Chemistry and Technology for Large-scale Synthesis of Graphene Nanoplatelets

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Abstract

Aim: To determine the synthesis conditions under which it would be possible to obtain high-quality graphene nanoplatelets (GNPs) on a large scale. **Materials and Methods:** The ability of graphite for cold expansion and exfoliation was found to depend on the degree of defectiveness of its crystal structure. Highly defective graphite structures are not prone to intercalation, exfoliation, and expansion, whereas perfect ones can be transformed more easily, which is important when setting up a large-scale pilot production of graphene-based nanomaterials. **Results and Discussion:** It is assumed that for efficient exfoliation of graphite materials, the power of ultrasonic radiation should be above a certain threshold value, whereas the concentration of that power in the working volume of the flow-through chamber and the contact time for the treated solution in that chamber should also exceed certain thresholds values. **Conclusion:** Furthermore, the following stages are proposed to transform the expanded graphite intercalation compound (EGIC) particles into GNPs: (1) Irreversible separation of worm-like EGIC particles into coarse GNPs and tight aggregates thereof, (2) irreversible separation of those GNPs and aggregates into thin GNPs and tight aggregates thereof, (3) irreversible separation of the tight GNP aggregates into smaller-size ones and individual thin GNPs, (4) reversible transformation of the coarse GNPs into exfoliated ones, and (5) reversible formation and decomposition of weak thin GNP aggregates. The efficiency and direction of those transformations were found to depend on the power of the ultrasonic radiation and the concentration of the processed graphite material.

Key words: Cold expansion, graphene nanoplatelets, graphite intercalation compounds, synthesis, ultrasonic exposure

INTRODUCTION

Graphene is one of the most promising carbon nanomaterials. The widespread use of graphene-based materials in various technical fields puts the development of technologies for their industrial production on the agenda. As far as it is known, for the first time, a graphene single layer (classically representing graphene) was obtained over substrates by transfer from single-crystal graphite using an adhesive tape. Further on, more advanced methods for growing and depositing graphene single layers on substrates have been developed, thereby allowing to create graphene electronic devices.[1-7] However, the present paper does not consider this field of technology and deals only with the issues of mass production and application of graphene nanomaterials in the form of dispersions, powders, and composites.

It is known that flat graphene single layers are stable over substrates, whereas in the free form they are unstable and tend to deform (e.g., to a roll up). However, considering graphene dispersions in condensed media, the graphene single layers can be stabilized due to their interactions with the environment. For instance, to stabilize such dispersions in aqueous and organic environments, surfactant adsorption is widely used.[8,9] Under certain conditions, the conversion of straightened graphene layers into rolls and back can be observed.[10] Nevertheless, the structure of graphene dispersions and powders synthesized in the laboratory and

offered by different manufacturers is usually far from perfect. In these materials, graphene particles are deformed to a greater or lesser extent and have ragged edges, structural defects as well as foreign atoms and chemical groups attached to the graphene skeleton. Besides, these dispersions and powders often possess significant impurities of other carbon structures. However, in many cases, this does not prevent their successful use and sometimes even improves the efficiency of their application. For instance, after alkaline activation, a highly defective graphene-like material synthesized via thermal (in this case, microwave) decomposition of graphite oxide (GO) possesses a high capacitance and can be employed in electric double-layer capacitors,[11,12] whereas graphene materials with a perfect structure cannot be activated by this method.

At present, the terms "graphene," "graphene materials," and "graphene nanoplatelets (GNPs)" are used to nominate the technical graphene materials, which, strictly speaking, do not present graphene in its classical sense. The mass production and application of such materials as single layers is often too expensive. Besides, technical compounds of graphene powders and dispersions produced by various companies are almost never monodisperse. However, GNPs, which consist of several or even several tens of layers, have been successfully used mainly as components of composite materials in a number of fields, of technology. Commercially available, GNPs can be divided into two types: Few-layered (comprised about 1-10 layers) and multi-layered (comprised about 10-60 layers).

