Carbon Nanoparticles from Thermally Expanded Graphite: Effect of the Expansion Conditions on the Derived Nanoparticles Morphology

Elena Raksha[1(✉)], Oksana Oskolkova[1], Valentiva Glazunova[2], Alina Davydova[1], Galina Volkova[2], Valerij Burchovetskij[2], Petr Sukhov[1], Viktoriya Gnatovskaya[1], Yuliya Berestneva[3], Ilya Verbenko[4], Yurij Yurasov[4], and Michael Savoskin[1]

[1] Department of Supramolecular Chemistry, L.M. Litvinenko Institute of Physical-Organic and Coal Chemistry, Donetsk, Ukraine
elenaraksha411@gmail.com

[2] Department of High-Pressure Physics and Advanced Technologies, Donetsk Institute for Physics and Engineering Named After A.A. Galkin, Donetsk, Ukraine

[3] Biotechnology Laboratory, Federal Scientific Centre of Agroecology, Complex Melioration and Protective Afforestation of the Russian Academy of Sciences, Volgograd, Russia

[4] Research Institute of Physics, Southern Federal University, Rostov-on-Don, Russia

Abstract. Liquid phase exfoliation of thermally expanded graphite (TEG) obtained from graphite nitrate cointercalation compound (GNCC) with acetic and formic acids allows obtaining dispersions of carbon nanoparticles, namely few-layer graphenes as well as small graphene structural fragments. TEG samples obtained at different temperature as well as in different heating modes were investigates as precursors of carbon nanoparticles. Effect of the expansion conditions on the derived nanoparticles morphology is discussed. The microstructure and morphology of obtained carbon nanoparticles were investigated by transmission electron microscopy (TEM). Planar sizes of the few-layer graphenes from TEG samples reached of $1–10\,\mu m$ and their thickness was within of $1–10$ atomic layers according to TEM data. It was found that TEG, obtained at 900 °C in thermal shock mode of heating, is more preferable for few-layer graphenes generation from TEGs.

Keywords: Liquid phase exfoliation · Graphite nitrate cointercalation compounds (GNCCs) · Thermally expanded graphite · Carbon nanoparticles · Few-layer graphenes · Sonication · Transmission electron microscopy (TEM)

1 Introduction

Thermally expanded graphite (TEG) is actively used in laboratory practice to obtain and study the properties of new materials due to a wide range of its practical applications [1–4]. The effect of various factors and conditions of TEG obtaining on its morphology and properties is actively studied [5, 6]. Thermally expanded graphite is a foam-like

carbon structure. High chemical and thermal stability, combined with controlled electrical and thermal conductivity, porosity, and well-developed specific surface create the prerequisites for the development of multifunctional materials based on TEG.

Graphite intercalation compounds (GICs) of the acceptor type are most often used as the precursors of TEG. 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 [7]. Equation (1) demonstrates the overall scheme of TEG obtaining. The cellular structure 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 [8].

$$\text{Graphite} \xrightarrow{\text{Intercalant}} \text{GIC} \longrightarrow \text{TEG} \tag{1}$$

The presence of graphite layers in the TEG structure opens prospects for its use as a carbon source in the obtaining of few-layer graphenes dispersions. The TEG structure is determined by the structural reorganization of the graphite matrix at the micro- and macro-levels at each stage of TEG obtaining [9]. The number of the intercalation stage (the number of graphite layers between neighboring intercalant layers) and the expansion temperature of the original GIC have a significant effect. It was established [5] that a decrease in the intercalation stage of GIC and an increase in the expansion temperature led to a decrease in the size of crystallites along the *c*-axis in TEG. It should be noted that already in the process of thermal expansion, exfoliation of a small amount of single- and few-layer graphenes is possible [10].

Liquid-phase exfoliation assisted with sonication [11–14], mechanical exfoliation [15], microwave method [16] and their various combinations are used to obtain nanoparticles based on TEG. Liquid phase exfoliation is currently one of the most widely used routs for graphene and few-layer graphenes producing. Typically, this process includes three stages: obtaining a dispersion of graphite in a solvent, exfoliation of graphite in dispersion via sonication, and isolation or purification of graphene.

This paper presents the results on the production of few-layer graphenes dispersions by exfoliation of a pre-thermally expanded graphite nitrate cointercalation compound with formic and acetic acids in *tert*-butanol assisted with sonication. This method 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:

 (i) synthesis and characterization of triple graphite nitrate cointercalation compound (GNCC) with formic and acetic acids as precursor for thermally expanded graphite;
 (ii) characterization of thermally expanded graphite samples as promising origin for carbon nanoparticles obtaining;
 (iii) liquid phase exfoliation of thermally expanded graphite obtained in different conditions.

