Triple graphite nitrate cointercalation compounds with acetic acid as precursors for thermally expanded graphite and carbon nanoparticles

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Abstract. Triple graphite nitrate cointercalation compounds (GNCCs) with acetic acid were synthesized, characterized by powder XRD and SEM methods, and used as a source of the thermally expanded graphite (TEG). Structural reorganization of graphite nitrate-acetate and triple GNCCs with acetic acid as a result of their exposition in air is discussed on the base of powder XRD data. Dispersions of carbon nanoparticles were prepared by liquid phase exfoliation of TEGs obtained from the GNCCs. It was demonstrated by TEM method that using of the studied TEGs as a source of carbon nanoparticles favours formation of few-layered graphene.

1. Introduction
Liquid phase exfoliation of graphite and related substances (graphite intercalation compounds, thermally expanded graphite) is one of the perspective (promising) routes to obtain carbon nanoparticles [1-5]. Graphite nitrate (GN) is one of the most labile graphite intercalation compounds of acceptor type, which can be quite easily obtained in the normal conditions. Possibility of the GN stabilization by the cointercalation was first predicted by Inagaki [6] and subsequently implemented in our laboratory on the example of the graphite nitrate cointercalation with acetic acid and water [7, 8]. Synthesis and structural characterization of binary graphite nitrate cointercalation compounds (GNCCs) with a variety range of organic compounds revealed key factors determining stability of such compounds [9]. Stabilization of graphite nitrate during its cointercalation with organic compounds is due to their protonation for account of nitric acid contained in the interlayer space. Stability index of cointercalated graphite nitrates was shown to correlate linearly with proton affinity of the organic cointercalants [8, 10]. Additional stabilization comes from formation of a continuous two-dimensional net of hydrogen bonds among the solvation ligands. Triple GNCCs contained two organic cointercalants in their structure were also synthesized [11-13] and have shown to exhibit good...
expansible properties [14]. Thermally expanded graphite (TEG) obtained from them demonstrated desirable structure for few-layered graphenes generating [11, 12] and good sorption properties [15].

Regular structure of binary and triple GNCCs as well as TEGs cellular structure can be considered as pre-organized ones for the few-layered graphenes and related carbon nanostructures generation. It was shown that triple GNCCs with acetic acid esters are perspective compounds for few-layered graphenes as well as nanoscrolls obtaining by liquid phase exfoliation in ethanol assisted with sonication [10].

This paper presents the results of complex investigations of structural features of triple graphite nitrate cointercalation compounds with acetic acid. Ethyl acetate, butyl acetate, formic acid, and acetic acid were used as additional cointercalants. Stability of the GNCCs as well as effect of the additional cointercalant in the GNCC structure on its structural and expansion properties are discussed. Triple GNCCs were used as a source for TEG 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.

2. Experimental

Natural flake graphite GT-1 (Zavalie Graphite Works, Kirovograd region, Ukraine) used for binary and triple GNCCs was preliminarily deashed by treatment with concentrated hydrochloric and hydrofluoric acids in three stages: (i) boiling in HCl, (ii) HF treatment, and (iii) reboiling in HCl. The ash content in graphite after purification was 0.01%. Organic intercalants (ethyl acetate, butyl acetate, formic acid, and glacial acetic acid) as well as tert-butanol were purchased from Merck-Schuchardt and used as received.

Synthesis of the binary cointercalation compound of graphite nitrate with acetic acid

Binary cointercalation compound of graphite nitrate with acetic acid (graphite nitrate – acetate) was prepared in a thermostatic reactor open to air at 20 °C as described elsewhere [10]. At the first stage nitric acid (0.6 cm³) with a density of 1.502 g·cm⁻³ was added to the sample of graphite (1 g), and the reaction mixture was stirred for 10 minutes. Then glacial acetic acid (6 ml) was added to the reaction mixture and the system was stirred again for 10 minutes. Resulted binary GNCC was separated by filtration and sample of as-prepared fresh GNCC was studied by powder X-ray diffraction (XRD) method. The rest of graphite nitrate - acetate sample was dried at 20 °C in air until the sample mass became constant.