In this regard, the question of nomenclature arises as to starting from which number of layers graphene and graphite should be distinguished from each other. As an example, such a distinction can be made based on the lattice vibrational properties of materials.[13] If the number of graphene layers in the material does not exceed 7-10, this material may be considered as graphene, but if it does, the material presents graphite. However, such theoretical criteria are not so important for technical applications, only the target performance characteristics (e.g., electrical conductivity, thermal conductivity and strength achieved by introducing a given amount of carbon nanomaterial into the polymer matrix, double-layer capacitance, etc.) really matter.

Nowadays, numerous methods for producing graphene materials (in particular, GNPs) have been developed. They make it possible to obtain nanoproducts with different quality indicators, which are to a varying extent suitable for scaling up to industrial production. Chemical/electrochemical reduction or decomposition (thermal, microwave, photochemical) of GO is one of the most flexible techniques for fabricating graphene and graphene-based nanocomposites.[14-19] When dissolved in water, GO spontaneously exfoliates to monolayers, thereby enabling the synthesis of graphene-based nanocomposites by adding various functional components to the GO aqueous solution or chemically modifying the GO layers. In the subsequent chemical reduction, the added nanoparticles

and groups become embedded into the structure of the resulting graphene nanocomposite. However, this method has two disadvantages: (1) The synthesis of high-grade GO compounds (water-soluble and monolayer-exfoliated) is rather time-/labor-consuming and hard to scale up and (2) the structure of graphene materials obtained from the GO is very defective.

There exist methods based on chemical vapor deposition of graphene layers on various substrates to create electronic devices. However, in most cases, the attempts of using them for mass producing graphene in powder form have yielded very defective and heterogeneous materials. Therefore, from our viewpoint, techniques based on exfoliation of graphite and different graphite materials could be more suitable for that purpose.

The exfoliation of crystalline (usually natural) graphite is most often carried out by sonication of a graphite suspension in organic solvents or aqueous surfactant solutions.[8,20] In the former case, surfactants highly effective in stabilizing CNTs dispersions in water (e.g., sodium dodecyl benzenesulfonate, Triton X-100, and others) can be used. In such experiments, the output of thin GNPs related to the weight of the original graphite is low, and the resulting GNP concentration is very low as well (about a few hundredths of grams per liter). The use of fluoro-organic surfactants can improve the effectiveness of graphite exfoliation.

The exfoliation can also be increased by employing pre-exfoliated graphite materials such as thermally expanded graphite (TEG) or highly exfoliated TEG obtained via thermal treatment of fluoro-containing graphite compounds.[6,21] There are a number of papers describing the graphite exfoliation under the conditions of electrochemical intercalation in various electrolytes including ionic liquids.[22-26] Some researchers have reported about GNPs synthesized by alcoholysis of graphite intercalation compounds with metallic potassium.[27,28] Graphite can also be exfoliated by grinding in a ball mill in the presence of solids which are supposed to introduce between the graphene layers and prevent them from closing.[29,30] Treating graphite in supercritical CO_2, including surfactant addition and ultrasound exposure, could be another very interesting and promising method.[31,32] Besides, graphene can be obtained by grinding graphite in a planetary mill in the presence of liquid CO_2.[33] Under these conditions, the CO_2 molecules are chemically attached to the graphene layers, thereby resulting in the formation of products which spontaneously spark when exposed to air.

Typically, when grinding graphite in aqueous surfactant solutions or organic liquids, the fraction of few-layered graphene obtained in a single technological cycle is extremely low and does not exceed 1-3% of the weight of original graphite. To develop large-scale production of GNPs via exfoliation of graphite materials, it is desirable that the GNP yield is 100% of the weight of original graphite, which

would exclude the very costly operation of particle fraction separation. Furthermore, the process must provide various types of good quality GNPs (few- or multi-layered) in the required range without ballast impurities, admit scaling, and be environmentally friendly.

