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SYNTHESIS OF GRAPHENE NANOPLATELETS FROM PEROXOSULFATE GRAPHITE INTERCALATION COMPOUNDS

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Ultrasonic exfoliation of expanded graphite compound obtained by cold expansion of graphite intercalated with peroxodisulfuric acid was shown to allow the creation of graphene nanoplatelets with thickness of about 5-10 nm. The resulting graphene material contained surface oxide groups. The expanded graphite intercalation compound was exfoliated by ultrasound much easier than thermally expanded graphite. A mechanism for the cleavage of graphite to graphene nanoplatelets is proposed. It includes: (1) formation of ionic graphite compound intercalated with peroxodisulfate anions; (2) decomposition of intercalated peroxodisulfate anions with formation of active free radicals which (3) attach covalently to carbon atoms; (4) cleavage and expansion of the graphite crystal due to the thickening of the peripheral region of graphene layers and release of gaseous oxygen between graphene layers; (5) hydrolysis of the expanded graphite compound; and, finally, (6) ultrasonic breaking of graphene nanoplatelet agglomerates.

Keywords: graphene, graphene nanoplatelets, peroxodisulfuric acid, graphite intercalation compounds, cold expansion.

1. Introduction

Currently graphene and graphene-based nanocomposites attract great attention. Both pure graphene and nanocomposite materials, such as graphene/carbon nanotubes, graphene/polyaniline, graphene/metal oxides and more complex systems, containing different functional groups, structures, and particles are currently being investigated. By definition, graphene is a monolayer of carbon atoms. However, sometimes "graphene" is used as a general term including few-layered and multi-layered graphene materials. Graphene nanoplatelets are one of the graphene materials produced by a number of carbon nanomaterial manufacturers, for example, xGnP by XG Sciences (http://xgsciences.com/). This is multi-layered graphene in the form of flakes or plates with thickness of 1–20 nm and size in plane of 1–50 microns (various grades available). Among the most promising applications of xGnP XG Sciences claims are for electrode materials for supercapacitors, anode materials for lithium batteries, conductive ink, heat-conductive films and coatings, additives for light composite materials, films and coatings shielding electromagnetic radiation, substrates for chemical and biochemical sensors, packing materials with improved barrier properties, additives which increase the strength of concrete, additives for composites with metal matrix. Furthermore, as follows from published data, the addition of graphene nanoplatelets into polymer composite materials, besides increasing electrical and heat conductivity, also increases strength, resistance to cracking, fire, wear and reduces the friction coefficient. Using graphene is highly efficient as an additive to liquid, consistent and solid lubricants. For example, the introduction of graphene nanoplatelets to polytetrafluoroethylene reduces friction wear by more than three orders of magnitude [1]. There are several reviews on graphene materials, their methods of preparation and applications in various fields [2-5].

It should be noted that although the terms “nanoplatelets”, “size in plane”, “diameter in plane” are often used, in fact, these particles usually are not flat but deformed flakes of irregular shapes, often aggregated.

Theoretically, graphene monolayers provide the highest performance in a variety of applications. However, graphene monolayers are very expensive and it is difficult to work with them because of their tendency to agglomerate in dry form and in suspensions. Currently, graphene monolayers were obtained as deposits on different supports or as dilute dispersions stabilized with surfactants in solvents. The use of such dilute graphene monolayer dispersions as additives into composite materials is problematic because of need to remove surfactant, which is strongly adsorbed on the surface of graphene. Multilayered graphene, in the form of graphene nanoplatelets, provides better effect-to-cost ratio than graphene monolayers in most applications, with the exception of nanoelectronics. In many applications, such as polymeric composite materials, graphene nanoplatelets and carbon nanotubes give similar results.

An analogy with single-walled and multiwalled carbon nanotubes (CNTs) can be used. Although by a number of parameters single-walled CNTs are most efficient, currently they are too expensive, and using multi-walled CNTs provides better effect-to-cost ratio. For some applications, graphene nanoplatelets can be more effective than multiwalled CNTs, due to higher electric and heat conductivity and low coefficient of friction.

For mass application of graphene-based materials, one of the key issues is the development of an effective, inexpensive and scalable process for their production. Various methods for obtaining graphene materials were reviewed in [2-5]. The first group of methods is based on the cleavage of crystalline graphite, expanded graphite or graphite intercalation compounds by ultrasonic treatment of the graphite materials suspended in organic solvents or in water in presence of surfactants. Thin flakes, consisting of single or multiple layers of graphene, were thus obtained by these methods.

In the second group of methods, crystalline graphite or thermally expanded graphite is oxidized to graphite oxide, which spontaneously exfoliates to monolayers when dispersed in water. Then graphite oxide is reduced to graphene in presence of substances, preventing the collapse of graphene layers back into the graphite structure. Such substances may be surfactants, nanoparticles of various compounds or water-soluble polymers.

