

Two-stage laser-induced synthesis of linear carbon chains

A.O. Kucherik, S.M. Arakelian, S.V. Garnov, S.V. Kutrovskaya,
D.S. Nogtev, A.V. Osipov, K.S. Khor'kov

Abstract. A method is proposed for the synthesis of linear carbon chains under irradiation of colloidal systems consisting of schungite nanoparticles by an ytterbium fibre laser with a pulse duration of 100 ns and an energy up to 1 mJ. Colloidal systems have been previously prepared by laser ablation of a schungite target in distilled water using a Nd³⁺:YAG laser with a pulse duration of 1 ms and an energy up to 10 J.

Keywords: laser ablation, linear carbon, colloidal systems.

1. Introduction

Despite the same chemical composition, carbon nanostructures (nanodiamonds, fullerenes, graphene, etc.) demonstrate a variety of physical and chemical properties due to differences in the formation of atomic bonds [1, 2]. The development of methods for the synthesis of carbon materials with a controlled structure has opened up new possibilities for one of them – a carbyne [3]. Carbyne [4–6] is an n-type semiconductor with an energy gap width ΔE up to 1 eV, in which electronic transport properties are structurally sensitive. Carbyne has a hexagonal lattice and represents a chain of covalently bonded carbon atoms with sp-hybridisation of orbitals of two possible types: alternation of n single and triple bonds ($-C\equiv C-$) _{n} , which is characteristic of α -carbyne, or alternation of n double bonds ($=C=C=$) _{n} in β -carbyne. These two types are commonly identified by the final products of chemical reactions under various conditions. The distance between the atoms in a carbyne chain is 0.128 nm, and the distance between the chains is 0.295 nm, which is substantially less than similar distances for graphite (0.142 and 0.335 nm, respectively); therefore, theoretically carbyne has an unrivaled specific strength as compared to graphene [7]. Optical and electrical properties of carbyne depend on its morphology [8–10]. Thus, the synthesis of carbyne with a variable structure of bonds is of considerable interest not only from a fundamental point of view, but also in the development of

new integrated circuits of advanced, next-generation hybrid electronic devices.

Synthesis of perfect single crystals of carbyne is a challenging process because linear carbon chains are unstable and undergo transition into other forms when they reach a certain critical size [11, 12].

Shi et al. [13] synthesised carbyne inside carbon nanotubes, which made it possible to stabilise its structure and produce a long and stable linear chain composed of 6000 carbon atoms.

For carbon materials, various scenarios of transitions between solid, liquid and gaseous states (see, e.g., [14]) can be implemented. A special place here is occupied by laser irradiation of carbon targets under which the state of the matter changes as a function of the heating rate of the sample [15] and the properties of a medium surrounding the sample [16]. Moreover, laser heating leads to a strong thermoelastic stress [17]. In the case of femtosecond laser irradiation one can even observe thermomechanical spalling [18] of the front surface of the irradiated sample. The authors of [19, 20] discussed theoretical and experimental conditions of carbyne synthesis from carbon targets exposed to nanosecond laser radiation. The primary mechanism of this process is the splitting of the graphite layers, followed by the formation of linear carbon chains. On the other hand, in using high-energy laser pulses with a duration of less than 20 ns it is possible to ensure a transition from amorphous carbon to nanodiamonds through Q-carbon [21].

By varying the laser pulse duration, one can control the dominant processes of the sample surface modification, and by varying the environment, one can change the kinetic conditions of their behaviour. During carbon ablation in a liquid, micro- and nanoparticles of various allotropic forms are formed in the volume of a colloidal solution [22]. Observation of the surface modification [23, 24] resulting from laser irradiation will allow one to control the formation of particles in a colloidal system. Note the results of the experiments presented in [25], where graphene-like layers were observed in the case of laser ablation of graphite in liquid nitrogen.

Under laser irradiation in liquid media, carbyne chains can be stabilised due to laser ablation in the presence of gold nanoparticles [20], which leads to the consolidation of the ends of linear chains on the surface of gold nanoparticles and prevents their further curling into coils.