Synthesis of the triple graphite nitrate cointercalation compounds with acetic acid

Triple cointercalation compounds of graphite nitrate were prepared in the same reactor as binary ones. At the first stage nitric acid (0.6 cm³) with a density of 1.502 g·cm⁻³ was added to the sample of graphite (1 g). The mixture was stirred for 10 minutes. Then organic cointercalants (6 cm³) in a ratio of 1 : 1 by volume were added to the reaction mixture and the system was stirred again for 10 minutes. Resulted triple GNCCs were separated by filtration and samples of as-prepared fresh GNCCs were studied by powder XRD method. The rests of samples were dried at 20 °C in air until the sample mass became constant.

Thermally expanded graphite preparation

Thermally expanded graphite samples were prepared from triple GNCCs by the thermal shock mode of heating as described elsewhere [13]. The thermal expansion coefficient of the graphite nitrate and its GNCCs was determined from the equation:

\[ K_v = \frac{V}{m} \]  

where \( K_v \) – the thermal expansion coefficient, cm³·g⁻¹; \( V \) – the graphite foam volume, cm³; \( m \) – the initial mass of the GNCC sample before heating, g.

Preparation of carbon nanoparticles dispersions
Dispersions of the carbon nanoparticles were prepared by liquid phase exfoliation of the TEG samples (0.04 g) at ambient temperature. Sonication (1 h, 22 kHz, 470 W, I 100-6 unit, Ultrasonic technique Inlab, Russia) was used to enhance the exfoliation process. Tert-butanol (40 cm³) was used as a medium for TEG liquid phase exfoliation.

Characterization of structure of the flake graphite, graphite nitrate cointercalation compounds, thermally expanded graphite and carbon nanoparticles

The structural features of graphite, GN, and GNCCs were studied by powder XRD method using a “DRON-3” diffractometer, CuKα radiation, wavelength λ = 1.5418 Å (U = 30 kV, I = 20 mA). Powder X-ray diffraction patterns of samples were recorded from 15° to 90° (2θ) with scanning speed 1°/min. The positions of the peaks in the diffraction patterns were determined with an accuracy of 0.02°.

The identity period (1ᵣ, Å) of intercalation compounds was calculated by the equation:

\[ Iᵣ = \frac{λ}{2 \sin \thetaᵣ} \]  

where λ – the radiation wavelength, (Å); θᵣ – the glide angle (deg); and l is the order of reflection at the angle θᵣ. The order of the strongest reflection l is related to the number of intercalation stage of graphite nitrate and GNCCs n by the equation \( l = n + 1 \). The height of the intercalant-filled layer (dᵣ, Å) for GNCCs was determined from the relationship \( dᵣ = Iᵣ \cdot 3.360 \) (n – 1), where Iᵣ is the identity period (Å), n is the number of intercalation stage (the number of graphite planes between neighboring intercalant layers), and, 3.360 Å is the interplanar distance in the initial graphite.

Studies of the surface morphology of the graphite, GNCCs, and TEG by scanning electron microscopy (SEM) were carried out using the scanning electron microscope JSM 6490 LV (JEOL). Imaging of samples deposited on a conductive graphite tape was carried out in two modes: backscattered electron imaging (BEI) mode for the elemental analysis of phases constituting the samples, and secondary electron imaging (SEI) mode for the study of investigated samples surface.

Morphology and inner microstructure of nanoparticles obtained from the TEG samples were investigated by transmission electronic microscopy (TEM). As-prepared dispersion was sprayed on TEM grid and subsequently investigated using JEOL JEM 200 transmission electronic microscope. The selected area electron diffraction (SAED) patterns were obtained by changing the focal area of the magnetic lens to determine the crystal structure of the sample.

