



Hexamethylenetetramine reaction with graphite oxide (GO) as a strategy to increase the thermal stability of GO: synthesis and characterization of a compound

ROBSON F. de FARIAS^{1*} and CLAUDIO AIROLDI²

¹*Departamento de Química, Universidade Federal do Rio Grande do Norte, Cx. Postal 1662, 59078-970 Natal, Rio Grande do Norte and* ²*Instituto de Química, UNICAMP, Cx. Postal 1664, 13083-97170 Campinas, São Paulo, Brazil*

(Received 17 July, revised 23 September 2009)

Abstract: In this paper, the synthesis and characterization of a GO–hmta compound (GO – graphite oxide; hmta – hexamethylenetetramine) are presented. It is shown that the presence of hmta molecules inside the GO matrix, with very strong interactions, stabilize the GO matrix from a thermal point of view. Such a fact could be used to explore possible applications of GO matrix, especially in catalysis.

Keywords: graphite oxide; hexamethylenetetramine; thermal stability.

INTRODUCTION

Graphite oxide (GO) can be defined/identified as an oxygen-rich carbogenic material that is typically derived by the strong oxidation of crystalline graphite and contains oxygen in the concentration range 30–40 % (w/w). This solid exhibits an extended lamellar structure with randomly distributed aromatic and aliphatic regions, as well as a high amount of hydroxyl/carboxyl functional groups embedded in its layers. Hence, GO is endowed with swelling, intercalation and ion exchange properties.^{1–7} This layered solid decomposes at relatively low temperature (< 200 °C), releasing CO₂ and H₂O. As a recent example of investigations on the chemistry of GO, the recently reported study of the intercalation of molecules of poly(ethylene oxide), poly(vinyl pyrrolidone), methyl cellulose, poly[oxymethylene(oxyethylene)], and poly[oligo(ethyleneglycol oxalate)] into GO can be mentioned.⁸ Possible usages of GO in catalysis have also been reported.⁹

It was verified that the forces of attraction between the polymers and GO are primarily dipole–dipole and/or hydrogen bonding arising from the polar groups in the polymers and the functional groups (COC, COOH, COH, and CTO) in the

* Corresponding author. E-mail: robsonfarias@pq.cnpq.br
doi: 10.2298/JSC090717018D



GO.¹⁰ Furthermore, it was verified that the addition of a small amount of dilute NaOH resulted in deprotonation of the acidic functionalities, which caused exfoliation of the layered structure.¹⁰ It was shown¹⁰ that GO is able to remove ammonia by two processes: intercalation and reactive adsorption. It was found that the total amount of adsorbed ammonia was significantly higher than that adsorbed on activated carbon. In an interesting interplay between GO and organosilanes (which are extensively used to modify amorphous or nanostructured oxide surfaces), there is report¹¹ of the preparation of intercalation compounds in which amino groups were inserted into the interlayer space of GO, using 3-aminopropylethoxysilanes. For such compounds, it was shown that the amino groups of 3-aminopropyltriethoxysilane were bonded to the hydroxyl groups of GO. It was also found that the temperature in which the intercalation occurred affected the interlayer distance, with larger distances been observed in products obtained at higher temperatures. On the other hand, it was shown that interactions with organic species can be used as a strategy to promote remarkable structural modifications in hybrid solids.¹²

In the present paper, the synthesis of a GO compound with hexamethylenetetramine (hmta) is reported.

EXPERIMENTAL

The graphite oxide was prepared as follows: 230 cm³ of 96 % sulfuric acid was transferred to a 3.0 dm³ Erlenmeyer flask which was cooled to 0 °C (ice bath). Graphite powder (10 g; Aldrich) was then added to the flask under mechanical stirring. K₂MnO₄ (30 g) was slowly added to the dark mixture with care being taken to maintain the reaction mixture below 20 °C. The reaction mixture was then allowed to cool to 2 °C and stirred at room temperature for 60 min. Then 230 cm³ of deionized water was slowly added to the system, whereby a rapid increase in temperature was observed. The reaction mixture stirred for 45 min, after which 230 cm³ of deionized water and 130 cm³ of 31 % H₂O₂ were added. Subsequently, deionized water was added to the system until a total volume of 2.0 dm³ was achieved. After standing for 72 h, the GO particles settled to the bottom of the flask and the excess liquid was withdrawn. The remaining liquid and solid particles were transferred to centrifuge tubes and centrifuged at 6000 rpm for 3 min. All samples were washed several times with deionized water and the supernatant reacted with a solution of barium nitrate until a negative test for sulfate was achieved.