In this paper we present new results on the laser-induced synthesis of carbyne in a colloidal system. At the first stage, as a result of laser ablation (a wavelength of 1.06 μm , a pulse duration of 1 ms at an energy up to 10 J and a pulse repetition rate of 50 Hz) of a schungite sample placed in distilled

A.O. Kucherik, S.M. Arakelian, S.V. Kutrovskaya, D.S. Nogtev,
A.V. Osipov, K.S. Khor'kov Vladimir State University named after
Alexander and Nikolay Stoletovs, ul. Gorkogo 87, 600000 Vladimir,
Russia; e-mail: kucherik@vlsu.ru;
S.V. Garnov A.M. Prokhorov General Physics Institute, Russian
Academy of Sciences, ul. Vavilova 38, 119991 Moscow, Russia;
National Research Nuclear University 'MEPhI', Kashirskoe shosse
31, 115409 Moscow, Russia

Received 10 May 2016
Kvantovaya Elektronika 46 (7) 627–633 (2016)
Translated by I.A. Ulitkin

water, we produced a colloidal system. The choice of schungite as a target is justified by the fact that its original structure is composed of a mixture of various carbon allotropes: fullerenes of natural origin [26] and nanostructured carbon [27], whose small lattices are connected with amorphous carbon.

At the second stage, we irradiated the colloidal system by an Yb laser with a pulse duration of 100 ns, an energy up to 1 mJ and a pulse repetition rate of 20 kHz, which made it possible to fragment the dispersed phase of the colloid and ensure the self-assembly of carbon chains (cf. [20]).

2. Experiment

2.1. Synthesis of nanoparticles by laser ablation of a carbon target in a liquid; initial formation of a colloidal system

Laser ablation in a liquid was used to prepare colloidal systems [22, 28–30]. The radiation source was a Nd³⁺:YAG laser with a pulse duration of 1 ms, a repetition rate of 50 Hz and a pulse energy up to 10 J.

The schungite target was placed in a cell with water so that the surface of the target was covered with water by more than 3 mm. During exposure to laser light, the cell with the target was moved on a translation stage at a speed of 100 to 1000 $\mu\text{m s}^{-1}$. The diameter of the laser spot on the target surface was from 100 to 500 μm , which made it possible to vary the laser intensity in the range $I \sim 10^5 - 10^7 \text{ W cm}^{-2}$. Thus, by changing the laser spot diameter and the scanning rate, as in [22], we implemented various regimes of surface modification (Fig. 1).

At a laser spot diameter of 1 mm on the surface of the sample, globules with a diameter of 2–5 μm were formed in the centre of the cavity, and a part of them were hollow (Fig. 1a). Together with the globules we observed the formation of threads. With increasing laser fluence, a porous film of the melt was formed in the centre of the cavity (Figure 1b) in whose pores one can also see globules. For a laser beam 250 μm in diameter, structures of ‘cauliflower’ type are formed in the centre of the cavity (Fig. 1c). These structures arise due to a disordered film growth during the reverse precipitation of vapour substances formed during ablation [31].

The particle size distributions $N(d)$ in the prepared colloidal system as functions of the irradiation conditions were measured by the dynamic light scattering intensity with a Horiba LB-550 particle size analyser.

The measurement results for the synthesised colloidal systems are shown in Fig. 2. It is seen that in all cases there is a considerable variation in the number of particles with respect to their average size. Along with particle measuring 100 nm in size, there were also formed submicron particles. Both the average size d of the particles and their variance in size increase with increasing laser pulse energy E . Changing the scanning speed of the laser beam across the surface also allows one to control the average size of the synthesised particles (Fig. 3). In all cases, the energy in the range from 4 to 5 J is transitional for the size of synthesised nanoparticles. With a further increase in E , we observe a sharp increase in the average particle diameter. This is due to the fact that an increase in the laser fluence leads to an increase in the depth of laser ablation of the sample, and therefore a large amount of material is removed from the target into the colloidal system volume.

Changes in the size and shape of the particles exposed to laser radiation with an energy $E = 1 - 10 \text{ J}$ are shown in Fig. 4. The particles in the colloidal solution obtained at $E = 1 \text{ J}$ (Fig. 4a) generally have a spherical shape and a uniform size; at the same time, they exhibit a tendency to clustering. With increasing laser pulse energy, the particles take the form of polyhedra and hardly aggregate into clusters (Figs 4b and 4c).

It should be noted that event after high-temperature treatment, schungite samples contain carbon globules or ‘bulbs’ that are resistant to heat up to temperatures of 2700 °C (cf. [30]). Consequently, the observed spherical particles are typical for schungite targets, the low energy of laser exposure making it possible to avoid significant changes in the material structure.

