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Intercalation of C₆₀-Fullerol into Graphite Oxide

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<http://dx.doi.org/10.5772/65999>

Abstract

Herein, we report on the intercalation of C₆₀-fullerol into graphite oxide. This was achievable due to the solubility of the guest species in water and the exfoliation/reconstruction properties of the layered host. The resulting nanocomposite materials were characterized using a wide variety of techniques, including infrared spectroscopy, powder X-ray diffraction, thermogravimetric analysis, and electron microscopy.

Keywords: intercalation, fullerol, graphite oxide, exfoliation, nanocomposite

1. Introduction

C₆₀-fullerene (or buckminsterfullerene) was the first compound to be discovered in the fullerene family of carbon allotropes. It is obtained by the purification of soot derived from the pyrolysis of graphite [1]. Each carbon is covalently bonded to three other carbon atoms in the nanostructure. The remaining electrons participate in delocalized double bonds which give rise to the electrical conductivity of the material. The atoms are arranged in a cage structure that confers excellent thermal stability to the material.

Fullerenes, and many of their derivatives, are relatively nontoxic and therefore have been considered as possible replacements for harmful substances such as heavy metals in some materials applications [2]. An interesting feature of fullerenes is the region of low electron density generated in the centre of the cage structure which allows for the possibility to trap other atoms or small molecules within, resulting in binary compounds known as endohedral fullerenes [3]. Hence, these materials could serve as protecting agents, for example, in protecting the active ingredients of medications from being eliminated too quickly by the immune system. However, the use of fullerenes in biological applications has been hampered due to

their insolubility in the aqueous environment of living cells. To explore such applications, water soluble derivatives of fullerene must therefore be synthesized, for example, by multiple hydroxylation of the fullerene cage structure to obtain fullerol. This synthesis can be achieved using a solvent-free reaction as described by Sheng et al. [4].

Graphite oxide (GO) is the oxidized form of graphite, which is usually obtained through the reaction of graphite with potassium permanganate in concentrated sulfuric acid in a process known as the Hummer's method [5]. This method adds oxygen-containing functional groups along the surface of the material, such as hydroxyl and carbonyl groups, and epoxide bridges, without breaking or severely interrupting the carbon sheet structure of graphite. Because of these functional groups, the material can be exfoliated in water and subsequently restacked, allowing other molecules such as polymers to be trapped between the layers [6]. Also, because GO is relatively nontoxic, this remarkably versatile substance has found use in biological applications, for example, as a biosensor for monitoring DNA hybridization [7].

Intercalating C_{60} -fullerol into GO may lead to the discovery of a hybrid material with interesting properties, especially for applications where the protection of small molecules is important. For example, the inclusion of an endohedral fullerene derivative into a lamellar material could allow for a more controlled release of the trapped molecule in the carbon cage. In general, intercalated materials have enhanced thermal and mechanical properties [8], which may also lead to more stable protecting properties. GO is an excellent choice as a host material for fullerol as both have been shown to form strong π -electron stacking interactions [9, 10]. Experiments were performed to determine whether C_{60} -fullerol can be successfully intercalated into GO via exfoliation and restacking of the layered host, as has previously been reported with compounds containing delocalized π -electrons [9].

2. Experimental section

2.1. Materials

C_{60} -fullerene, sodium hydroxide, hydrogen peroxide, methanol and hydrochloric acid were purchased from Aldrich. Graphite oxide was prepared as described in Ref. [5].

2.2. Synthesis of C_{60} -fullerol

C_{60} -fullerol was prepared using the solvent-free method as described in Ref. [4]. C_{60} -fullerene was placed in a mortar with 60 equivalents of both solid sodium hydroxide and 30% aqueous hydrogen peroxide, forming a suspension. These were ground together for at least 15 min to ensure complete reaction. The resulting yellow-brown sludge was dissolved by stirring in deionized water and then filtered by gravity to remove impurities. The resulting solution was concentrated under high vacuum until a brown precipitate appeared. The solid was fully precipitated by adding methanol and separated from the solution by centrifuging for 30 min, followed by decanting of the excess methanol. The solid was washed with methanol and

centrifuged twice more to remove any remaining sodium hydroxide, and then freeze-dried to obtain the brown hydroxylated product.

