Obtaining graphene nanoplatelets from various graphite intercalation compounds

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Abstract. The work compares the exfoliation ability of different graphite materials (expanded graphite intercalation compound, thermally expanded and oxidatively intercalated graphites) and describes the properties of graphene nanoplatelets (GNPs) obtained dependently on intercalation/deintercalation conditions and reagents. Among the studied materials, the graphite intercalated with ammonium persulfate in sulfuric acid and expanded at 40 °C possesses the maximum ability for ultrasonic exfoliation in the presence of a surfactant. The exfoliation efficiency strongly depends on the content of water in sulfuric acid during the intercalation. The highest efficiency was achieved for the expanded graphite intercalation compound (EGIC) prepared in sulfuric acid containing diluted oleum, which may be explained by increased acidity of the medium and, correspondingly, redox potential of the persulfate compound. This is also related to increased amounts of oxygen groups in the GNPs obtained from the EGIC synthesized in 100% sulfuric acid and diluted oleum. Besides, the nature of surface groups on the GNPs strongly depends on the nature of a deintercalating reagent. Thus, the treatment of the EGIC with different nucleophilic molecules (such as water, ammonia, carbamide, hexamethylenetetramine, organic amines, etc.) can yield GNPs with various surface groups. The interaction between the EGIC and nucleophilic molecules does not only include the substitution of sulfate groups, but also redox reactions with participation of graphene layers. Depending on the nature of the nucleophile, those reactions can lead to the formation of different groups attached to the graphene surface. GNPs with almost pure surface were obtained when using ammonia and carbamide.

1. Introduction
Nowadays, graphene-based nanostructures are of great interest for many technological applications (e.g., chemical current sources, adsorbents, sensors, polymer composites, etc.) due to their unique thermal, electrical, optical and mechanical properties [1-3]. They are usually produced as multi- or, especially, few-layered graphene nanoplatelets (GNPs) comprised of thin stacks of platelet-shaped graphene sheets. These nanoparticles have a wide range of thickness (0.34-20 nm) and may consist of up to 30-50 (or even more) monolayers.

In this regard, surfactant-assisted ultrasonic exfoliation of well-ordered crystalline graphite and its subsequent dispersion in water or organic solvents has recently been widely used to mass-fabricate GNPs [4-5]. Usually, surfactants and solvents efficient in dispersing carbon nanotubes (CNTs) can
also be employed to obtain GNPs [6-7]. Therefore, previous studies performed on CNTs can provide useful information when working with GNPs.

However, the direct exfoliation of native graphite is not actually sufficiently effective. This process is slow, and only a small fraction of pristine graphite is transformed into thin (few-layered) GNPs. Separation of this few-layered fraction may become a serious problem in the large-scale fabrication of GNPs. Some promising approaches for the exfoliation of native graphite are under development nowadays; for instance, one of them is based on using supercritical carbon dioxide optionally combined with surfactants and ultrasonic irradiation [8].

To increase the efficiency of the exfoliation process, a certain kind of energy should be applied to a graphite material, either ultrasonically treated or not. In the case of applying chemical energy, some chemical transformations with large jumps in free energy take place. For instance, one treats starting graphite with a reagent and then with another one opposite in chemical nature, or after treating graphite with a reagent, the obtained graphite material is further processed under conditions, under which the previously treated material is highly unstable and decomposes quickly. It may be supposed that the free energy evolved during such chemical reactions can be transformed into the desired structural transformation. Sometimes, it is possible to find an effective combination of chemical reactions and physical treatments. The thermal expansion of graphite usually performed via oxidative intercalation of graphite and thermal shock resulting in chemical decomposition of graphite intercalation compounds accompanied by partial exfoliation appears to be a well-known example. However, the preparation of GNPs by ultrasonic exfoliation of common expanded graphite is not sufficiently effective, because rather thick platelets can only be obtained [9]. Much more interesting graphene materials were synthesized through exfoliation of so-called “highly thermally exfoliated graphite”, which, in its turn, was obtained by thermal treatment of ClF$_3$-intercalated graphite [10]. Few-layered graphene products so fabricated contain fluorine and are hydrophobic, which makes them attractive as additives to various non-polar matrix composite materials. However, using such highly aggressive and toxic intercalating reagents demands special precautions and is potentially dangerous. Besides, to obtain high-yield GNPs, graphite is intercalated with potassium, followed by treatment with a reagent (water or alcohol) that can vigorously react with that metal, as well as with microwaves and ultrasound [11]. Such a combination of chemical and physical actions results in great jumps in the free energy of the system at several stages and, theoretically, can promote structural transformations. However, GNPs obtained according to this technique are rather thick. Treatment with such aggressive reagent as oleum is (sulfuric acid containing free sulfur trioxide) was also tried for exfoliation of graphite to GNPs [12].

