SYNTHESIS AND CHARACTERIZATION OF FULLERENE FROM GRAPHITE ORE

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Abstract

This research work concerned with synthesis and characterization of fullerene from graphite ore. The graphite ore was collected from Thabeikkyin Township, Mandalay Region. The synthesis of fullerene was carried out by Modified Hummer's method in which graphite powder was oxidized with the help of oxidizing agent H₂SO₄ and KMnO₄. Moreover, the various amounts of NaNO₃, H₃PO₄, KMnO₄ and H₂SO₄ were used to produce fullerene. The crystal lattice size of graphite and fullerene were characterized by X-ray diffraction (XRD). The prepared fullerenes were analysed by Thermo gravimetric analysis (TG-DTA). The morphology of the graphite and the synthesized fullerene were investigated by scanning electron microscope (SEM).

Keywords: Graphite, Fullerene, Hummer's method, XRD, TG-DTA, SEM

Introduction

The prefix "nano" has found in last decade on ever-increasing application to different fields of the knowledge. Nanoscience, nanotechnology, nanomaterials or nanochemistry are only a few of the new nano-containing terms. The nanosized world is typically measured in nanometers $(1 \text{ nm}=10^{-9} \text{ m})$ (Hahens *et al.*, 2007).

Nowadays, nanotechnology research is developed as a cutting-edge interdisciplinary technology involving chemistry, physics, material science, biology and medicine (Roco, 2004). Nanomaterials and nanoparticles exhibit high strength, high thermal stability, low permeability and high conductivity properties, among other unique properties which stimulate the scientific commonly to focus their research on developing new applications and products related to nanotechnology. Nanoparticles are 1 nm to 100 nm in size. They have very small sizes and large surface area to volume ratios. Their atoms may also be arranged into tubes or rings. Carbon can form nanoparticle stimulates with a variety of shapes (Fears *et al.*, 2011).

Graphite is a crystalline form of carbon, a native element mineral and one of the allotropes of carbon. Graphite is the most stable form of carbon under standard conditions. Graphite occurs in metamorphic rocks. Minerals associated with graphite include quartz, calcite, micas and tourmaline (Anthony *et al.*, 1990).

The fullerenes are the third allotrope of carbon after graphite and diamond. Each molecule of fullerene family (C_n) consists of 12 pentagons and m number of hexagons conforming to the relation m = (n-20/2) (Euler's theorem). C₆₀ fullerene was produced from a graphite (Dietz *et al.*, 1981). The most abundant from of fullerenes is Buckminster fullerene (C₆₀) with 60 carbon atoms arranged in a spherical structure (Kratschmer *et al.*, 1990). It contains 12 pentagons and 20 hexagons. The pentagonal rings contain only single bonds (Hawkins *et al.*, 1991).

Fullerenes are used in a wide range of applications such as in optical and electronic devices (polymer additives, solar cells, photovoltaic) (Kronholm and Hummelen, 2007), in commercial cosmetic products (Xiao *et al.*, 2005), and in biomedicine (antiviral, anti-cancer, and antioxidant agents, in drug delivery systems) (Tagmatarchis and Shinohara, 2001). The aim of this research work is to synthesize and characterize fullerene from graphite ore.

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Graphite structure

Materials and Methods

Sample Collection

The graphite ore was collected from Thabeikkyin Township, Mandalay Region. The graphite ore was ground to get the powder. The graphite powder samples were stored in a well-stoppered bottle and used through out this research and presented in Figure 1.



(a)



Figure 1 (a) Graphite ore (b) Graphite powder

Preparation of Fullerene from Graphite with NaNO₃, KMnO₄ and H₂SO₄ by Modified Hummer's Method under Different Conditions

Preparation of fullerenes (C-1) and (C-2) from graphite with NaNO3, KMnO4 and H2SO4

A 0.5 g of graphite powder sample and 0.25 g of sodium nitrate were mixed and stirred in ice bath by using magnetic stirrer. 20 mL of concentrated sulphuric acid and 2.0 g of potassium permanganate were added into the solution. The solution was stirred for 1 h. After stirring 1 h, this solution was removed from ice bath and again stirred for 3 h at room temperature. Then, 50 mL of distilled water was added into the solution and stirred for another 1 h at room temperature. 50 mL of hot water and 7.5 mL of 30 % hydrogen peroxide were added into the solution. The solution was obtained. This solution was centrifuged and the precipitate was collected and washed with 5 % hydrochloric acid and then with distilled water until it became neutral. Fullerene (C-1) was obtained.