2.3. Intercalation of C₆₀-fullerol into GO

The process for the intercalation of C₆₀-fullerol into GO was adapted from Ref. [9]. C₆₀-fullerol and GO were placed in separate round bottom flasks. Deionized water was added to the flasks, and they were then sonicated for 30 min to ensure dispersion/dissolution of the solids. The fullerol solution was then added to the flask containing GO which was again sonicated for 30 min, then stirred overnight. Five drops of concentrated hydrochloric acid were then added, followed by another night of stirring. The reaction mixture was cast on a glass substrate in order to monitor the change in structure of the material by XRD, heated to 60°C for 90 min and then allowed to cool to room temperature. A small portion of the resulting suspension was cast on another glass substrate for XRD analysis, and the rest centrifuged for 30 min. The wet solid was then collected and freeze-dried to give the final product.

3. Instrumentation

Nuclear magnetic resonance spectroscopy was performed on samples of the synthesized C₆₀-fullerol on a Bruker 300 MHz NMR spectrometer. All samples were prepared in D₂O, and a total of 6228 scans were performed for ¹³C NMR and 174 scans for ¹H NMR.

C₆₀-fullerol, GO and all intercalation products, were analyzed using a Bruker ALPHA FT-IR spectrometer equipped with an attenuated total reflectance (ATR) sampling unit. The samples were run over the range 4000–400 cm⁻¹. The resolution of the instrument was 0.9 cm⁻¹, and 17 scans were used.

Powder X-ray diffraction was performed on all materials using a Bruker AXS D8 Advance diffractometer, equipped with a graphite monochromator, variable divergence and antiscattering slits, and a scintillation detector. Cu (Kα) radiation ($\lambda = 1.542 \text{ \AA}$) was used for the measurements which were run in air from 2 to 60° (2θ). Intermediate samples were prepared as casts on glass substrates as mentioned in Section 2.3, while samples of the final products were pressed on double-sided scotch tape on silicon substrates.

Thermogravimetric analysis was performed on a TGA Q500 from TA instruments using a heating rate of 20°C/min.

Scanning electron microscopy (SEM) was performed using a Hitachi TM 3000 tabletop scanning electron microscope. An accelerating voltage of 15 kV was used. The samples were mounted on a carbon black tape prior to the imaging.

High resolution transmission electron microscopy (TEM) was performed on a Hitachi 7500 Bio-TEM, using an accelerating voltage of 80 KV. The powdered samples were dispersed in deionized water with the help of ultrasonication, and the dispersed samples were cast on carbon-coated copper grids.

4. Results and discussion

C₆₀-fullerol synthesized in this research was characterized using various techniques to confirm hydroxylation of the fullerene structure and the number of hydroxyl groups added, in order to determine average molar mass and product yield. The intercalated product was characterized in order to confirm insertion of fullerol and determine the material's properties such as stoichiometry, structure, thermal properties, and solubility in water.

Hydroxylation of fullerene was confirmed using IR and NMR spectroscopy. The IR data are summarized in (Table 1), and NMR data are provided in (Table 2).

Compound	Frequency (cm ⁻¹)	Intensity	Assignment
Fullerene (Aldrich)	1427	w	C=C stretch
	794.8	m	C—C stretch
Fullerol (Batch 1)	2446	w, broad	O—H stretch
	1419	s	C=C stretch
	855.7	m	C—C stretch
Fullerol (Batch 2)	2447	w, broad	O—H stretch
	1423	s	C=C stretch
	877.2	m	C—C stretch
Fullerol (Batch 3)	3323	w, broad	O—H stretch
	1419	s	C=C stretch
	877.1	m	C—C stretch

Table 1. IR signals for fullerene and derivatives.

Compound	NMR type	Shift (ppm)	Multiplicity	Assignment
Fullerol (first batch)	¹ H	3.353	s	—O—H
	¹³ C	166.0	s	—C—OH
Fullerol (third batch)	¹ H	3.349	s	—O—H

Table 2. NMR chemical shifts.

The IR spectra contain the characteristic fullerene C=C stretch peak at 1420 cm⁻¹, although the intensity differs. This is because some double bonds are lost when electrons are used

to form bonds to the hydroxyl groups. During hydroxylation, double bonds also rearrange so that only carbons with single bonds are hydroxylated, in order to maintain the integrity of the cage structure. As a result, the position of the C=C signal remains virtually unchanged, while the C—C signal is shifted to higher frequency due to the effects of the hydroxyl group. However, the hydroxyl signal in the IR spectrum is much less intense and is usually observed at around 3323 cm⁻¹ (batch 3). However, for batch 1 and batch 2, the —OH band is shifted to a lower wave number ca 2440 cm⁻¹, and this is attributed to hydrogen bonding between the fullerol molecules, via the hydroxyl groups.