For subsequent irradiation of the targets we used a colloidal system comprising carbon nanoparticles with a size no larger than 100 nm. To this end, the colloids were processed in a centrifuge separating particles by size, the particle concentration in the system being 1 mg mL⁻¹. It is experimentally shown that the particles of this size retain the structure of the original material and thus an increase in the number of lattice defects allows one quite successfully to

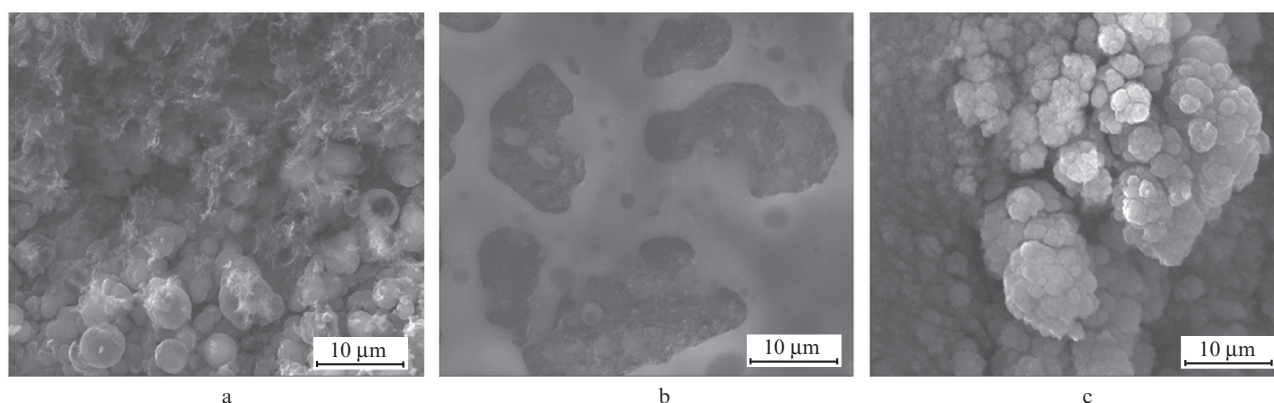


Figure 1. SEM images of the schungite surface after irradiation by a repetitively pulsed laser with a pulse duration of 1 ms, energy of 0.5 J and pulse repetition rate of 50 Hz. The diameter of the laser beam on the target surface is (a) 1000, (b) 500 and (c) 250 μm . The scanning speed of the laser beam along the sample surface is 250 $\mu\text{m s}^{-1}$.

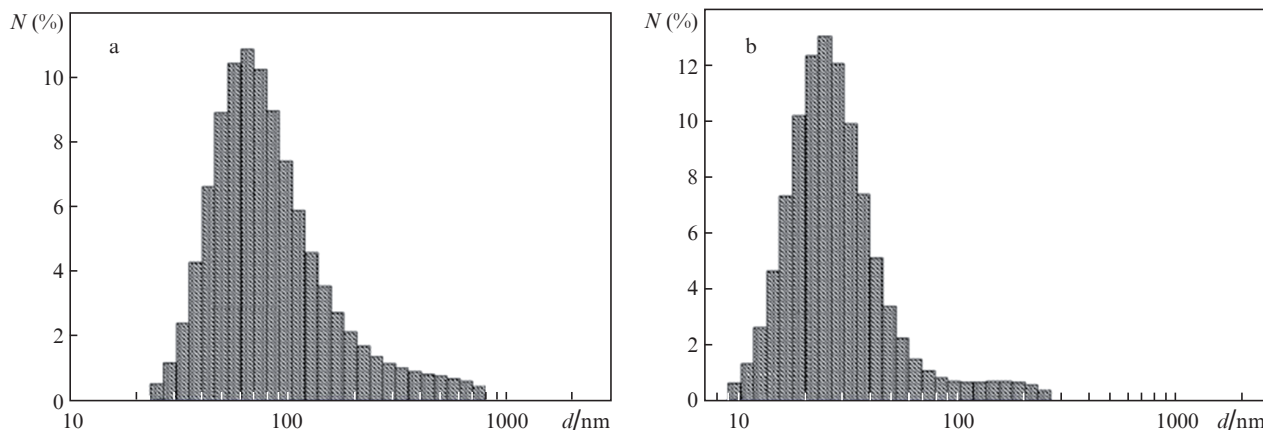


Figure 2. Histograms of particle size distributions d under laser irradiation with a pulse duration of 1 ms and an energy of (a) 5 and (b) 1 J. The scanning speed is $250 \mu\text{m s}^{-1}$, and the laser spot diameter is $250 \mu\text{m}$.

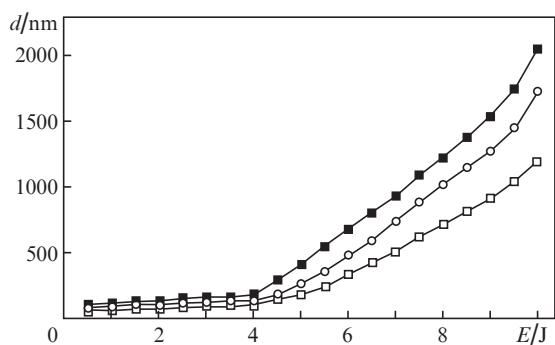


Figure 3. Dependences of the mean particle size d in the colloidal systems on the laser pulse energy E at a scanning speed of the laser beam along the sample $v = (\blacksquare)$ 250, (\circ) 500 and (\square) 1000 $\mu\text{m s}^{-1}$. The diameter of the laser beam on the sample surface is $250 \mu\text{m}$.

carry out the fragmentation of the particles at relatively moderate laser intensities.

