Mechanisms of graphene exfoliation under the action of femtosecond laser radiation in liquid nitrogen

K S Khorkov, D A Kochuev, V A Ilin, R V Chkalov, V G Prokoshev and S M Arakelian
Vladimir State University named after Alexander and Nikolay Stoletovs, 87 Gorky Street, Vladimir 600000, Russia

E-mail: freeod@mail.ru

Abstract The processes of graphene structures formation under the action of the femtosecond laser radiation on carbon samples in liquid nitrogen are discussed. Mechanisms of graphene sheets exfoliation are proposed depending on the power density of the laser radiation: in the first case, the separation occurs due to the volumetric expansion during heating the region occupied by nitrogen molecules; at a laser radiation energy exceeding the ablation threshold, the surface of graphite begins to breakdown in the region of the action, followed by separation into graphene layers.

1. Introduction
Graphene is a two-dimensional crystal consisting of carbon atoms arranged in a hexagonal lattice. The term "graphene" appeared in 1962, but the discovery of real graphene occurred only in 2004 using the method of mechanical splitting of graphite. According to this method, graphene sheets are separated from crystalline graphite, either as a result of friction of pieces of crystalline graphite against each other, or in "peeling" them off the graphite surface with a special adhesive tape, followed by its dissolution. The micromechanical splitting of graphite became the main way of obtaining graphene in the early studies of its properties, and formed the basis for a whole series of new production methods, initiating active research in the field of graphite layers’ separation. To date, their results have been generalized in a number of review papers [1-5].

Now, there is a large abundance of methods for the production of graphene, one of which is the "liquid-phase exfoliation of graphene". This method is based on the intercalation of foreign atoms or molecules in the interlayer space of graphite. Because of the introduction of impurities, the energy of interaction between layers is weakened by increasing the distance between them. Thus, further separation of the graphite into its constituent monolayers becomes possible. As penetration substances are used surfactants having a high energy of interaction with graphene layers such as N, N-dimethylacetamide, g-butyrolactone (GBL) and 1,3-dimethyl-2-imidazolidinone (DMEU). For example, in [1] a suspension was prepared from N-polyethyleneoxide and a finely dispersed graphite powder, which was subsequently subjected to ultrasonic treatment and centrifugation. As a result of this treatment, a suspension is formed in the surface active liquid containing suspended single-layer graphene sheets, as well as multilayers graphene. Thermodynamically, this possibility is due to the higher energy of interaction of the surfactant with the surface of the graphene sheet than the energy of the interaction of the neighboring layers with each other.
To further study the properties of the resulting material, a drop of the treated suspension was applied to a carbon mesh. The obtained samples contained flat and curved graphene scales, as well as flakes consisting of several layers. Another, more complex example of such an approach, is described in [2]. The authors managed to achieve a 90% yield of single-layer graphene films in the following way: graphite powder was pre-annealed for 1 minute at 1000 °C and finely ground, and then subjected to multistage surfactant interaction together with ultrasonic treatment and centrifugation. Another common method of liquid-phase separation of graphite is the Hammer’s method [3], according to which the inner layers of graphite are oxidized by an anhydrous mixture of concentrated sulfuric acid with sodium nitrate and potassium permanganate. After the course of the reaction accompanied by active gas evolution, the mixture is dried and formed an aqueous suspension of graphene oxide (GO) flakes which has enhanced stability by electrostatic repulsion of the layers of GO in water.

2. Experiment

Targets from highly oriented pyrolytic graphite (HOPG) HOPG-1.7-10x10x1-1 and glassy carbon (GC) SU-2000 were used as initial samples for graphene production. HOPG is fundamentally the best material for the elimination of graphene, since it is formed from high-quality graphite layers, almost parallel to each other. The glassy carbon has a rather complex structure. It is a bundle of randomly intertwined carbon ribbons crosslinked by carbon bonds of varying multiplicity. Obviously, glassy carbon cannot be a source of flat graphene sheets. However, for a number of applications of graphene, for example, as a material for electrodes of ionistors (supercapacitors) or for reinforcing nanoceramics, it is necessary that it has a complex extended surface [6].

The surface treatment of the targets was carried out by radiation of ytterbium femtosecond TETA-10 laser. Parameters of the laser radiation: \( \lambda = 1029 \text{ nm}, \tau = 280 \text{ fs} \), repetition rate \( f = 10 \text{ kHz} \), pulse energy \( \varepsilon = 150 \mu \text{J} \). The polarization of laser radiation is linear. The exposure scheme is shown in Figure 1. The surface treatment of graphite was performed in a liquid nitrogen medium, which covered it with a layer about 1 cm thick. The diameter of the laser spot on the target surface reached \( 100 \mu \text{m} \) [7].

