



Carbon Nanoparticles from Thermally Expanded Cointercalates of Graphite Nitrate with Organic Substances

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Abstract. Thermally expanded graphite (TEG) is a vermicular-structured carbon material that can be prepared by heating expandable graphite compounds. Liquid phase exfoliation of TEG obtained from graphite nitrate cointercalation compounds (GNCCs) with organic substances allows obtaining dispersions of carbon nanoparticles, namely few-layer graphenes as well as small graphene structural fragments. This paper presents the results of complex investigations of structural features of triple GNCCs with acetic acid, formic acid, ethyl acetate and acetonitrile as well as TEGs on their base. X-Ray powder diffraction and scanning electron microscopy were used for studied GNCCs and TEGs characterization. GNCCs were used as a source for thermally expanded graphite which can be considered as perspective precursor for graphene and related structures. Morphology of the carbon nanoparticles formed from corresponded TEGs by liquid phase exfoliation in *tert*-butanol assisted with sonication is discussed. The most promising results were observed for the TEG sample obtained from a triple GNCC with acetic acid and acetonitrile.

Keywords: Graphite Nitrate · Cointercalation · Liquid Phase Exfoliation · Carbon Nanoparticles · Few-Layer Graphenes

1 Introduction

Thermally expanded graphite (TEG) is a vermicular-structured carbon material that can be prepared by heating expandable graphite compounds up to 1000 °C. TEG is actively used for the production of graphite paper [1], graphite foil [2], protection coatings [3], fillers for polymer composites [4–6], adsorbent [7, 8], cathodes for aluminum-ion batteries [9] or anodes for lithium-ion batteries [10, 11], components of catalysts [12, 13], for energy storage, phase change and sensor materials [14–16] etc. The effect of various

factors and conditions of TEG obtaining on its morphology and properties is actively studied [2, 17, 18].

The main method for producing thermally expanded graphite in laboratory practice is still the thermal expansion of graphite intercalated compounds (GICs) [19, 20]. GICs are compounds with a regular layered structure in which chemical particles (intercalants) are intercalated between the carbon layers. Graphite foam or TEG is formed due to the effect of thermal shock, microwave radiation or electric current on the GIC. Usually, TEG production is carried out in several stages: the synthesis of thermally expanding GIC, its stabilization, and heat treatment. The honeycomb microstructure of TEG is formed as a result of heat treatment of GIC. The volume of the cellular structure significantly exceeds the volume of the original GIC. The cell walls are a multilayer structure of graphite layers, the width of the walls is comparable to the size of graphite crystallites along the *c*-axis [21]. The structural features of thermally expanded graphite make it possible to suggest it as a source for carbon nanostructures. Methods for obtaining nanoparticles with different morphologies based on TEG have been proposed [8, 22, 23].

This paper presents the results on the production of few-layer graphenes dispersions by exfoliation of a pre-thermally expanded graphite nitrate cointercalation compounds (GNCCs) with organic substances in *tert*-butanol assisted with sonication. Organic cointercalates, used for GNCCs obtaining, were acetic and formic acids, ethyl acetate, acetonitrile as well as their combinations. Liquid phase exfoliation makes it possible to obtain suspensions of few-layer graphene particles containing also single-layer graphene. The formation of few-layer graphene particles was confirmed by transmission electron microscopy. At this study, we consider the following frameworks of the problem:

- Synthesis and characterization of triple graphite nitrate cointercalation compounds (GNCCs) with organic compounds as precursors for thermally expanded graphite;
- Characterization of thermally expanded graphite samples as promising origin for carbon nanoparticles obtaining;
- Liquid phase exfoliation of thermally expanded graphites, obtained from different precursors.