2.2. Laser irradiation of colloidal systems. Analysis of the conditions of synthesis of linear structures in a liquid

For the fragmentation of the dispersed phase of the obtained colloidal system, we used an ytterbium fibre laser ($\lambda = 1.06 \mu\text{m}$) with a pulse duration of 100 ns, pulse repetition rate

of 20 kHz and pulse energy up to 1 mJ. The radiation was focused into the volume of the colloid into a spot of $50 \mu\text{m}$ in diameter; the scanning speed of the beam over the colloid volume was varied from 1 to 10mm s^{-1} . The irradiation time was varied from 5 to 15 min in view of the fact that the characteristic time of graphite–carbyne conversion is 25 s [14]. Thus, the exposure time was certainly sufficient for the formation of carbyne structures. In this case, the energy that is absorbed by 100-nm particles should provide their partial fragmentation without destroying the linear bonds. The energy absorbed by a spherical particle of radius r_0 can be determined from the relation

$$E_{\text{abs}} = \pi r_0^2 Q_{\text{abs}} \int_0^t I(t) dt, \quad (1)$$

where $I(t)$ is the temporal distribution of the laser light intensity; and Q_{abs} is the efficiency factor for absorption.

To calculate Q_{abs} , we will use the stationary Mie theory [32] for a spherical particle of amorphous carbon of radius $r_0 = 50 \text{nm}$ with allowance for the data for the key parameters of amorphous carbon at a laser wavelength $\lambda = 1.064 \mu\text{m}$ [33]:

$$Q_{\text{abs}} = \frac{8\pi r_0}{\lambda} \text{Im} \frac{\varepsilon^2 - 1}{\varepsilon^2 + 2}, \quad (2)$$

where $\varepsilon = n + ik$; $n = 2.106$; and $k = 0.945$.

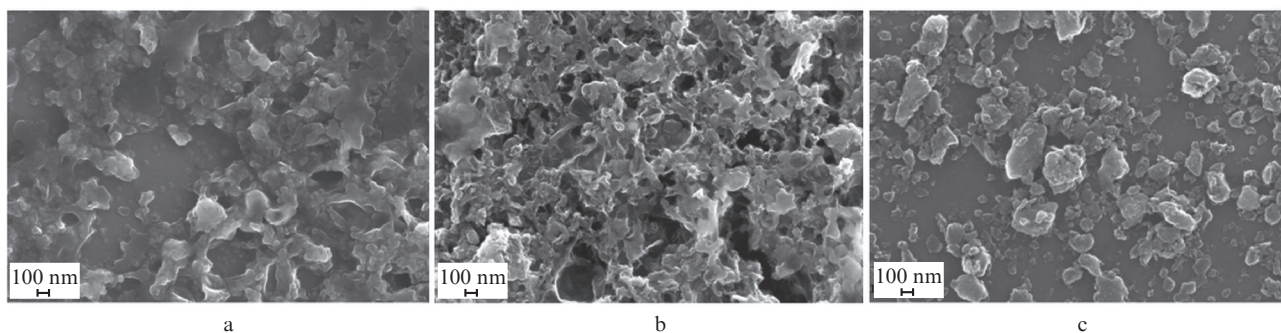


Figure 4. SEM images of carbon particles in the colloid, produced by laser pulses of millisecond duration with an energy of (a) 1, (b) 5 and (c) 10 J at a scanning speed $v = 500 \mu\text{m s}^{-1}$. The diameter of the laser spot on the target surface of the sample is $250 \mu\text{m}$.

Depending on the laser irradiation conditions, the absorbed energy for a single pulse is 10^{-6} – 10^{-9} J. Given that, due to a small size the particles do not have their own thermal capacity, we determine the maximum achievable temperature of the laser radiation by the formula [34]

$$T_{\max} = \frac{I_p k_a d}{8\chi}, \quad (3)$$

where I_p is the peak power of laser radiation; χ is the coefficient of thermal conductivity of the liquid phase of the colloid; and the coefficient k_a takes into account the smallness of the particle size as compared to the wavelength in accordance with the Mie theory:

$$k_a = \exp[-0.2(\sqrt{n^2 + k^2} - 1)] \left[1 - \exp\left(\frac{4\pi kd}{\lambda}\right) \right]. \quad (4)$$

For the conditions of our experiments, the maximum temperature T_{\max} under irradiation by a single pulse does not exceed the carbon sublimation temperature (~ 5000 K). However, in the case of multi-pulse irradiation with allowance for the fact that the conditions for the phase transition of a liquid surrounding the particles will be implemented, it is possible to reach temperatures that are close to the carbon sublimation temperature [14]. Of key importance is the fact that conditions for the possible formation of carbyne will be

fulfilled in our case much earlier with regard to both temperature and pressure [35].