3. Results and discussion

3.1 Binary cointercalation compound of graphite nitrate with acetic acid

Graphite nitrate - acetate (binary GNCC) was obtained by the introduction of acetic acid into graphite nitrate. The overall scheme of the process involves graphite nitrate synthesis as a first stage followed by cointercalation with acetic acid:

\[
\text{Graphite} \xrightarrow{\text{HNO}_3} \text{Graphite nitrate} \xrightarrow{\text{CH}_3\text{COOH}} \text{Graphite nitrate - acetate}
\]

Structural changes in graphite during its interaction with nitric acid and subsequent treatment with acetic acid have been studied by powder XRD method. Figure 1 shows the X-ray powder diffraction patterns of the binary GNCC in coordinates \( \theta^{55-2θ} \) in the range \( 2θ = 15°- 65° \). The diffraction pattern of freshly prepared GNCC sample differs little in appearance from the patterns of graphite nitrate (figure 2); however, a shift of reflections towards larger or smaller angles is observed. Indexing of X-ray diffraction patterns of the graphite nitrate - acetate performed similarly to GN and binary GNCCs [8, 10], revealed the presence of stage II (β phase) and stage IV (α phase) intercalation compounds in the investigated cointercalate.
Storage of the sample in air is accompanied by appreciable reorganization of the cointercalate structure along with the deintercalation process. A gradual transformation \( \alpha \rightarrow \beta \) for the stage IV compound is observed for graphite nitrate - acetate during sample storage in air. Position of the peak with maximum intensity is shifted towards larger angles (\( \Delta 2\theta = 0.96^\circ \) after 88 days of exposition), which indicates a gradual decrease of the identity period (\( I_C, \) Å) and height of the intercalant-filled layer (\( d_i, \) Å) (\( \Delta d_i = 0.665 \) Å after 88 days of exposition) (figure 1-b). Peak position for the stage II (\( \beta \) phase) compound is shifted from \( 2\theta_{1h} = 26.88^\circ \) up to \( 2\theta_{20d} = 26.64^\circ \) after 20 days of exposition and \( 2\theta_{88d} = 26.60^\circ \) after 88 days of exposition (figure 1-a). The latter value is within reach to the 002 peak of initial graphite (\( 2\theta = 26.52^\circ \)) and points on the deintercalation process proceeding. Ratio of the peak intensities for the stage IV and stage II compounds of the graphite nitrate – acetate is observed to be \( I_{IV} : I_{II} = 5 : 1 \) in fresh sample, \( 2 : 1 \) after 20 days of exposition, and \( 1 : 1 \) after 88 days of exposition.

Thus the crucial structural reorganization of stage IV compound was shown to occur during first 20 days of the GNCC sample exposition in air, but after that deintercalation processes were uppermost. However noticeable structural changes for more stable stage II compound (\( \beta \) phase) were observed only after 20 days of sample exposition.
3.2 Triple graphite nitrate cointercalation compounds with acetic acid

Triple graphite nitrate cointercalation compounds were obtained by the introduction of two organic intercalants into GN. The overall scheme of the process involves GN synthesis as a first stage followed by cointercalation with two organic substances: acetic acid and ethyl acetate, acetic and formic acids, acetic acid and butyl acetate.

Structural changes in graphite matrix resulted from its interaction with nitric acid and subsequent treatment with organic cointercalants have been studied by powder XRD method. Figure 3 shows the diffraction patterns of the triple GNCCs in coordinates $I^0.5 - 2\theta$ in the range $2\theta = 20^\circ - 65^\circ$. Indexing of X-ray diffraction patterns of the triple GNCCs performed by analogy with graphite nitrate and binary GNCCs [8, 10], revealed the presence of stage II (β phase) and stage IV (α phase) intercalation compounds in the investigated cointercalates.

It should be noted that formation of studied triple GNCCs is accompanied by an activation of the intercalated structure as compared with GN and graphite nitrate-acetate. All discussed triple GNCCs (both stage II and stage IV compounds) are characterized by higher values of identity period (table 1).