Ultrasonic exfoliation of various forms of graphite usually gives graphene nanoplatelets with a wide distribution of thicknesses, containing some amount of graphene monolayers. Concentration of the graphene nanoplatelets in dispersions obtained by these methods is very small, on the order of 0.01–0.1 g/l. Furthermore, the content of surfactant in the dispersions obtained is usually much higher than the content of graphene materials itself. For these reasons, the mass production of graphene materials by these methods is rather expensive, which is reflected in high cost of various forms of graphene materials, including graphene nanoplatelets offered by manufacturers of carbon nanomaterials.

Methods of obtaining graphene via graphite oxide, principally, are most flexible for the synthesis of various graphene-based nanostructures and other nanosized components [5]. However, the known methods of graphite oxide syntheses, for example by oxidation of crystalline graphite with potassium chlorate in nitric acid or potassium permanganate in sulfuric acid, are very expensive, take long time and become dangerous (risk of explosion) when performed at larger scales. So the cost of graphite oxide is also high.

In [6-8], graphite material was described called as “microflaky graphite”. In modern terminology, this material was graphene nanoplatelets. In these studies, the key step was intercalation of graphite with solution of peroxide compounds (peroxomonosulfuric acid, peroxodisulfuric acid, ammonium persulfate) in sulfuric acid. Under certain conditions, the graphite intercalation compounds were formed containing intercalated anions of peroxosulphuric acids (peroxomonosulphuric or peroxodisulfuric). These compounds are unstable at room temperature and decompose, forming molecular oxygen between graphene layers, swelling the crystal, so a phenomenon similar to the thermal expansion of graphite was observed, but at room temperature. The extent of such “cold” expansion, defined by the apparent volume, is close to thermal expansion which occurs at high-temperature treatment (thermal shock) of graphite intercalated compounds in the common technology of the thermally expanded graphite production. In worm-like particles of both expanded graphite compounds and thermally expanded graphite, the graphite crystal is already split into nanoplatelets and all that remains is to break their aggregates and remove intercalated species if needed.

The purpose of this paper is to explore the possibility of obtaining graphene materials from expanded graphite formed by cold expansion of graphite intercalated with peroxosulfate compounds and determine the parameters of materials obtained depending on the preparation conditions.

2. Experimental

2.1. Starting materials

The following starting materials were used in this study.

Natural graphite GSM-1, 99.9% purity (supplied by “Resource-C” Ltd., Russian Federation).

Ammonium persulfate (APS), “Pure for analysis” grade.

Thermally expanded graphite with bulk density of 4 kg/m^3, produced by UniChimTek-Graflex Ltd. (Russian Federation).

Surfactant “NF” (Russian standard GOST 6848-79) produced by “Pigment” Ltd. (Russian Federation), comprises oligomeric product of polycondensation of naphtalenesulfonic acid with formaldehyde, sodium salt.

100% sulfuric acid was prepared by addition of pre-calculated amount of 65% oleum to 95% sulfuric acid.

Ultrasonic treatment was performed with IL-10-2.0 installation (electrical power up to 2 kW). Optical density was measured with KFK-3 spectrophotometer.

2.2. Synthesis procedure

Synthesis of expanded graphite compound was performed as described previously [6-8]. Graphite was treated with a solution of APS in sulfuric acid (6.67 g APS per 1 g graphite). In a few minutes, the blue intercalation compound of graphite formed, which, according to [8], was graphite peroxodisulfate of the composition $C_{22.5}\ HS_2O_8^-\ 2.5H_2SO_4$. This compound gradually decomposed at room temperature with expansion of the crystals due to the evolution of gaseous oxygen between graphene layers. The rate of expansion depended on temperature. For example, at 40° C, 2 hours was sufficient for complete expansion. Very bulky mass formed consisting of yellow-brown worm-like particles. This process was called “cold expansion of graphite” [8]. The apparent volume of expanded graphite compound at the above specified ratio of reactants was 300 cm^3/g of starting graphite. The resulting expanded graphite compound was treated with water and washed on filter to neutral pH. Upon hydrolysis, the color of the expanded material changed from yellow-brown to gray. This material, containing 0.9% of dry substance, was used in following experiments in wet form without drying. Mass content of sulfur in the dry substance was 0.7%. Worm-like particles of this product were very similar to thermally expanded graphite and represented aggregates of interconnected graphene nanoplatelets, forming a very bulky porous structure. Drying resulted in dramatic decrease of the apparent volume and bonding of graphene nanoplatelets, probably due to capillary forces.