The wet powders were then dried at room temperature in a fume hood for 72 h and then at 30° for 3 h in an oven.

The GO intercalation compound was prepared by magnetically stirring (3 h) 2.0 g of GO with 50 cm³ of an aqueous solution prepared by dissolution of 10.0 g of hexamethylenetetramine, hmta (Aldrich), C₆H₁₂N₄ (1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane)*. The compound settled to the bottom of the flask and was filtered off, washed with deionized water and dried at room temperature for 72 h in a fume hood.

The CHN elemental analysis was performed using a Perkin–Elmer instrument, Bomem, model MB 102. The infrared (FTIR) spectra were recorded on a Bomem instrument using the

* Hmta is also known under the names hexamine, methenamine and urotropine.

KBr disc technique. The thermogravimetric analysis was performed in a Shimadzu TGA-50 instrument under a dynamic nitrogen atmosphere ($50 \text{ cm}^3 \text{ min}^{-1}$), in platinum sample holders at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

RESULTS AND DISCUSSION

The elemental analysis results are summarized in Table I. Based on the nitrogen elemental analysis result, it can be calculated that the GO-hmta matrix contained 123 mmol of hmta per gram of sample.

TABLE I. Elemental analysis results (%) for GO and GO-hmta samples

Compound	C	H	N	O
GO	39.7	2.6	–	57.7
GO-hmta	53.0	3.3	6.9	36.8

The obtained FTIR spectra are shown in Fig. 1. In the spectrum of GO, bands at 3450 cm^{-1} (OH stretching), 1654 cm^{-1} (COOH), 1383 cm^{-1} and 1058 cm^{-1} (COC/COH)

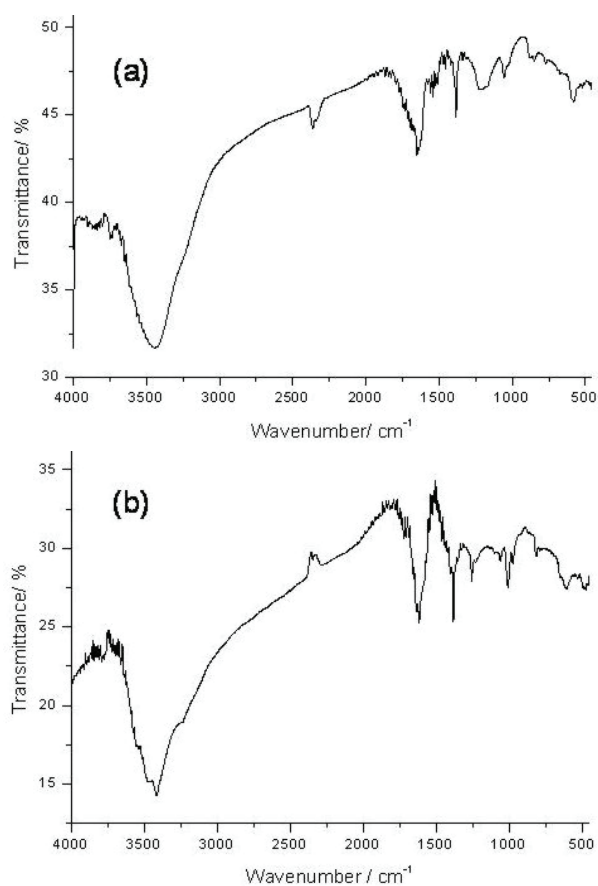


Fig. 1. FTIR Spectra for a) GO and b) GO-hmta.

can be observed. Such bands are, of course, not exhibited by graphite. The spectrum of GO-hmta exhibited respective bands at 3426, 1630, 1381 and 1015 cm^{-1} . The significant shift to lower wave numbers of these bands, due to stretching of OH, COOH and COC/COH groups, shows that there were strong interactions between these groups and the hmta molecules, probably by hydrogen bonding. Taking into account the symmetric nature of hmta, the structure of which is shown in Fig. 2, it can interact simultaneously with many sites in the GO matrix.