The fullerene (C-2) was also prepared according to the same procedure as (C-1) preparation. However, the stirring time 3 h and sonication time 3 h were taken for preparation of C-2.

Preparation of Fullerene from Graphite with H₃PO₄, KMnO₄ and H₂SO₄ by Modified Hummer's Method under Different Conditions

Preparation of fullerenes (C-3) and (C-4) from graphite with H₃PO₄, KMnO₄ and H₂SO₄

A 0.25 g of graphite powder sample and 27 mL of concentrated sulphuric acid and 3 mL of phosphoric acid were mixed and stirred in ice bath by using magnetic stirrer. 1.32 g of potassium permanganate was slowly added to this solution and stirred for 1 h. After stirring 1 h, this solution was removed from ice bath and again stirred for 5 h at room temperature. Then dark green solution was obtained. 1 mL of hydrogen peroxide was added drop by drop and stirred for 0.5 h at room temperature. 10 mL of concentrated HCl and 30 mL of deionized water were added into the solution. This solution was centrifuged. The resultant precipitate was washed with 5 % HCl and distilled water until neutral. Finally, fullerene was obtained.

The fullerene (C-4) was prepared according to the same procedure of (C-3). However, the stirring time 9.5 h was taken for preparation of C-4.

Results and Discussion

Fullerene nanoparticles were synthesized from graphite ore by modified Hummer's method. The preparation of fullerene nanoparticles were performed under four different conditions. And the graphite ore powder and prepared fullerene nanoparticles were characterized by advanced methods such as XRD, TG DTA and SEM.

Characterization of Graphite Ore and Prepared Fullerene by XRD

The graphite ore powder was characterized by XRD and the chromatogram and results are presented in Figure 2 and Table 1-2. According to the results, the graphite sample shows a sharp peak ($2\theta = 26.141^{\circ}$) which corresponds to the diffraction line (002) with the intercellular spacing in the crystal (d) respectively is 3.4061. The range of particle size of graphite were found to be 152.76-855.98 nm and average particle size is 490.47 nm. Phase ID reported that graphite sample was graphite 2H. According to graphite grading HB scale, the collected graphite ore sample was found to be hard



Figure 2 XRD diffraction pattern of graphite ore

Peak	Bragg	Miller indices	FWHM of peak	Inter cellular	Particle size,
No.	angle (20)	(h k l)	(β) radians	spacing d (nm)	D (nm)
1.	26.141	002	0.0018	3.4061	761.74
2.	44.129	101	0.0034	2.0505	435.12
3.	49.930	102	0.0099	1.8250	152.76
4.	54.270	004	0.0018	1.6889	855.98
5.	59.461	103	0.0064	1.5532	246.73

 Table 1
 The Results from XRD Pattern of Graphite Ore

 Table 2
 The Peak ID Report of Graphite Ore

Peak No.	Bragg angle (2θ)	Miller indices (h k l)	Area (%)	Phase ID
1.	26.141	002	100.0	Graphite 2H
2.	44.129	101	6.0	Graphite 2H
3.	49.930	102	1.0	Graphite 2H
4.	54.270	004	4.0	Graphite 2H
5.	59.461	103	1.0	Graphite 2H

Fullerene nanoparticles were synthesized by using H_2SO_4 , NaNO ₃, KMnO₄, H_2O_2 , HCl and H_3PO_4 under four different stirring times and shaking time. The highest yield of C-4 was 88.40 % followed by C-2, C-3 and C-1 as shown in Table 3.