The speed of movement of the laser beam along the surface of the target was from 10 to 100 cm/s. Accordingly, depending on the scanning speed of the beam, each region of the target surface was exposed from 1 to 10 femtosecond pulses (upper left corner of Figure 1). Graphene splitting occurs at a laser beam velocity of 25 cm/s, when the graphite surface is exposed to four laser pulses (overlapping - 75%). With a larger overlap, a strong destruction of the surface of the target and at the same time an exfoliated carbon material begins.
At the end of the laser treatment, the targets were kept under natural conditions until liquid nitrogen evaporated completely, after which their surface became accessible for investigation by microscopic methods. The results of laser action on graphite targets were studied on the basis of images obtained with the scanning electron microscope Quanta 200 3D (SEM-images) and a probe nanoscale laboratory Integra Spectra (Raman spectra).

3. Processing results
Microscopic studies of the carbon material detached from the surface of HOPG under the influence of femtosecond laser radiation confirmed the production of graphene sheets of various shapes. Graphene tapes with a width of up to 50 μm and a length of more than 150 μm have been identified (Figure 2a), as well as graphene plates of arbitrary shape with a characteristic size of more than 150 μm (Figure 2b).

Graphene tapes obtained during the experiments, although have folds and bends, also have rather large areas (up to 2000 μm²) of flat areas of the surface.

![Figure 2](image-url)

Figure 2. Graphene tapes (a) and plates (b), cleaved from the main sample, under the expose of femtosecond laser radiation at HOPG in liquid nitrogen

The synthesized plates (flakes) also exhibit numerous folds and bends, as well as significant flat areas of the surface. It should be noted that on the surface of large graphene sheets, much smaller (characteristic sizes of the order of 1 μm) and crumpled structures are observed.

On the SEM images (Figure 3) on the graphene structure, can be seen areas (highlighted by an arrow) that have a different number of graphene layers. At the same time, such "steps" are formed at the edges of the sheets, which follow from the process of laser-induced exfoliation of graphene.
Figure 3. SEM-images of formed graphene structures, the edge region is highlighted and shown by an arrow

Graphene structures obtained by laser treatment of the surface of glassy carbon have a fundamentally different shape (Figure 4). Graphene sheets form lumps with a complex folded structure. Clumps with a characteristic size of the order of 1 μm are recorded.

Figure 4. SEM-image of graphene structures on the surface of glassy carbon

4. **Discussion of graphene exfoliation mechanisms**

A comparison of the results of treatment of HOPG and GC by femtosecond laser radiation in a liquid nitrogen environment showed that the use of the first material is preferable for the purpose of obtaining the flattest and thin graphene structures. Obviously, in this case the primary internal structure of the irradiated materials plays a decisive role.

The thermal expansion of the graphite lattice is anisotropic, as are the values of the thermal and electrical conductivity of this material. The anisotropy for graphite is the stronger, as the higher the ordering of the lattice. The temperature coefficient of linear expansion in the direction of the basal planes is much less than in the perpendicular direction, thereby contributing to exfoliation of the structure under intense heating.

The cooling of graphite to the temperatures of liquid nitrogen reduces the lattice vibrations of the graphite starting material, so that the interlayer distance is reduced to 3.339Å, and when heated, it
increases to 3.465 Å (at 1000 °C) [8]. Cooling of samples with liquid nitrogen is often used in view of availability, which satisfies the boiling point and the small size of the nitrogen molecule, which ensures its high fluidity. At low temperatures, the graphite lattice becomes less "plastic", which, probably, will make it possible to destroy interplane bonds by a smaller energy contribution at the site of local heating of nitrogen molecules diffused into the interplanar distance.

In [9] proposed a mechanism for obtaining carbon "nanoscrolls" – twisted graphene sheets in a spiral. A sample of natural graphite was immersed in liquid nitrogen and irradiated with microwave radiation for 5 seconds. Upon irradiation, the initial sample of graphite was heated to a high temperature, as a result of which it increased in volume. At the same time, the graphene sheets on the graphite surface are cooled by liquid nitrogen and compressed. Thus, a stress state is formed between the cooled surface of the sample and the main volume of the heated graphite. As a result of the stresses created at the boundary, the interplane bonds break, the graphene sheets are peeled off, followed by folding into carbon nanostructures due to a more favorable energy state. Further processing consisted in the action of ultrasound that facilitated the further separation of the resulting structures from the graphite sample. The allocation of the necessary fractional structural composition of the nanoscrolls was carried out by means of centrifugation.