2   Experimental

Graphite nitrate (GN) as well as graphite nitrate cointercalation compound with acetic and formic acids were prepared as a starting material for the generation of thermally expanded graphite. GN and GNCC were synthesized in a thermostatic reactor using nitric acid (98%) and natural flake graphite GT-1 (Zavalie Graphite Works, Kirovograd region, Ukraine). A mixture of graphite (1 g) and HNO_3 (0.6 mL) was stirred for 10 min at 20 °C to obtain a GN. Triple GNCC with acetic and formic acids was obtained by treatment of as-prepared GN with mixture of acids (1:1 by volume) and reaction system was stirred for 10 min. Resulted GNCC was separated by filtration and dried at 20 °C until the sample mass became constant.

Thermally expanded graphite was obtained from GNCC in the thermal shock mode of heating (at 500, 700 and 900 °C) as well as in the linear one (at 900 °C).

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 500 °C (TEG^{Ts500}) and 900 °C (TEG^{Ts900}). Then the cuvette with expanded graphite was removed from the furnace, the contents were gently transferred to a beaker for further use.

Linear mode of heating. About 0.2 g of the GNCC was inserted into the cuvette at ambient temperature. Then the cuvette was placed in the furnace at 900 °C and has been kept for 120 s (TEG^{L900}). 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 for obtained GNCC in different modes of heating were determined by heating of the samples within the thermal shock mode at 900 °C as described in [17].

X-ray diffraction (XRD) measurements were performed on DRON 3 diffractometer (CuKα radiation, λ = 1.54181 Å). Only freshly prepared samples of graphite nitrate and GNCC were used for XRD studies. Surface morphology of the synthesized GNCC as well as TEGs was estimated by scanning electron microscopy (SEM) using a complex analytical scanning electron microscope JSM 6490 LV (JEOL).

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 of samples were obtained using JEOL JEM-200 transmission electronic microscope.

3   Results and Discussion

3.1   Graphite Nitrate Cointercalation Compound with Carboxylic Acids as Precursor for Expanded Graphite

Triple graphite nitrate cointercalation compound with acetic and formic acids was used as precursor for expanded graphite. GNCC was synthesized by treatment of natural flake graphite with fuming nitric acid following by treatment of the formed graphite nitrate with co-intercalants—carboxylic acids. General scheme of the GNCC synthesis

is provided in Fig. 1. Representative SEM images of initial graphite and discussed GNCC are presented in Fig. 2. All samples demonstrate the layer structure, but GNCC formation is accompanied with a reorganization of the graphite microstructure, namely besides introducing of the co-intercalants particles into interlayer space the delamination of flakes is observed.
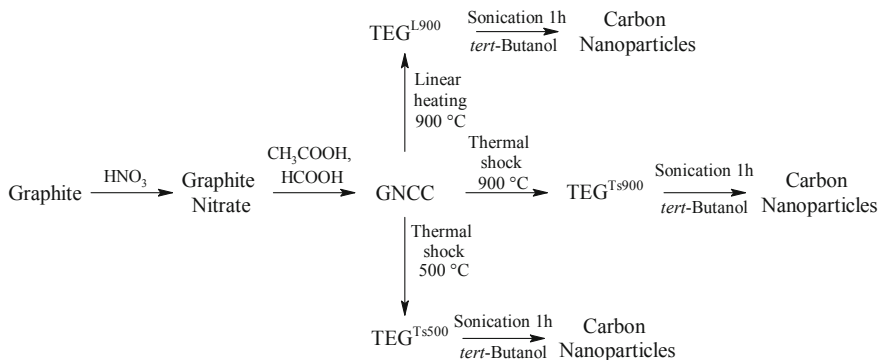