2 Experimental

2.1 Synthesis of Graphite Nitrate Cointercalation Compounds and Thermally Expanded Graphite Preparation

Graphite nitrate (GN) as well as graphite nitrate cointercalation compounds were prepared as a starting material for the generation of thermally expanded graphite. GN and GNCCs were synthesized in a thermostatic reactor using nitric acid (98%) and natural flake graphite GT-1 (Zavaliy Graphite Works, Kirovograd region, Ukraine). A mixture of graphite (1 g) and HNO₃ (0.6 ml) was stirred for 10 min at 20 °C to obtain a GN. Triple GNCCs were obtained by treatment of as-prepared GN with corresponding organic cointercalants (1: 1 by volume) and reaction system was stirred for 10 min. Resulted GNCCs were separated by filtration and dried at 20 °C until the sample mass became constant.

Thermally expanded graphite samples were obtained from GNCCs in the thermal shock mode of heating. About 0.2 g of the GNCC was inserted into the pre-heated cuvette

and has been kept in the furnace for 120 s at 900 °C. Then the cuvette with expanded graphite was removed from the furnace, the contents were gently transferred to a beaker for further use.

The thermal expansion coefficients (K_V , $\text{cm}^3 \cdot \text{g}^{-1}$) for obtained GNCCs were determined by heating of the samples within the thermal shock mode at 900 °C as described in [23].

2.2 GNCCs and TEG Sample Characterization Methods

X-ray diffraction (XRD) measurements were performed on DRON 3 diffractometer ($\text{CuK}\alpha$ radiation, $\lambda = 1.54181 \text{ \AA}$). Surface morphology of the studied TEGs was estimated by scanning electron microscopy (SEM) using a complex analytical scanning electron microscope JSM 6490 LV (JEOL).

2.3 Dispersions of Carbon Nanoparticles

Dispersions of carbon nanoparticles were prepared by liquid phase exfoliation of the TEGs. Sonication of the TEGs samples in *tert*-butanol (22 kHz and 470 W) was used for enhancement of the exfoliation process. The duration of the sonication was 1 h. Morphology of the prepared nanoparticles was estimated by transmission electron microscopy (TEM). Only freshly prepared samples of carbon nanoparticles dispersions were used for TEM studies. The TEM images of the dispersions samples were obtained using JEOL JEM-200 transmission electronic microscope.

3 Results and Discussions

3.1 Graphite Nitrate Cointercalation Compounds as Precursors of Thermally Expanded Graphite

The general strategy for obtaining carbon nanoparticles used in this work included following main stages: (i) natural graphite intercalation, (ii) cointercalation of graphite nitrate, (iii) thermal expansion of GNCC and (iv) liquid phase exfoliation of TEG (for general scheme see Fig. 1). At the first stage, graphite nitrate with a regular structure was obtained. GN was further stabilized by treatment with organic compounds, namely acetic acid or its combination with formic acid, ethyl acetate and acetonitrile. As a result, stable binary and ternary GNCCs were obtained. For comparison purposes, compounds in which acetic acid was one of the cointercalants were studied. For ternary compounds, additional co-intercalants were formic acid, ethyl acetate, or acetonitrile.

Structure of the synthesized binary and triple GNCCs was characterized by X-ray powder diffraction method. In obtained samples compounds of the IVth (α -phase) and of the IInd (β -phase) stages of intercalation were presented. From the results of X-ray diffraction analysis values of interplanar space filled with cointercalants species (d_i) were estimated for studied GNCCs and listed in Table 1. The determined d_i values for GNCCs are increased up to 6.532–8.072 Å as compared with 3.359 Å for initial graphite. It should be noted that the d_i values for ternary compounds are greater than corresponding one for a binary GNCC with acetic acid.

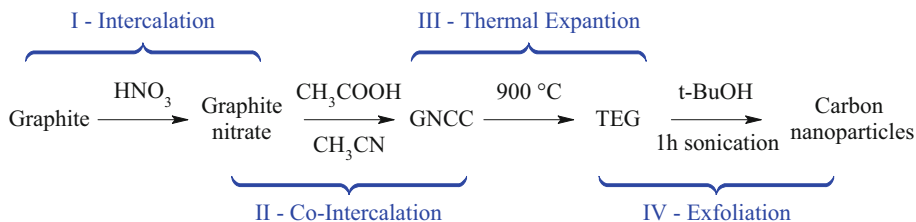


Fig. 1. Step-by-step scheme of the carbon nanoparticles obtaining.