One promising approach to the exfoliation of graphite materials is the electrochemical exfoliation of graphite [13-15]. In this case, the intercalation is followed by spontaneous or ultrasonic exfoliation. The electrochemical methods basically allow for more flexible tuning of intercalation and exfoliation processes, because the oxidation potential, particle nature and intercalation medium can be varied independently (within the limits of their compatibility). However, these techniques are sophisticated for laboratory experiments and, moreover, for industrial production because of arising numerous difficulties (e.g., more complex equipment, problems with stability of electrode materials, and limitations of ion/molecule diffusion and mass transfer). Considering this fact, purely chemical and physical methods of graphite exfoliation seem to be more attractive for the large-scale production of GNPs. The problem is to find an efficient combination of chemical reactions and physical treatments ensuring the desired structural transformations.

Previously, we have proposed a new method for producing GNPs that consists in cold expansion of peroxodisulfuric acid-intercalated graphite, spontaneous pre-exfoliation with the formation of an expanded graphite intercalation compound (EGIC) having an apparent volume of 300-320 cm$^3$g$^{-1}$ of the starting material, and its ultrasonic exfoliation into GNPs [16].

It should be noted that the idea of better exfoliation of the EGIC compared to the other intercalated materials (e.g., thermally expanded (TEG) and oxidatively intercalated (OIG) graphites) has come
from the fact that the former consists of “live” GNPs that are not subjected to “hard” treatment like thermal shock. In this “live” expanded compound, the nanoplatelets are not only separated by vacant spaces, but also these spaces are filled with molecules of a reaction medium (acid or, after hydrolysis, water). When, for example, thermally expanded graphite is obtained after the thermal decomposition of intercalated graphite, the nanoplatelets have sintered edges which hinder their ultrasonic exfoliation.

Taking into account the aforementioned, the present work aims to compare the exfoliation ability of different graphite materials and study the properties of GNPs obtained under various intercalation/deintercalation conditions and reagents.

2. Research target and methods

Starting materials. Graphite GSM-1 (purity 99.9 %) was acquired from “Resurs-S” Ltd. (Ekaterinburg, Russia) and used as an initial material for obtaining GNPs. Ammonium persulfate (APS, analytical reagent grade) was purchased from “Reakhim” Ltd. (Moscow, Russia); it was used as an intercalation medium. To prevent aggregation of the synthesized GNPs in the system, surfactant NF (a sodium salt of naphthalenesulfonic acid/formaldehyde polycondensate) prepared according to the Russian National Standard GOST 6848-79 at “Pigment” Ltd. (Tambov, Russia) was employed.

Preparation of graphite intercalation compounds. The EGIC was synthesized through cold expansion of the graphite intercalated with an APS solution in 95 % and 100 % sulfuric acid, as well as in 100 % sulfuric acid containing 1% of free SO3, and used for ultrasonic exfoliation. The detailed description of the technique for obtaining the EGIC is given in our previous work [16].

As for the TEG and OIG, their production included oxidative intercalation of natural graphite in an acidic medium. In the case of the TEG, it was followed by rapid heating to high temperatures (thermal shock). Sulfuric acid combined with an oxidant (nitric acid, hydrogen peroxide, ammonium persulfate, etc.) is frequently used as intercalation medium. In some cases, other acids or oxidants can be used if the sulfur content in the TEG is undesirable [17-18].

