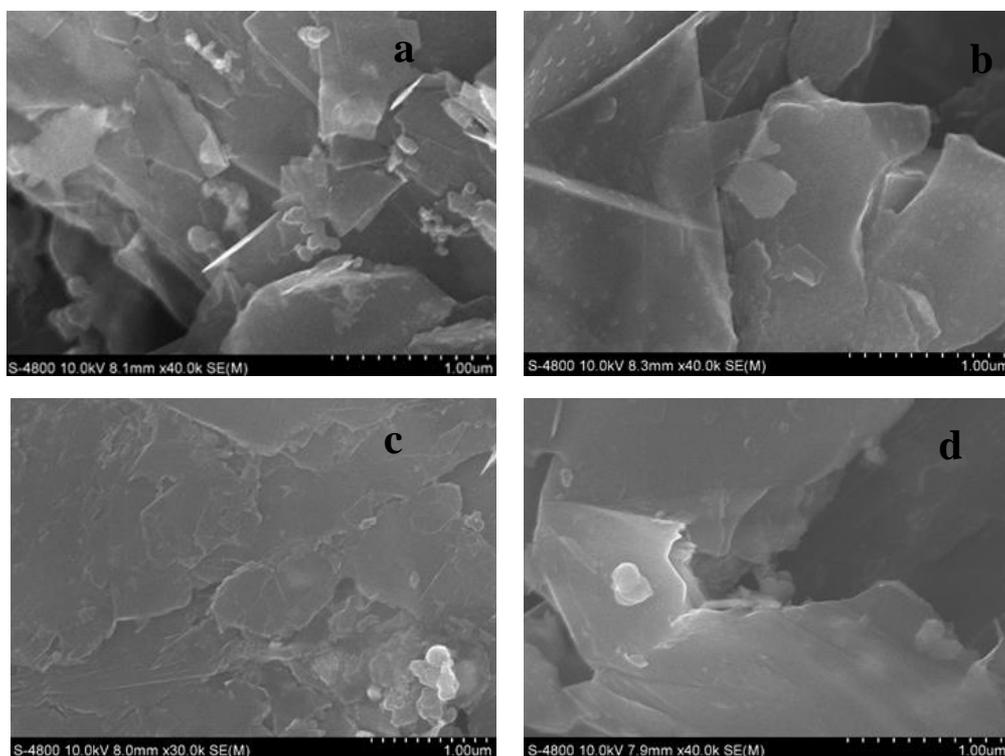


Fig. 7. SEM images of G0 (a), EG0 (b) and G40 (c), EG40 (d)

The morphologies of graphite and expanded graphite are shown as in Figure 7. The SEM images of the G and EG0 present graphite with multilayers structure and impurity. Defects are observed in the G40 sample irradiated at 40 kGy, while, the SEM

image of the EG40 shows expanded graphite with thinner structure.

IV. CONCLUSIONS

Electron beam radiation has significantly influenced the characteristic properties of

Vietnamese graphite. The analysis results of FTIR, Raman, SEM and XRD spectra showed the dependence of the self-assembled and defects of the graphite structure on the absorbed dose. EG40 sample showed the most expanded graphite lattice structure, corresponding to an expansion coefficient of 35% higher than that of pristine graphite. The results of this study are the premise for further studies such as improvement and application of Vietnamese's expanded graphite as oil absorption materials, pigments or raw materials for the fabrication of graphene oxide...

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