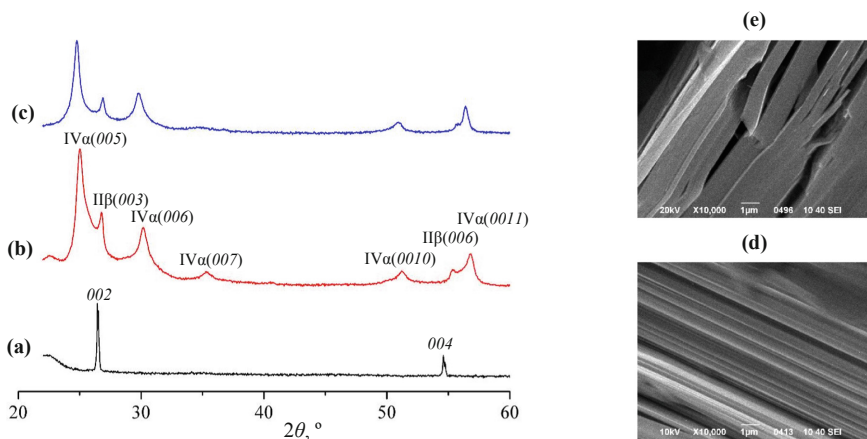**Fig. 1** Summarized scheme of carbon nanoparticles obtaining from TEGs

Fig. 2 X-ray diffraction patterns of graphite (*a*), graphite nitrate (*b*), and GNCC (*c*) with acetic and formic acids and representative SEM images (side view) of graphite (*d*) and GNCC (*e*)

Structure of the synthesized triple GNCC was characterized by X-ray diffraction method. Figure 2 demonstrates diffraction patterns of graphite, graphite nitrate and GNCC in $I^{(0.5)} - 2\theta$ coordinates. In obtained samples compounds of IVth and IInd stages of intercalation are presented. From the results of X-ray diffraction analysis values of interplanar space filled with co-intercalants species (d_i) were estimated for studied GN and GNCC. The d_i values for GN and GNCC are increased up to 6.634–7.899 Å (Table 1) as compared with 3.359 Å for initial graphite.

Formation of GNCC with acetic and formic acids leads to additional reorganization of graphite matrix as well as to enhancement of ability to thermal expansion as compared with GN: coefficient of thermal expansion determined for studied GN and GNCC are 249 and 380 $cm^3 g^{-1}$, respectively. Thus, the investigated GNCC can act as an effective precursor of thermally expanded graphite.

Table 1 Structural characteristics of the graphite nitrate and GNCC with acetic and formic acids as well as coefficients of thermal expansion of the studied compounds

GNCC	Co-intercalant	IV-α compound		II-β compound		K_V (cm^3 g^{-1})
		2θ (°)	d_i (Å)	2θ (°)	d_i (Å)	
1	–	25.00	7.729	26.76	6.634	249
2	$HCOOH + CH_3COOH$	24.76	7.899	26.88	6.590	380

3.2 Thermally Expanded Graphite, Obtained from GNCC with Acetic and Formic Acids

Thermally expanded graphite, based on GNCC, was obtained using two heating modes—thermal shock (at 500 and 900 °C) and linear heating (at 900 °C). It should be noted that the value of the thermal expansion coefficient of GNCC depends on the temperature and heating mode (Table 2). The highest value of the thermal expansion coefficient was observed at 900 °C in the thermal shock mode.

Table 2 Thermal expansion coefficients of GNCC, based on formic and acetic acids, at different temperatures and heating modes

T, °C	500	700	900	900
Heating mode	Thermal shock	Thermal shock	Thermal shock	Linear
K_V, cm^3 g^{-1}	220	325	380	165

Reflexes, which are typical for the graphite phase, are observed on the X-ray diffraction patterns of TEG samples, obtained from GNCC (Fig. 3). The absence of uncharacteristic reflexes for crystalline graphite on TEGs XRD patterns was established by the XRD method, residual intercalation compounds were also not detected, namely there are no reflexes typical for the initial GNCC. Broadening, splitting and shift of the reflexes towards smaller angles on the X-ray diffraction pattern occur upon GNCC thermal expansion. TEG is less ordered than initial graphite.

Figure 4 shows typical SEM images of TEGs at various 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
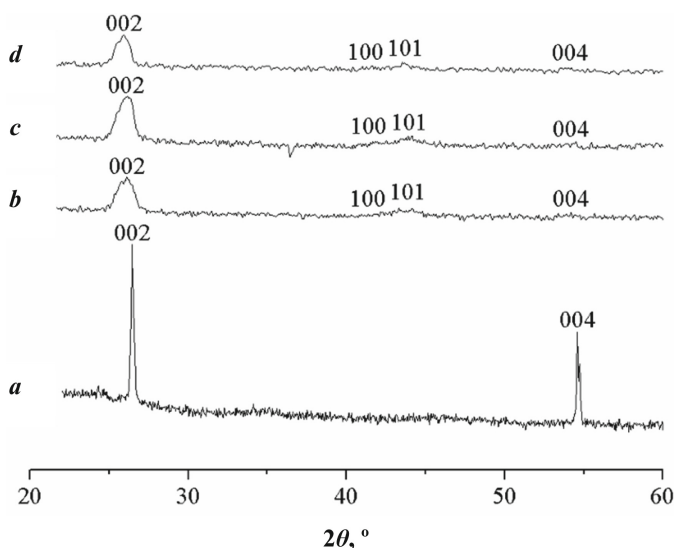
Fig. 3 X-ray diffraction patterns of graphite (*a*), TEG^{Ts500} (*b*), TEG^{Ts900} (*c*), and TEG^{L900} (*d*) samples