¹H NMR spectroscopy was performed on the synthesized fullerol (batch 1 and batch 3), and the observed chemical shifts were compared to the literature [11]. A singlet is observed at 3.35 ppm which corresponds to the fullerol hydroxyl proton and is in good agreement with the literature. ¹H NMR spectroscopy does confirm the successful synthesis of fullerol.

¹³C NMR was also performed on fullerol (batch 1), and a single strong peak is observed at 166 ppm. This is in very good agreement with the literature and represents the fullerene carbon signal shifted upfield due to the deshielding effect of the oxygen atoms [11].

TGA was conducted on the synthesized fullerol (batch 1 and batch 3). The data show that the fullerene cage structure is more stable when hydroxylated, as it decomposes above 900°C, while fullerene itself decomposes between 500 and 600°C. Using the residue percentage at the final decomposition along with the hydroxyl decomposition observed at an early stage in the thermogram allows for calculation of the molecular formula and hence molecular weight of the fullerol. The assumption made in the calculation is that the compound fullerol consists of 60 carbon atoms similar to the starting fullerene. Knowledge of the molecular formula and molecular weight allowed for calculation of the percent yield of the synthesized fullerol. The average molecular formula, molecular weight, and percentage yield are tabulated in (Table 3).

Batch	Molecular formula	Molecular weight (g/mol)	% Yield
First	C ₆₀ (OH) _{5.897}	820.9	87.7
Second	C ₆₀ (OH) _{5.897}	820.9	100.0
Third	C ₆₀ (OH) _{10.32}	896.1	86.3

Table 3. Reaction products and yields for fullerol synthesis.

Powder X-ray diffraction shows that the synthesized fullerol is completely amorphous. The powder pattern is featureless as there are no diffraction peaks present (Figure 1).

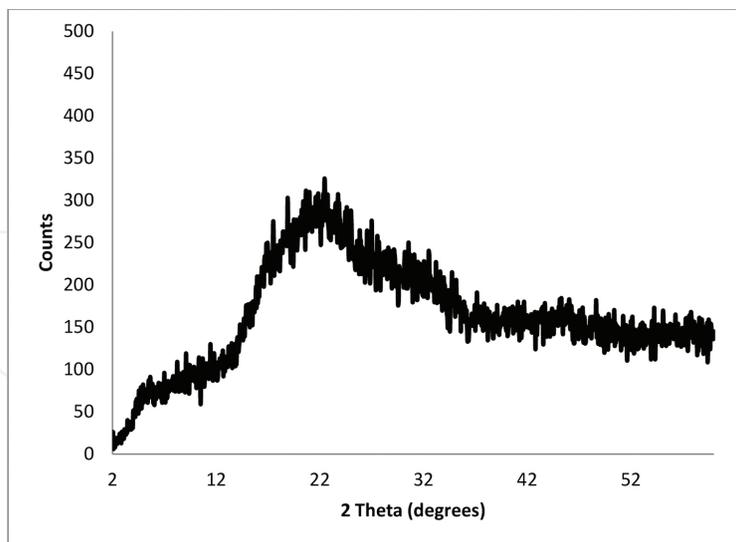


Figure 1. XRD of fullerol.

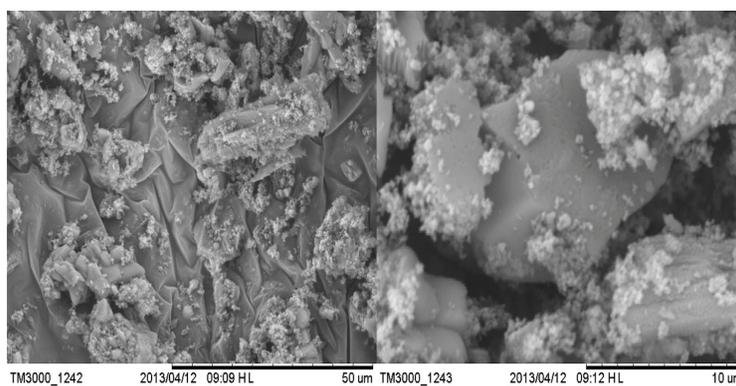


Figure 2. SEM images of fullerol.