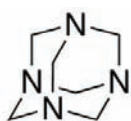


Fig. 2. Structural formula of hmta.

The thermogravimetric curves obtained for GO and the GO-hmta compound are shown in Fig. 3 and the TG data are summarized in Table II. The data given

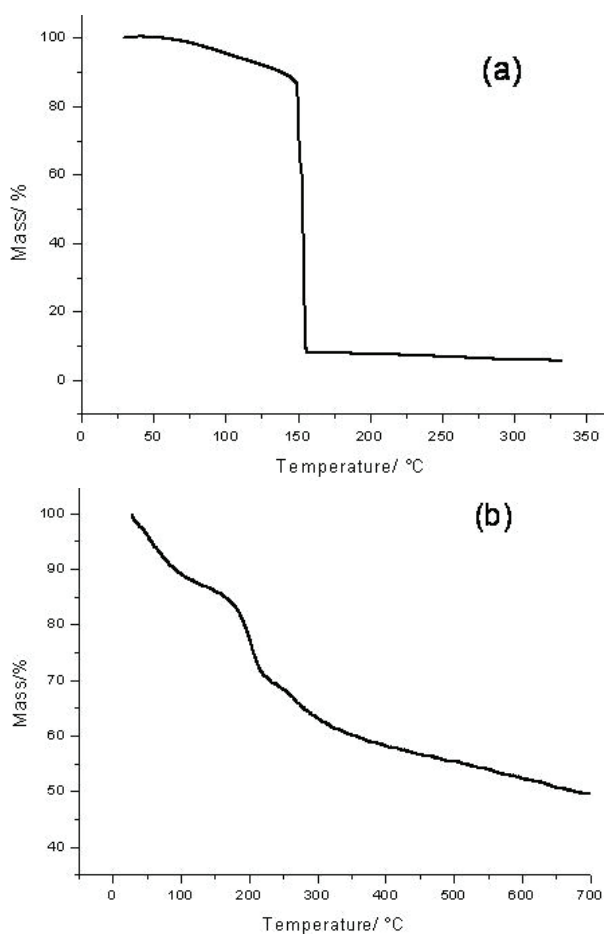


Figure 3. The thermogravimetric curves for a) GO and b) GO-hmta.

in Table II verify that the presence of hmta molecules inside the interlayer space of GO promoted stabilization of the matrix, since pure GO lost 80 % of its mass in the 150–160 °C range, whereas even with the hmta molecules, the mass loss in the 125 to 700 °C was only 39 %. The corresponding carbon residue increased from 8 % for GO to 49 % for the hybrid matrix.

TABLE II. Thermogravimetric data summary for GO and GO–hmta samples

Compound	Temperature range, °C	Mass loss, %	Process
GO	40–145	12	Release of physisorbed water molecules $2\text{C}_3\text{H}_3\text{O}_{4.5}(\text{s}) \rightarrow 6\text{CO} + 3\text{H}_2\text{O}$
	150–160		
GO–hmta	40–120	12	Release of physisorbed water molecules $2\text{C}_3\text{H}_3\text{O}_{4.5}(\text{s}) \rightarrow 6\text{CO} + 3\text{H}_2\text{O}$ Release of hmta molecules and $2\text{C}_3\text{H}_3\text{O}_{4.5}(\text{s}) \rightarrow 6\text{CO} + 3\text{H}_2\text{O}$
	125–220		
	225–700		

It is noteworthy that the thermal degradation profile for GO shown in Fig. 3a, with two mass loss steps, is completely different from those previously presented.⁸ In that study, three distinct mass loss steps were observed at 40, 185 and 433 °C, assigned to the release of water, CO and CO₂, respectively, with a final residue of approximately 5 %. This discrepancy can be explained remembering that the elemental analysis results were also quite different in both cases: C, 47.16 %; H, 1.72 %, and O, 40.27 %, giving to the GO sample the formula C₈H_{3.5}O_{5.1},⁸ whereas in the present work the results were C, 39.7 %; H, 2.6 %, and O, 57.7 %, giving the formula C₄H₃O₄. Hence, the oxygen percentage of the matrix prepared in the present study surpassed the “usual” 30–40 % for GO. Such a difference in composition can be attributed to the larger volume of H₂O₂ used in this study in comparison with the previously described preparation.⁸ Thus, in the present GO compound there were equal amounts of C and O. However, if one takes into account the final carbon residue of 8 % after the thermal degradation and recalculates the carbon percentage based on this, the formulae C₃H₃O_{4.5} is obtained, giving rise to the thermal degradation process: $2\text{C}_3\text{H}_3\text{O}_{4.5}(\text{s}) \rightarrow 6\text{CO} + 3\text{H}_2\text{O}$.