![Figure 3](image.png)

Table 1. Structural characteristics of the GN and its cointercalation compounds on the base of powder XRD data.

| GNCCs   | Cointercalant(s)       | 1 h stage IV $2\theta$, °  | 1 h stage II $I_C$, Å | 480 hs stage IV $2\theta$, °  | 480 hs stage II $I_C$, Å |
|---------|------------------------|----------------------------|------------------------|-------------------------------|--------------------------|
| 1 HNO$_3$ |                        | 25.00 17.809 26.76 9.994 | -                      | -                             | -                        |
| 2 HNO$_3$/acetic acid |                     | 24.88 17.893 27.04 9.892 | 25.36 17.560 26.64 10.038 | -                             | -                        |
| 3 HNO$_3$/acetic acid/formic acid |                             | 24.76 17.979 26.88 9.950 | 25.40 17.533 26.76 9.994 | -                             | -                        |
| 4 HNO$_3$/acetic acid/butyl acetate |                         | 24.68 18.036 26.84 9.965 | 25.08 17.753 26.64 10.038 | -                             | -                        |
| 5 HNO$_3$/acetic acid/ethyl acetate |                         | 24.56 18.123 26.88 9.950 | 24.88 17.893 26.60 10.053 | -                             | -                        |

Storage of the GNCCs samples in air is accompanied by appreciable reorganization of the cointercalates structure along with the deintercalation process. A gradual transformation $\alpha \rightarrow \beta$ for the stage IV compound is also observed for studied GNCCs. Table 1 demonstrates changes in GNCCs structural characteristics after 20 days of the samples exposition in air. Values of identity period for stage IV compounds are reduced as compared to the fresh samples, thus an $\alpha \rightarrow \beta$ transformation occurs. Corresponded $I_C$ values for the stage II compounds increased after 20 days of exposition. Such changes can be explained by additional water molecules intercalation into the GNCCs structure.
Meanwhile $2\theta$ values for the stage II compounds are within reach to the 002 peak of initial graphite and points on the deintercalation process proceeding. Probably water intercalation and deintercalation processes occur simultaneously in studied compounds and observed at $2\theta = 26.60^\circ - 26.70^\circ$ peak should be considered as superposition of two phases – graphite and stage II intercalation compound. Thus more detailed investigations of these processes are needed. Ratio of the peak intensities for the stage IV and stage II intercalation compounds after 20 days of exposition in air were $I_{IV} : I_{II} = 3 : 2$ for GNCCs with formic acid and butyl acetate as the second cointercalants, and $I_{IV} : I_{II} = 2 : 3$ for GNCC with ethyl acetate as the second cointercalant indicating less stability of triple GNCCs as compared with binary GNCC with acetic acid.

The surface morphology of the flake graphite and obtained GNCCs samples was investigated by scanning electron microscopy method. Representative SEM images of initial graphite and discussed GNCCs are presented in figure 4. All samples demonstrate the layer structure, but GNCCs formation is accompanied with a reorganization of the graphite microstructure – besides introducing of the cointercalant particles into interlayer space the delamination of flakes occurred.

Triple GNCCs demonstrated good thermal expansion ability. Thermal expansion coefficients determined for considered compounds along with corresponding values for GN as well as binary GNCC with acetic acid are listed in table 2. In all studied cases, the use of cointercalant(s) leads to an increase in the $K_V$ value in comparison with corresponding value for the GN and graphite nitrate-acetate. The values of the expansion coefficient of the triple compounds exceed the $K_V$ value for the corresponding binary one. This fact indirectly indicates an increase in the intercalants molar content in the obtained triple cointercalates. A marked increase in $K_V$ values was observed for binary and triple GNCCs excluding GNCC with acetic and formic acids after 20 days of samples exposition in air (table 2). Taking into account powder XRD investigation results presented above one can assume that during GNCCs exposition in air additional water intercalation is preferable for the graphite nitrate-acetate and compounds with ethyl and butyl acetates whereas for the GNCC with acetic and formic acids deintercalation process is preferable.

![Figure 4. Representative SEM-images of initial graphite (a), triple GNCCs with acetic acid and ethyl acetate (b), acetic and formic acids (c), acetic acid and butyl acetate (d), and TEGs based on them (e – g).](image)

| GNCCs | Cointercalant(s) | $K_V$, cm$^3$·g$^{-1}$ |
|-------|-----------------|----------------------|
|       |                 | 1 day | 20 days |
| 1     | HNO$_3$         | 250   | -       |
| 2     | HNO$_3$ / acetic acid | 354   | 400     |
| 3     | HNO$_3$ / acetic acid / ethyl acetate | 300   | 375     |
| 4     | HNO$_3$ / acetic acid / formic acid | 380   | 350     |
| 5     | HNO$_3$ / acetic acid / butyl acetate | 395   | 400     |

Table 2. The thermal expansion coefficients of the graphite nitrate and its cointercalation compounds determined after 1 and 20 days of samples exposition in air.
3.3 Carbon nanoparticles generated from TEGs based on triple graphite nitrate cointercalation compounds with acetic acid.

