Microwave-Assisted Exfoliation Synthesis of Exfoliated Graphite and Their Oil Adsorption Ability

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Abstract—An EG was successfully synthesized by microwave-assisted exfoliation method and characterized by SEM, FT-IR, and BET. We also investigated the adsorption ability of EG fo sorption of engineering oils (DO, FO and CO) in the mixed oil-water. The results indicated that EG with high surface area (100.97 m^2/g) can effetely adsorb oils. The maximum DO, CO, and FO adsorption capacity is 75.35 ± 1.13, 74.11667 ± 2.97, and 48.71667 ± 5.34 g/g, respectively.

Keywords—*Microwave-assisted exfoliation synthesis, exfoliated graphite, oil adsorption*

I. INTRODUCTION

Exfoliated graphite (EG) is a graphite which has a degree of separation of a substantial portion of the carbon layers in the graphite [1]. EG has been received much attention due to its larger application such as heat insulating material, fire-retardant material, packings, and adsorbent. Especially, EG with large sorption capacity and high sorption rate have been suggested as a promising adsorbent for oil adsorption in oil spill accidents [2], [3].

EG can be fabricated by some methods such as micromechanical cleavage, liquid phase exfoliation [4], chemical vapor deposition [5], molecular beam epitaxy [6], ultrasonic irradiation [7], and microwave (MW) irradiation [8]–[10]. Among of the aforementioned methods, MW irradiation has been believed as one of the best choices for its many benefits, including rapid, easy and efficient synthesis.

In this page, we prepared an EG using MW-assisted exfoliation process. The influent of MW power, time and the weight ratio of precursors in the exfoliation volume of EG was investigated. The as-synthesized products were characterized by SEM, FT-IR, and BET. Besides, we also investigate the oil adsorption ability of EG.

II. EXPERIMENT

A. Preparation of EG

All chemical were used as received. EG was synthesized from natural graphite flake (GF) with carbon content 87.68% supplied by the Yen Bai region of Vietnam. The synthesized procedure includes two following steps: (1) GF, $KMnO_4$, $HClO_4$, and $(CH_3CO)_2O$ were mixed in different weight ratios with a 50 mL glass beaker for 10 s to produce graphite intercalation compounds (GIC); (2) GIC was taken in a 50 mL ceramic beaker and take into a 2.45 GHz microwave oven (SANYO) operated at different MW power P_w (W) for different time t_w (s).

B. Characterization of EG

The as-synthesized samples were observed by scanning electron microscope (SEM, S4800, Japan) at an accelerating voltage source of 10 kV with a magnification of 7000. The FT–IR spectra were recorded by using the Nicolet 6700 spectrophotometer instrument. The N_2 adsorption/desorption isotherm was obtained using the Micromeritics 2020 volumetric adsorption analyzer system. BET surface area was measured using the isotherm equation.

The exfoliated volume of EG (EV, ml/g) was calculated by the following equation:

$$EV = \frac{V}{m} \qquad (1.1)$$

where V is the volume of EG and m is the quantity of EG. 0.2 g EG was transferred into a 50 mL graduated cylinder lightly, then V and M of EG were recorded.

C. The oil sorption capacity of the EG

For oil adsorption test, we used oils such as diesel oil (DO, kinematic viscosity 2.742 mm^2/s, density 850 kg/m^3), crude oil (CO, kinematic viscosity mm^2/s, density kg/m^3), and fuel oil (FO, kinematic viscosity mm^2/s, density kg/m^3). 15g of oil and 100 mL simulated seawater (salinity 3.5 %, ASTM 1141) were added in a Petri dish at room temperature. Then, 0.2g EG was individually added to the simulated seawater containing oil. After adsorption process, the mixture of EG and oil was filtered through a grille to remove water and the remaining oil for 5 min, followed by balancing to determine the oil sorption capacity of the EG (g/g).The oil sorption capacity of the EG was determined by changing the weight ratio of oil to EG.

Therefore, sorption capacity was the weight of oil sorbed per 1 g of EG (g/g). All experiment was repeat three times.

III. RESULTS AND DISCUSSION

A. The preparation of the EG

It is well known that the mechanism of the exfoliated processes of EG based on the vapor processes of GICs in between graphite layers resulting the formation of worm-like structure. GICs can be decomposed by temperature and oxidizing agents. In this study, we employed MW irradiation with rapid and uniform local heating, and therefore the decompose of GICs took place rapidly, as a comparison with conventional heating.

