Nanosecond pulsed laser ablation of synthetic graphite in liquids for the synthesis of spherical graphene

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M. B. Shavelkina, M. M. Malikov, P. P. Ivanov, T. I. Borodina, and G. E. Valyano

AFFILIATIONS
Joint Institute for High Temperatures of the Russian Academy of Sciences, Moscow 125412, Russia

Author to whom correspondence should be addressed; electronic mail: mshavelkina@gmail.com

ABSTRACT
Pulsed laser ablation in liquids has become a simple, fast, and environmentally friendly method for the synthesis of carbon nanostructures since it does not require the use of toxic chemicals. The great advantage of this method is its ability to control the size, shape, and structure of the products by combining parameters of the laser, target material, and liquid. By ablation of two types of synthetic graphite with a high-power copper vapor laser in ethanol and distilled water, spherical graphene was obtained. The composition of the gas phase and the condensation temperature of carbon in the temperature range of 1000–5000 K were determined by means of thermodynamic modeling. The precursors for the formation of spherical graphene during laser ablation in alcohol and water are discussed.

Key words: laser ablation in liquid, graphite, colloids, graphene spheres, thermodynamic modeling

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I. INTRODUCTION
Graphite is widely used as a feedstock for the synthesis of fullerenes, carbon nanotubes, graphene, and diamondlike films. The main problem in the making of composites (for example, construction materials, magnetic data carriers, rapid adsorbents, additives for oils, lubricants, and lubrication-cooling liquids in the biochemical synthesis) using this kind of nanomaterials is the complexity of their distribution in volume due to their dimensional effect. One of the ways to solve this problem is the insertion of nanoparticles into composites like stable suspensions, produced by means of ultrasonic machining, surfactants, or centrifugation. Laser ablation in liquid is considered as another way to solve the same problem. During the ablation in liquid, the collision frequency of particles from target and liquid is by many orders of magnitude greater compared with the collision frequency in vacuum or gas. It means a more intense generation of nanoparticles and structures. The liquid hinders the spread of ablation products; therefore, the pressure within the plasma might be as high as several GPa, the temperature—up to 4000–5000 K and density—$10^{22}$–$10^{23}$ cm$^{-3}$. Under high collision frequency of atoms and molecules, there appear in the plasma nanocomplexes of particles both from the material of target and liquid and from the products of their chemical interaction. After the end of the laser pulse plasma recombines in microseconds, vapor of liquid mixed with the ablation products condenses into a colloidal solution of nanoparticles. Parameters of laser radiation, target composition, and confining liquid composition are easy to specify. Therefore, the method of laser ablation of solid material in liquid is capable to produce various nanostructures with determined functional properties.

This work is aimed to investigate the influence of the composition of the environment on the structure morphological properties of carbon nanoparticles during the ablation of two kinds of graphite under the pulse-periodic radiation of a copper vapor laser (CVL), which pertains to the class of lasers based on the self-contained transition in metal atoms. These lasers work in pulse regime generating due to transitions from the resonance level to the metastable one.

II. MATERIAL AND METHODS
A. General principles and design of the experimental setup
The ablation of samples has been performed under the laser radiation power $\sim 9.5$ W with pulse power $2.7 \times 10^{9}$ W/cm$^2$ and
pulse energy around 54 J/cm². The optical layout of the experiment is presented at Fig. 1. CVL (1) with commercial discharge tube (GL-201) was used as a source of radiation. This laser tube is provided by an unstable resonator with a great coefficient of increment M ~ 200 and by a spatial filter (collimator) for the isolation of a small divergence beam. It was being generated at two wavelengths—510 and 578 nm (green and yellow lines), with corresponding related powers 2:1. Pulse duration was in the range of 20–25 ns, the frequency 10 kHz, and average power—10–15 W. There was the power source up to 4 kW. The laser beam was being focused on the surface of the target by means of an achromatic objective (2) with a focal length of 280 mm, providing a spot size of less than 100 μm. Graphite sample (3), cut out from the rod, was being placed at the bottom of the rectangular quartz cuvette (4), filled with distilled water or ethanol. A vessel with cooling water and the cuvette was placed on the moving table (6), providing a constant drift of the focal spot along the graphite surface in order to prevent the formation of deep craters there.