Under laboratory conditions, the heat treatment of the OIG can be carried out by placing a sample into a hot muffle (900-1000 °C) for a short time. In the industrial production of the TEG, the thermal shock is performed by continuous blowing up the dust of dry OIG into a furnace heated by electricity or combustion of natural gas.

Sonication procedure and optical measurements. The sonication procedure was performed on an IL-10 device (electric power of the emitter 2 kW) under cooling a glass with a processed solution in a cold water bath. The optical density (absorbance) was measured with a KFK-3 photoelectric colorimeter (Russia) in a 1 cm cuvette at a wavelength of 500 nm.

In these systems, the Beer-Lambert law was obeyed, and thus, the light absorption coefficient (K, dm$^3$/g·cm) can be estimated according to Eq. (1).

$$K = \frac{D}{CL}$$

where D is the optical density (dimensionless), C is the graphite concentration (g/dm$^3$), and L is the path length of the cuvette (cm).

To eliminate any uncertainties caused by the weight of oxygen groups, all K values were calculated considering the weight of the initial graphite, unless other stated. It was found that in experiments conducted under the similar conditions, the K value correlates with the dispersion/exfoliation degree— the smaller the thickness of GNPs and the lower their aggregation, the higher the K value. Thus, these parameters were evaluated through the K. In our previous experiments, the K values lied in the range of 19-33 dm$^3$/g·cm for the multi-layered GNPs (15-30 layers), and 50-63 dm$^3$/g·cm for the few-layered GNPs (2-5 layered). Besides, we calculated, with some assumptions, that the maximum theoretically possible K value for the dispersion of randomly oriented flat, non-aggregated graphene monolayers is 65.83 dm$^3$/g cm [16].
3. Results and discussion

In the Figure 1, there is compared efficiency of ultrasonic exfoliation of different graphite materials in aqueous solutions of the surfactant NF. To estimate the acoustic power, we assumed that (according to the manufacturer information) the efficiency of electric-to-acoustic energy transformation for the ultrasonic installation used was about 50%. We related the acoustic power to the volume of the solution processed (i.e., in kWt-h/dm\(^3\)). It is a very approximate evaluation, since numerous technological factors affecting the exfoliation efficiency can hardly be considered correctly. From the Figure 1, it follows that the lowest exfoliation takes place for the TEG (which is known to be exfoliated better than common crystalline graphite). The OIG in sulfuric acid (after hydrolysis and washing with water) is exfoliated better than the TEG. There are data in the literature that the OIG so obtained (which is a common starting substance for producing the TEG) consists of pre-exfoliated crystals. Probably, this facilitates the ultrasonic exfoliation of this material compared to the common crystalline graphite. The EGICs in the system “graphite – sulfuric acid – ammonium persulfate (APS)” are exfoliated much better. This is natural, because the cold expansion process observed in these systems is extensive pre-exfoliation. The mechanism of the cold expansion was considered in our previous research [16]. Worm-like particles formed during this process consist of GNPs bound by edges, and it remains only to split these nanoparticles apart.

Figure 1. The ultrasonic exfoliation efficiency of different graphite intercalation compounds in aqueous solutions of the surfactant NF: 1 – TEG; 2 – OIG in 100 % sulfuric acid; 3 – EGIC in 95% sulfuric acid; 4 – EGIC in 100% sulfuric acid; 5 – EGIC in 100 % sulfuric acid containing 1 % of free SO\(_3\). A dashed line indicates a theoretical limit for obtaining flat, non-aggregated graphene monolayers (K = 65.83 dm\(^3\)/g.cm)