2.3. Samples properties and methods of testing

The crude material, obtained as described above, consisted of worm-like particles. Under ultrasonic treatment of an aqueous suspension, these particles were dispersed to graphene nanoplatelets. The degree of dispersion was evaluated by optical density (D) of treated dispersions. Thinner graphene particles, in general, produced larger D values. Aggregation tended to decrease D values. To determine the optical density, 0.250 g surfactant NF, 200 cm^3 water and a weighed portion of wet graphene material were placed in a 250 cm^3 beaker, so that the mass concentration of solids in the resulting mixture was from 0.02–0.035 g/dm^3, an optical density range convenient for measurement. The mixture was sonicated under cooling in a water bath and periodically, samples were taken for optical density measurement. The absorbance was measured in a 1 cm optical length cuvette at wavelength of 500 nm. Determination was carried out for no more than 2 minutes after ultrasound was off, because optical density slowly dropped over time, probably due to reversible particle aggregation. The resulting dispersions exhibited the characteristic pearlescence due to orientation of nanoplatelets in stream of liquid under stirring. Lambert-Beer law was observed in these systems. This allowed the calculation of the light absorbance coefficient (K):

$K=D/(CL)$, where

K – Light absorbance coefficient, dm^3/g.cm;

D – Optical density (corrected by subtraction of slight absorbance of surfactant NF at 500 nm), dimensionless;

C – Concentration of graphene material, g/dm^3;

L – Optical length of cuvette, cm.

The K value relatively weakly dropped with increasing wavelength in the visible region of spectrum (reduced by 15% from 500 to 800 nm).

Electronic images of samples were obtained using a dual-beam scanning electron microscopic complex Neon 40, Carl Zeiss.

3. Results and discussion

3.1. Preparation of graphene nanoplatelets via graphite intercalation compounds

At first glance, intercalation of foreign particles between the layers of graphite could weaken the bond between them and allow easier exfoliation. This might work with covalent attachment of fluorine atoms to the graphene skeleton. However, almost all known intercalants, capable of penetrating between the graphite layers are strong electron donors or acceptors and form charge transfer or ionic structures with graphene layers in which the bonding between graphene layers is reinforced due to electrostatic forces.

However, many graphite intercalation compounds are able to undergo secondary thermal or chemical transformations that result in a profound restructuring of the crystal structure, accompanied with exfoliation of crystalline intercalated compounds to graphene nanoplatelets and even graphene monolayers. The most common example is the thermal expansion of graphite intercalation compounds (mostly graphite sulfate or nitrate), which leads to the formation of expanded graphite. Thermally expanded graphite may be dispersed by sonication to graphene nanoplatelets in alcohol solution. However, graphene nanoplatelets obtained in this way were relatively thick, on the order of 50 nm [2].

Highly exfoliated thermally expanded graphite (HETEG) was obtained, which can be split into much finer nanoplatelets. HETEG was obtained by thermal decomposition of the graphite compound C_2F*nClF_3 at 573–723 K. As a result, molecular chlorine and chlorofluoro-carbons were generated as by-products. The HETEG easily dispersed in organic solvents or in aqueous solutions of sodium dodecylbenzenesulfonate, and formed one-, two-, and few-layered graphene [2, 9]. However, this method has a serious disadvantage – very toxic and dangerous reagents and by-products, so it is hardly acceptable for the mass production of graphene.

In [10], expanded graphite with a structure resembling the thermally expanded graphite was obtained by treatment of graphite intercalation compound KC_8 with water or ethanol. Processing alcoholic suspension of the product obtained by microwave radiation resulted in graphene nanoplatelets with thickness of about 10 nm.

3.2. Preparation of graphene nanoplatelets via expanded graphite peroxosulfate compound

Fig. 1 shows the dependence of light absorption coefficients for ultrasonic treatment time for different forms of expanded graphite in aqueous suspensions containing surfactant NF (1.25 g/dm^3) as stabilizer. Four types of expanded graphite or expanded graphite compounds were examined in these experiments:
1) thermally expanded graphite (TEG);
2) expanded compound of graphite obtained by cold expansion (at 40° C) of graphite intercalated with ammonium persulfate solution in concentrated (95%) sulfuric acid;
3) expanded compound of graphite obtained by cold expansion (at 40° C) of graphite intercalated with ammonium persulfate solution in 100% sulfuric acid;
4) expanded compound of graphite obtained by cold expansion (at 40° C) of graphite intercalated with ammonium persulfate solution in 100% sulfuric acid containing 1% of free SO_3.

As it follows from Fig. 1, thermally expanded graphite showed the least ultrasonic exfoliation in our experiments.

As can be seen from Fig. 1, the expanded graphite compounds obtained by cold expansion of graphite intercalated with APS in sulfuric acid was dispersed ultrasonically significantly better than thermally expanded graphite. Moreover, the dispersal strongly depends on content of water in the sulfuric acid used as a solvent. The presence of 5% water in sulfuric acid significantly retards dispersing ability. Considering the data obtained earlier [6-8, 11], we can assume the following mechanism for the processes occurring in this system. The first step is formation of blue graphite intercalation compound containing intercalated anions of peroxodisulfuric acid. Its composition was determined to be $C_{22.5}HS_2O_8^-$*$2.5H_2SO_4$ [11]. This compound gradually decomposed at room temperature with the evolution of oxygen gas (with admixture of ozone) and formed worm-like particles of expanded graphite compound with apparent volume up to 300 cm^3/g of starting graphite. A similar graphite intercalation compound formed (at low temperature) with peroxomonosulfuric acid, but it