In comparison with experiments on heating a graphite sample with microwave radiation using laser radiation, the peeled graphene structures do not take the form of nanoscrollers, but form flat shapes. This can be due, firstly, to the characteristic heating time of the region exposed to the effect – with short laser pulses there is a rapid local heating, in contrast to uniform heating by microwave radiation. Secondly, in the case of a laser-induced exfoliation, a sufficiently large number of graphene layers is separated, which does not allow the graphene lattice to deform in the general layer and to perform sheet folding in a spiral.

As it suggested in [8], when a graphite sample is immersed in liquid nitrogen, the latter penetrates into the interlayer distance of the graphite planes as a monolayer of the liquid ("mono-layer 2D-fluid"). Having a smaller size, nitrogen molecules penetrate into the interplanar distance in places that have defects (cracks, chips, layering), and also from the ends of the sample itself (Figure 5).

![Figure 5. Schematic representation of the process of nitrogen diffusion into the interlayer distance of the graphite lattice](image)

For nanosecond laser pulses, the main process that affects the heating of nitrogen molecules is the transfer of target energy due to thermal conductivity. The laser pulse duration is much longer than the electron-phonon energy transfer time, i.e. during the time of the laser pulse, the electrons transmit energy to the lattice of the substance, and its heating occurs within the laser exposure region, including diffused nitrogen. As a result of laser heating and, as a consequence, an increase in the amplitude of vibrations of nitrogen molecules, a volumetric expansion of the region occupied by nitrogen molecules occurs (a transition from the liquid phase to the gas phase). Thus, interplanar carbon π-bonds (16-40 kJ/mol) are destroyed, which are weaker than σ-bonds (of the order of 450 kJ/mol) [10]. Effective
heating of nitrogen is carried out due to the transfer of thermal energy from the graphite lattice in the absence of nitrogen absorption bands at the working wavelength.

In the interaction of ultrashort laser pulses with a graphite sample in a liquid nitrogen medium, several variants of the course of the processes of structural changes in the material can be identified. When the laser radiation power is insufficient for laser ablation processes to occur, the photon energy is absorbed by the carbon lattice and diffused nitrogen. In view of the sharp increase in the lattice vibrations and nitrogen molecules, weak interplane π-bonds collapse (Figure 6). The splitting and splitting of the graphite layers takes place mainly on the defects of the processed structure (cracks, chips, scratches, including heterogeneous lattice defects in view of the gaps facilitating the diffusion of liquid nitrogen molecules.) Accordingly, an increase in the number of nitrogen atoms in the lattice of the material promotes more intensive exfoliation of graphene sheets.

Figure 6. Schematic representation of the process of graphene peeling as a result of thermal expansion of nitrogen

Figure 7 shows the result of the detachment of graphene structures on the surface of the HOPG in the region of the crack. It is clearly seen that the detachment starts from the center of the crack according to the mechanism described above. On a SEM image with a large magnification, it is seen that individual structures exfoliate and bend in the direction from the beginning of the detachment, holding at the base and in some places also exfoliating. The next step in using the obtained graphene structures is to separate from the original sample using ultrasonic treatment, form a solution and deposit on the required substrates.

Figure 7. SEM-images of the edges of graphene sheets (with different magnifications)
At laser radiation energy above the ablation threshold, the surface of graphite starts to breakdown in the area of the impact. As a result of the processes, occurs during laser ablation, a high-pressure region forms on the walls of the formed cavity. The separation of the graphite structure to multilayer graphene under such mechanism occurs as a result of the reactive action of ablation products. In view of the presence of various defects, the graphene layers are separated from the main sample.

Figure 8 schematically shows the process of graphene structures exfoliation upon reaching the ablation process: black bars denote graphite layers; red hemisphere – laser-induced plasma plume; black arrows – the directions of expansion of the ablation products, directions of propagation of the pressure front. In the case of scanning by laser radiation, the main parameter at the start of the mechanism is the exposure time at a specified value of the density power (Figure 9).

The increase of the energy of laser radiation leads to an increase of temperature and pressure in the impact area due to insignificant heat removal and the impossibility of expanding deep into the material. In this case, nonequilibrium conditions are forming and leads to a change in the phase composition at some depth of the sample and to subsequent formation of bulk crystal structures [11].

5. Conclusion
Thus, the general mechanism of graphene exfoliation by femtosecond laser action in liquid nitrogen is the separation of surface layers of the target as a result of disruption of interplanar bonds of carbon
samples due to the expansion of the induced transition of diffused nitrogen to the gas phase under laser heating.

At the same time, from the surface of the HOPG are separated flat layers, of which it consists. On the surface of the glassy carbon, a sufficiently thick layer containing both graphene ribbons and amorphous material is pinched. With the using of glassy carbon as a material, this effect becomes more complex, allowing forming crumpled type structures.

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