During the laser action we observed the bleaching of colloidal systems (Fig. 5), which can be associated with the synthesis of carbyne, the formation of which is accompanied by this effect (see, e.g., [1, 36]).

The study with the employment of the laser particle size analyser shows that the diameters of the particles of the dispersed phase of the colloid depend on the irradiation time. When exposed to nanosecond pulses, the particle size distribution becomes bimodal with time, because apart from the fragmentation of particles, in the interaction region we observe a competing process, i.e. aggregation, in the peripheral volume of the colloid. However, the average particle size in the system decreases with increasing exposure time (Fig. 6). In general, this behaviour of colloidal systems is consistent with the typical mechanisms of laser fragmentation of liquid systems [37–39].

The first peak of the histogram is shifted to the region of small sizes (10 nm), and the particle size distribution is narrowed, while the second maximum is shifted to ~ 30 nm. Further laser irradiation does not lead to a significant change in the particle size. It can be assumed that these small particles are ‘transparent’ to laser radiation at $\lambda = 1.06$ μm and therefore a longer exposure does not alter the particle size in the volume of the colloid.

Replacing the liquid phase of the colloid can significantly change the process of the particle fragmentation and the conditions of the carbyne formation. However, the use of water for this purpose has a number of significant advantages, since it allows one to avoid the formation of new carbon phases due to reactions of carbon atoms and molecules with molecules of the medium. Even if irradiation leads to the formation of compounds with oxygen or hydrogen, they will be volatile and leave the laser interaction region and the liquid.

During the laser action, we observed in all cases a change in the morphology of the particles produced in the colloid. After a 5-min exposure to radiation with an intensity of 5×10^6 W cm^{-2} , mainly carbon crystallites with an average size of 80 nm are formed (Fig. 7a). When irradiated for 10 min (Fig. 7b), the average particle size is reduced to 50 nm and threads are formed. In the case of 15-min irradiation (Fig. 7c), ‘dendrites’ consisting of particles with a size from 10 to 30 nm are formed in the sediment, and the extended linear structures are observed.

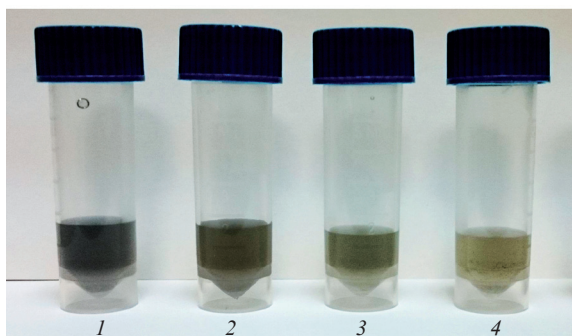


Figure 5. (Colour online) Colloidal systems before and after laser irradiation: (1) initial system, and after irradiation for (2) 5, (3) 10 and (4) 15 min.

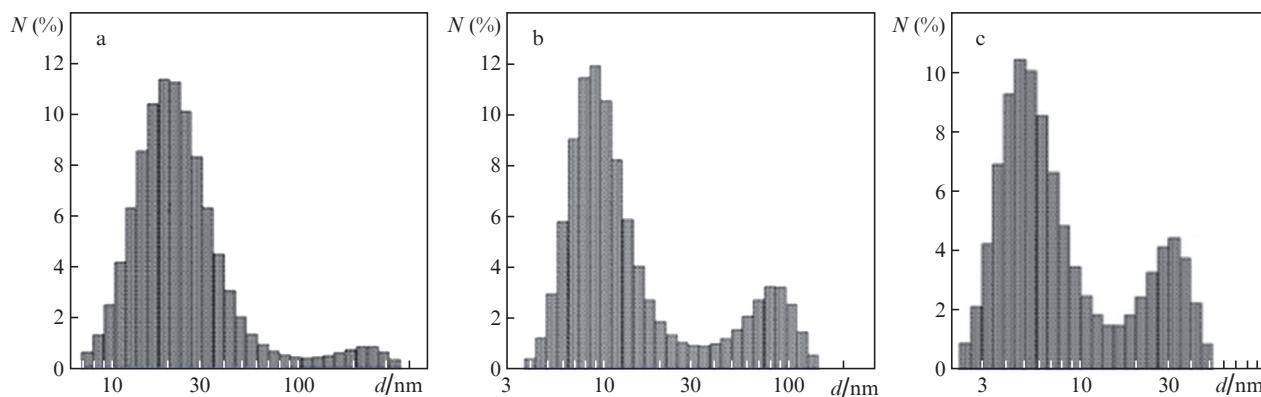


Figure 6. Histograms of particle sizes in the colloidal systems at a laser irradiation time of (a) 5, (b) 10 and (c) 15 min.