In our prior work,[34] we have proposed a method for fabricating GNPs through ultrasonic exfoliation of a graphite material obtained after cold expansion of graphite intercalated using an ammonium persulfate solution in sulfuric acid and showed that, despite the similarity in the particle morphology, expanded graphite intercalation compounds (EGICs) are exfoliated by ultrasound considerably easier than TEG. Besides, it has been found that in the laboratory, it is possible to obtain GNPs from almost any graphite material under sufficiently intense sonication. However, as shown by our experience of developing a pilot technology for producing GNPs, the ultrasonic treatment stage appears to be a bottleneck that restricts productivity of the entire process. Therefore, searching for or and synthesizing easily exfoliated graphite materials is important for developing large-scale industrial production of graphene-based materials.

Considering the aforementioned, the objective of the present research is to determine the optimum synthesis conditions under which it would be possible to obtain high-quality GNPs through the ultrasonic exfoliation of an EGICs on a large scale.

MATERIALS AND METHODS

Starting materials and reagents

In the present research, the following starting graphite materials were used: GSM-1, GSM-2, GAK-1, and colloidal ball-milled C-0 (all – from Resource-C Ltd., Ekaterinburg, Russia). Their characteristics are presented in Table 1. Among these materials, GSM-1, with its highest particle size, has the less defective structure, whereas C-0, with its lowest particle size, possesses the most defective structure.

Ammonium persulfate (APS, 98 %, reagent grade) and sulfuric acid (95%, reagent grade) were obtained from Reakhim Ltd. (Moscow, Russia), whereas oleum (65 %, reagent grade) was acquired from pigment Ltd. (Tambov, Russia). Sodium salt

Table 1: Characteristics of the starting materials used in the study

Graphite mark	Carbon content (%)	Particle size (mm)
GSM-1	99.9	0.1-0.5
GSM-2	99.5	0.1-0.2
GAK-1	99.5	0.08-0.15
C-0	99.0	≈0.004

of naphthalene sulfonic acid/formaldehyde polycondensate (NF), polyvinylpyrrolidone (PVP, M ≈10,000 g/mol), and Triton X-100 were purchased from Pigment Ltd. (Tambov, Russia), AppliChem GmbH (Darmstadt, Germany) and Dow Chemical Co. (Midland, MI, USA), respectively, and employed as surfactants.

GNP synthesis procedure and surface measurements

The details of the GNP synthesis procedure performed at NanoTechCenter Ltd. (Tambov, Russia) are presented in our previous work.[34] First, the starting graphite materials were oxidatively intercalated using an APS solution in sulfuric acid or diluted oleum (obtained by mixing concentrated sulfuric acid with oleum in various proportions). After that, the cold EGICs were performed at 40°C for 3 h to obtain EGICs. The latter were hydrolyzed and rinsed in aqueous suspensions (with or without the addition of the surfactants) to remove the acid (so-called "de-intercalation)."

Then, the EGICs were subjected to sonication for their exfoliation to obtain dispersed few- or multi-layered GNPs. The ultrasonic treatment was carried out under laboratory and industrial conditions. Under the laboratory conditions, the aqueous dispersions (volume 1.0-1.5 dm^3 each) were sonicated using an IL-10 ultrasonic device (Ultrasonic Techniques-Inlab Ltd., Saint-Petersburg, Russia; electric power 2 kW) equipped with a mechanical mixer (400-500 rpm) and cooling running-water bath. Under the industrial conditions, the sonication of the dispersions (volume 20-100 dm^3 each) was performed using a unit consisting of three Bulava-P flow-through ultrasonic dispersers (Center for Ultrasonic Technologies Ltd., Biysk, Altay Region, Russia, with a total electric power of 16 kW). The temperature of the processed solutions was fixed by controlling the flow rate of cooling water.