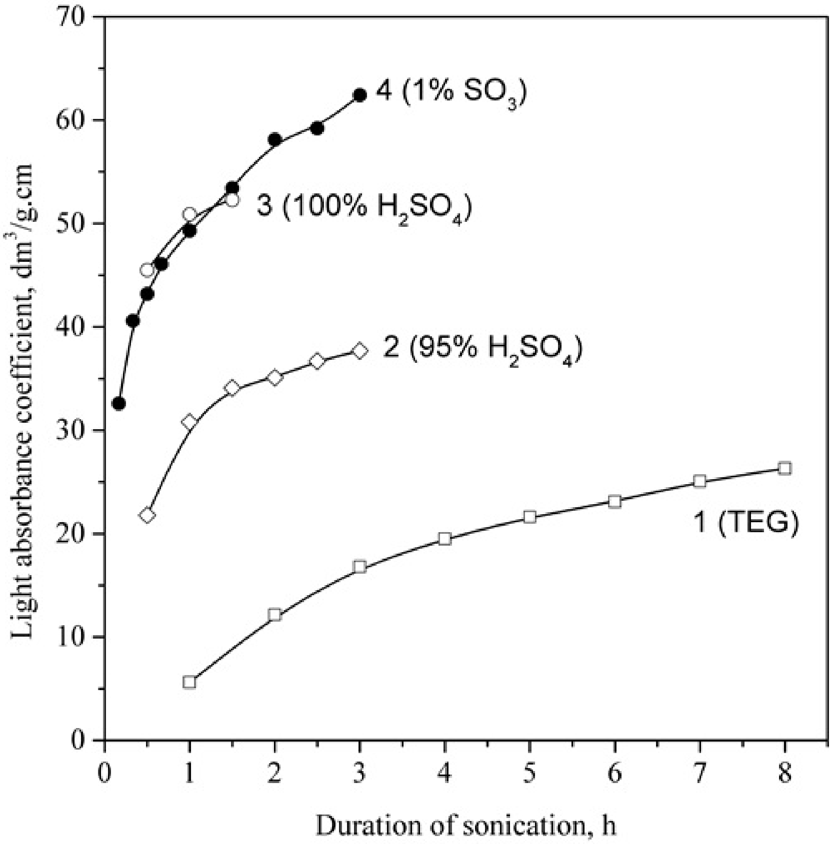

FIG. 1. Dependence of light absorbance coefficient on time of ultrasonic treatment for different forms of expanded graphite in aqueous suspensions containing surfactant NF (1.25 g/dm^3) as a stabilizer

was less stable and its decomposition, accompanying with "cold" expansion, proceeded even at 0° C. Visually, the process of cold expansion of graphite peroxosulfate compounds is very similar to the thermal expansion of intercalated graphite, however, occurs at temperature close to room temperature.

This process consists of complex chemical and structural transformations. Presumably, the cold expansion process begins with the decomposition of intercalated and dissolved peroxosulfate compounds, which give rise to highly reactive species:

$$H_2S_2O_8 \rightarrow 2HSO_4^{\cdot} \qquad (1)$$

$$H_2SO_5 \rightarrow HSO_4^{\cdot} + OH^{\cdot} \qquad (2)$$

$$HS_2O_8^{-} \rightarrow HSO_4^{-} + SO_4 \qquad (3)$$

$$SO_4 \rightarrow SO_3 + O \qquad (4)$$

$$S_2O_8^{2-} \rightarrow 2SO_4^{-\cdot} \qquad (5)$$

These active species react with graphene layers, forming covalent bonds with carbon. The color of the resultant expanded graphite compound is yellow to yellow-brown. XRD data for the expanded substances show a broad halo with no sharp peaks characteristic for crystalline graphite compounds [11]. Increasing the apparent volume and conversion of the crystalline flake graphite particles into worm-like ones is due to the evolution of oxygen gas between the graphene layers. This gas was produced simultaneously in peroxide compounds decomposition and the oxidation of the graphene skeleton.

We can assume that in the yellow expanded graphite compound, the flat aromatic system of graphene layers is broken by the covalent attachment of -OSO_3H groups to carbon atoms, similarly to graphite fluoride and graphite oxide. In [11], based on the measurements of the volume of oxygen gas evolved in the process of "cold" expansion, the degree of oxidation of carbon skeleton was determined for the expanded graphite compounds obtained in the graphite-$H_2S_2O_8$-H_2SO_4 ternary system.

It was found that one group -OSO_3H (attached covalently or as an anion) corresponds to x=7 carbon atoms, wherein, the x value decreases with excess $H_2S_2O_8$ in the starting system. It should be noted that for ionic compounds of graphite particles with electron accepting species characteristic value of x usually is in the range of 22 to 24, while for graphite fluorides x value usually is 1 to 6. However, in graphite monofluoride CF the C-F bond is purely covalent, carbon layers are non-planar, non-aromatic and do not conduct electric current. In lower graphite fluorides (C_2F, C_4F, C_6F), the fluorine bond with carbon skeleton becomes more ionic, and carbon layers become more planar and gain conductivity. Possibly, by degree of oxidation of carbon skeleton the products of "cold" expansion of graphite intercalated with peroxosulfates can be compared with lower graphite fluorides.