1610 cm^{-1} (Fig. 9). The D peak (1380 cm^{-1}) is observed for all samples, although its intensity varies, depending on the irradiation conditions. The widths of the peaks corresponding to carbyne with polyyne bonds are reduced to 2100–2200 cm^{-1} . This behaviour of the spectrum suggests that in the process of evaporation of the colloid, carbyne chains undergo a transition into sp^2 -hybridised carbon structures.

With increasing exposure time, the spectra feature bands in the range from 800 to 900 cm^{-1} , corresponding to bending vibrations [5]. Thus, linear carbon chains in the process of the drying of a colloid drop are transformed into complex molecules [50]: bundles and globules consisting essentially of β -carbyne.

3. Discussion of the factors determining the stability of carbyne structures

Conditions for the formation of a linearly ordered carbon structure in our experiment can be related to the peculiarities of modification of carbon nanoparticles in the liquid: in the process of laser splitting of carbon nanostructures, the isotropic colloidal systems in general allow carbyne chains to be stabilised.

The role of the interaction of laser radiation with nanoparticles and the role of viscous forces on the part of the liquid are determined by the structural characteristics of carbon materials (cf. Refs [51, 52], in which a similar two-stage synthesis of carbon structures is used).

Indeed, the number of repeating units in carbon (organic) polymers can vary significantly. Such polydispersity of a macromolecular system leads to a globular, and/or linear and/or branched, and/or network structure (compare with the analysis carried out in [53]).

For the linear macromolecular structure that is characteristic of carbyne, each repeating unit is connected to two adjacent units. However, such a structure is not stable, especially in the conditions of the random/external action. Energetically favourable is a bundle structure, i.e. a globule, when the intramolecular interaction forces exceed the intermolecular interaction forces. This structure is actually closed and passive.

The two remaining structures are stable, especially in certain environments. As for one of them – the network structure, it is similar to the stable lattice structure of crosslinked linear structures. Thus there appear several crystalline and amorphous regions, which determine the reactivity of these structures in general. However, more complex aggregates with a varying degree of ordering are in fact formed.

We failed to observe the formation of carbyne in the case of irradiation by laser pulses of femtosecond duration, which can be, apparently, explained by the local processes of destruction of matter in the field of such intense laser radiation.

Deposition of the carbon material from the colloid onto a solid surface in this case led to a drastic decrease in the concentration of carbyne. This may be due to a violation of the isotropy of the medium in which the substance is already placed (two-dimensional structure). For the same reason, a change in the type of the liquid in the colloidal system also affects the stability of the one-dimensional carbyne chain (cf. [36, 42]). Indeed, in a more viscous medium carbyne should be more stable. In this sense, the known method of the carbyne synthesis during laser sublimation and its deposition onto a substrate is not the most efficient process, because in the gas–dust phase the self-organisation of the system into sp^2 -

and sp^3 -structures should dominate even before the surface substrate itself can exert the orienting influence.

The maximum formation efficiency of carbyne was observed in our experiments with schungite. This can be explained by the fact that due to the initial amorphous structure and the presence of nanostructured carbon, the synthesised nanoparticles under continuous laser irradiation tend to form linear structures attached to nanoparticles (fullerenes, nanodiamonds, etc.) In this case, we observe the bleaching of the colloidal system, typical for the formation of carbyne (see photos in Fig. 5).

The synthesis process and the stability of carbyne can be determined by substantially reduced melting point at the grain boundaries in an inhomogeneous medium (cf. [53]). It is through such an intermediate ‘liquid stage’ that the formation of carbyne is, probably, energetically more favourable (see, e.g., [23, 25]).