the microstructure of graphite during the formation of GNCC and subsequent thermal expansion is determined by the nature of graphite, intercalants, the stage of intercalation, and thermal expansion conditions [5]. For graphite bisulfate, it was shown [5] that a decrease in the intercalation stage and an increase in temperature during the preparation of TEG lead to a greater degree of disorder and destruction of the walls that form the cellular structure of TEG. TEGs, based on GNCC with formic and acetic acids, are characterized by a clear cellular structure (Fig. 4), however, the cell sizes in the case of TEG, obtained in the linear heating mode, are smaller compared to those for TEG obtained in thermal shock mode. During linear heating, fragments with a non-exfoliated structure also observed in the TEG structure (Fig. 4, c).
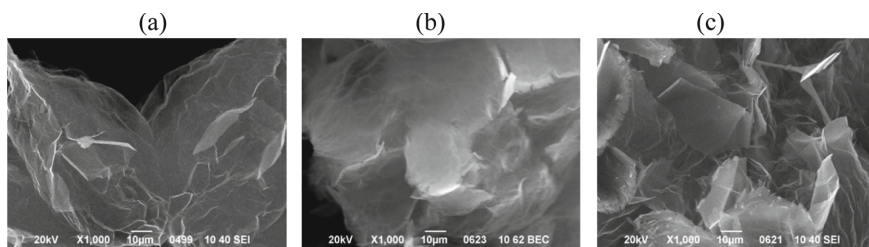

Fig. 4 Representative SEM images of TEG samples at various magnifications: (a) TEG^{Ts900}, (b) TEG^{Ts500}, and (c) TEG^{L900}

Thus, TEGs, obtained from studied GNCC with carboxylic acids in various heating modes, demonstrate a structure pre-organized for the generation of few-layer graphenes.

3.3   Carbon Nanoparticles Obtained from TEGs

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 temperature and heating mode used for the TEGs obtaining. Figures 5, 6 and 7 show representative TEM images of carbon nanoparticles, obtained by TEGs exfoliation in *tert*-butanol, induced by ultrasound.

According to TEM data, the dispersion based on TEG, obtained at 900 °C in the linear (TEG^{L900}) and thermal shock (TEG^{Ts900}) modes, contained predominantly few-layer graphenes. The planar dimensions of the observed particles varied in the range of 1–20 µm, and the thickness of the particles, ranged from 2 to 10 layers. Figures 5 and 6 show typical TEM images of the obtained particles. The electron diffraction patterns of the selected areas (SAED) indicate the crystalline nature of the particles and the presence of several disordered layers.

Exfoliation of the TEG^{Ts900} sample in *tert*-butanol via sonication leads to the generation of the few-layer graphenes with planar dimensions up to 6 µm (Fig. 5). Formed amorphous nanoparticles in this case were of small quantity.
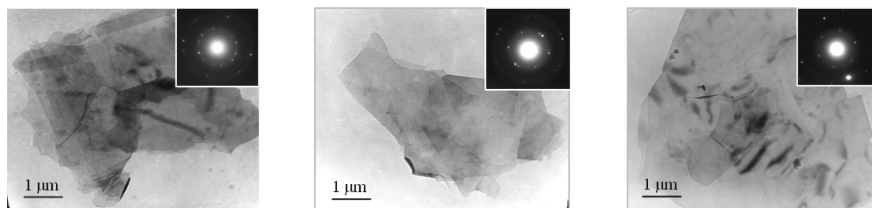

Fig. 5 Representative TEM images of carbon nanoparticles obtained in *tert*-butanol by sonication of the TEG^{Ts900} sample and corresponding SAED patterns