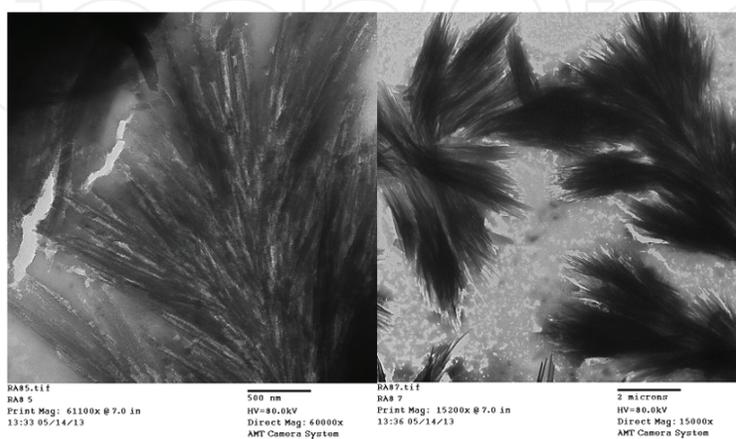


Figure 3. TEM images of fullerol.

SEM (**Figure 2**) and TEM (**Figure 3**) provide supporting evidence that the synthesized fullerol is, in fact, amorphous. The SEM and TEM micrographs display complete lack of crystallinity, and hence the absence of long range structural order in fullerol in the solid state.

Intercalation of fullerol into GO was performed by adapting the synthetic methodology described in Ref. [9]. Using the molecular weight of fullerol as calculated from TGA, the mole ratio of fullerol to GO used in the intercalation experiments were 0.6:1, 1.2:1, and 2.4:1, and the resulting products will be referred to as the first, second, and third intercalate, respectively. Confirmation of intercalation and elucidation of the structural features of the intercalates were performed using IR, XRD, SEM, and TEM.

Compound	Frequency (cm ⁻¹)	Intensity	Assignment
GO	3201	s, broad	O—H stretch
	1717	m	C=O stretch
	1575	m	C=C stretch (GO)
	1368	m	C—C stretch
	1045	s	C—O stretch
First intercalate (fullerol:GO = 0.6:1)	3100	s, broad	O—H stretch
	1717	s	C=O stretch
	1576	m	C=C stretch (GO)
	1375	w	C—C stretch
	1223	m	C—O stretch (C ₆₀)
	1053	s	C—O stretch (GO)
Second intercalate (fullerol:GO = 1.2:1)	3210	s, broad	O—H stretch
	1714	s	C=O stretch
	1582	m	C=C stretch
	1371	w	C—C stretch
	1217	s	C—O stretch (C ₆₀)
	1036	s	C—O stretch (GO)
Third intercalate (fullerol:GO = 2.4:1)	1716	s	C=O stretch
	1565	m	C=C stretch (GO)
	1428	w	C=C stretch (C ₆₀)
	1227	s	C—O stretch (C ₆₀)
	1046	s	C—O stretch (GO)

Table 4. IR signals for GO and intercalated products.

It is worthy to note that the IR spectrum of graphite oxide contains, as expected, peaks characteristic of hydroxyl, carbonyl, and other C–O functional groups. The IR spectra of the first two intercalates closely resemble that of graphite oxide; however, they also contain two different absorptions in the region for C–O stretching. The one just above 1200 cm^{-1} may be related to the fullerol C–O bond as it is more intense for the second intercalate where a higher ratio of fullerol was used in its formation. For the third intercalate, where almost twice as much fullerol was used in comparison to the second intercalate, the intensity of the peak is reduced, and the hydroxyl peak disappeared. However, a peak at 1428 cm^{-1} characteristic of the fullerene cage structure is observed. This is a good evidence for intercalation, as it suggests that adding enough fullerol causes the hydroxyl groups in the material to react with functionalities on the GO layers in some way that prevents them from absorbing in the IR region. This could, for example, be a hydrolysis reaction of the hydroxyl groups, creating an ester linkage between the fullerene cage and graphite oxide layers. The major peaks from the IR spectra are recorded in (Table 4).