Fig. 1 shown the EV of EG samples synthesized using different microwave power and time. From Fig.1A, when MW power is 360 W, the maximum EV is 215.00 mL/g. When MW power is less than 360 W, the EV of EG was reduce because the energy was not enough for expanded volume processes. Increasing MW power, the EV of EG was also decreased. The reason is that a part of GIC was burned. The effect of MW time on the expanded volume of EG was shown in Fig. 1B. As shown in Fig. 1B, the EV reached the highest value when MW time was 50 s. Therefore, in our experiment condition, the synthesis of EG at 360W for 50 s are optimal conditions.
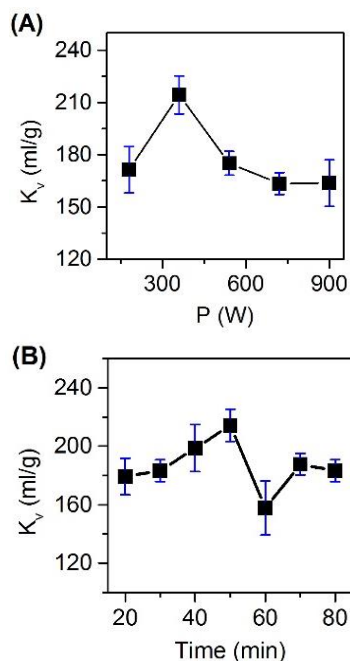

Fig. 1. The exfoliated volume of EG prepared at different MW power (A) and for different time (B).

The influence of the weight content of oxidizing agents and intercalating agent on the EV of EG was also investigated. $KMnO_4$ and $HClO_4$ were used as oxidizing agents while $(CH_3CO)_2O$ was used as an intercalating agent. The results were shown in Table 1. This result indicated that with an increase of the $(CH_3CO)_2O$, the EV of EG increased and reached the maximum value 214.33 ± 10.97 ml/g for 1:1:1:0.4 (sample no.8 in Table 1). When oxidizing ratio varied by keeping the others constant, the maximum EV = 243.67 ± 28.87 ml/g obtained for 1:0.5:1:0.4 (sample no.1 in Table 1).

TABLE I. THE EXFOLIATED VOLUME OF EG PREPARED AT DIFFERENT MIXED PRECURSOR.

No.	Mixture ratio by weight $GF: KMnO_4: HClO_4: (CH_3CO)_2O$	EV (ml/g)
1	1:0.5:1:0.4	243.67 ± 28.87
2	1:1.5:1:0.4	114.33 ± 9.24
3	1:0.5:0.5:0.4	239.67 ± 43.43
4	1:1.5:0.5:0.4	59.33 ± 1.53
5	1:0.5:1.5:0.4	64.67 ± 14.05
6	1:1.5:1.5:0.4	179.33 ± 12.50
7	1:1:1:0.3	187.67 ± 7.51
8	1:1:1:0.4	214.33 ± 10.97
8	1:1:1:0.5	171.00 ± 6.93

B. Characterization of EG

Fig.2 shows the morphology of GF and EG by SEM analysis. From Fig. 2(A), the morphology of GF amorphous particle. As shown in Fig. 2(B), after MW process, the morphology and shape of GF were transformed to the adjacent carbon layers. It is concluded that MW irradiation with rapid and uniform local heating can destroy GICs to free graphite layers.
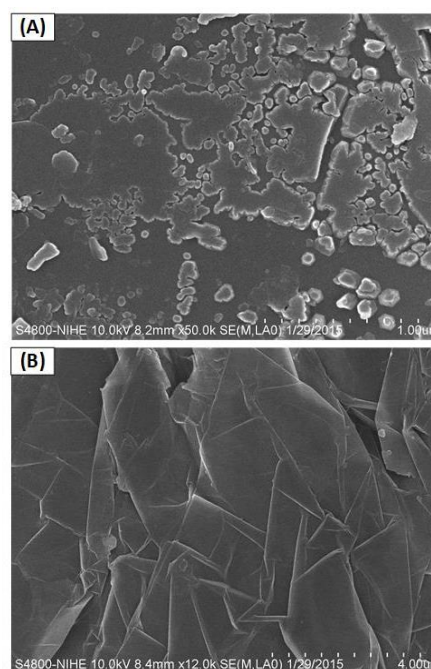

Fig. 2. SEM image of (A) GF and (B) EG .