Exfoliation of the TEG^{L900} sample in *tert*-butanol via sonication also leads to generation the few-layer graphenes with planar dimensions up to 20 µm (Fig. 6, a, b). The presence of a fraction of amorphous particles up to 100 nm in size (Fig. 6, c) was also revealed in the dispersion. Thus, changing the heating regime from thermal shock to linear, on the one hand, contributes to an increase in the planar dimensions of the generated few-layer graphenes, but, on the other hand, leads to an increase in the number of amorphous particles formed in the dispersion.
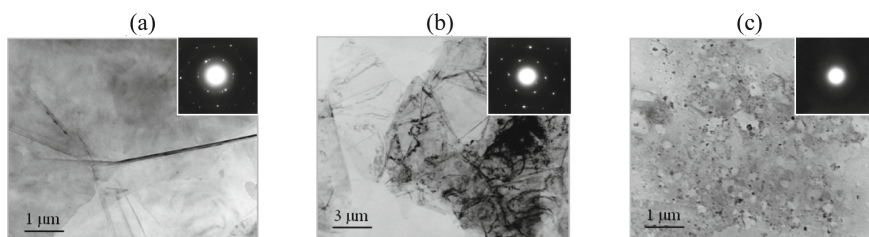
Fig. 6 Representative TEM images of carbon nanoparticles obtained in *tert*-butanol by sonication of the TEG^{L900} sample and corresponding SAED patterns

The temperature, used to obtain TEG sample, affects the morphology of the nanoparticles, generated during TEG exfoliation in *tert*-butanol. During exfoliation under the same conditions (frequency and power of sonication, duration of exposure, medium) for TEG, obtained at a lower temperature (TEG^{Ts500}), the formation of few-layer graphenes with a large number of layers in a package was expected. However, the TEM analysis of dispersion, based on TEG^{Ts500}, showed the presence of few-layer graphenes with a thickness from 2 to 10 layers and with planar dimensions up to 5 µm. The SAED pattern of the particle in Fig. 7, a gives clear reflections of the hexagonal structure, while the intensity of the reflections of the outer circle is greater than the inner one, which is typical for two-layer particles.

In addition to reducing the planar sizes of nanoparticles, the dispersion also contained a significant quantity of defragmented planes and small amorphous carbon nanoparticles with sizes up to 100 nm (Fig. 7, d), characterized by the absence of any reflections in the electron diffraction pattern. The resulting particles were also characterized by a large number of visually observed surface defects. An enlarged particle fragment in Fig. 7, b, with more than three layers (on the SAED pattern the intensities of reflections of the inner and outer circles are equal) demonstrates a large number of upper layer defects (dashed square). However, the discussed particle is crystalline, since the SAED pattern of this fragment has a clear hexagonal structure, the reflections of which correspond to the luminosity region in the dark field mode, as can be seen from Fig. 7, c.

Since the exfoliation of graphite via sonication involves formation of surface defects (kinks, bends) [18], 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 [19]. The difference in particle morphology may be due to the peculiarities of the change in the structure at the microlevel during the formation of TEG, which is used as a source of carbon nanoparticles. The authors of [6], when studying dispersions of TEG in isopropanol by the TEM method, showed that the microstructure of TEG, obtained at 1000 °C, is characterized by the presence of narrow graphene packets with layers of turbostratic carbon at the boundaries, while the TEG, obtained at a lower temperature (600 °C), contains fairly large areas of amorphous carbon. Apparently, in our case, the appearance of a significant number of amorphous carbon particles in the
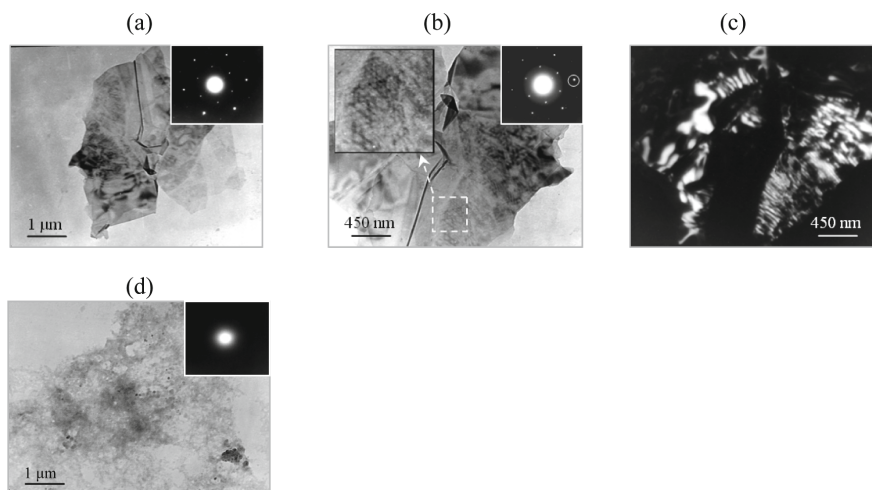
(a)   (b)   (c)