 Table 3
 Yield Percent of Fullerene (C-1 to C-4)

No	Fullerene	Yield (%)
1	C-1	73.02
2	C-2	76.08
3	C-3	74.52
4	C-4	88.40

The prepared fullene (C-1 to C-4) were characterized by XRD and the results are presented in Figure 3-6 and Table 4-12.



Figure 3 XRD diffraction pattern of fullerene (C-1)

Peak No.	Bragg angle (2θ)	Miller indices (h k l)	FWHM of peak (β) radians	Particle size D (nm)
1.	10.218	(1 0 0)	0.0060	23.735
2.	10.840	(0 0 2)	0.0152	9.061
3.	17.651	(1 1 0)	0.0093	14.921
4.	20.621	(1 1 2)	0.0098	14.220
5.	21.530	(0 0 4)	0.0034	41.049
6.	30.888	(3 0 0)	0.0027	52.683
7.	32.650	(0 0 6)	0.0044	32.470

Table 4 The Results from XRD Diffractogram of Fullerene (C-1)

According to Table 4, the range of particle size of prepared fullerene (C-1) were found to be 9.061-52.683 nm and average particle size is 26.877 nm.

Peak No.	Bragg angle (2θ)	Miller indices (h k l)	Area (%)	Phase ID
1.	10.218	(1 0 0)	20.6	C ₆₀
2.	10.840	(0 0 2)	97.5	C ₆₀
3.	17.651	(1 1 0)	14.5	C ₆₀
4.	20.621	(1 1 2)	18.7	C ₆₀
5.	21.530	(0 0 4)	6.6	C ₆₀
6.	30.888	(3 0 0)	3.2	C ₆₀
7.	32.650	(0 0 6)	5.5	C ₆₀

 Table 5 The Peak ID Report of Fullerene (C-1)

For C₆₀, the localized peaks at $2\theta = 10.218^{\circ}$, 10.840° , 17.651° , 20.621° , 21.530° , 30.888° and 32.650° that referred to plane reflections of (100), (002), (110), (112), (004), (300) and (006), respectively. According to Table 5, phase ID of prepared C-1 was confirmed as C₆₀ and should be fullerene.



Figure 4 XRD diffraction pattern of fullerene (C-2)

Peak	Bragg	Miller indices	FWHM of peak	Particle size
No.	angle (2θ)	(h k l)	(β) radians	D (nm)
1.	10.220	(100)	0.0122	29.025
2.	10.841	$(0\ 0\ 2)$	0.0116	18.162
3.	17.550	$(1\ 1\ 0)$	0.0071	19.542
4.	20.831	$(1 \ 1 \ 2)$	0.0114	12.054
5.	30.638	$(3\ 0\ 0)$	0.0066	21.539
6.	32.668	$(0\ 0\ 6)$	0.0040	35.721

 Table 6 The Results from XRD Diffractogram of Fullerene (C-2)

According to Figure 4 and Table 6, the range of particle size of prepared fullerene (C-2) were found to be 12.054-35.721 nm and average particle size is 27.829 nm.

Peak No	Bragg angle (2θ)	Miller indices (h k l)	Area (%)	Phase ID
1.	10.220	(1 0 0)	100.0	C ₆₀
2.	10.841	(0 0 2)	88.1	C ₆₀
3.	17.550	(1 1 0)	5.9	C ₆₀
4.	20.831	(1 1 2)	10.6	C ₆₀
5.	30.638	(3 0 0)	4.0	C ₆₀
6.	32.668	(0 0 6)	2.3	C ₆₀

 Table 7 The Peak ID Report of Fullerene (C-2)

For C₆₀, the localized peaks at $2\theta = 10.220^{\circ}$, 10.841° , 17.550° , 20.831° , 30.638° and 32.668° that referred to plane reflections of (100), (002), (110), (112), (300) and (006), respectively. According to Table 7, prepared C-2 was confirmed as C₆₀ and should be fullerene.