As can be seen from Fig. 1, the expanded graphite compound obtained by using anhydrous sulfuric acid, dispersed under ultrasonic treatment was significantly better than that obtained using 95% sulfuric acid. This can be attributed to the difference in acidity. It is known that auto-dissociation of concentrated sulfuric acid occurs according to the scheme:

$$H_2SO_4 + H_2O \leftrightarrow HSO_4^- + H_3O^+ \tag{6}$$

Thus, acidity of concentrated sulfuric acid corresponds to ion H_3O^+. Auto-dissociation of anhydrous sulfuric acid proceeds in another way:

$$2H_2SO_4 \leftrightarrow HSO_4^- + H_3SO_4^+, \quad [H_3SO_4^+] \cdot [SO_4^-] = 2 \cdot 10^{-4} \tag{7}$$

$$2H_2SO_4 \leftrightarrow HS_2O_7^- + H_3O^+, \quad [H_3O^+] \cdot [HS_2O_{7}-] = 4 \cdot 10^{-5} \tag{8}$$

Molecular-ion composition of anhydrous sulfuric acid can be described by the following data [12]:

H_2SO_4 — 99.5%
HSO_4^- — 0.18%
$H_3SO_4^+$ — 0.14%
H_3O^+ — 0.09%
$HS_2O_7^-$ — 0.05%
$H_2S_2O_7$ — 0.04%

Even a small admixture of water (tenths %) inhibits reactions (7) and (8), and dissociation scheme (6) becomes dominant [12].

Thus, in anhydrous sulfuric acid, the $H_3SO_4^+$ cation dominates among ions, causing acidity, and it is a much stronger acid than H_3O^+. In a solution of ammonium persulfate in anhydrous sulfuric acid, peroxodisulfuric acid is formed:

$$(NH_4)_2S_2O_8 + 2H_2SO_4 \leftrightarrow 2NH_4HSO_4 + H_2S_2O_8 \tag{9}$$

In an anhydrous sulfuric acid medium it can be protonated:

$$H_2S_2O_8 + H_3SO_4^+ \leftrightarrow H_3S_2O_8^+ + H_2SO_4 \tag{10}$$

Obviously, the protonated form of peroxodisulfuric acid is a much stronger oxidant than peroxodisulfuric acid, and this results in higher oxidation state of graphite in the compounds formed. It is also obvious that the presence of ammonium salts somewhat reduces the acidity of the system because HSO_4^- anions are basic in the medium of sulfuric acid and form a buffer system with acidic cations. For this reason, using peroxodisulfuric acid without ammonium salts (obtained by mixing sulfuric acid with concentrated hydrogen peroxide and oleum as described in [7]) would be more efficient for oxidative intercalation of graphite. However, the preparation and use of this system is dangerous because of great evolution of heat when mixing the components.

Hydrolysis of the cold-expanded graphite compounds formed in the systems studied resulted in transition of yellow or yellow-brown color to gray, and this was accompanied by some evolution of oxygen gas (with admixture of ozone). One can suppose that addition of water not only leads to hydrolytic cleavage of sulfate groups attached to carbon or removing hydrosulfate anions from interlayer space, but also causes redox disproportionation according to the scheme proposed in [13]. Namely, the central area of the carbon layers is reduced to graphene structure and peripheral area is oxidized to graphite oxide structure.

According to [14], samples of "microflaky graphite" contained 6% of the graphite oxide phase on the surface of graphite microflakes (nanoplatelets in modern terminology). It is due to the presence of these hydrophilic graphite oxide groups that the hydrolyzed material is well dispersed in water by ultrasonication (however, aggregation takes place in the absence of a surfactant). When dried, the relatively strong bonding of graphene nanoplatelets occurs with formation of elastic films [7]. This feature of graphene nanoplatelets, obtained via peroxosulfate graphite intercalation compounds, favors application of this material in composites with polar polymers (epoxy, phenol-formaldehyde, etc.).