As seen on the Figure 1, the efficiency of the ultrasonic exfoliation of the EGICs strongly depends on the contents of water in sulfuric acid used as a medium for oxidative intercalation with APS.
Previously, we assumed that in those admixtures, water influences the acidity of sulfuric acid and, in its turn, the oxidative potential of peroxosulfate species [16]. The higher the oxidative potential, the more efficient the oxidation of the graphene framework and the cold expansion is. This also correlates with the increasing mass content of oxygen groups in the expanded graphite materials obtained after hydrolysis and washing (nearly 9 wt% for 100% sulfuric acid, 13 wt% for sulfuric acid containing 1.5% of free SO₃). We have studied in detail the effect of the water content in sulfuric acid used as a medium and solvent for APS on the K values obtained for GNPs. GNPs were synthesized through ultrasonic exfoliation of expanded graphite compounds in aqueous dispersion (3 g/dm³) without surfactant. Then, to determine the K values, samples of the multi-layered GNPs so obtained were suspended in the solution of the surfactant NF (concentration of graphene material 0.025-0.035 g/dm³), and additionally treated by ultrasound. The results are shown in the Figure 2. In this figure, the concentration of sulfuric acid below 100 % means simply “100% - content of water”. To plot in the same scale concentration of sulfuric acid above 100%, we calculated the “negative” content of water by dividing the content of free SO₃ by its molecular weight (80) and by multiplying the molecular weight of water (18). Thus, 101% sulfuric acid corresponds to the content of 1%-80/18=4.44% of free SO₃ (Figure 2).

![Figure 2](image.png)

**Figure 2.** Effective K values for GNPs samples obtained from graphite intercalated by APS in sulfuric acid with different content of water or free SO₃. The K values calculated with respect to dry weight of GNPs including oxygen groups. An aqueous solution of surfactant NF was used in the process of ultrasonic exfoliation

The Figure 2 demonstrates the pronounced effect of the concentration of sulfuric acid on ability of the EGICs for the ultrasonic exfoliation. Even little admixtures of water in sulfuric acid substantially retard ability to exfoliation. On the other hand, a small content of free SO₃ facilitates exfoliation. These data prove the interpretation made in our previous work [16].
The other essential factor determining the exfoliation effectiveness of the EGICs under the ultrasonic treatment, is the absence or presence of a surfactant. Generally saying, it is practically impossible to exfoliate common graphite materials in water without adding a surfactant, because of bad wettability of graphene planes with water. On the other hand, graphite oxide (GO) is spontaneously exfoliated in water due to large amounts of oxygen groups attached to the graphene skeleton. The expanded graphite materials obtained by the cold expansion of graphite intercalated with APS in sulfuric acid after hydrolysis contain 9-13 wt% oxygen groups. This in insufficient for spontaneous exfoliation of the GO in water, but greatly facilitates the ability for the ultrasonic exfoliation in pure water and aqueous solutions of surfactants compared to common graphite materials. For instance, the morphology of the EGICs is very similar to that of the TEG (worm-like particles, length up to 1-2 cm). However, as it was shown in the Figure 1, the TEG is much less exfoliated than the EGICs, which can be explained by the absence of oxygen groups in the TEG (they are eliminated after the high-temperature expansion process).

Principally, there are different methods of post-treatment of EGICs prior to ultrasonic exfoliation. The simplest one is hydrolysis and washing with water. Under these conditions, molecules of water behave as nucleophile and react with the positively charged graphene skeleton. As a result, the hydrolyzed product contains the oxygen groups. However, oxidized graphene layers are very reactive and easily interact with a lot of substances, even with inert hydrocarbons. In all the cases, the initial yellow-to-khaki color of the EGICs changes to dark-gray. One could think that different graphene substances can be obtained after post-treating the EGICs by varying reagents. However, our experiments indicate that in most cases it is not true. It seems that the treatment of the EGICs with water, alcohols and a large variety of organic compounds essentially result in similar, if not the same, product, namely, graphene containing oxygen groups. The reason of this is that positively charged graphene layers in the EGICs are very strong oxidizers, and the redox process is the first one occurring after the interaction with the organic compound. Usually, almost all organic compounds (with rare exceptions) contain hydrogen atoms connected to carbon. Thus, any oxidation process in an oxygen-containing medium (sulfuric acid) generates water, and, finally, almost the same oxygen-containing graphene product as after the direct hydrolysis with water can be obtained.