Table 1. Structural characteristics of the GNCCs along with coefficients of thermal expansion of the studied compounds.

GNCCs	Cointercalants	IV- α compound		II- β compound		K_V ($\text{cm}^3 \cdot \text{g}^{-1}$)
		2θ ($^\circ$)	d_i (Å)	2θ ($^\circ$)	d_i (Å)	
1	$\text{CH}_3\text{C}(\text{O})\text{OH}$	24.88	7.813	27.04	6.532	350
2	$\text{CH}_3\text{C}(\text{O})\text{OH} + \text{HC}(\text{O})\text{OH}$	24.76	7.899	26.88	6.590	380
3	$\text{CH}_3\text{C}(\text{O})\text{OH} + \text{CH}_3\text{C}(\text{O})\text{OC}_2\text{H}_5$	24.52	8.072	26.88	6.590	300
4	$\text{CH}_3\text{C}(\text{O})\text{OH} + \text{CH}_3\text{CN}$	24.80	7.870	26.84	6.605	350

Formation of GNCCs with organic compounds leads to additional reorganization of graphite matrix as well as to enhancement of ability to thermal expansion as compared with graphite nitrate: values of coefficient of thermal expansion (K_V), determined for graphite nitrate and studied GNCCs, are $249\text{ cm}^3 \cdot \text{g}^{-1}$ [24] and within $300\text{--}380\text{ cm}^3 \cdot \text{g}^{-1}$, respectively (Table 1). Thus, the investigated GNCCs can act as effective precursors of thermally expanded graphite.

3.2 Pre-organized TEGs for Carbon Nanoparticles

Thermally expanded graphite samples based on GNCCs were obtained using thermal shock (at $900\text{ }^\circ\text{C}$) method of heating. Coefficient of thermal expansion (K_V), estimated for studied GNCCs were within $300\text{--}380\text{ cm}^3 \cdot \text{g}^{-1}$ (see Table 1) and ternary GNCC with acetic and formic acids was found to demonstrate the highest K_V value.

The structure of the obtained TEGs was studied by powder X-ray diffraction. Reflexes typical for the graphite phase are observed on the X-ray diffraction patterns of studied samples. The absence of uncharacteristic reflexes for crystalline graphite on TEGs XRD patterns (Fig. 2) was established, residual intercalation compounds were also not detected, that is there are no reflexes typical for the initial GNCCs. Broadening, splitting and shift of the reflexes towards smaller angles on the X-ray diffraction pattern occur upon GNCCs thermal expansion. TEG is less ordered as compared with initial graphite (Fig. 3).

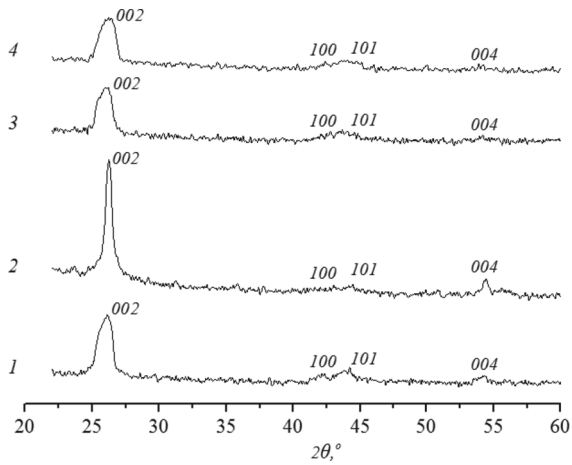


Fig. 2. X-ray diffraction patterns of investigated TEGs samples in $I^{(0.5)} - 2\theta$ coordinates (numbers on figure correspond to precursor GNCCs listed in Table 1).