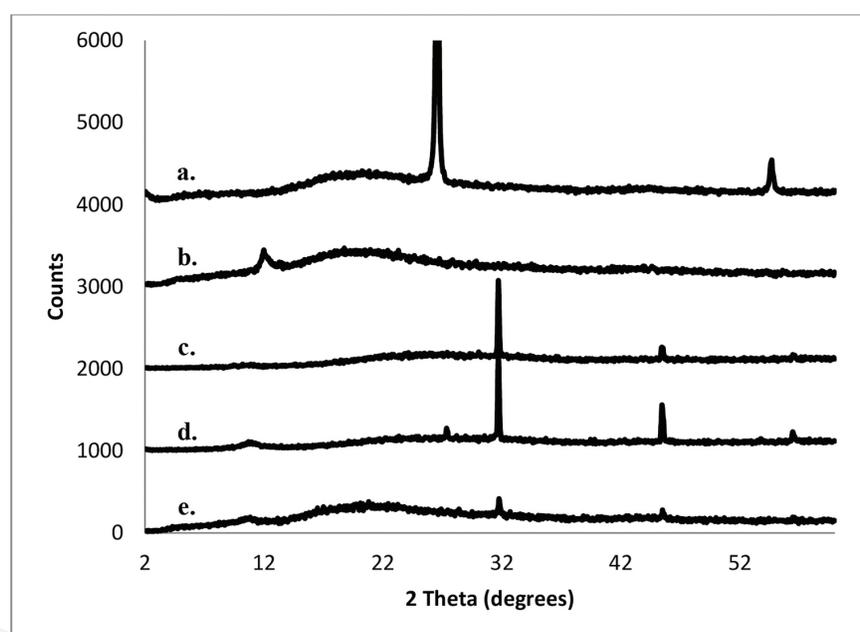


Figure 4. XRD of (a) graphite, (b) graphite oxide, (c) first intercalate after acid treatment (cast), (d) first intercalate, after acid followed by heat treatment (cast), and (e) first intercalate (final solid, freeze-dried product).

XRD was performed on the final solid products of the three intercalation reactions. In addition, XRD was run on cast samples during the formation of the first intercalate, after acid and heat treatments (**Figure 4**). For comparison, the XRD scans of graphite and GO are also included in **Figure 4**. The X-ray diffractograms show that addition of acid and heat treatment during the intercalation process leads to the formation of a more ordered intercalated material. Acid and heat treatments cause the appearance of a peak with a d-spacing value of 2.8 \AA ($2\theta = 32$) which is not seen in the diffractograms of the starting materials. This is actually supporting evidence for the hydrolysis mechanism proposed from the IR data, a likely mechanism for the intercalation of fullerol into GO. The appearance of a peak with a d-spacing of 8 \AA (higher than that

of GO) is also good evidence for intercalation, and this peak is much more intense in the product with higher fullerol content. However, it is interesting to note that the final freeze-dried product does contain an amorphous character, and this could be due to the fact that the XRD was run on the solid sample adhered to double-sided scotch tape on silicon substrate.

Although the above experiments offer excellent evidence for intercalation, full intercalation would, however, result in a d-spacing value higher than 8 Å, as the diameter of the fullerene cage is over 1 nm. Therefore, the most likely explanation is partial intercalation of fullerol into the graphite oxide layers. Hence, the best evidence for determining the detailed structure of these materials is by SEM (Figure 5) and TEM (Figure 6). With these techniques, one can directly observe the surface of the materials and between the layers, as well. In some of the images shown in Figures 5 and 6, amorphous clumps resembling those of fullerol can be seen packed between the layers, as well as attached to the surface of the layers. This is the clearest evidence that at least partial intercalation did occur.