The targets were made from two types of synthetic graphite electrodes, differing in diameter and strength. Disks 3 mm in thickness were cut out from graphite rods 6 and 10 mm in diameter as targets for the subsequent investigation of their properties.

As a result of the target ablation, the colloidal solution is produced in the confining liquid, containing the solid carbon phase. The solution was being centrifuged for 10 min long at 10 000 revolutions per minute. Samples for analysis used to be prepared by the repeated deposition of wet sediment on the object carrier and the copper substrate with consequent drying under 312–323 K and atmospheric pressure.

C. Thermodynamic modeling

Thermodynamic analysis of the equilibrium composition of multicomponent systems is performed for the wide range of temperature, pressure, and initial composition. Program code is developed using the approach of Refs. 14 and 15 (a comparison of methods is performed in Ref. 16). The algorithm is based on the minimization of Gibbs energy in the space of reaction coordinates accounting for all possible states—gaseous (including the ionization) and condensed ones (liquid, solid)—by means of sequential execution of reactions, supplemented by the scheme of optimization of the basis. Every single step is the solution of the equation of the mass conservation for the single reaction. The gas phase is considered a mixture of ideal chemically reacting and ionizing gases. For the condensed state, the model of nonsolving pure substances is used. Thermodynamic properties of individual substances are imported from IVTANTHERMO data base. The carbon is presented there as condensed matter (graphite) and as gaseous molecules, composed of several, from 1 up to 5, atoms. In the high temperature range, pure carbon exists as atoms and ions. Under low temperatures, the condensed phase appears—graphite. Usually, multiatomic carbon molecules appear and vanish only in the transitional zone.

III. RESULTS AND DISCUSSION

Two kinds of graphite rods differing by specific density were used as a raw material. The specific density of the first sample (N1 hereinafter, diameter 6 mm) is 1.48 g/cm³ and of the second (N2 diameter 10 mm) is around 1.63 g/cm³. Laser ablation of the graphite target in distilled water and ethanol produces the gray coloration of the liquid, giving evidence of the formation of the suspension of dispersed particles. After some time, the solution becomes transparent due to the settling out of large particles. Figure 2 shows the images of particles on the slide surface after deposition and drying of the suspension, produced by the pulse laser ablation of graphite.

Analysis of the diffraction image of sample N1 shows that the produced material consists of two carbon phases, everyone having a hexagonal crystal structure. The average size of the area of coherent dissipation (ACD) along the crystallographic axis “c” for both phases is 28 nm. The volumetric part of the first phase is 75 vol. %, and its parameter of order is 0.49. Corresponding values for the second phase are 25 vol. % and 0.04.

In sample N2, the domineering phase (83% vol.) is a graphite-like phase with a turbo-striated structure, and its average size of ACD is less than 1 nm. This material includes three phases, one of them has the rhombohedral crystal structure, and two others have the hexagonal one with parameters of three-dimensional ordering using standard technique. X-ray diffraction spectra were produced from the basic surfaces of samples and their perpendicular slices.

Morphology analysis of the macrostructure of dried colloid on a copper substrate was performed by means of a scanning electron microscope Nova NanoSem 650 using the standard technique (SEM-analysis).

For the local determination of the sample composition, an energy dispersion spectrometer, installed on the microscope Nova NanoSem 650, was used (EDS-analysis).

B. Material characterization

Phase analysis was performed using x-ray diffraction data obtained on the DRON-2.0 powder diffractometer (CuKα-radiation)
0.85 and 0.16. The content of the first hexagonal phase is 9 vol. % and of the second is 5 vol. %. The content of rhombohedral graphite is 3 vol. %.