The value of the light absorbance coefficient (Fig. 1) depends on the thickness of the graphene nanoplatelets and their aggregation in an aqueous dispersion. The smaller the average thickness of graphene nanoplatelets and the less they are aggregated, the greater should be the value of K. Unfortunately, due to overlap of these two factors, it is not possible to evaluate each of them separately by the value of K. However, in the presence of a sufficiently effective surfactant, such as dispersant NF, sonication of graphene material suspensions resulted in completely transparent dispersions, while ultrasonic treatment without the addition of a surfactant led to transformation of the initial worm-like particles (which can be regarded as strong agglomerates of nanoplatelets chemically bonded at their edges) into the large loose flakes (weak agglomerates of nanoplatelets connected by adsorption forces). Thus, we can assume that in the presence of an effective surfactant, agglomeration is minimal and change in the K value is mainly due to splitting of the initial worm-like particles and changing the average thickness of graphene nanoplates depending on the preparation conditions and dispersion. Furthermore, observing of the Lambert-Beer law indicates that agglomeration is minimal in the systems studied. It is interesting to compare our data (Fig. 1) with similar data in literature. In [15], the ultrasonic cleavage of graphite crystal in an aqueous solution of sodium dodecylbenzene sulfonate (graphite starting concentration of 0.1 g/dm^3, DDBS 0.5 g/dm^3) was investigated. The light absorbance coefficient of the sonicated substance at 660 nm (after separation of the coarse fraction by centrifugation) was found to be 1390 ml/mg.m, which is equivalent to 13.9 dm^3/g.cm. The number of monolayers in graphene nanoplatelets so obtained, as estimated by transmission electron microscopy, was in the range of 1–15, with maximum at the distribution of about 5 monolayers.

In [16], the optical properties of aqueous dispersions of chemically derived graphene monolayers were studied. It was found that optical density vs. concentration plots in this system deviate from Lambert-Beer law. From the data given in this work, the effective light absorbance coefficient can be estimated (very approximately because of deviation from Lambert-Beer law) to be 33 dm^3/g.cm at 400 nm and 25 dm^3/g.cm at 600 nm. It was shown in [16] that at concentrations of graphene over 10 mg/dm^3 aggregation of graphene nanoplatelets was observed, but at lower concentrations spontaneous curling of graphene layers into scrolls occurred. Thus, the optical properties of aqueous dispersions of chemically derived graphene were dependent on aggregation and scrolling of graphene nanoplatelets.

It is difficult to compare our data with the above-cited, because it is obvious that aggregation strongly depends on the nature of surfactant and surface groups on graphene nanoplatelets. Relatively large values of K observed in the present work probably are due both factors — presence of hydrophilic surface groups and efficient surfactant used.

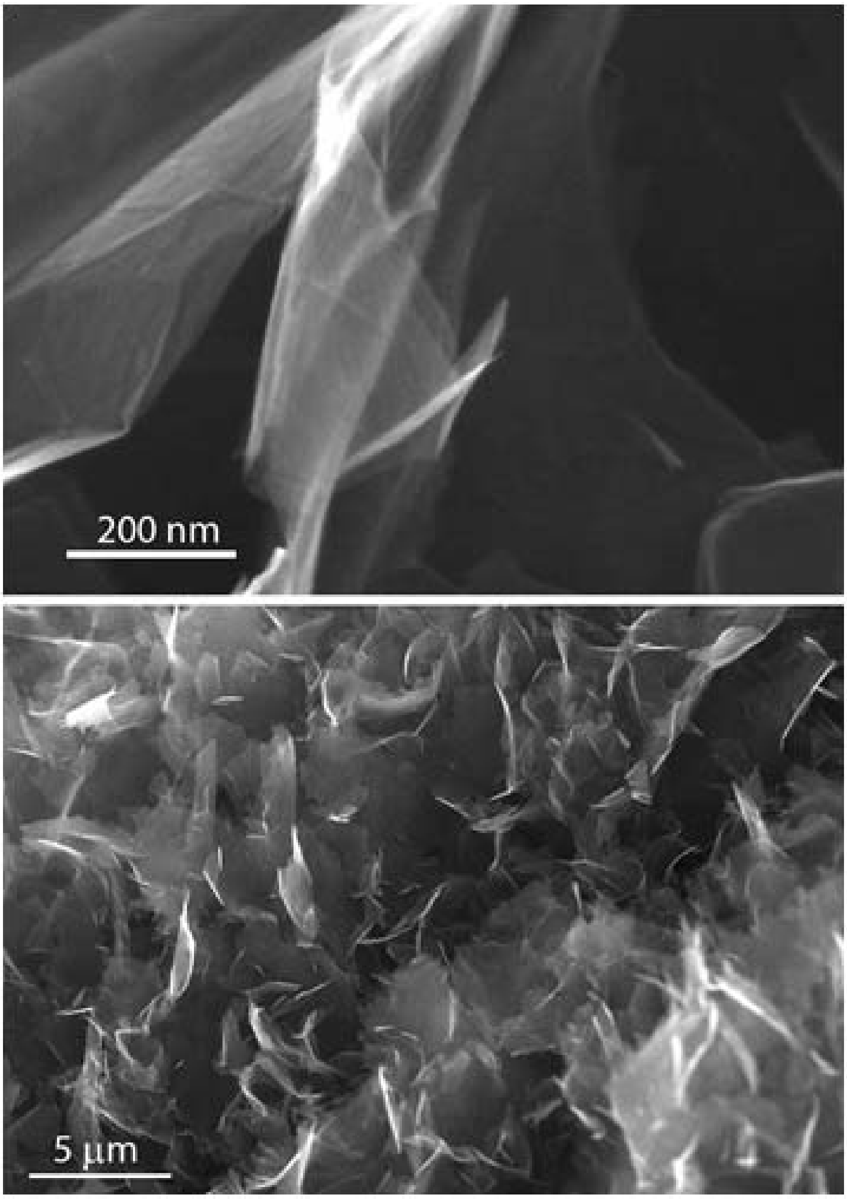

Fig. 2. SEM images of graphene material obtained by sonication of expanded graphite compound in aqueous suspension without addition of surfactants