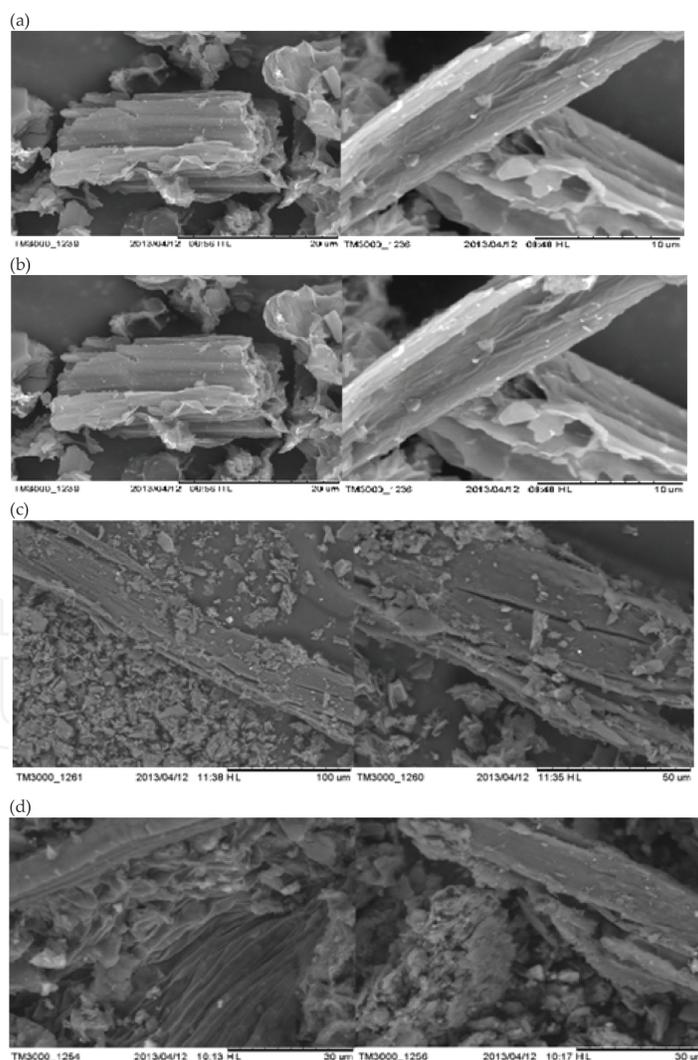


Figure 5. SEM micrographs of (a) graphite oxide, (b) first intercalate, (c) second intercalate, and (d) third intercalate.