During the ablation of N1 in water, the particles of irregular shape are formed with the range of lateral sizes from submicrometers up to tens of micrometers. Morphology of the surface of particles consists of deformed layers. Sometimes particles are composed of the stack of layers with scaly goffer. On the upper layers of the stack, there are spherical nanostructures with diameters 5–10 and 100–500 nm (Fig. 3).

By means of energy dispersion analysis (Fig. 4), it is established that the main element of the dried colloid is carbon. Most pronounced from the admixtures are the atoms O, Na, and Cu. The latter most probably is provided by the copper substrate. The presence of oxygen (~15 vol. %) is usual for carbon nanostructures due to the high reactivity of carbon within the structure of the graphite layer. The experiment was performed in ethanol and water, so it is no wonder that there are oxygen containing functional groups, which sorb on the surface of carbon particles. However, during the drying of the powder in atmospheric conditions under the contact with air, the oxygen sorption is going on due to the high concentration of surface defects.

Morphology of the ablation products of N1 in ethanol is presented at Figs. 5 and 6. Investigations show that the particles...
consist of stacks of layers with sizes in the range from micrometers up to several tens of micrometers. Aggregates are coated with dispersed formations and porous films. Multiple spherical particles sized \( \sim (0.1 - 1) \mu m \) are visible also.

According to the energy dispersion analysis of the ablation products of N1 in ethanol, the main element of the suspension material is carbon, and there are also the same admixtures as those during the ablation in water.

Microscope analysis of the ablation products of N2 in water shows that in the dried suspension there is a significant share of spherical formations (Fig. 7) sized \( \sim (0.1 - 0.9) \mu m \) and of greater aggregates of nanosized particles. In individual cases, one can see their striated “bulbous” structure (Fig. 8).

As stated above, x-ray structural analysis of ablation products of sample N2 demonstrated, that the particles are x-ray-amorphous, and that their microstructure prevents the dispersion of the beam. This effect might be conditioned by the thickness of particles in a moderate number of graphene layers and by the presence of a significant number of defects distorting the interplanar spacings. Probably, it corresponds to the observed spherical particles, which might be graphene bubbles with an envelope consisting of several layers like few-layered graphene. Formation of similar structures proves the peculiarity of the ablation in the confining liquid—under the pulse-periodic laser radiation, a fragmentation of the target occurs accompanied by sequential interaction of melted drop with confining vapor. In Ref. 18, after ablation of graphite in ethanol, the composition of the suspension was determined. It was found that the main components, there were polyynes \((C_{n+1}H_2)\), which are known to be predecessors of carbon particles\(^{19}\) as well as of onions.\(^{20}\) Both kinds of particles have the spherical morphology. Investigations of the graphene formation mechanism in the high temperature plasma of RF discharge demonstrated that the formation of flaky structures goes on through the striation of spherical structures.\(^{21}\) Likewise, in Ref. 22, there established the possibility of the formation of onions within the plasma jet, generated by the DC plasma torch. The formation of graphene bubbles was observed during the reduction of graphene oxides.\(^{23,24}\)

In order to investigate the influence of the gas phase composition on the synthesis of carbon nanostructures during the ablation of graphite confined in liquid, thermodynamic modeling of plasma was performed under the pressure 4 GPa in the temperature range 5000–1000 K, using the properties of individual substances from the database IVTANTHERMO.\(^{17}\) In this database, the carbon is presented as condensed matter (graphite) and gas molecules containing up to five atoms. Under high temperatures, only atoms and ions of carbon are accountable. Condensed phase-graphite appears at low temperatures. It is known from experience that carbon molecules appear and vanish in some transition zone. The problem is
the determination of this temperature zone and the establishment
of predecessors of spherical particles.