(d)

Fig. 7 Representative TEM images in bright (a, b, d) and dark (c) field modes of carbon nanoparticles, obtained in *tert*-butanol by sonication of the TEG^{Ts500} sample, and corresponding SAED patterns. On the SAED (b), the circle indicates the reflex, used to obtain the image (c) in the dark field mode

dispersion on the base of TEG^{Ts500} sample can also be due to the presence of amorphous carbon regions in the structure of TEG, obtained at 500 °C.

Thus, in accordance with the results of the TEM analysis, it was shown that the obtained dispersions, regardless of the conditions for obtaining the TEG sample, contained predominantly few-layer graphenes. However, lowering the processing temperature of the initial GNCC and changing the processing mode from thermal shock to linear heating led to an increase in the content of small aromatic and amorphous nanoparticles in the system.

4 Conclusion

The structure of TEGs, based on graphite nitrate cointercalation compound with carboxylic acids, is pre-organized for the formation of few-layer graphene particles. The presence of few-layer graphenes in the exfoliation products of TEG samples, based on graphite nitrate cointercalation compound with formic and acetic acids in *tert*-butanol medium, has been established by the transmission electron microscopy method. It was shown that varying the temperature as well as heating mode of TEG obtaining makes it possible to regulate a degree of formed amorphous nanoparticles. Exfoliation of TEG, obtained at 900 °C in thermal sock heating mode, leads to generation of the few-layer graphenes. Formed amorphous nanoparticles in this case were of small account. Descent of TEG obtaining temperature contributes to a significant increase in amorphous nanoparticles fraction, formed during TEG exfoliation in *tert*-butanol. Changing the heating regime from thermal shock to linear, on the one hand, contributes to an increase in the planar dimensions of the generated few-layer graphenes, but, on the other hand, leads to an increase in the number of amorphous particles, formed in the dispersion.

The presented results revealed that TEGs, based on graphite nitrate cointercalation compound with carboxylic acids, are 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.

References

1. Obraztsova E, Barshutina MN, Bakunin ES, Rukhov AV, Shipovskaya AA, Shuklinov AV (2020) Mendeleev Commun 30(2):174
2. Frąc M, Pichór W, Szołdra P, Szudek W (2021) Constr Build Mater 275(11):122126
3. Asalieva E et al (2020) Appl Catal A 601:117639
4. Chriaa I, Karkri M, Trigui A, Jedidi I, Abdelmouleh M, Boudaya C (2021) Polymer 212:123128
5. Ivanov AV, Maksimova NV, Kamaev AO, Malakho AP, Avdeev VV (2018) Mater Lett 228:403
6. Ivanov AV et al (2021) J Mater Sci 56:4197
7. Sorokina NE, Redchitz AV, Ionov SG, Avdeev VV (2006) J Phys Chem Solids 67:1202
8. Chen P-H, Chung DDL (2013) Carbon 61:305
9. Afanasova IM et al (2010) Carbon 48:1862
10. Dideikin AT, Sokolov VV, Sakseev DA, Baidakova MV, Vul' AY (2010) Tech Phys 55(9):1378
11. Kulakova II, Lisichkin GV (2020) Russ J Gen Chem 90:1921
12. Chen G et al (2004) Carbon 42:753
13. Veca LM et al (2009) Adv Mater 21:2088
14. Gu W, Zhang W, Li X (2009) J Mater Chem 19:3367
15. Ma F, Liu L, Wang X, Jing M, Tan W, Hao X (2020) Compos Sci Technol 187:107895
16. Janowska I, Chizari K, Ersen O (2010) Nano Res 3:126
17. Berestneva Y, Raksha EV, Voitash AA, Arzumanyan GM, Savoskin MV (2020) J Phys: Conf Ser 1658:012004
18. Li Z, Young RJ, Backes C, Zhao W, Zhang X, Zhukov AA, Tillotson E, Conlan AP, Ding F, Haigh SJ, Novoselov KS, Coleman JN (2020) ACS Nano 14:10976
19. Tapia JI, Larios E, Bittencourt C, Yacamán MJ (2016) Carbon 99:541