Light absorption coefficient and surface measurements

To assess the efficiency of ultrasonic exfoliation of different graphene-based materials, a certain easily measured parameter is required. Generally speaking, the average thickness of GNPs or thickness distribution of their particles, estimated based on transmission, and atomic force spectroscopy measurements could be the physically precise criterion for exfoliation efficiency.[8,10,20,30,35-40] Besides, for sufficiently thin (i.e., few-layered) GNPs, Raman spectra can be used for indirectly estimating their thickness.[13,41-46] However, the above-mentioned methods are too complicated and expensive for mass analysis. In this regard, we have proposed an indirect method consisting in determining the effective light absorption coefficient (K, dm^3/g cm) of GNP dispersions, for which the Beer-Lambert law is obeyed,[47] considering the ideal GNP model and related assumptions.

Since the Beer-Lambert law was obeyed for all the systems under study, that method was used in the present research as well. The optical density of the obtained GNP dispersions was measured on a KFK-3 photoelectric colorimeter (ZOMZ Ltd., Sergiev Posad, Moscow Region, Russia) in a cuvette with 1 cm optical path length at a wavelength of 500 nm. To calculate the K, the carbon weight without oxide groups was considered. The studied GNP dispersion samples were diluted with water or a surfactant solution (Triton X-100, 1.0 g/dm³) in order that the measured density lied in a suitable range (0.1-1.0).

As we have previously determined,[47] calculated *K* values decrease with an increase in the thickness (number of graphene layers) of randomly oriented GNP dispersions. For GNPs with rather large lateral dimensions, their aggregation, and non-flat shape appear to be the main factors causing the deviation of measured *K* values from calculated ones. For those reasons, the former are always smaller than the latter. However, the proposed method is suitable for comparison of samples obtained when changing a certain process parameter under otherwise identical conditions.

The morphology of the GNP surfaces was studied by scanning electron microscopy (SEM) using a Neon 40 instrument (Carl Zeiss Jena GmbH, Jena, Germany), whereas the number of graphene layers in the GNPs was estimated by transmission electron microscopy (TEM) on a JEM-200CX instrument (JEOL Ltd., Tokyo, Japan).

RESULTS AND DISCUSSION

The experiments demonstrated that the graphite materials used herein are susceptible with varying degrees to intercalation and cold expansion [Figure 1]. When treating the GSM-1, GSM-2 and GAK-1 materials with the APS solution in sulfuric acid, blue GICs are initially formed followed by the formation of yellow-brown (in the cases of GSM-1 and GSM-2) and brown (in the case of GAK-1) compounds as a result of the expansion. Unlike the above-mentioned materials, the C-0 colloidal graphite material does not change the color and volume after treating with the intercalating solution and aging at 40°C. The apparent volume of the EGICs correlates with the size of particles of the starting graphite materials and, correspondingly, with their degree of defectiveness: GSM-1 > GSM-2 > GAC-1 >> C-0. Based on this finding, it is probable that the intercalation of the C-0 material does not occur under the cold expansion conditions. From optical measurements, it was found that the sonication of this graphite after the oxidation thereof does not lead to the formation of a superfine product. It may be due to the fact that in this case, the intercalation of C-0 does not depend on the defectiveness of its structure. If the oxidation takes place, it probably affects only the particle surface. For the other graphite, the sonication of the EGICs in the aqueous suspensions (after the hydrolysis and acid removal) results in exfoliation with the formation of GNPs.