Pure ethanol (C\textsubscript{2}H\textsubscript{5}OH) was being used in experiments. Under 4 GPa due to the contact with confining liquid, the fragments of the target cool down from 5000 K. Earlier investigations have shown that the carbon condensation in plasma volume begins at the temperature range 2432–2609 K. Addition of 5% of carbon (with relation to ethanol) leads to higher temperatures of the beginning of concentration. Figure 9 shows the beginning of the concentration of carbon—result of ablation in ethanol—in the temperature range of 2960–3060 K. CO, H\textsubscript{2}, and CH\textsubscript{4} are the dominating components in plasma. There are no carbon atoms in the temperature range before the point of condensation. Carbon is present in molecules vanishing after the condensation: C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, and CH\textsubscript{3}. Some of them appear immediately before the condensation: C\textsubscript{2}H\textsubscript{5} and C\textsubscript{2}H\textsubscript{2}. Relatively long after condensation continues to be present C\textsubscript{2}H\textsubscript{4}. The sharp bend of the curve CO shows that the carbon in this molecule actively participates in the condensation process.

During the ablation in distilled water, the carbon condensation in plasma is significant for the carbon content over 30% (weight). The evolution of concentrations of gas components after ablation in water at a carbon content of 40% is shown in Fig. 10. The process of condensation begins near 2100 K. The main component is CO with weak competition of H\textsubscript{2}–CH\textsubscript{4}. Sharp bend of the curve CO in the vicinity of concentration temperature is accompanied by the increase of CO\textsubscript{2}. The behavior of component C\textsubscript{2}H\textsubscript{6} is similar to that of C\textsubscript{2}H\textsubscript{4}—appears just before and vanishes immediately after the condensation. In addition, their concentrations are at the same level.

So, the thermodynamic modeling show that during the ablation in the vapor environment, there appear in abundant quantities oxygen containing components, first of all—CO (Figs. 9 and 10). Their simultaneous intrusion into the surface layer of the striated structures tends to hinder the diffusion, and gas accumulates in the thin surface layer (up to 0.5 \(\mu\)m of thickness), forming the pores and bubbles. Under high pressure, the bubbles collapse, forming the craters on the surface of layered nanoparticles and spheres.

It may be supposed that autonomous structures like spheres, constructed from multiaatomic carbon planes, are framed by oxidized graphene layers due to the interaction of carbon with gases like CO and H\textsubscript{2}O, forming on the surface of the structure carbonyl (\(-\text{CO}\)) and hydroxyl (\(-\text{OH}\)) groups.\textsuperscript{26–27} It corresponds to the high content of oxygen.

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{fig9.png}
\caption{Evolution of the gas phase composition during the ablation of graphite in confining ethanol. Two ranges of mole fraction are presented—0–0.5 (upper part) and 0–0.05 (lower part).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{fig10.png}
\caption{Evolution of the gas phase composition during the ablation of graphite in confining water. Two ranges of mole fraction are presented—0–0.5 (upper part) and 0–0.01 (lower part).}
\end{figure}
IV. CONCLUSIONS

The sheet graphene has demonstrated its excellent mechanical, thermal, electronic, and optical properties. These particularities enabled its use in multiple applications. Spherical graphene stands separately because the methods of its production are yet under development. There are many ways of synthesizing of spherical graphene. The impulse laser ablation in liquids is the most simple, fast, and ecologically friendly among them. It does not use toxic chemicals, expensive vacuum chambers, and super clean rooms. The main advantage of this method is the possibility to control the size, shape, and structures of the product by the selection of laser parameters and the liquid to use. Due to the ablation of artificial graphite in distilled water and ethanol by means of a copper vapor laser during 60–65 min, spherical particles were produced. Two kinds of graphite with different diameters were used as targets. It is established that there are no fundamental differences in the structure of ablation products. In both cases, carbon is the structural unit. The formation of carbon structures depends mainly on the nature of liquid. The experiment proves the greater content of graphene in the case of ethanol compared with water. The formation of carbon structures depends mainly on the nature of liquid. The experiment proves the greater content of graphene in the case of ethanol compared with water.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

M. B. Shavelkina: Conceptualization (lead); Methodology (lead); Writing – review & editing (lead). M. M. Malikov: Investigation (lead); Writing – original draft (lead). P. P. Ivanov: Data curation (lead); Formal analysis (lead); Software (lead); Validation (equal). T. I. Borodina: Investigation (equal); Validation (equal). G. E. Valyano: Investigation (lead); Validation (lead).

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