Fig. 3 shows FT-IR of GF and EG. In details, the presence of hydroxyl groups, O-H stretching, and adsorbed water was confirmed by stretching vibration of broadband around 3420 cm^{-1}. The shape peaks positioned around 1629 cm^{-1} was attributed to the existence of the C=O group. The peaks at about 2350 cm^{-1} represent the C-O-C stretch vibration. The –CH_3 stretch vibration could be recognized by the present of the peak at 2917 cm^{-1}.
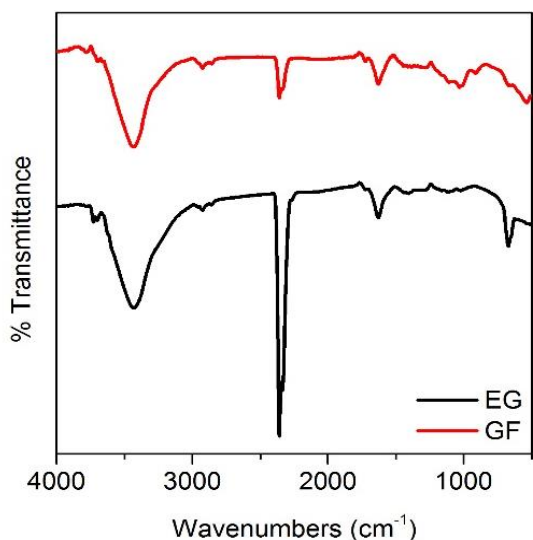
Fig. 3.   FT-IR of GF and EG.

The pore size distribution and BET surface area of AC were observed. The results were shown in Table 1. The surface area EG were about sixteen times greater than those of GF, corresponding to the increase of the EV value. Similarly, the pore volume of EG increased from 0.007 to 0.106 $cm^3/_g$. However, the pore size remained unchanged.

TABLE II.   THE PHYSICAL PROPERTIES OF EG AND GF.

Samples	SBET (m2/g)	Pore size (A)	Pore volume (cm3/g)	EV (ml/g)
GF	6.52	12.6	0.007	1.6
EG	100.97	12.6	0.106	243.67 ± 28.87

C. The oil sorption capacity of the EG

The oil sorption capacity of the EG was shown in Fig.4. The results indicated that EG can rapidly adsorb DO and FO. The maximum DO, CO, and FO adsorption capacity is 75.35 ± 1.13, 74.11667 ± 2.97, and 48.71667 ± 5.34 g/g, respectively. The FO sorption capacity of the EG showed small value due to its high viscosity.
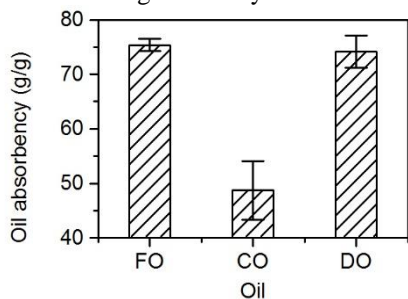

Fig. 4.   The oil sorption capacity of the EG.

IV.   CONCLUSION

The oil sorption capacity of the EG was shown in Fig.4. The results indicated that EG can rapidly adsorb DO and FO. The maximum DO, CO, and FO adsorption capacity is 75.35 ± 1.13, 74.11667 ± 2.97, and 48.71667 ± 5.34 g/g, respectively. The FO sorption capacity of the EG showed small value due to its high viscosity. We have synthesized EG by microwave-assisted exfoliation method and also investigated the adsorption ability of EG for sorption of engineering oils (DO, FO and CO) in the mixed oil-water. The samples were synthesized at 360 W and for 50 s showed the highest EV values. Besides, EG with high surface area (100.97 m2/g) can effetely adsorb oils. The maximum DO, CO, and FO adsorption capacity is 75.35 ± 1.13, 74.11667 ± 2.97, and 48.71667 ± 5.34 g/g, respectively. It was suggested that EG is a promising adsorbent for oil adsorption in oil spill accidents.

ACKNOWLEDGMENT

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