If one wants to obtain graphene products with different nature, the EGIC must be treated with nucleophiles which cannot be easily oxidized, or the oxidation reaction must not be the first one. There is a very restricted assortment of such reagents. We used, with some success, ammonia, urea, and hexamethylenetetramine. In the case of ammonia, the first stage of its interaction with the EGIC is protonation by sulfuric acid. The final graphene material obtained after the treatment of the EGIC with dry gaseous ammonia does not contain oxygen groups. It is obvious that some redox processes should occur for the reduction of the oxidized graphene skeleton, but now it is not possible to identify the nature of the processes taking place. Principally, the similar process occurs when the EGIC reacts with urea. In this case, carbon dioxide evolves, and amide groups react as base, substituting the sulfate functionality. However, contrary to the hydrolysis of the EGIC, its ammonolysis with gaseous ammonia or urea results in obtaining hydrophobic GNP s, the weight of which is precisely equal to the weight of the initial graphite. This indicates that no functional groups are attached to the surface of the GNP s so obtained. It may be that the positive charge of oxidized graphene layers is neutralized due to the redox reaction with ammonia or amide groups.

In the Figure 3, the plots of K vs. time of ultrasonic treatment for the samples of the EGICs deintercalated with ammonia (plot 3) and urea (plot 2) are demonstrated and compared to the original graphite (plot 1). In these experiments, the original graphite was GSM-2, and dimethylacetamide was used as a solvent instead of an aqueous surfactant solution.
Figure 3. K vs. ultrasonic treatment time dependencies obtained for the EGIC samples deintercalated with ammonia (plot 3) and urea (plot 2) compared to the original graphite (plot 1). The concentration of the graphite materials in dimethylacetamide is 0.5 g/dm³.

One can see that after the cycle “intercalation→expansion→deintercalation”, the ability of the graphite material for the exfoliation considerably increases, which can be explained by the pre-exfoliation of graphite after that cycle. Multi-layered GNPs were obtained in these experiments, as indicated by K values.

However, the variants of deintercalation of EGICs with ammonia or urea, resulting in obtaining hydrophobic GNPs, are more complicated for scaling because of the evolution of heat and multiple technological stages. Up today, the hydrolysis remains the most simple and practical method for post-treating EGICs to synthesise GNPs, if the presence of surface oxide groups is allowable or favorable. Dependent on the absence or presence of surfactants, multi- or few-layered GNPs can be obtained by ultrasonic exfoliation. The typical SEM and TEM images of different kinds of GNPs so obtained are shown in the Figures 4-7.

Figure 4. SEM images of multi-layered (15-25 layers) GNPs obtained by ultrasonic exfoliation of the hydrolyzed EGIC in water without surfactant.
Figure 5. TEM images of multi-layered (15-25 layers) GNPs obtained by ultrasonic exfoliation of the hydrolyzed EGIC in water without surfactant.

Figure 6. SEM images of few-layered (3-5 layers) GNPs obtained by ultrasonic exfoliation of the hydrolyzed EGIC in water with the surfactant.

Figure 7. TEM images of few-layered (3-5 layers) GNPs obtained by ultrasonic exfoliation of the hydrolyzed CEGIC in water with the surfactant.
4. Conclusions
In the process of cold expansion of the graphite using the APS, a covalent attachment of hydrosulfate groups to graphene layers probably takes place. Under the sonication, the cold EGICs are exfoliated into GNPs more easily than those ones obtained after hydrolysis or thermal expansion. The efficiency of the ultrasonic exfoliation of those EGICs strongly depends on the content of water in sulfuric acid (as oxidative intercalation medium): smaller amounts facilitate the process; this may be explained by increased acidity of the medium and redox potential of the APS compounds, as well as by larger amounts of oxygen groups available in the obtained GNPs.

The nature of groups available on the surface of the GNPs depends on the nature of a deintercalating reagent. This fact can be used regarding further applications of the synthesized GNPs (e.g., supercapacitor electrodes, composite materials, etc).

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