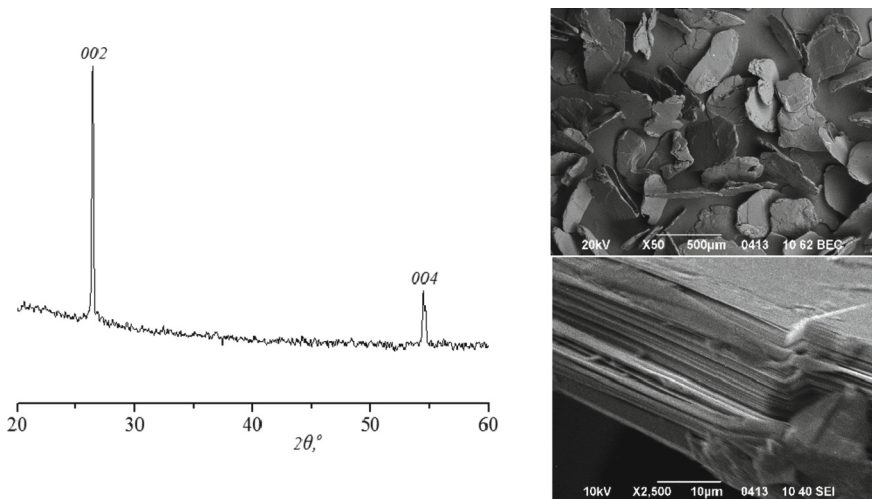


Fig. 3. X-ray diffraction pattern in $I^{(0.5)} - 2\theta$ coordinates and representative SEM images of natural graphite (GT-1), used as a starting material for GNCCs and TEGs obtaining.

Figure 4 shows typical SEM images of studied TEGs at the same magnifications. The width of visible pores in such structures varies from 1.0 to 20 μm . It should be noted that individual few-layered fragments are already present in the samples. The change in the microstructure of graphite during the formation of GNCCs and subsequent thermal expansion is determined by the nature of graphite, intercalants, the stage of intercalation, and thermal expansion conditions [2, 17, 21]. TEGs based on studied GNCCs are characterized by a clear cellular structure. There are no significant differences in the structure and morphology of the studied samples. All TEGs obtained from binary

and triple GNCCs with organic compounds demonstrate a structure pre-organized for the generation of few-layer graphenes.

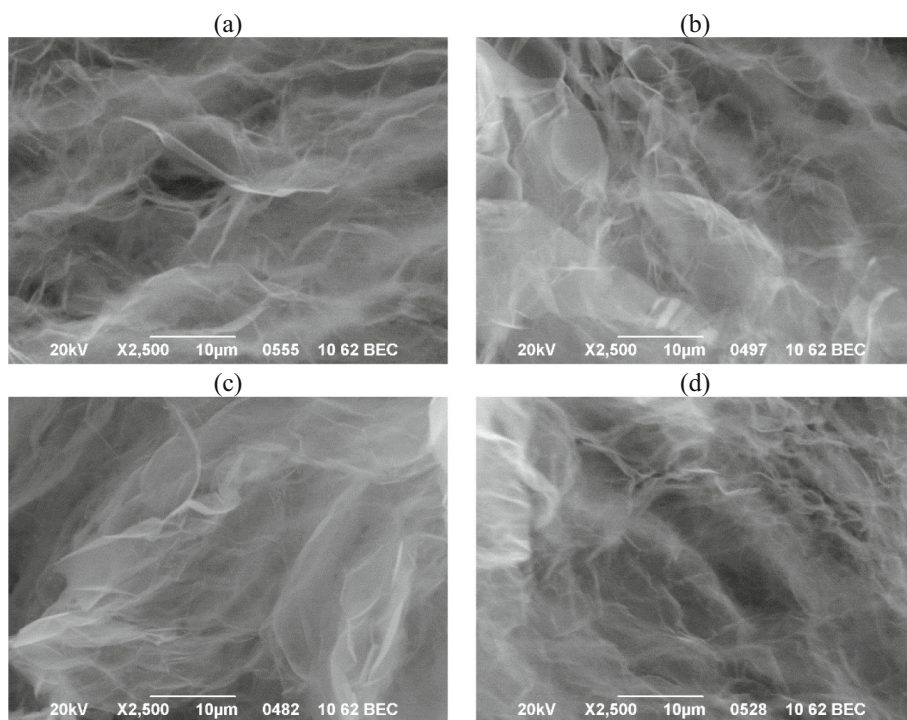


Fig. 4. Representative SEM images of studied TEG samples at the same magnifications. Correspondence to the original GNCCs listed in Table 1 is the following: (a) – 1; (b) – 2; (c) – 3; and (d) – 4.