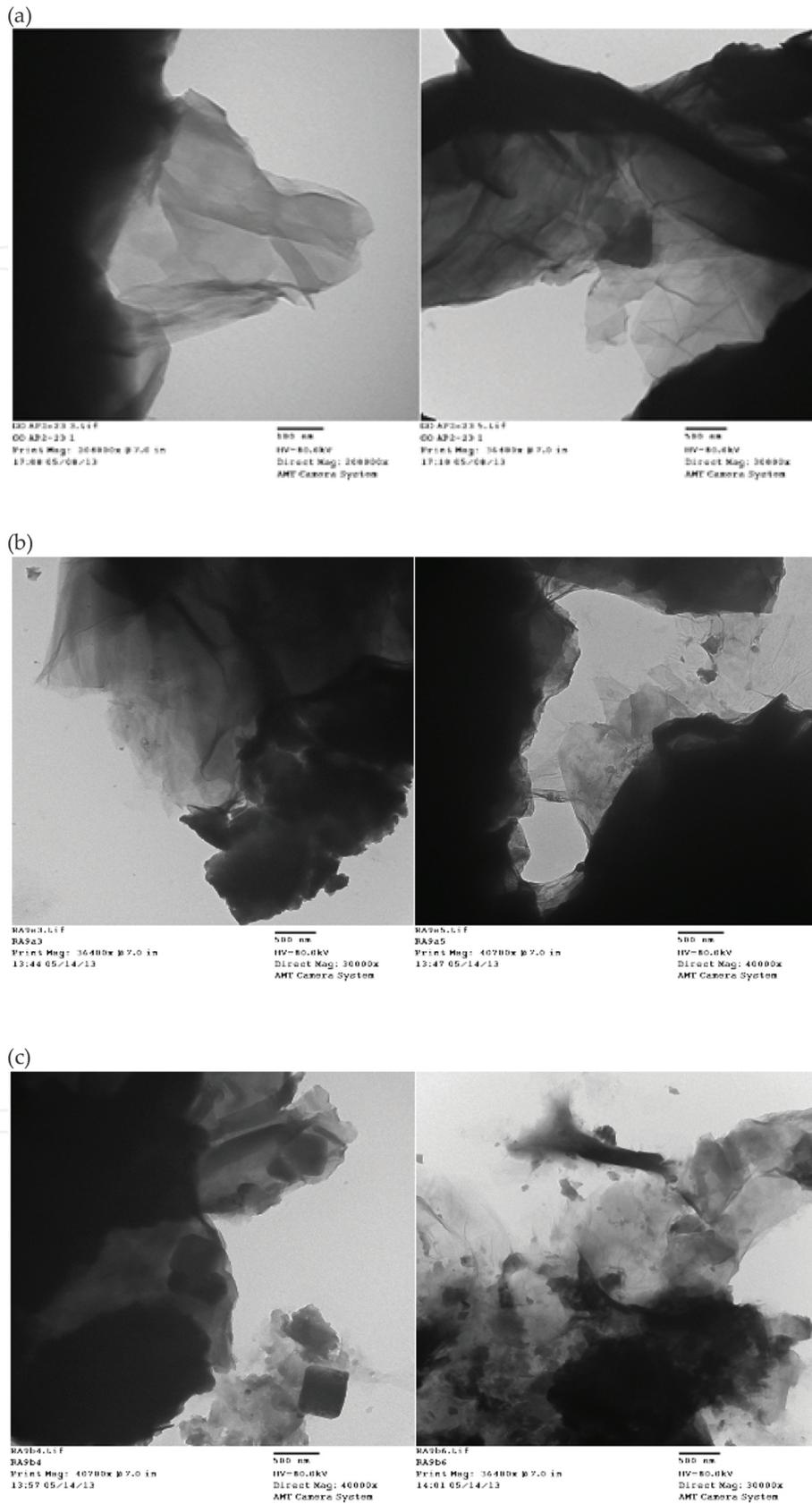


Figure 6. TEM micrographs of (a) graphite oxide, (b) second intercalate, and (c) third intercalate.

TGA studies were used to determine the stoichiometry of the intercalated materials by making use of the observed mass losses, molecular weight of fullerol, and that of GO as reported in Ref. [9]. As an illustration, the thermogram of the second intercalate (fullerol:GO = 1.2:1) is depicted in **Figure 7**; the other two intercalates show similar decomposition patterns. The mass loss seen at around 400°C is due to the release of the fullerene cage structure from the intercalated material, and the loss at around 800°C is attributed to be oxidation of carbon residues remaining from graphite oxide (**Figure 7**). Using this information, the stoichiometries of the intercalated materials were calculated and are shown in (**Table 5**). The evidence suggests that increasing the fullerol ratio increases the amount of fullerol contained in the final product, but not all of the fullerol ends up in the gallery space of the GO, especially at higher molar ratios where any excess fullerol will end up on the surface and edge of the layered structure as evidenced by SEM.

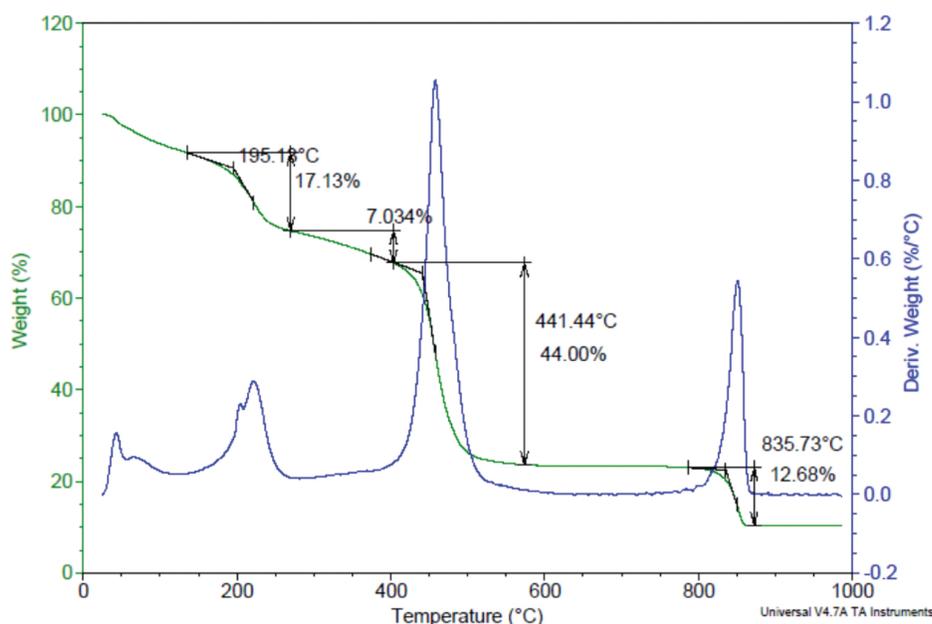


Figure 7. TGA of second intercalate.