Figure 2 shows the increasing dependencies of the *K* values obtained for GNP dispersions formed under the ultrasonic treatment of the EGICs in aqueous solutions of various surfactants on the sonication time. As can be seen, among the surfactants used herein, Triton X-100 is the most efficient one. Furthermore, these *K* values also depend on the concentration of the graphene material (G): When increasing the concentration from 1.0 to 2.0 g/dm³ in the presence of the same surfactant (Triton X-100), the *K* values considerably decrease. This finding may be explained by irreversible exfoliation of worm-like EGIC particles (which represent aggregates of tightly bound GNPs) into separate nanoplatelets in the systems under study, followed by dynamic equilibrium established between the nanoplatelets and weak aggregates. The higher the concentration of the graphene material, the more the steady state is shifted toward the GNP aggregates.
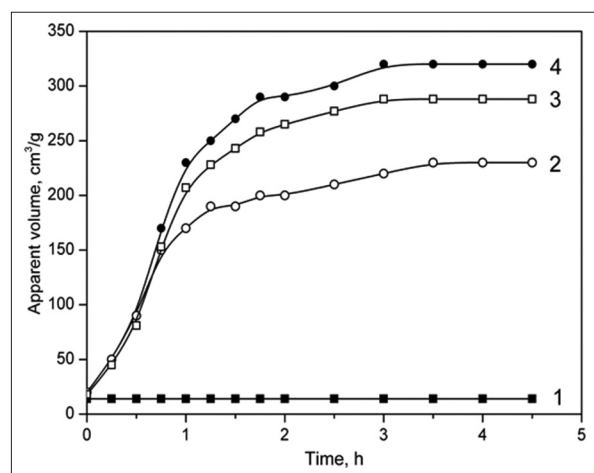
Figure 1: Dependencies of the apparent volume on the time of expansion at 40°C for the APS-intercalated graphites. Medium – 100 % sulfuric acid; 1 – C-0; 2 – GAK-1; 3 – GSM-2; and 4 – GSM-1
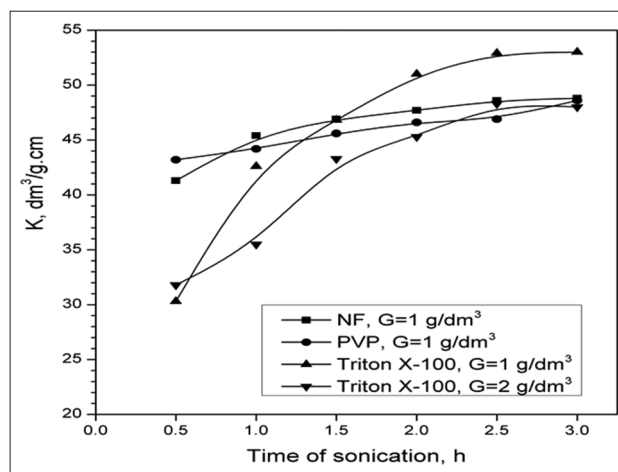
Figure 2: Dependencies of the light absorption coefficient (*K*) of the GNP dispersions on the time of sonication of the expanded graphite intercalation compounds in the aqueous solutions of different surfactants.

When performing the laboratory experiments, there is no problem of diluting the system as required for minimum aggregation. However, the dilution means decreasing the productivity of the ultrasonic exfoliation stage, which is the bottleneck of the overall process. To achieve reasonable productivity on an industrial scale, a smart approach is needed.

Considering these features of the ultrasonic dispersion of the EGICs, a processing scheme can be proposed to increase the productivity of the ultrasonic exfoliation of graphite materials. First, the concentrated system should be sonicated to break tight GNP aggregates (i.e., particles of the initial EGIC) and transform them into weak aggregates. Then, the resulting dispersion must be diluted and sonicated once again to break the weak aggregates (these aggregates are separated significantly faster than the tight aggregates). As a result, the ultrasonic power required for preparing GNP dispersions with the desired K values can be reduced, and the overall productivity can be substantially increased.

The conducted experiments showed that the sonication of the EGICs in the pilot industrial ultrasonic device runs somewhat differently than in the laboratory device. In the industrial case, the K values are significantly higher than those obtained in the laboratory experiments at the same graphene and surfactant concentrations in the dispersions (3.0 g/dm³ graphene, and 4 g/dm³ Triton X-100), as can be seen from the dependencies of K values on the electrical power of the ultrasonic emitters related to the volume of the treated dispersion (i.e., specific electrical power) presented in Figure 3. From this Figure 3, it can be observed that the greater the power in the ultrasonic device chamber, the more efficiently the exfoliation occurs.