3.3 Morphology of Carbon Nanoparticles from Expanded Graphite Nitrate Cointercalants

Dispersions of carbon nanoparticles were prepared by liquid-phase exfoliation of the TEGs samples in *tert*-butanol, assisted with sonication (22 kHz, 470 W, 1 h). The dispersions obtained were investigated by TEM method. Overall scheme of carbon nanoparticles obtaining is summarized in Fig. 1. An analysis of the dispersions obtained in *tert*-butanol by the TEM method revealed that carbon nanoparticles of various morphologies can be obtained by this technique. Most commonly, a mixture of particles is formed, which includes graphene-like particles of various sizes (both single-layer and few-layer) and small amorphous carbon nanoparticles.

Morphology of the observed nanoparticles was revealed to depend on the intercalant's nature in GNCCs, used for the TEGs obtaining. Figure 5 show representative TEM images of carbon nanoparticles, obtained by TEGs exfoliation in *tert*-butanol induced

by ultrasound. During exfoliation under the same conditions (frequency and power of sonication, duration of exposure, medium) for TEGs obtained from studied GNCCs, the formation of few-layer graphenes with different planar sizes was observed. The TEM analysis of dispersion, based on thermally expanded binary GNCC-1 (with acetic acid), showed the presence of few-layer graphenes with a thickness from 2 to 10 layers and with planar dimensions up to 5 μm . Exfoliation of thermally expanded triple GNCC-2 under these conditions leads to the formation of few-layer graphenes with sizes of 1–5 μm . Processing of TEG samples based on GNCC-3 and GNCC-4 makes it possible to obtain dispersions of few-layer graphenes with planar dimensions up to 20–50 μm (fragments are presented in Fig. 5c, d). In the case of thermally expanded GNCC-4, individual particles up to 75 μm were observed.