Fig. 2 shows SEM images of the graphene material obtained upon ultrasonic treatment of cold-expanded graphite compound (after hydrolysis) in aqueous suspension without the addition of surfactants. These images are very similar to the analogous materials described in numerous literary sources and avenues of firms producing graphene materials. The thickness of nanoplatelets can be estimated very roughly from nanoplatelets butt-ends

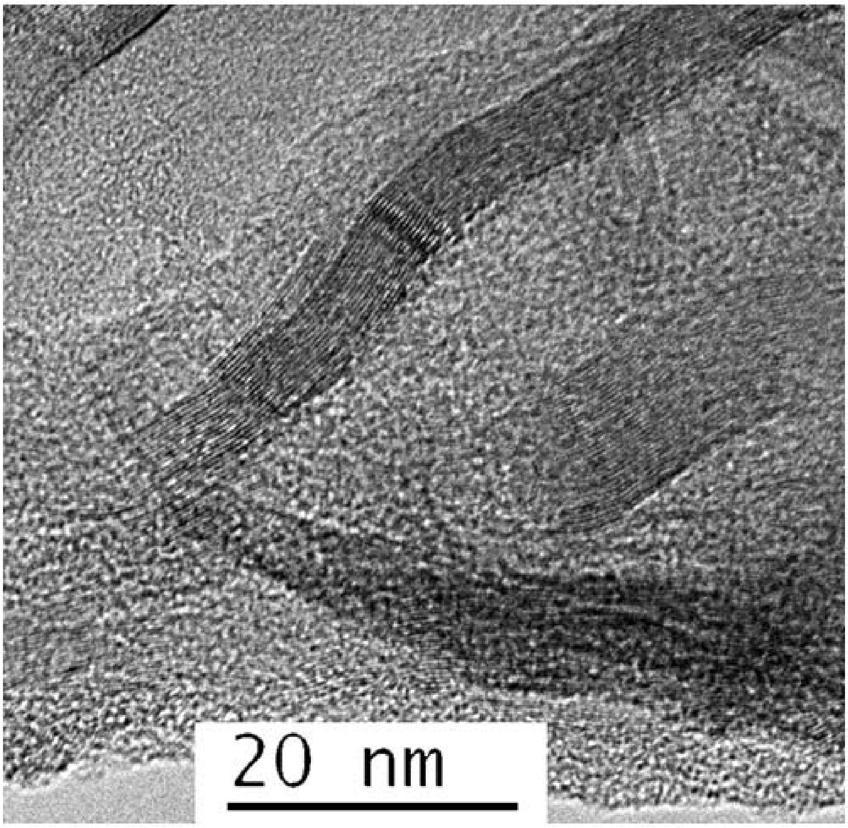

Fig. 3. TEM images of graphene material obtained by sonication of expanded graphite compound in aqueous suspension without addition of surfactants

as the order of not more than 5–10 nm. More accurate estimation from SEM images is not possible because of limited resolution of the scanning electron microscope.

In Fig. 3 there are images of the material in transmission electron microscope. In places where nanoplatelets fragments were directed along electron beam, images were observed allowing estimation of the number of graphene layers. As is seen from Fig. 3, the platelets are of different thickness. Two platelets in the field of view contain nearly 15 and 25 carbon layers correspondingly. Attempts to determine average thickness of nanoplatelets via surface area of dry samples were unsuccessful because drying resulted in strong glueing of nanoplatelets. The surface area of graphene nanoplatelet samples obtained by sonication of expanded graphite compound in aqueous suspension (without surfactant) was determined by adsorption of Methylene Blue in acidic aqueous solution according to Russian standard GOST 13144-79 (Graphite. Methods of determination specific surface area) to be 120 m^2/g. If compared to the theoretical surface area of graphene monolayer, 2630 m^2/g, this corresponds to 22 layers as the average-by-weight number of graphene layers in the material obtained, and average thickness of 7.4 nm. Probably, more prolonged sonication or addition of surfactants could decrease the average thickness of nanoplatelets in the material obtained.