4. Conclusions

In this paper, we have shown the possibility of synthesis of linear carbon structures under laser irradiation of colloidal systems containing carbon nanoparticles. The use of laser pulses of nanosecond duration apparently allows for the partial particle fragmentation, which leads to destruction of bonds between the layers, and then to the splitting of graphene layers into linear structures. The irradiation time at a certain critical value of intensity (in this case, 10^6 W cm^{-2}) is the dominant factor in the synthesis of carbyne. In the conditions of laser irradiation of the colloidal system, sp -fragments of linear chains, experiencing a kink and entering into chemical bonds with the formation of sp^2 - and sp^3 -bonds, are produced. However, during ablation in a liquid, linear chains due to viscous forces become more resistant, which is observed in the measured Raman spectra.

Acknowledgements. The work was performed within the framework of the State Research Task of Vladimir State University (Grant No. 2014/13) and partially by the Russian Foundation for Basic Research (Grant Nos 16-32-60067 mol_a_dk, 16-32-00759 mol_a and 16-42-330531 r_a). Measurements of the structural properties of carbon materials were performed in conjunction with the Resource Research Centres of ‘Nanomaterials’ and ‘Laser and optical materials research’ at St. Petersburg State University.

References

1. Belenkov E.A., Greshnyakov V.A. *Fiz. Tverd. Tela*, **8**, 1640 (2013).
2. Konov V.I. *Kvantovaya Elektron.*, **45**, 1043 (2015) [*Quantum Electron.*, **45**, 1043 (2015)].
3. Mel'nichenko V.M., Sladkov A.M., Nikulin Yu.N. *Usp. Khim.*, **51**, 736 (1982).
4. Korshak V.V., Kasatochkin V.I., Sladkov A.M., et al. *Dokl. Akad. Nauk SSSR*, **6**, 1342 (1961).
5. Sladkov A.M. *Polisopryazhennyye polimery* (Polyconjugated Polymers) (Moscow: Nauka, 1989) p. 253.
6. Babaev V.G., Guseva M.B., in *Carbyne and Carbonyl Structures* (Dordrecht–Boston–London: Kluwer Academic Publishers, 1999) p. 159.
7. Liu M., Artyukhov V.I., Lee H., et al. *ACS-Nano*, **7** (11), 10075 (2013).
8. Akagi K., Nishiguchi M., Shirakawa H., et al. *Synth. Met.*, № 1-3, 557 (1987).
9. Demishev S.V., Pronin A.A., Glushkov V.V., et al. *Zh. Eksp. Teor. Fiz.*, **1** (7), 140 (2002).