To understand the obtained results, it should also be taken into account that as shown by our experiments on sonication of the
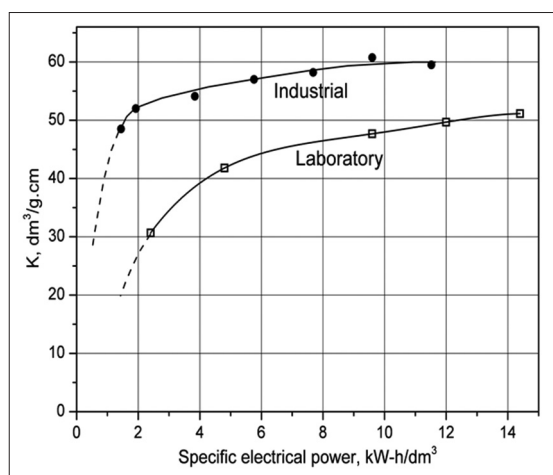
Figure 3: Dependence of the light absorption coefficient (*K*) on the specific electric energy of the ultrasonic emitters per unit volume of the processed dispersions for the laboratory and industrial ultrasonic devices. Concentrations: Graphene - 3 g/dm³, and Triton X-100 - 4 g/dm³

same volume of the dispersions using the ultrasonic units with different number of emitters, when increasing the number of emitters, the exfoliation efficiency grows faster than it could be expected from the arithmetic sum of the emitter power. The same effect was observed when decreasing the volume of the dispersions for the same set of ultrasonic emitters. Based on the conducted experiments, it can be assumed that for efficient exfoliation of graphite materials, the power of ultrasonic radiation should be above a certain threshold value, whereas the concentration of that power in the working volume of the flow-through chamber and the contact time for the treated solution in that chamber must also exceed certain thresholds values. If the values of those parameters are not sufficient, the exfoliation efficiency sharply decreases, and the lack of power cannot be compensated by increasing the time of the ultrasonic treatment.
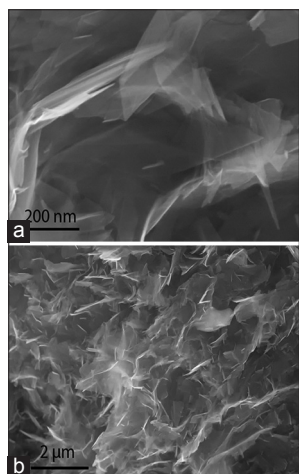
Thus, the following transformation stages can be proposed to elucidate the experimental transformation of the EGICs into the GNPs through the ultrasonic exfoliation: (1) Irreversible transformation of the worm-like EGIC particles into coarse GNPs and tight aggregates thereof, (2) irreversible transformation of those GNPs and aggregates into thin GNPs and tight aggregates thereof, (3) irreversible transformation of the tight GNP aggregates into smaller-size ones and individual thin GNPs, (4) reversible transformation of the coarse GNPs into exfoliated ones, and (5) reversible formation and decomposition of weak thin GNP aggregates.

Apparently, the concentration of the ultrasonic power mostly affects stages 4 and 5. If the concentration the concentration of that power in the working volume of the flow-through chamber and the contact time for the treated solution in that chamber are not sufficient, the exfoliation of coarse GNPs that has already started is reversed after the particles have been released from the zone of high ultrasonic radiation power. After a certain time, arisen cracks (which began bundle) spontaneously merge due to the elasticity of the GNPs (which is probably accompanied by ejection of the adsorbed surfactant molecules from the exfoliation zone). This may take place because of weak ultrasonic radiation that penetrates through, like it does through waveguides, into the tank containing the processed dispersion. The greater the dispersion volume, the less the effective time of the dispersion contact with the zone of powerful ultrasonic radiation, and thus, the reversibility of process (4) leads to a steady state, at which an increase in the time of the ultrasonic treatment does not result in a significant improvement of the product quality (if the "quality" is meant as the average GNP thickness and the lack of tight GNP aggregates).