Experiment	Fullerol:GO ratio	Calculated stoichiometry
1	0.60:1	(C ₆₀ (OH) _{5.897}) _{0.67} GO
2	1.2:1	(C ₆₀ (OH) _{10.32}) _{0.80} GO
3	2.4:1	(C ₆₀ (OH) _{10.32}) _{1.7} GO

Table 5. Stoichiometries of intercalated products.

The intercalation compounds were tested for their solubility in water. The third intercalate dissolved readily, while the first and second intercalates could only be dispersed in water, with observed pieces of solids settling down over time. This suggests a clear trend that having more

fullerol in the composite material increases its polarity and thus its solubility in a polar solvent such as water.

5. Potential applications of materials

The intercalated materials synthesized in this research could potentially be used as drug delivery systems. Graphite oxide (GO) and fullerol are both nontoxic materials which can be dispersed or solubilized in an aqueous environment. Our research shows that fullerol can be partially intercalated into GO. Hence, drug molecules entrapped within the cage structure of fullerol can potentially be inserted into layered GO, and the resulting intercalated systems would allow for the slow and controlled release of these drugs in humans and animals.

6. Conclusion

C₆₀-fullerol was successfully synthesized and partially intercalated between the layers of graphite oxide. The stoichiometry of these nanocomposite materials was determined via TGA, and their structure elucidated using a variety of techniques. Solubility tests showed that the intercalate with highest fullerol content was more soluble in water, and IR analysis suggests that the mechanism of intercalation is the hydrolytic formation of bonds between the fullerene cage structure and functionalities on the GO layers. The lower than expected d-spacing value of the intercalates as observed by XRD suggests partial intercalation of the fullerol into the GO layers. SEM and TEM proved to be valuable characterization techniques for this research, as they allowed for direct observation of the fact that fullerol was, indeed, partially intercalated into the layered structure.

In perspective, if endohedral fullerenes can be successfully intercalated into GO, the chemical and thermal stability of the resulting intercalated nanocomposites materials could make them useful in applications that require protection for sensitive or reactive molecules. In addition, their water solubility could make them useful materials as drug delivery systems, since fullerene and GO are both nontoxic allotropes of carbon. Further research is required in order to determine the types of fullerenes that can be intercalated into GO, as well as the properties of the resulting nanocomposite materials.

Acknowledgements

Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Prince Edward Island is gratefully acknowledged.

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References

- [1] Kroto HW et al. Fullerenes studies at sussex. In *Buckminsterfullerenes*; VCH: New York, 1993.
- [2] Prato M. [60] Fullerene chemistry for materials science applications. *Journal of Materials Chemistry*. 1997; 7: 1097–1109.
- [3] Chai Y et al. Fullerenes with metals inside. *Journal of Physical Chemistry*. 1991; 95(20): 7564–7568.
- [4] Sheng W et al. Novel and efficient synthesis of water-soluble [60] fulleranol by solvent-free reaction. *Synthetic Communication*. 2005; 35(13): 1803–1808.
- [5] Hummers WS Jr., Offeman RE. Preparation of graphitic oxide. *Journal of American Chemical Society*. 1958; 80: 1339.
- [6] Bissessur R, Scully SF. Intercalation of solid polymer electrolytes into graphite oxide. *Solid State Ionics*. 2007; 178: 877–882.
- [7] Wu J et al. A biosensor monitoring DNA hybridization based on polyaniline intercalated graphite oxide nanocomposite. *Sensors Actuators B*. 2004; 104: 43–49.
- [8] Ray SS, Okamoto M. Polymer/layered silicate nanocomposites: a review from preparation to processing. *Progress in Polymer Science*. 2003; 28: 1539–1641.
- [9] Bissessur R et al. Encapsulation of polyanilines into graphite oxide. *Langmuir*. 2006; 22: 1729–1734.
- [10] Sygula A et al. A double concave hydrocarbon buckycatcher. *Journal of American Chemical Society*. 2007; 129(13): 3842–3843.
- [11] Alves GC et al. Synthesis of C₆₀ (OH) 18–20 in aqueous alkaline solution under O₂-atmosphere. *Journal of the Brazilian Chemical Society*. 2006; 17(6): 1186–1190.