Figure 5 XRD diffraction pattern of fullerene (C-3)

Peak No.	Bragg angle (2θ)	Miller indices (h k l)	FWHM of peak (β) radians	Particle size D (nm)
1.	10.150	(1 0 0)	0.0167	8.242
2.	10.750	(0 0 2)	0.0095	14.496
3.	17.655	(1 1 0)	0.0054	25.694
4.	20.906	(1 1 2)	0.0027	51.638
5.	21.632	(0 0 4)	0.0131	10.656
6.	30.533	(3 0 0)	0.0038	37.402
7.	32.470	(0 0 6)	0.0063	22.668

 Table 8 The Results from XRD Diffractogram of Fullerene (C-3)

According to Figure 5 and Table 8, the range of particle size of prepared fullerene (C-3) were found to be 8.242-51.638 nm and average particle size is 24.399 nm.

Peak No	Bragg angle (2θ)	Miller indices (h k l)	Area (%)	Phase ID
1.	10.150	(1 0 0)	51.4	C ₆₀
2.	10.750	(0 0 2)	100.0	C_{60}
3.	17.655	(1 1 0)	3.8	C_{60}
4.	20.906	(1 1 2)	2.2	C_{60}
5.	21.632	(0 0 4)	9.5	C_{60}
6.	30.533	(3 0 0)	1.8	C_{60}
7.	32470	(0 0 6)	3.0	C_{60}

 Table 9
 The Peak ID Report of Fullerene (C-3)

For C₆₀, the localized peaks at $2\theta = 10.150^{\circ}$, 10.750° , 17.655° , 20.906° , 21.632° , 30.533° and 32.470° that referred to plane reflections of (100), (002), (110), (112), (004), (300) and (006), respectively. According to Table 9, the phase puity of prepared C-3 was confirmed as C₆₀ and should be fullerene.



Figure 6 XRD diffraction pattern of fullerene (C-4)

Peak No.	Bragg angle (2θ)	Miller indices (h k l)	FWHM of peak (β) radians	Particle size D (nm)
1	10.180	100	0.0065	21.206
2	10.730	002	0.0099	13.910
5	17.606	110	0.0078	17.788
6	20.640	112	0.0086	16.205
8	21.332	004	0.0069	20.220
9	32.570	006	0.0068	21.007

Table 10 The Results from XRD Diffractogram of Fullerene (C-4)

According to Table 10, the range of particle size of prepared fullerene (C-4) were found to be 13.910-21.206 nm and average particle size is 18.389 nm.

Peak No.	Bragg angle (2θ)	Miller indices (h k l)	Area (%)	Phase ID
1	10.180	100	65.7	C ₆₀
2	10.730	002	99.8	C_{60}
3	17.606	110	5.2	C_{60}
4	20.640	112	7.4	C_{60}
5	21.332	004	4.1	C_{60}
6	32.570	006	2.6	C_{60}

 Table 11
 The Peak ID Report of Fullerene (C-4)

For C₆₀, the localized peaks at $2\theta = 10.180^{\circ}$, 10.730° , 17.606° , 20.640° , 21.332° , and 32.570° that referred to plane reflections of (100), (002), (110), (112), (004) and (006), respectively. According to Table 11, prepared C-4 was confirmed as C₆₀ and should be fullerene. Average particle size for four prepared fullerenes (C-1 to C-4) are listed in Table 12. From these data the average particle size of prepared fullerene were nano.

 No.
 Fullerene
 Average Particle Size (nm)

 1.
 C-1
 26.877

 2.
 C-2
 27.829

 3.
 C-3
 24.399

 4.
 C-4
 18.389

 Table 12
 Average Particle Size for Fullerene (C-1 to C-4)



Thermal Stabilities of Prepared Fullerene by TG -DTA

Figure 7 TG-DTA thermogram of fullerene C-1

Table 13	TG-DTA	Analysis	of Fullerene	C-1
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No.	Temperature (°C)	Weight loss (%)	Type of peak	Remark
1.	229.42	13.421	exothermic	Due to the loss of moisture and impurity
2.	479.91	39.888	exothermic	Break down of some bonds and degradation occur

According to Figure 7and Table 13, the maximum degradation was found to be 479.91°C and the weight loss is 39.888 %. The thermal analysis of C-1 shows basically two mass loss steps (TG) with corresponding thermal events in the DTA curves. The first steps up to 229.42 °C show mass losses 13.421 % due to the physically adsorbed water on the material and impurity, probably occurred during storage. The second mass loss step (479.91 °C) may be the break down of some bonds and degradation of carbon skeleton.