Furthermore, if the ultrasonic power values are not sufficient, this does not eliminate the reversible aggregation at step (5), when equilibrium (steady-state condition) is established between the thin GNPs and their weak aggregates. The less the initial weight concentration of the graphene material, the more that equilibrium is shifted to the left, which seems to

be favorable for producing a product of quality. However, when working with low concentrations, the productivity of the technological process decreases, and moreover, very dilute dispersions are unsuitable for their subsequent use (e.g., for synthesizing nanocomposite materials). It should also be considered that in weak GNP aggregates containing the adsorbed surfactant molecules; the GNP surface is available for various functionalization and modification reactions (e.g., for depositing polyaniline and metal oxide nanoparticles oxides, and reactions involving hydroxyl, carboxyl, and epoxy groups). Thus, it can be assumed that in many applications, the use of GNP dispersions in the form of weak aggregates is quite acceptable, and there is no sense in working with very low concentrations. Under the conditions of the experiments described herein, the optimum weight concentration of graphene during the ultrasonic exfoliation can be chosen within the range of 3.0-5.0 g/dm³ (depending on the surfactant used).

Figures 4 and 5 present typical SEM and TEM images, respectively, of the GNPs, obtained through the ultrasonic exfoliation of the EGICs in the aqueous surfactant (Triton X-100) solution. As can be seen from Figure 4, the GNPs are
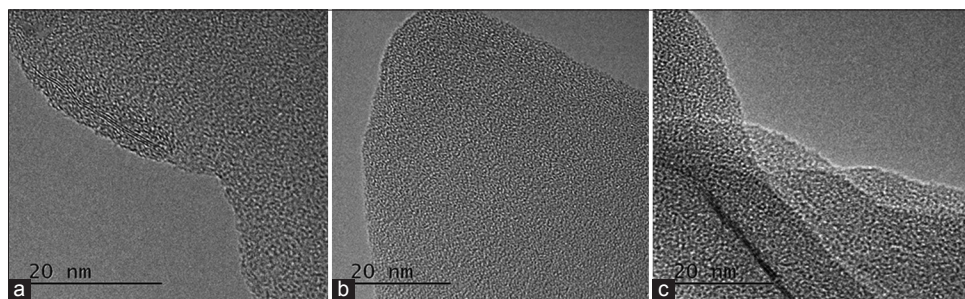
strongly deformed which appears to be one of the reasons (along with aggregation) for the decrease in the observed K values compared with the calculated data. In Figure 5, it can be seen than in some regions of the GNPs surface, the number of graphene layers in the GNPs can be directly counted at the folds.

For the GNP samples synthesized herein in the presence of surfactants, the number of layers was found to range from 2 to 5. It is possible that these samples contain single graphene layers but it is difficult to observe them based on the proposed method.

CONCLUSION

The ultrasonic exfoliation of EGICs obtained by cold expansion of various graphite materials was investigated, and the optimum conditions for the pilot industrial production of GNPs were determined. It was found that the size (and correspondingly, the defectiveness) of graphite particles affects the cold expansion process: The materials with larger particle sizes (less defectiveness) are expanded better.

The large-scale GNP synthesis comprises graphite intercalation and cold expansion with the formation of worm-like particles, their irreversible exfoliation under sonication and reversible aggregation with the formation of weak aggregates. The higher the ultrasonic power applied per unit volume of the suspension, the more efficiently the exfoliation occurs. As regards the technological aspect (large-scale GNPs production), to increase the productivity of the ultrasonic exfoliation of the EGICs, a two-step treatment was proposed. At the first stage, the concentrated suspension is sonicated, whereas, at the second stage, the obtained dispersion is diluted and repeatedly sonicated to break the weak aggregates.

Figure 4: Scanning electron microscopy images (at different magnifications – [a and b]) of the few-layered graphene nanoplatelets obtained by sonication of expanded graphite intercalation compounds from the GSM-2 graphite material in the presence of the Triton X-100 surfactant

ACKNOWLEDGMENT

Figure 5: Transmission electron microscopy images of different regions (a-c) in the few-layered graphene nanoplatelets obtained by sonication of expanded graphite intercalation compounds from the GSM-2 graphite in the presence of the Triton X-100 surfactant

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