Analysis of the thermal degradation profile of the GO–hmta matrix gives more interesting results. The carbon percentage is increased from 39.7 (GO) to 53.0 % (GO–hmta), a difference of 13.3 %. However, after thermal degradation, the final carbon residues were 8 (GO) and 49 % (GO–hmta), a difference of 41 %. Hence, by comparison of the TG curves shown in Fig. 3, as well as on these carbon residues, it is clear that the presence of hmta molecules change, in a remarkable way, the thermal degradation profile of GO. This is a very uncommon effect in lamellar matrices. In lamellar MoO₃ for example,^{13–18} after the release of the organic moiety, the lamellar matrix exhibits its “normal” degradation processes.

Taking into account that hmta sublimates in the range 285–295 °C,¹⁹ it is valid to assume that in the temperature range covered by the TG curve, all the

hmta molecules had left the interlayer space. Hence, the mass loss steps observed in the TG curves for the GO–hmta matrix are assigned as shown in Table II. Such a proposal suggests that after the release of physisorbed water molecules, the release of CO and H₂O from the GO matrix not interacting with hmta molecules commences but that this is interrupted when the decomposition of the GO parts that are interacting with the hmta molecules begins. Thus, the presence of hmta molecules inside the GO matrix, with very strong interactions, increases the thermal stability of the GO matrix. Such a fact could be explored to investigate possible applications of the GO matrix (in catalysis, for example). In the range 225–700 °C, hmta and GO decompose slowly: the GO parts decompose after the release of hmta molecules, *i.e.*, the main step (rate determining) of the thermal degradation is the release of hmta molecules.

The obtained X-ray diffraction patterns are shown in Fig. 4, from which it can be seen that the crystallinity of GO is enhanced after reaction with hmta. Fur-

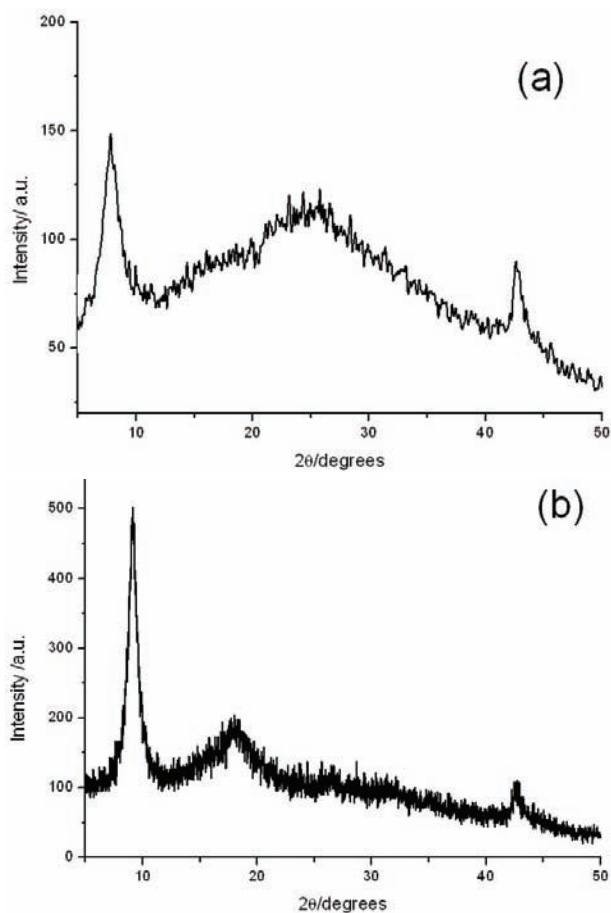


Fig. 4. X-Ray diffraction patterns for a) GO and b) GO–hmta.

thermore, the interlayer distance decreased from 1.13 nm (7.8°) to 0.96 nm (9.2°) after reaction with hmta – taking into account the (001) diffraction peaks. The peak at 18.4° can be assigned to the GO–hmta (002) diffraction peak.