Figure 8 TG-DTA thermogram of fullerene C-2

No.	Temperature (°C)	Weight loss (%)	Type of peak	Remark
1.	252.09	36.735	exothermic	due to the loss of moisture and impurity
2.	484.05	39.796	exothermic	break down some bonds and degradation occurs
3.	599.80	80.612	exothermic	break down some bonds and degradation occurs

Table 14 TG-DTA Data Analysis of Fullerene C-2

According to Table 14, the maximum degradation was found to be 599.80 °C and the weight loss is 80.612 %. The thermal analysis of C-2 (Figure 8) shows three mass loss steps (TG) with corresponding thermal events in the DTA curves. The first steps up to 252.09 °C show mass losses 36.735 % due to the physically adsorbed water on the material and impurity. The second mass loss step (484.05 °C) and the third mass loss step (599.80 °C) can be assigned to the break down of some bonds and degradation of carbon skeleton.



Figure 9 TG-DTA thermogram of fullerene C-3

Table 15 TG-DTA Analysis of Fullere	ne C-3	
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No.	Temperature (°C)	Weight loss (%)	Type of peak	Remark
1.	253.44	23.185	exothermic	Due to the loss of moisture and degradation occur in some extent
2.	300.20	100.00	exothermic	Complete degradation occur

According to Table 15, the maximum degradation was found to be 300.20 °C and the weight loss is 100.00 %. The thermal analysis of C-3 (Figure 9) shows two mass loss steps (TG) with corresponding thermal events in the DTA curves. The first step up to 253.44 °C show mass losses 23.185 % due to the physically adsorbed water on the material and impurity. The second step at 300.20 °C can be assigned to occur complete degradation (100% mass loss).

Morphology of Prepared Fullerenes by SEM

The morphology of graphite, prepared C-1 and C-3 were analysed by SEM microscopy (Figures 10).



Figure 10 SEM image of graphite and prepared fullerenes (C-1) (C-2)

According to SEM microscopy, in graphite, graphene sheets are packaged with a distance between sheets. The SEM image of C-2 shows disorganization of material and a greater distance between sheets that indicates there was an expansion and change of graphite due to the aspect of crumpled and exfoliated.

Conclusion

In this research, the preparation of fullerene (C-1 to C-4) was carried out from graphite by the changing amount of NaNO₃, H₃PO₄, KMnO₄ and H₂SO₄ with various time intervals such as stirring times and sonication times, respectively. The yield percent of fullerene were found to be 73.02 % for C-1, 76.08 % for C-2, 74.52 % for C-3 and 88.40 % for C-4. The crystalline size and crystal nature of graphite and fullerene were investigated by XRD spectra. From the XRD result, the particle size of graphite was found to be 152.76-855.98 nm. The average particle size of graphite was found 490.47 nm. The average particle size of prepared fullerene were found to be 26.877 nm in C-1, 27.829 nm in C-2, 24.399 nm in C-3 and 18.389 nm in C-4 respectively. From the XRD data, the prepared fullerene C-1 to C-4 were confirmed according to 20 value and ID phase. Furthermore, the thermal stability of fullerene was determined using thermo-gravimetric analysis (TG-DTA). From the TGA data, the fullerene started to degrade at 229.42 °C (13.421%) in C-1, 252.09 °C (36.735 %) in C-2 and 253 °C (23.185 %) in C-3. The maximum degradations were found to be 479.91 °C (39.888 %) in C-1, 599.80 °C (80.612 %) in C-2 and 300.20 °C, (100.0 %) in C-3. Among them, C-3 was completely decomposed at 300.2 °C. Finally, the surface morphology of graphite and prepared fullerene were analyzed by SEM microscopy. According to SEM microscopy, the morphology of graphite was found as packaged sheets. The SEM image of C-2 shows disorganization of graphite.

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