10. Korobova Yu.G., Bazhanov D.I. *Pis'ma Zh. Eksp. Teor. Fiz.*, **9**, 524 (2012).
11. Mel'nichenko V.M., Sladkov A.M., Nikulin Yu.N. *Usp. Khim.*, **51**, 736 (1982).
12. Bulychev B.M., Udod I.A. *Rus. Khim. Zh.*, **39**, 9 (1995).
13. Shi L., Rohringer P., Suenaga K., et al. *Nat. Mat.* DOI: 10.1038/NMAT4617 (2016).
14. Asinovskii E.I., Kirillin A.V., Kostanovskii A.V. *Usp. Fiz. Nauk*, **172**, 8 (2002).
15. Downer M.C., Ahn H., Reitze D.H., et al. *Int. J. Thermophys.*, **14** (3), 361 (1993).
16. Wang C.X., Yang G.W., in *Laser Ablation in Liquids – Principles and Applications in the Preparation of Nanomaterials* (Singapore: Pan Stanford Publishing, 2012) Ch. 3, p. 157.
17. Vovnenko N.V., Zimin B.A., Sud'nikov Yu.V. *Zh. Tekh. Fiz.*, **81** (6), 57 (2011).
18. Bulgakov A.V., Bulgakova N.M., Burakov I.M., et al. *Sintez nanorazmernykh materialov pri vozdeistvii moshchnykh potokov energii na veshchestvo* (Synthesis of Nanoscale Materials Under Irradiation of the Matter by High-power Energy Fluxes) (Novosibirsk, Institute of Thermal Physics SB RAS, 2009) p. 462.
19. Christopher B. *J. Phys. Chem. C*, **37**, 21605 (2015).
20. Pan B., Xiao J., Li J., et al. *Sci. Adv.*, **9**, e1500857 (2015).
21. Jagdish N., Anagh B. *APL Mater.*, **3**, 100702 (2015).
22. Antipov A.A., Arakelian S.M., Garnov S.V., et al. *Kvantovaya Elektron.*, **45** (8), 731 (2015) [*Quantum Electron.*, **45** (8), 731 (2015)].
23. Abramov D.V., Arakelian S.M., Galkin A.F., et al. *Pis'ma Zh. Eksp. Teor. Fiz.*, **84** (5), 315 (2006).
24. Bagayev S.N., Prokoshev V.G., Kucherik A.O., et al. *Dokl. Akad. Nauk*, **395** (2), 183 (2004).
25. Abramov D., Arakelian S., Kochuev D., et al. *Nanosist.: Fiz., Khim., Mat.*, **7** (1), 220 (2016).
26. Rozhkova N.N., Gribanov A.V., Khodorkovskii M.A. *Diamond Relat. Mater.*, **16**, 2104 (2007).
27. Razbirin B.S., Rozhkova N.N., Shcheka E.F., et al. *Zh. Eksp. Teor. Fiz.*, **145** (5), 838 (2014).
28. Arakelian S.M., Kucherik A.O., Prokoshev V.G., et al. *Vvedenie v femto–nanofotoniku: fundamental'nye osnovy i lazernye metody upravlyaemogo polucheniya i diagnostiki nanostrukturirovannykh materialov* (Introduction to Femto- and Nanophotonics: The Fundamentals and Laser Methods for Controlled Synthesis and Diagnostics of Nanostructured Materials) (Moscow: Logos, 2015).
29. Abramov D.V., Antipov A.A., Arakelian S.M., et al. *Laser Phys.*, **24**, 074010 (2014).
30. Kholodkevich S.V., Berezkin V.I., Davydov V.Yu. *Fiz. Tverd. Tela*, **41** (8), 1412 (1999).
31. Abramov D.V., Gerke M.N., Kucherik A.O., Kutrovskaya S.V., Prokoshev V.G., Arakelian S.M. *Kvantovaya Elektron.*, **37** (11), 1051 (2007) [*Quantum Electron.*, **37** (11), 1051 (2007)].
32. Bohren C.F., Hoffman D.R. *Absorption and Scattering of Light by Small Particles* (New York: Wiley, 1983; Moscow: Mir, 1986).
33. <http://refractiveindex.info/?shelf=main&book=C&page=Hagemann>.
34. Simak A.V., Voronov V.V., Shafeev G.A. *Trudy IOFAN*, **60**, 83 (2004).
35. Whittaker A.G. *Nature*, **276** (5689), 695 (1978).
36. Rozhkova N.N., Emel'yanova G.I., Gorlenko L.E., et al. *Fiz. Khim. Stekla*, **37** (6), 853 (2011).
37. Kirichenko N.A., Shcherbina M.E., Serkov A.A., Rakov I.I. *Kvantovaya Elektron.*, **45** (12), 1161 (2015) [*Quantum Electron.*, **45** (12), 1161 (2015)].
38. Maximova K., Aristov A., Sentis M., Kabashin A. *Nanotechnology*, **26**, 065601 (2015).
39. Kirichenko N.A., Sukhov I.A., Shafeev G.A., Shcherbina M.E. *Kvantovaya Elektron.*, **42** (2), 175 (2012) [*Quantum Electron.*, **42** (2), 175 (2012)].
40. Ferrari A.C., Robertson J. *Philos. Trans. R. Soc. London, Ser. A*, **362**, 2477 (2004).
41. Kholodkevich S.V., Poborchii V.V. *Pis'ma Zh. Tekh. Fiz.*, **20** (3), 22 (1994).
42. Cataldo F. (Ed.) *Polyynes: Synthesis, Properties, and Applications* (Boca Raton: CRC-Press, 2005).
43. Ravagnan L., Manini N., Cinquanta E., et al. *Phys. Rev. Lett.*, **102**, 245502 (2009).
44. Zhao X.L., Ando Y., Liu Y., et al. *Phys. Rev. Lett.*, **90**, 187401 (2003).
45. Zhao C., Kitaura R., Hara H., et al. *J. Phys. Chem. C*, **115**, 13166 (2011).
46. Shi L., Sheng L., Yu L., et al. *Nano Res.*, **4**, 759 (2011).
47. Agarwal N.R., Lucotti A., Fazzi D., et al. *J. Raman Spectrosc.*, **44**, 1398 (2013).
48. Kijima M., Kinoshita I., Shirakawa H. *J. Mol. Struct.*, **521**, 279 (2000).
49. Ravagnan L., Siviero F., Lenardi C., et al. *Phys. Rev. Lett.*, **89** (28), 285506 (2002).
50. Mel'nik N.N., Korobov D.Yu., Plyashechnik O.S., et al. *Kratk. Soobshch. Fiz.*, **7**, 24 (2013).
51. Semenov A.P., Semenova I.A. *Zh. Tekh. Fiz.*, **85** (3), 1443 (2015).
52. Rozhkova N.N. *Ekol. Khim.*, **4**, 204 (2012).
53. Straumal B.B. *Fazovye perekhody na granitsakh zeren* (Grain Boundary Phase Transitions) (Moscow: Nauka, 2003).