TEG samples obtained from triple GNCCs were used as a source of carbon nanoparticles. GNCCs samples were undergoing thermal shock at 900 °C. The increase in gas pressure in GNCCs with increasing temperature leads to deformation of graphite layers during thermal shock and the formation of cracks in flakes (wedge-shaped defects). In addition, in the process of thermal expansion crystallites are split along the c axis, as well as an increase of the specific surface area of the samples is observed. The surface morphology of the TEGs obtained as a result of heat treatment of the investigated GNCCs was studied by SEM. Typical SEM micrographs of the TEG samples are shown in figure 4. Studied TEGs demonstrated cellular structure, the width of visible pores in the particles varies from 0.5 to 50 μm. The cell walls are formed by graphite layers. Destruction of TEG cellular structure during sonication in liquid phase may result in generation of single as well as few-layer graphenes and related structures due to exfoliation.

Step-by-step scheme of the carbon nanoparticles obtaining starting from graphite is presented in figure 5. Dispersions of carbon nanoparticles were obtained by corresponded TEGs liquid phase exfoliation assisted with sonication in tert-butanol.

![Figure 5. Step-by-step scheme of the carbon nanoparticles obtaining (with representative SEM-images of initial graphite, intermediate graphite nitrate, GNCC with acetic and formic acids, TEG, and representative TEM-image of the final few-layer graphene particle).](image)

The microstructure of as-prepared nanoparticles was estimated by transmission electron microscopy and representative TEM images are listed in figure 6. The SAED patterns of resulted graphenes (figure 6) displayed sixfold symmetry consistent with the typical hexagonal crystalline structure. Planar sizes of the as-prepared few-layer graphenes reached several tens of μm, the thickness varied within 2 - 10 atomic layers (visible parts in figure 6 are of 6 - 7 μm).

![Figure 6. Representative TEM-images along with SAED patterns of the final few-layer graphene particles obtained from triple GNCCs with acetic acid and ethyl acetate (a), formic acid (b), butyl acetate (c) by sonication in tert-butanol.](image)

It was demonstrated that liquid phase exfoliation of GNCCs assisted with sonication lead to the formation of carbon nanoparticles of different morphology – few-layer graphenes, nanoscrolls, small amorphous particles [10, 11]. Acid medium caused by the presence of deintercalated HNO₃, HCCOH.
and CH$_3$COOH during exfoliation of triple GNCC with formic and acetic acids resulted in considerable structural defects of graphene-like particles [16]. TEG as a precursor of carbon nanoparticles favours mainly few-layer graphene formation.

4. Conclusions
A number of new triple GNCCs with acetic acid have been obtained. Studied products contained stage IV ($\alpha$ phase) and stage II ($\beta$ phase) intercalation compounds. They are characterized by larger identity periods in comparison with the initial graphite nitrate and graphite nitrate-acetate. Exposition of graphite nitrate - acetate and triple GNCCs with acetic acid in air leads to structural reorganization of the cointercalates due to the competing intercalation/deintercalation processes. Considerable structural reorganization of stage IV compounds ($\alpha \rightarrow \beta$ transformation) were shown to occur during first 20 days of the GNCC sample exposition in air, but after that deintercalation processes were uppermost. Noticeable structural changes for more stable stage II compounds ($\beta$ phase) were observed only after 20 days of sample exposition. It was demonstrated that the treatment of graphite nitrate with two cointercalants leads to an excess of the thermal expansion coefficient of triple CCNGs compared to the $K_v$ value for the corresponding graphite nitrate-acetate. The ultrasound-assisted liquid phase exfoliation of TEGs based on the triple GNCCs in tert-butanol leads to the major formation of few-layer graphenes. The resulting nanoparticles can be used as reinforcing fillers for polymers, rubbers and building materials, as well as sensors, sorption materials, and substrates for various catalysts.

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