In aqueous dispersions without added surfactant, despite the presence of hydrophilic graphite oxide groups, particles of the investigated graphene materials form large aggregates in the form of fuzzy flocks with visual size up to several millimeters. Apparently, these aggregates are weak. Obviously, ultrasonic treatment of much diluted aqueous dispersion of expanded graphite compound (after hydrolysis) in presence of a surfactant could provide most efficient separation of graphene nanoplatelets and retard aggregation. However, such

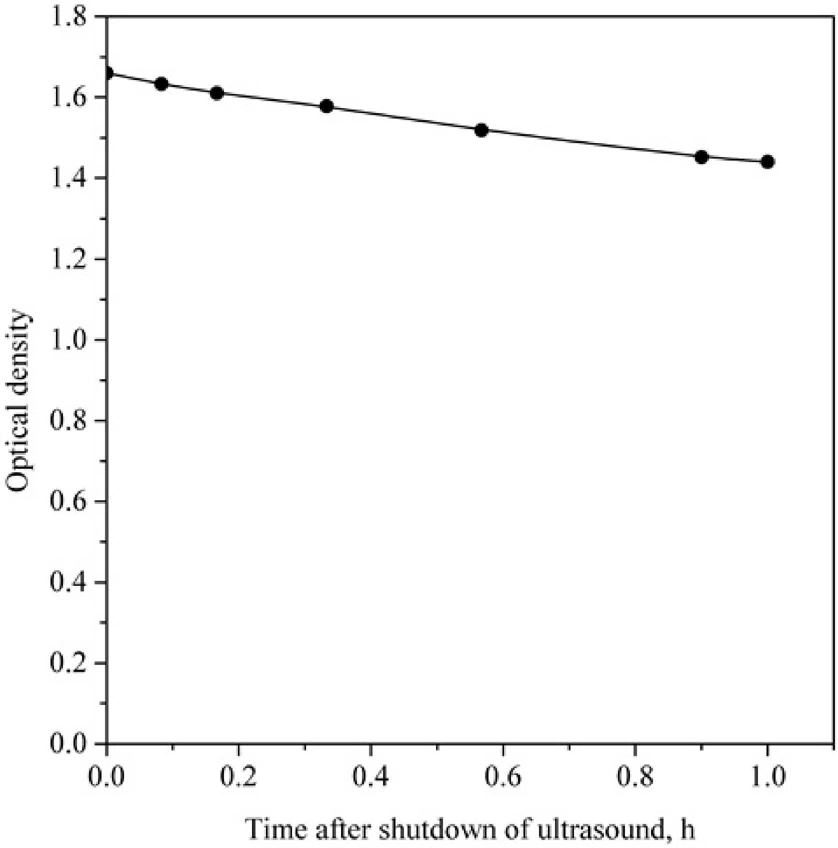

FIG. 4. Dependence of optical density of graphene nanoplatelets dispersion in aqueous solution of 1.25 g/dm^3 surfactant NF on time after switching off ultrasonic apparatus

a method is too expensive for mass production. Besides, surfactants commonly used for stabilization of graphene (monolayer and multilayered) dispersions in water, are strongly adsorbed on graphene surface and it is very difficult to remove them by washing. This creates a problem if the graphene material is intended for application in polymeric composite materials. Sonication of the aqueous dispersions of the expanded graphite compound in water without adding a surfactant gives aggregated material, consisting of weak agglomerates, without problems caused by the presence of surfactant. This material can be easily produced large scale and can be introduced into organic formulations by exchange of water for organic solvent. So, sonication without surfactant is a compromise between suitability of preparation and quality of the graphene nanoplatelets obtained, if we accept thickness of nanoplatelets and degree of aggregation as criteria of quality.

When storing aqueous dispersions of graphene nanoplatelets, obtained by sonication of dilute suspensions of graphene material (0.02-0.035 g/dm^3) in the presence of surfactant NF (1.25 g/dm^3), optical density slowly decreases after shutdown of ultrasound (Fig. 4). This most likely indicates reversible aggregation of nanoplatelets.

With prolonged standing (several days), the initially transparent dispersion of graphene nanoplatelets partially precipitated in form of flocks, but formed again transparent brownish-gray solution at shaking. The solution exhibited characteristic pearl effect due to orientation of nanoplatelets in flow of liquid. It can be assumed that aggregates of nanoplatelets formed in these conditions are not strong and aggregation is easily reversible upon stirring. It is possible that there would be no aggregation when using a more efficient surfactant.

Thus, the process of cold expansion of peroxosulfate graphite intercalation compounds can be used to obtain graphene nanoplatelets.

4. Conclusions

1. Expanded graphite compounds formed upon cold expansion of the graphite intercalated with peroxosulfate compounds easily exfoliate under sonication to form graphene nanoplatelets.

2. Intercalation of graphite with a solution of ammonium persulfate in anhydrous sulfuric acid gives more fine graphene nanoplatelets compared to intercalation in concentrated (95%) sulfuric acid. Presumably, admixture of water reduces the medium acidity and oxidative efficiency of the intercalation system, and this, in its turn, decreases the degree of carbon skeleton oxidation.

3. Presumably, covalent attachment of hydrosulfate groups to graphene layers occurs during the cold expansion process, resulting in yellow expanded graphite compound.

4. Expanded graphite compounds, obtained by cold expansion, exfoliate to graphene nanoplatelets under sonication significantly easier than thermally expanded graphite.

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