Since the interlayer distance of GO decreased and did not increase after reaction with hmta, it can be concluded that the hmta molecules are not intercalated into the GO. However, it is possible to suppose that the insertion of hmta molecules into the GO interlayer space could provoke very intense interactions (via hydrogen bonds) between the layers, provoking the observed distance contraction. This second hypothesis is considered the most probable taking into account the increased thermal stability (Fig. 3 and Table II). The higher crystallinity of the hybrid matrix in comparison with pure GO also reinforces this hypothesis.

ИЗВОД

РЕАКЦИЈА ХЕКСАМЕТИЛЕНТЕТРАМИНА СА ГРАФИТНИМ ОКСИДОМ (GO)
КАО СТРАТЕГИЈА ПОБОЉШАЊА ТЕРМИЧКЕ СТАБИЛНОСТИ GO:
СИНТЕЗА И КАРАКТЕРИЗАЦИЈА ЈЕДИЊЕЊА

ROBSON F. de FARIAS¹ и CLAUDIO AIROLDI²

¹Departamento de Química, Universidade Federal do Rio Grande do Norte, Cx. Postal 1662,
59078-970 Natal, Rio Grande do Norte и ²Instituto de Química, UNICAMP,
Cx. Postal 1664, 13083-970 Campinas, São Paulo, Brasil

У раду је приказана синтеза и карактеризација оксид графита–хексаметилентетрамин (GO–hmta) једињења. Показано је да молекули хексаметилентетрамина у GO матрици имају врло јаку интеракцију што доводи до стабилизације и побољшања термичких особина GO матрице. Та чињеница отвара могућности примене GO матрице, посебно у катализи.

(Примљено 17. јула, ревидирано 23. септембра 2009)

REFERENCES

1. R. F. de Farias, *Chemistry on modified oxide and phosphate surfaces – fundamentals and applications*, Academic Press, Amsterdam, 2009
2. I. Dákány, R. Krüger-Grasser, A. Weiss, *Colloid Polym. Sci.* **276** (1998) 570
3. A. B. Bourlino s, D. Gour nis, D. Petridis, T. Szabó, A. Szer i, I. Dákány , *Langmuir* **19** (2003) 60505
4. A. Lerf, H. He, M. Forster, J. Klinowski, *J. Phys. Chem. B* **102** (1998) 4477
5. N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva, *Chem. Mater.* **11** (1999) 771
6. T. Szabá, A. Szeri, I. Dákány, *Carbon* **43** (2005) 87
7. T. Szabá, O. Berkesi, P. Forgó, K. Josepovits, Y. Sanaki s, D. Petridis, *Chem. Mater.* **18** (2006) 2740
8. R. Bissessur, S. F. Scully, *Solid State Ionics* **178** (2007) 877
9. J. Bian, M. Xiao, S. J. Wang, Y. X. Lu, Y. Z. Meng, *Catal. Commun.* **10** (2009) 1529
10. M. Sereych, T. J. Bandosz, *Carbon* **45** (2007) 2126
11. Y. Matsuo, Y. Nishino, T. Fukutsuka, Y. Sugie, *Carbon* **45** (2007) 1384
12. R. F. de Farias, C. Airoidi, *J. Non-Cryst. Solids* **261** (2000) 181
13. R. F. de Farias, *Int. J. Inorg. Mater.* **3** (2001) 303

14. R. F. de Farias, *Int. J. Inorg. Mater.* **3** (2001) 931
15. R. F. de Farias, *J. Phys. Chem. Solids* **64** (2003) 2199
16. R. F. de Farias, *Mater. Chem. Phys.* **90** (2005) 302
17. R. F. de Farias, *J. Phys. Chem. Solids* **64** (2003) 1241
18. R. F. de Farias, M. S. Refat, H. A. Hashem, *J. Incl. Phenom. Macrocyc. Chem.* **61** (2008) 113
19. G. R. Maxwell, *Synthetic nitrogen products – a practical guide to the products and processes*, Springer, New York, 2006.