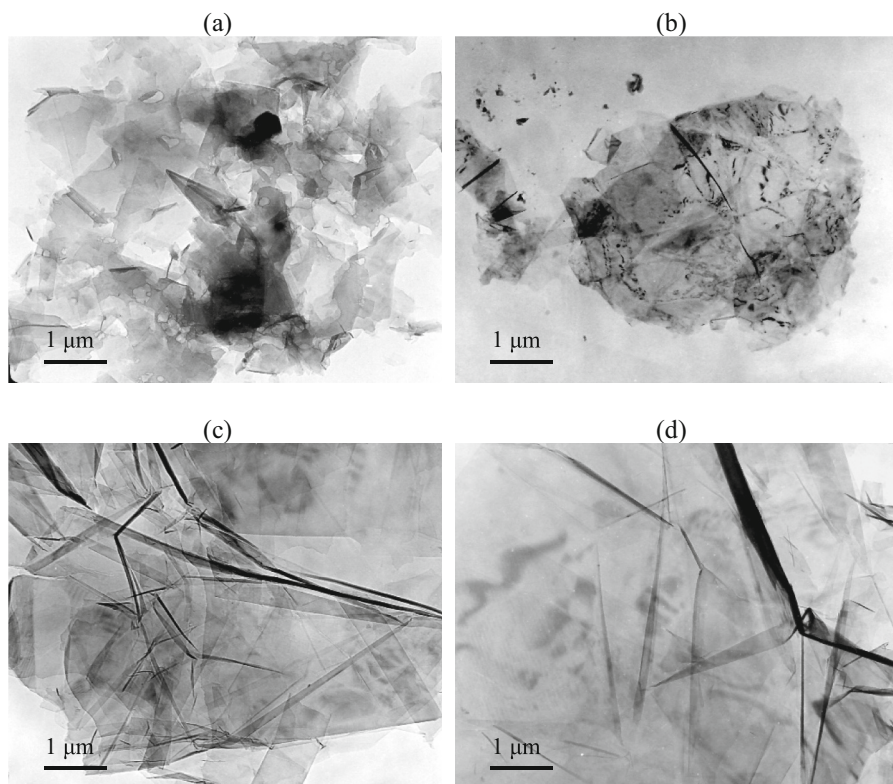


Fig. 5. Representative TEM images of carbon nanoparticles, obtained in *tert*-butanol by sonication of the TEGs samples and corresponding SAED patterns. Correspondence to the original GNCCs listed in Table 1 is the following: (a) – 1; (b) – 2; (c) – 3; and (d) – 4.

In the case of TEG, based on GNCC-2 with acetic and formic acids, the resulting dispersion, in addition to few-layer graphenes, contained also a significant amount of small amorphous graphene-like particles, as well as particles with obvious surface defects (Fig. 6).

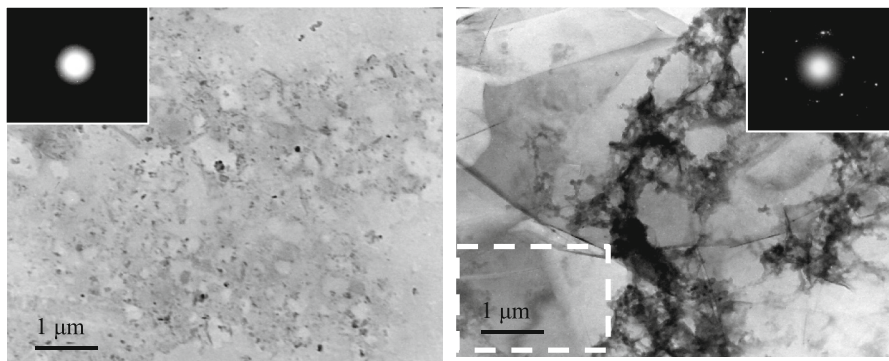


Fig. 6. TEM images of carbon nanoparticles obtained in *tert*-butanol by sonication of the TEG on the base of GNCC-2 with acetic and formic acids.

Since the exfoliation of graphite via sonication involves formation of surface defects (kinks, bends) [25], the presence of small amorphous particles in the dispersion can be caused by the destruction of nanoparticles with a large number of surface defects. The appearance of oxygen-containing groups on the surface due to partial oxidation also contributes to the destruction of nanoparticles with the formation of small polyaromatic fragments [26]. It was shown previously [27] that exfoliation under similar conditions of a ternary GNCC with acetic and formic acids leads to the generation of few-layer graphenes, nan scrolls as well as small graphene-like particles in the system. The presence of a large number of visible defects on the surface of the resulting nanoparticles was also noted. These data are in good agreement with the results of exfoliation of TEG, based on GNCC with acetic and formic acids, observed in present work. Therefore, the formation of particles in the system with a large lot of visible surface defects may be due to the morphological features of the initial GNCC, which was used to obtain TEG.

4 Conclusions

The structure of TEGs based on graphite nitrate cointercalation compounds with organic substances is pre-organized for the formation of few-layer graphene particles. The presence of few-layer graphenes in the exfoliation products of TEG samples in *tert*-butanol medium has been established by the transmission electron microscopy method. It was shown that varying the cointercalates nature in the precursor GNCCs makes it possible to regulate planar sizes of few-layer graphenes as well as degree of formed amorphous nanoparticles. Exfoliation of TEGs, based on triple GNCCs with acetic acid and ethyl acetate as well as with acetic acid and acetonitrile, lead to generation of the few-layer graphenes with planar sizes up to 20–50 μm . Formed amorphous nanoparticles in this case were of small account. The presented results revealed TEGs, based on graphite nitrate cointercalation compound with acetic acid and its derivatives to be a promising source of carbon nanoparticles. Exfoliation of TEGs in liquid media by sonication can be simple and effective route for carbon nanoparticles obtaining under mild conditions.

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